



Summary and Synthesis of the Available Literature on the Effects of Nutrients on Spring Organisms and Systems

Mark T. Brown and Kelly Chinnners Reiss

Center for Environmental Policy
Department of Environmental Engineering Sciences

Matthew J. Cohen and Jason M. Evans

Forest Water Resources Laboratory
School of Forest Resources and Conservation

K. Ramesh Reddy, Patrick W. Inglett, and Kanika Sharma Inglett

Department of Soil and Water Science

Thomas K. Frazer, Charles A. Jacoby, and Edward J. Philips

Department of Fisheries and Aquatic Sciences

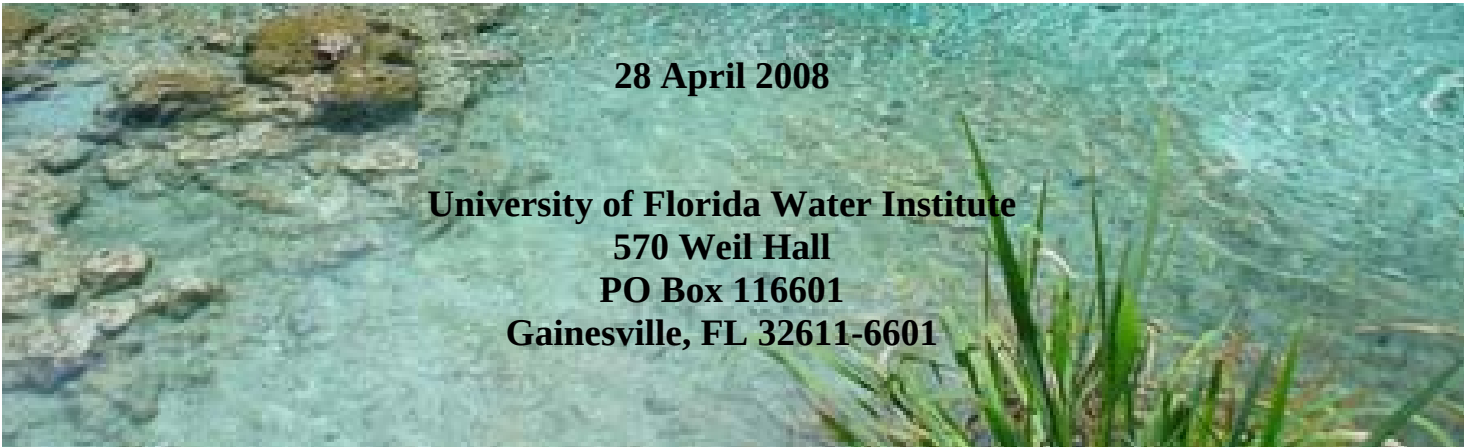
Robert L. Knight¹ and Sky K. Notestein

Wetland Solutions, Inc.

¹Department of Environmental Engineering Sciences

Kathleen A. McKee

University of Florida Water Institute



28 April 2008

University of Florida Water Institute

570 Weil Hall

PO Box 116601

Gainesville, FL 32611-6601

Executive Summary

This summary of the state of the knowledge related to nutrient effects on spring ecosystems and biota represents a synthesis of the most important findings from the literature. The report was commissioned by the Springs Initiative of the Florida Department of Environmental Protection (DEP) to review the pertinent literature related to nutrient effects on spring ecosystems and biota.

To address the complexity of spring ecosystems, this literature synthesis was prepared by a diverse team of spring researchers at the University of Florida's Water Institute, Center for Environmental Policy, School of Forest Resources and Conservation, Department of Environmental Engineering Sciences, Department of Soil and Water Science, Department of Fisheries and Aquatic Sciences, and The Center for Governmental Responsibility; as well as expertise from the environmental consulting firm, Wetland Solutions, Inc.

The report is organized into eight chapters:

1. Springs as Ecosystems
2. Springshed Nutrient Loading, Transport and Transformations
3. Biogeochemical Processes and Implications for Nutrient Cycling
4. Nutrient Effects on Spring Flora and Fauna
5. Invasive Aquatic Plants and Aquatic Plant Control in Florida Springs
6. Effects of Nutrients on Spring Ecosystems
7. Managing Nutrient Inputs to Florida Springs: The Legal Framework
8. Synthesis of Nutrients and Springs

DEP's mandate was threefold: 1) to prepare a review of what is known about the interactions between nutrients and springs, 2) to identify what information gaps exist that inject substantial uncertainty for springs restoration and management, and 3) make recommendations for public policy and research to address these gaps. The following summary draws the most important highlights from each chapter according to this mandate.

Chapter 1: Springs as Ecosystems

This chapter focuses on describing the abiotic and biotic components of spring and spring run ecosystems, their forcing functions and inputs, and the known ecology of these unique aquatic ecosystems.

The Literature: What is Known

From this review of the existing literature on spring ecosystems there are several conclusions that can be drawn:

- ***Springs and spring runs represent a unique class of aquatic ecosystems*** typified by high water clarity, relatively constant water temperature and chemical conditions, and complex biotic interactions.
- ***In their natural state, springs persist in a quasi environmental steady-state*** and due to this stability have developed complex biological systems that are highly efficient at converting solar energy into useful productive work.
- ***During the past century humans have been exerting an increasing variety of external and internal stresses on spring ecosystems in Florida***, the most pervasive include:
 - Alteration of discharge regimes resulting from increased groundwater withdrawals,
 - Increased levels of nutrients, particularly nitrate-N in groundwaters discharging from springs,
 - Extensive recreational disturbance of springs and spring runs, and
 - Increased disturbance in the form of management actions, for instance exotic species control.

The Literature: What is not Known, with Emphasis on Future Research Directions

Several studies suggest that multiple stressors can affect the productivity of spring ecosystems, suggesting that the measurement of ecosystem metabolism may allow for the quantification of these stressors as well as the *health* of spring ecosystems. To further develop these concepts the following research directions are suggested:

- ***Development of a holistic management strategy for springs to foster better understanding*** of the relative importance and synergism of direct stressors at the local level and indirect stresses that occur at the regional scale.

- ***Ecosystem-level information such as monitoring of ecosystem metabolism may provide a more sensitive and quantifiable indicator*** of the response of springs to nutrient increases and the myriad other anthropogenic stresses.
- ***Use of whole-spring and in situ mesocosm manipulation experiments to clarify the effects*** of individual forcing functions on spring ecosystem response.

Chapter 2: Springshed Nutrient Loading, Transport and Transformations

This chapter focuses on nutrient loading to springsheds, with an emphasis on processes of transport and attenuation that are germane to their delivery to springs. It discusses intrinsic vulnerabilities of karst areas to nitrogen loading, and examines the effects of changes land use/land cover and hydrology on various aspects of water quality decline. The chapter ends with an examination of the state of our understanding of springsheds as closed systems of water and solutes, with an emphasis on areas of uncertainty that are relevant questions for future research.

The Literature: What is Known

From this review of the existing literature on nutrient loading there are four essential areas for which managers can proceed with relative certainty:

- ***Complex flowpaths and a wide distribution of residence times characterize the hydrogeology of the Floridan Aquifer.*** The timeline and source area of water delivered to springs is of critical importance to springshed management,
- ***Karst landscapes are vulnerable to pollutants from anthropogenic activities at the surface.*** It is clear that the risks of aquifer contamination are greatly attenuated in regions of the state where regional confining layers (e.g., Hawthorn Formation) limit the rate of interaction between surface and Floridan Aquifer waters.
- ***Water quality is changing in dramatic ways including:*** nitrogen enrichment, hardness, dissolved oxygen concentrations, and trace quantities of pharmaceuticals.
- ***The preponderance of N pollution appears to be from fertilizer sources.*** While there are several reasons to treat this finding as an over-generalization, most of the accumulated evidence from mass balance computations and isotopic tracer studies suggests that mineral fertilizers, and therefore not septic tanks and wastewater sprayfields, are the principal sources of N pollution. However, since fertilizer use is highly diffuse and based on hundreds of thousands of individual decisions, control of N from point sources such as municipal wastewater effluent disposal activities may be a more cost effective form of N load reduction.

The Literature: What is Not Known, with Emphasis on Future Research Directions

What is not known about loading, transport and transformations injects substantial uncertainty that has key implications on pollutant delivery in karst systems and thus represent important areas of future research.

- ***What are the temporal dynamics of water age?*** It is clear from the literature that there remain large uncertainties about the age mixture of water discharging from spring vents.
- ***What is the natural variability in spring flow, and how vulnerable is this to human appropriation?*** Ongoing efforts to set minimum flows and levels (MFLs) should consider the role of flow in water quality response variables.
- ***What are the sources of N in springsheds?*** While there is accumulating evidence that the source of N is principally mineral fertilizer, there remains significant uncertainty about the interpretation of bulk stable isotope measurements in complex karst hydrologic systems.
- ***What are the causes and effects of water quality changes beyond elevated nitrate?*** The synthesis of the literature on springs is dominated by information about nitrogen, but essentially devoid of similarly detailed studies of other water quality parameters.
- ***What is the assimilative capacity of the landscape and aquifer for nutrients and other contaminants?*** Understanding the assimilative capacity and how it might be affected by development and enhanced by management, should be a research priority.
- ***How responsive are springsheds to management interventions?*** As we begin to understand the links between springshed activities and declining water quality in spring ecosystems, evaluating the extent to which parameters are management-sensitive is relevant to both timelines for recovery and prioritization of management efforts.

Chapter 3: Biogeochemical Processes and Implications for Nutrient Cycling

The potential biogeochemical reactions and pathways occurring in springs are numerous, and have been studied in varying levels of detail. In this chapter the following three issues are presented: 1) a description of the biogeochemical processes related to nutrient cycling in spring systems, 2) a summary of the available literature related to biogeochemistry in Florida spring systems, and 3) a discussion of the needs and directions for future spring research.

The Literature: What is Known

- ***In springs and spring runs, biogeochemical processes occur in the water column, sediments and flood plains and can regulate the role of springs as a ‘source’ or ‘sink’ for nutrients and pollutants.*** The effect of biogeochemical processes on spring water

composition begins immediately upon emergence from the boil and continues throughout the entire length of a spring run.

- ***Key interfaces involved in elemental cycling in springs environments are biofilms, algal mats and hyporheic sediments zones.*** A variety of processes can occur in these zones of high microbiological activity including organic matter decomposition, nitrogen fixation, nitrification, denitrification, iron reduction, sulfate reduction, and associated processes involving phosphorus.
- ***Organic matter compositions and distributions greatly affect the variety and importance of biogeochemical processes*** especially those requiring anaerobic conditions (e.g., denitrification).
- ***There is a high likelihood that the effect of increased nitrate may be coupled to other nutrient levels*** (e.g., phosphorus or metals) or physico-chemical parameters (e.g., dissolved oxygen). Some of the observed association of increased nitrate with increased algal growth could be the result of other reactions occurring during groundwater emergence (e.g., sulfide oxidation and calcium carbonate precipitation).

The Literature: What is Not Known

- ***Because there are so few data characterizing the physical, chemical and microbiological conditions in most springs, it is extremely difficult to describe the exact nature and extent of biogeochemical reactions that are occurring in these systems.***
- ***There is little information to ascertain the involvement of other nutrient processes/cycles in controlling nitrate levels,*** including nitrate conversion and loss (e.g., iron and sulfur involvement in denitrification or alternative loss processes)
- ***Among the studies which could advance our understanding of springs as sinks, sources, and transformers of nutrients are:***
 - Expanding water quality data collection to include additional geochemical parameters (e.g., sulfide) could improve our ability to explain and predict individual spring responses to nutrients.
 - Increasing the frequency of water quality data collection (e.g., diel patterns) will offer additional insight into our ability to identify pathways (e.g., aerobic vs. anaerobic, phototrophic vs. heterotrophic) involved in spring processing/cycling of nutrients.
 - Basing the collection of water quality data on upstream and downstream locations of stream segments will improve our ability to understand processes and spring run characteristics contributing to nutrient uptake and transformation.
 - Characterization of sediments (e.g., nutrient storages, organic matter distributions, mineral composition) would enable better assessments of benthic and hyporheic

processes affecting current and future storages and fluxes of sediment nutrients (sediment memory).

- o Studies are needed to document the potential for aquatic plant management efforts to alter biogeochemical conditions (i.e., creating anoxic zones) and nutrient cycles (e.g., increasing denitrification loss of nitrate or increasing release of ammonium and phosphorus).
- o More studies are needed to document the involvement of individual system components in observed declines in nitrate with distance in spring runs (i.e., dilution vs. biotic uptake vs. denitrification).
- o More exploratory work is necessary to determine the existence and importance of novel pathways of nitrate conversion (e.g., anammox and lithotrophic nitrate reduction).

Chapter 4: Nutrient Effects on Spring Flora and Fauna

Many of Florida's springs and spring runs are enriched in nitrate due to broad-scale contamination of groundwater supplies, which fosters two primary and interrelated concerns regarding the effects on flora and fauna in spring systems:

- 1) high nitrate concentrations can promote eutrophication that can lead to a variety of changes in flora and fauna
- 2) high nitrate concentrations in Florida's springs and spring runs can affect fauna directly through toxicity.

The Literature: What is Known

- ***A eutrophication progression scheme suggests that increased nutrient delivery to aquatic systems may induce change***, by favoring production of fast-growing algae that ultimately out-compete and displace native vascular plants (see Duarte 1995).
- ***In some of Florida's spring systems, both the apparent proliferation of nuisance algae and the apparent decline of native vascular plants are consistent with the proposed eutrophication progression scheme***, which a cue that management actions are needed.
- ***In general, nutrients can affect the faunal assemblages in aquatic systems in three primary ways:*** 1) toxicity, 2) changes to trophic webs and 3) changes in habitats.
 - o Elevated concentrations of ammonia and nitrate can lead to increased mortality and sublethal effects.
 - o At this time, lethal effects are not an overwhelming concern in most spring systems.

- Toxicity needs to be factored into management of spring systems, especially given uncertainty factors that could be applied to most criteria
- The potential for changes in trophic webs and habitats, along with flow-on effects on faunal assemblages does exist.
- The form and magnitude of any changes are determined by complex interactions among bottom-up and top-down processes, such as grazing pressure, habitat use and predation pressure.
- The outcomes of ecological interactions clearly relate to sustainable management of spring systems

The Literature: What is Not Known

- ***There are few quantitative data that definitively link changes comprising the eutrophication progression scheme to increased nitrate loads in spring systems***
 - The eutrophication progression scheme predicts that nonlinear responses may have “decoupled” these systems from contemporary concentrations of nutrients in the water column.
 - Currently, patterns in the distribution and abundance of plants and algae do correlate with other physical and chemical parameters, such as light availability.
 - Little is known about the individual or combined effects of the various forcing factors or the form and strength of potential feedback mechanisms, including those linked to nutrient concentrations.
- ***There are no data to support rigorous evaluation of bottom-up and top-down influences on faunal communities***
 - Changes in faunal assemblages have not been linked to changes in vegetated communities and changes in grazer abundance have not been linked to changes in floral assemblages.
 - Sublethal effects of nitrate may not translate to effects on populations, assemblages or ecosystems.

Recommendations for Future Research

- ***Management of nutrients in spring ecosystems would benefit from compilation of inventories and collection of baseline data.*** Initial suggestions for discussion include inventories and baseline data collection designed to:
 - Measure nutrients, oxygen, carbon, light, flow, substrates, grazing, algae, plants, invertebrates, fish, and other key drivers and valued components of spring systems chosen with the best available information and, eventually, with guidance from the results of diagnostic studies.

- target systems where effectiveness of management can be assessed (e.g., systems with total maximum daily loads, minimum flows and levels, pollution load reduction goals, surface water improvement plans or basin management action plans).
- Sample synoptically or at spatial and temporal scales that support rigorous analyses of interactions (note that these inventories and baselines form the platform for adaptive management).
- Balance breadth with depth (e.g., optimize taxonomic detail and replication).
- ***Diagnostic studies focused on bottom-up and top-down interactions are also critical.***
Initial suggestions include the following recommended diagnostic studies to:
 - Determine assimilation of nutrients by flora as a key component of nutrient budgets, including assimilation by epiphytes, macroalgae, vascular plants and microphytobenthos or microalgae found in sediments.
 - Determine how nutrients and other drivers affect overgrowth, shading and other relationships among periphyton, macroalgae and vascular plants in an effort to ascertain the need for management actions, including aquatic plant management and restoration of native species.
 - Clarify limitations to growth of algae and plants by:
 - focusing on species of algae and plants that are hypothesized or known to play major roles in nutrient assimilation
 - including potentially limiting factors other than nitrogen and phosphorus and interactions among limiting factors that can significantly influence the outcomes of management (e.g., micronutrients, iron, oxygen, carbon, light, flow and substrate type)
 - exploring relationships and consequences across multiple levels of biological and ecological complexity, including uptake and other physiological responses, growth and reproduction of individual organisms, and ecological changes in populations or assemblages to promote the success of management actions at the system level (note that some of the key, large-scale relationships form the core of an adaptive management approach)
 - elucidating the direction, magnitude and form of limitations (e.g., nonlinear and nonreversible) to identify suitable targets and goals for management actions.
 - Identify and elucidate changes in composition and function of faunal assemblages related to changes in habitats in an effort to identify habitats to be protected or restored by management actions.

- o Determine palatability of flora to grazers, rates of grazing, and the form and magnitude of predation by primary consumers in an effort to identify flora, grazers and trophic links to be protected or restored by management actions.
- o Identify and elucidate the toxic effects of ammonia and nitrate beyond physiological and individual levels of organization (e.g., population and assemblage effects) in an effort to determine threshold levels, safety factors and the need for management actions.

Chapter 5: Ecosystem Implications of Invasive Aquatic Plants and Aquatic Plant Control in Florida Springs

Nonnative and nuisance plants such as water hyacinth, water lettuce, and hydrilla are a primary management concern in many Florida springs. In fiscal year 2005 – 2006, the DEP's Bureau of Invasive Plant Management spent approximately \$173,000 to control these plants in springs, primarily through the use of chemical herbicides.

This chapter reviews a broad range of literature to outline what is known and, in some cases, unknown about: 1) the history of these plants and their control in Florida, 2) the growth potential of the nonnative plants in springs as a function of elevated nitrate-nitrogen concentrations, 3) the social and ecological consequences of aquatic plant overgrowth, 4) the ecological risks associated with current aquatic plant control methods, and 5) the potential benefits of alternative aquatic plant management approaches in some springs systems. The following are the chapter's major findings and research suggestions:

The Literature: What is Known

- ***Major problems with nonnative plants in Florida began with the introduction of water hyacinth, into the St. Johns River in the late 19th century.*** Water hyacinth was documented in several springs ecosystem along the St. Johns River by the mid 1890s. Chemical control programs have maintained water hyacinth populations at low levels throughout Florida since the mid-1970s.
- ***Historical sightings by William Bartram indicate that water lettuce, a floating aquatic plant, has been present in a number of Florida springs since at least 1765.*** Scientists disagree as to whether water lettuce was present in Florida before European colonization, or was introduced by early Spanish settlers. Chemical control programs have maintained water lettuce at low levels throughout Florida since the mid-1970s.
- ***Hydrilla became established in several areas of Florida, including the Kings Bay/Crystal River springs complex, by 1960.*** Sustained control of hydrilla, a submersed aquatic plant, has proven more difficult than the floating plants in Florida. Most aquatic plant management costs in Florida springs ecosystems over 2005 – 2006 were associated with chemical control of hydrilla.

- **Observations from several springs suggest a “boom-bust” successional sequence in which nonnative plants first out-compete native plant communities, and then suffer catastrophic population crashes associated with aquatic plant control or natural disturbances.** Succession of springs into algal-dominated ecosystem states may be promoted by the nutrient pulses and ecological openings associated with the rapid loss of aquatic plant populations.
- **Water hyacinth and water lettuce emit allelopathic compounds capable of suppressing a number of algal taxa.** The effects of such allelopathic compounds on algal dynamics in springs ecosystem are not presently known.
- **Ecosystem surveys indicate that water hyacinth, water lettuce, and hydrilla provide attractive habitat for crayfish, apple snails, amphipods, fish, manatees, and other springs fauna at moderate levels of coverage.**
- **Observational accounts suggest that aquatic plant control activities may sometimes have significant adverse effects on springs fauna.** Depression of dissolved oxygen due to decaying biomass is a primary concern to animals following aquatic plant control. Copper and diquat herbicides also pose concerns in terms of direct toxicity to some animals at levels used for aquatic plant control.
- **Water hyacinth and water lettuce are currently being managed for algal-suppression, nutrient recovery, and biomass utilization in a number of tropical countries, including places in which they are considered nonnative.** Careful experimentation with similar ecosystem recovery methods may be worthwhile in highly degraded springs ecosystems where these plants are established.
- **Biotypes of hydrilla that are resistant to fluridone, a systemic herbicide commonly used for hydrilla control in Florida lakes, have been documented in recent years.** Thus, there is increased concern about the potential evolution of hydrilla strains that are resistant to Aquathol®, the contact herbicide most commonly used to control hydrilla in springs.
- **Establishment of selective biological control organisms is increasingly viewed as a priority for sustainable control of hydrilla in Florida.** A potential biological control for hydrilla, the hydrilla tip mining midge (*Cricotopus lebetis*), has been documented in Kings Bay/Crystal River, and may be suitable for experimental introduction into other springs systems.

The Literature: What is Not Known

- **Although scientific literature indicates clear relationships between nitrogen enrichment and increased growth of water hyacinth, water lettuce, and hydrilla in non-flowing aquatic systems, the few studies available for springs and other flowing waters have not definitively determined a concentration of nitrate-nitrogen in springs that would be limiting to any of the nonnative plants.** Nutrient assays in flowing water mesocosms would be necessary to develop nitrate-nitrogen limitation values for these plants in springs conditions.

- **Although the scientific literature suggests that copper and diquat herbicides can have significant adverse effects on algal community dynamics, these potential effects have not been well-studied in the specific context of Florida springs.** *Lyngbya wollei*, a filamentous cyanobacterium of great concern in many Florida springs, is notable for its relative resistance to these compounds as compared to other common algal and cyanobacteria taxa.

Chapter 6: Effects of Nutrients on Spring Ecosystems

There exists a wide-spread recognition of the environmental and economic importance of artesian springs in Florida. An ecosystem approach is essential to provide a greater understanding of the relative interactions between the myriad physical, chemical, and biological fluxes present in springs and their normal responses to rising nutrient levels. A focused and logical research agenda will be critical to pulling these precious but threatened natural resources back from their current declining path.

The Literature: What is Known

- ***The best evidence suggesting a decline in the health of Florida's spring ecosystems comes from studies that have been conducted over a half-century time period in Silver Springs.*** Both the direct measurements and the estimated system metabolism analyses indicate that the Silver Springs ecosystem may be considerably less productive than it was fifty years ago (Munch *et al.* 2006). The key findings from that study are:
 - *Sagittaria kurziana* remains the dominant submersed aquatic plant species in Silver Springs and represents one of the main physical features of the ecosystem.
 - Biomass estimates for submersed aquatic plants in the summer season were not significantly different from estimates made by Odum in the early 1950s. However, estimates for winter biomass were 31% lower than Odum's, who reported no seasonal difference in submersed aquatic plant biomass.
 - Biomass estimates for the epiphyte community in the summer were approximately three-fold higher than those reported by Odum, while winter values were not significantly different between the two studies.
 - The largest disparity between the Munch *et al.* (2006) estimates of primary producer community biomass and those of Odum from the 1950s was the substantial increase in biomass for the benthic algal mat community.
 - Total species richness for birds, fish, and reptiles in the Munch *et al.* (2006) study were similar to historical records at Silver River.

- Estimated annual average fish live-weight biomass in the Munch *et al.* (2006) study has declined in Silver Springs since Odum's study in the early 1950s by about 96%; and by 61% since Knight's 1978-79 study (Knight 1980).
- Annual average gross primary productivity (GPP) and community respiration declined 27% and 26% respectively in the period between the 1950s and today and net community production declined by about 59%.
- ***Recent studies of the Wekiva River and Rock Springs Run (WSI 2007a) (spring runs averaging 0.69 and 0.84 mg/L of nitrate nitrogen, respectively) found similar results as those observed at Silver Springs with significantly lower gross primary productivity and photosynthetic efficiency demonstrating an inverse correlation between rising nitrate concentrations and reduced aquatic ecosystem metabolism.***

The Literature: What is Not Known, with Emphasis on Future Research Directions

Despite a wide variety of springs' research, there remains a significant knowledge gap between the real and perceived threats that nitrate pollution plays on the ecology of spring ecosystems. In summary the following recommended applied research activities are suggested:

- ***Baseline data on ecosystem-level structure and response to key forcing functions, including sunlight, flow, and nutrient levels are lacking.*** Studies are needed that are fairly long-term (multiple years of repeated measures) and conducted over a representative sample of springs with a range of forcing functions including discharge rates, groundwater chemistry, nutrient concentrations, and recreational intensities;
- ***Community response to increasing nutrients under controlled conditions are lacking.*** We suggest the design of *in situ* complex (multi-species) mesocosm studies to allow replication of spring plant community responses to a range of nutrient conditions under realistic and relevant spring environmental conditions;
- ***Understanding of impacts and effects of management interventions are lacking.*** Whole-spring manipulation studies are suggested to test the effects of possible management techniques such as controlling levels of springshed nutrient loading, human recreational activities, alternative control methods for invasive species, and estimation of optimal consumer carrying capacities (*e.g.*, manatee density).

Chapter 7: Managing Nutrient Inputs to Florida Springs: The Legal Framework

The legal framework for managing the nutrient pollution of Florida springs is potentially as broad as the scope of human activities that contribute nutrients to the springshed. Regulations on the discharge of wastewater are key elements.

The Literature: What is Known

- ***The federal Clean Water Act provides a set of mandates and incentives for state programs.*** The focus of the Clean Water Act is protecting surface waters through the regulation of point source discharges under the National Pollutant Discharge Elimination System (NPDES). Discharges to groundwater may be regulated under this program if there is a “significant nexus” to the quality of navigable surface waters.
- ***The Safe Drinking Water Act (SDWA) protects public water supplies by establishing minimum criteria for drinking water quality and requiring states to regulate the underground injection of pollutants.*** Groundwater quality standards for nutrients are thus focused on the protection of public health. Florida has been delegated NPDES permitting authority by the Environmental Protection Agency (EPA) and implements an Underground Injection Control (UIC) program that is consistent with the SDWA. In addition, Florida regulates certain sources of nutrient pollution that do not fall within the direct jurisdiction of the federal program, such as nonpoint sources, agricultural discharges, and additional discharges to groundwater.
 - The regulatory program requires discharges to achieve effluent limitations based on the application of specified levels of technology or to achieve water quality standards, whichever is more stringent. Domestic wastewater treatment plants are generally only required to use secondary treatment, except in areas where the Legislature has required advanced wastewater treatment (AWT). Concentrated Animal Feeding Operations (CAFOs) are currently regulated under state rules pending the adoption by EPA of a new federal rule. Those stormwater dischargers subject to NPDES permitting are required to reduce the discharge of pollutants to the Maximum Extent Practicable.
 - Florida’s surface water quality standards must be reviewed and approved by EPA every three years. They consist of designated uses, narrative and numeric criteria for each of those uses, and moderating provisions.
- ***Waters designated as Outstanding Florida Waters (OFW) have a general limitation on their degradation.*** A narrative nutrient standard prohibits altering nutrient concentrations “so as to cause an imbalance in natural populations of aquatic flora or fauna.” Numeric standards can also be developed, most commonly as Total Maximum Daily Loads (TMDL).
- ***The TMDLs process begins with determining whether a particular waterbody is “impaired” and demonstrating it does not meet water quality standards for a specific criterion.*** If there is sufficient data demonstrating the concentration of the specific pollutant causing the impairment, it can be added to the verified list. A TMDL is then calculated and the load reasonably and equitably allocated to the various sources and basins contributing pollutants. A Basin Management Action Plan (BMAP) is developed for implementing the adopted TMDL.

- ***Stormwater is a significant source of pollutants that can be regulated as a point source, because much of it is collected into pipes or channels, or as a nonpoint source, because much of it comes from diffuse sources and activities.*** The NPDES program regulates many of the larger stormwater systems and stormwater associated with industrial activities. Systems subject to NPDES permitting must be periodically reviewed and ways to reduce pollution must be considered in permit renewals.
- ***Most stormwater systems in Florida are either unpermitted or regulated under an Environmental Resource Permit program.*** Although they must be operated and maintained, there is no program for periodic review for compliance or enhancements.
- ***Septic tanks and other Onsite Treatment and Disposal Systems (OSTDS) are another major potential source of nutrient pollution.*** The Department of Health has adopted regulations for the construction and siting of septic tanks and drainfields. In some areas where nutrients are a concern, such as the Florida Keys, performance-based systems have been required. Local governments can adopt more stringent requirements.
- ***Local governments are required to periodically revise and implement comprehensive plans that can provide a framework for local springs protection.*** Local comprehensive plans and land development regulations can limit the intensity and design of land development to limit the contribution of nutrients to springs. They can provide for improved stormwater and wastewater management.
- ***The Florida Legislature may require special protections or enact other legislation that could protect springs and springsheds.*** The Legislature has specifically required local governments in the Wekiva Study Area to amend their comprehensive plans to enhance springs protection. It has also limited the ability of local governments to regulate agricultural land uses and the conversion of agricultural land to urban uses. A Consumer Fertilizer Task Force has recommended new restrictions on the ability of local governments to regulate the application of fertilizers.

Chapter 8: Synthesis of Nutrients and Springs: Knowns, Unknowns, Research Priorities and Management Implications

This chapter represents a synthesis of the most important findings; greater details can be found within each of the chapters.. This synthesis chapter is organized into three parts:

- 1) a summary of the “knowns” regarding nutrient effects on springs and spring biota,
- 2) the unknowns and suggestions for future research, and
- 3) suggestions for a research and adaptive management program for spring ecosystems in Florida.

Part 1: NUTRIENTS and SPRINGS: State of the knowledge

There is growing evidence that nitrate concentrations are increasing in the water discharging from springs. Given the importance of nitrate-N and its role as a driver of primary production in

many aquatic systems, N appears to be the aspect of springs that has received the most study. Chapter 8 summarizes the current state of knowledge concerning nutrients in springs.

PART 2: SPRINGS RESEARCH PRIORITIES

Our review of the available literature has shown that we do not have a systematic understanding of historic changes, fundamental processes, or mechanisms of ecosystem function sufficient to definitively manage springs and their contributing areas. Summarized in previous sections of this Executive Summary are topic areas in need of research related to spring and the effects of nutrients and other stressors on spring biota.

Overall we propose a rather holistic research agenda that includes diagnostic studies, paired comparative studies of springs, manipulation studies, and fine grained monitoring to elucidate cause and effect relationships and to test various hypotheses regarding the impacts of stressors on spring ecosystems and biota. In particular we suggest:

- that a number of smaller springs be selected that represent a variety of stressors acting separately and in combination as a means of testing various hypotheses regarding the impacts of stressors on spring ecosystems and biota. Tests might involve, for instance, choosing springs with low versus high DO, presence and absence of grazers, low versus high nitrate-N, absence versus presence of recreation and so forth; then changing environmental conditions such as nitrate-N concentrations or DO concentrations in springs to support grazers, etc
- a relatively intense monitoring campaign in a like number of springs that is designed to elucidate spatial variability and temporal dynamics of stressors and impacts.

Sustaining this long term research program will require a sustained source of funding. We suggest a simple source of funding, tied directly to the resource that is not a tax, but rather is a contribution for springs research.

- One-cent per bottle of water sold in Florida contributed for spring research will raise up to \$21 million per year.
- Companies who contribute will use the contribution as a marketing tool with a green sustainable water logo on each bottle.

PART 3: RECOMMENDATIONS for SPRINGS POLICY and MANAGEMENT

Florida's springs are important, unique resources and are under considerable pressure from changes in environmental drivers, direct human use, and indirect alteration of their chemical and physical environment.

- Our ability to understand causality between stressors and indicators in spring ecosystems is not sufficient to allow a fine grain approach to management.

- The complexity of the issues as well as the complexity of the springs' social ecological system, comprised of a multitude of actors from microbes to state government, requires an ***Adaptive Management*** (AM) approach.
- An AM approach required are new institutions and institutional frameworks as well as new science and experimental frameworks. We propose the creation of up to 6 ***Adaptive Springshed Action Programs*** (ASAPs).
- The proposed ASAPs build on the Springs Working Groups model by developing overall management goals and objectives, and then initiating a round of management interventions to test hypotheses concerning the causes of current apparent declines in spring ecosystem condition.
- The social framework of the ASAP team should include a tripartite of individuals from government, science, and the citizenry at large.
- Research within the AM context is designed for the purpose of producing results that may be applied to and answer management questions.
 - It must be able to operate under conditions of complexity, uncertainty and risk, and generally be applied over large spatial and temporal scales.
 - AM research crosses many ecological and organizational boundaries increasing its complexity and the lead time required for accomplishing its objectives
- The research within each of the ASAPs should ultimately be formulated by their participants, as they each have their particular ecological issues, management potentials, and socio-economic constraints.

TABLE OF CONTENTS

Chapter 1 - Springs as Ecosystems	1
Summary	1
INTRODUCTION TO FLORIDA SPRINGS	1
Background.....	1
Springs as Ecosystem Laboratories	3
Spring Stability and the Evolutionary Time Scale.....	4
SPRINGS ECOSYSTEM DIAGRAMS	5
Global/Regional Scale	5
Springshed Scale.....	5
Spring Scale	9
ENVIRONMENTAL FORCING FUNCTIONS.....	13
Solar Inputs	13
Atmospheric Forcing Functions.....	15
Groundwater Inputs	16
Anthropogenic Forcing Functions	20
ENERGY/MATERIAL STORAGES IN SPRINGS	22
Spring Basin/Spring Run	22
Water and Dissolved Constituents	24
Primary Producers.....	25
Primary Consumers.....	27
Higher-Level Consumers	29
Decomposers.....	29
Spring Biomass Pyramid.....	30
ECOSYSTEM-LEVEL PROCESSES.....	31
Primary Productivity	31
Community Respiration	34
Productivity/Respiration Ratio.....	34
Photosynthetic Efficiency	34

Community Export.....	35
Pollutant (Nutrient) Assimilation.....	35
Secondary Productivity	35
HUMAN AND AESTHETIC USES	36
Recreational Uses.....	37
Visitation Seasonality	38
Visitation Numbers	39
Economic Impacts.....	42
Effects of Recreation on Spring Ecosystems	42
Human Use Carrying Capacity	43
DISCUSSION	44
REFERENCES	46

Chapter 2 - Springshed Nutrient Loading, Transport and Transformations.. 53

Summary	53
The Literature: What is Known	53
The Literature: What is Not Known, with Emphasis on Future Research Directions	54
INTRODUCTION	57
HYDROGEOLOGY	61
Hydrology in a Karst Environment.....	61
Typology of Florida's Springs	65
Springshed Delineation.....	67
Hydrogeology and Nutrient Loading.....	73
Assessing Aquifer Vulnerability.....	74
Timescales of Water and Nutrient Fluxes.....	75
TRENDS IN WATER QUANTITY AND QUALITY	77
Water Quantity.....	77
Nitrogen	79
Phosphorus.....	85
Carbon.....	87
Other Water Quality Parameters.....	89

SOURCES OF NUTRIENTS	92
Nitrogen	92
Natural Sources.....	94
Inorganic Sources.....	95
Organic Sources	99
Isotope Tracing of N Sources	101
Synthesis of N Springshed Budgets.....	104
Phosphorus.....	107
Carbon (BOD).....	108
Other Water Quality Parameters.....	109
SINKS AND TRANSFORMATIONS OF NUTRIENTS	110
Nutrient Sinks in Karst Landscapes.....	111
Nitrogen	111
Phosphorus.....	113
Carbon.....	114
Other Water Quality Parameters.....	114
Springshed nutrient budget – Synthesis of Sinks.....	114
UNKNOWNNS AND RESEARCH PRIORITIES	118
Hydrologic and Geochemical	118
Nutrient Loading.....	118
Subsurface Nutrient Processing	119
REFERENCES	121

Chapter 3 - Biogeochemical Processes and Implications for Nutrient Cycling

.....	135
Summary	135
The Literature: What is Known	135
The Literature: What is Not Known	136
INTRODUCTION	137
SPRING ENVIRONMENT	137
Spring water chemistry	137

Reactive Zones.....	139
Biofilm	140
Benthic Algal Mats	141
Sediments	142
BIOGEOCHEMICAL PROCESSES.....	144
Carbon.....	144
Carbon Sources	144
Decomposition	145
Nitrogen	148
Biological Nitrogen Fixation	149
Nitrogen uptake.....	150
Nitrogen mineralization	151
Denitrification	152
Alternative N pathways.....	153
Overall N Cycle	156
Phosphorus.....	156
Forms of phosphorus in water column and sediments.....	157
Mineralization of organic phosphorus	159
Biotic and Abiotic Ca Interactions.....	160
Biotic and Abiotic Fe Interactions	161
Overall P Cycle	162
Sulfur.....	162
Sulfide Oxidation	162
Sulfate Reduction.....	163
Overall S Cycle	164
EFFECTS OF INCREASED NUTRIENTS	164
Carbon/Organic Matter Impacts	164
Nitrogen Impacts.....	164
Phosphorus Impacts	165
Sulfur Impacts.....	166
SUMMARY AND CONCLUSIONS	166

Management and Policy Implications.....	167
RESEARCH NEEDS.....	168
Specific Research Recommendations.....	168
Biogeochemical Characterization.....	168
Source and Fate of N.....	169
Carbon Dynamics.....	169
Sulfur Distribution and Function.....	170
Coupled Biogeochemical Cycles.....	170
REFERENCES.....	171
 Chapter 4 - Nutrient Effects on Spring Flora and Fauna.....	 179
Summary.....	179
The Literature: What is Known.....	179
The Literature: What is Not Known.....	179
Recommendations for Future Research.....	180
INTRODUCTION.....	182
Nitrate as a Compound of Concern.....	183
PRIMARY PRODUCERS IN SPRING ECOSYSTEMS AND FACTORS AFFECTING THEIR ABUNDANCE AND DISTRIBUTION.....	183
Light.....	184
Carbon and Oxygen Balance in Macrophytes.....	186
Stream Velocity and Substrate.....	187
Nutrients.....	188
Community Responses to Increased Nutrients.....	192
EFFECTS OF NUTRIENTS ON FAUNA.....	194
Components of Spring Ecosystems.....	195
Relationships Between Nutrients and Invertebrates in Florida Springs.....	196
Relationships Between Nutrients and Fish in Florida Springs.....	200
Summary of Relationships Between Nutrients and Fauna in Florida Springs.....	207
Nutrient Effects Operating Through Ecosystem Processes.....	207
Nutrient Effects Operating Through Toxicity.....	210

Toxicity of Ammonia.....	211
Toxicity of Nitrate.....	213
Summary of Nutrient Effects on Fauna in Springs.....	217
RESEARCH TO IMPROVE MANAGEMENT OF NUTRIENTS IN SPRINGS	218
REFERENCES	220

Chapter 5 - Ecosystem Implications of Invasive Aquatic Plants and Aquatic

Plant Control in Florida Springs.....	231
Summary.....	231
The Literature: What is Known	231
The Literature: What is Not Known, and Recommendations for Future Research	232
INTRODUCTION	234
Major Invasive Aquatic Plants: History and Control in Florida.....	235
Water Hyacinth	235
Water Lettuce.....	239
Hydrilla	240
NITRATE-NITROGEN AND NONNATIVE PLANTS IN SPRINGS.....	242
Water Hyacinth and Nitrogen Limitation	242
Water Lettuce and Nitrogen Limitation.....	244
Hydrilla and Nitrogen Limitation	244
NONNATIVE PLANTS AND ALGAL COMMUNITY DYNAMICS	245
Boom-Bust Hypothesis	245
Allelopathy Hypothesis.....	247
AQUATIC PLANT CONTROL AND ALGAL SUCCESSION	248
Herbicide Selection Hypothesis.....	248
Copper.....	249
Diquat.....	249
Endothall	250
Glyphosate	250
2,4-D	251
Attractor – Catastrophe Hypothesis.....	251

Habitat Values of Water Hyacinth.....	251
Habitat Values of Water Lettuce and Hydrilla	253
Non-Target Concerns.....	254
RECOMMENDATIONS FOR FURTHER RESEARCH	256
Alternative Management of Floating Plants	258
Alternative Management of Hydrilla	259
CONCLUSION.....	260
REFERENCES	261
 Chapter 6 – Effects of Nutrients on Spring Ecosystems	271
Summary	271
ECOSYSTEM STRUCTURE	273
Primary Producers.....	273
Algae	274
Vascular Plants.....	279
Primary Consumers.....	280
Invertebrates.....	280
Vertebrates	280
Secondary Consumers.....	281
Fish.....	281
Higher-Level Consumers	281
Humans	282
ECOSYSTEM FUNCTION.....	282
Community Metabolism	282
Gross and Net Productivity	283
Respiration	287
Productivity/Respiration Ratio.....	287
Photosynthetic Efficiency	287
Community Metabolism Conclusions.....	288
HUMAN AND AESTHETIC USES	289
Visitor Satisfaction.....	289

Economic Impacts.....	289
Effects of Eutrophication on Human Recreation	289
DISCUSSION	290
RECOMMENDATIONS FOR FURTHER RESEARCH	296
Proposed Research Priorities	297
Recommendations.....	298
REFERENCES	299

Chapter 7 - Managing Nutrient Inputs to Florida Springs: The Legal

Framework	305
Summary	305
REGULATION OF DISCHARGES.....	307
Clean Water Act.....	307
State Discharge Permitting	309
Domestic Wastewater	310
Industrial Discharges and Concentrated Animal Feeding Operations (CAFO).....	311
WATER QUALITY STANDARDS.....	312
Groundwater Quality Standards.....	312
Surface Water Quality Standards.....	313
TOTAL MAXIMUM DAILY LOADS	315
Impaired Waters.....	316
The Verified List.....	317
Calculation and Allocation	317
Basin Management Action Plans (BMAP).....	318
STORMWATER.....	319
NPDES Stormwater Permitting	321
SEPTIC TANKS.....	321
LAND USE PLANNING AND REGULATION	322

Chapter 8 - Synthesis of Nutrients and Springs: Knowns, Unknowns,

Research Priorities and Management Implications	327
Summary	327
INTRODUCTION	329
PART 1 - NUTRIENTS and SPRINGS: State of the knowledge.....	329
Fate, Transport, and Transformation: <i>What we know</i>	329
Effects of Nutrients on Spring Organisms and Systems: <i>What we know</i>	331
Effects on Flora and Fauna	332
Effects on Invasive Plants and Invasive Plant Effects on Springs.....	334
Ecosystem Scale Effects	334
The Legal Framework.....	335
PART 2: SPRINGS RESEARCH PRIORITIES	336
Nutrient Fate, Transport, and Transformation: <i>What we don't know</i>	336
Nutrient Effects on Flora and Fauna: <i>What we don't know</i>	338
Invasive Plants and Springs: <i>What we don't know</i>	338
Ecosystem Scale Effects: <i>What we don't know</i>	339
Summary of Research Recommendations	340
PART 3: RECOMMENDATIONS for SPRINGS POLICY and MANAGEMENT	341
The Springs Initiative: Protecting Florida's Springs	342
Adaptive Management: An Approach to Springs Protection	343
A Tragedy of the Commons.....	343
Managing in the Face of Uncertainty.....	344
Adaptive Springshed Action Programs (ASAPs)	344
Adaptive Spring and Springshed Research.....	347
REFERENCES	349

Springs as Ecosystems

Robert L. Knight,^{1, 2} and Sky K. Notestein¹
¹ Wetland Solutions, Inc.

² Department of Environmental Engineering Sciences, University of Florida

Summary

Springs and spring runs represent a unique class of aquatic ecosystems typified by high water clarity and relatively constant water temperature and chemical conditions. Structurally, springs are best characterized by their basin morphometry (shape and volume), their position in the landscape, and their flora and fauna. A classic aquatic food web and biomass pyramid in spring ecosystems includes numerous primary producers and smaller numbers of primary and secondary consumers. Research has demonstrated that in their natural state, many springs are highly productive and persist in an approximate steady-state compared to most other aquatic ecosystems. During the past two centuries humans have been exerting an increasing variety of stresses on spring ecosystems in Florida. These external and internal stresses include decreasing groundwater supplies and increasing levels of nutrients, extensive recreational disturbance, and management alterations. Due to their physical and biological complexity combined with their adaptations to provide optimal levels of system productivity, a holistic ecosystem-level approach to spring studies is necessary to provide a greater understanding of anthropogenic effects (such as nutrient enrichment) on spring ecosystems. Development of a management strategy for springs will be dependent upon a better understanding of the relative importance and synergism of direct stressors at the local level and indirect stresses that occur at the regional scale. Systems-level metrics have promise for providing a better understanding of the properties that many springs have in common. Use of ecosystem-level information is expected to provide a more sensitive indicator of the response of springs to nutrient increases and concurrent alterations due to the myriad other anthropogenic stresses.

INTRODUCTION TO FLORIDA SPRINGS

Background

Springs and their associated spring runs are a unique class of aquatic ecosystems. Since their principal water source is groundwater, many springs have water that is crystal clear, yet rich with dissolved nutrients and gases. Often this water quality provides the basis for a diverse assemblage of aquatic flora and fauna whose productivity is primarily determined by light availability and secondarily affected by the availability of macro and micro nutrients and by the ambient groundwater temperature. Additional factors that may affect spring productivity include external forcing functions such as diffusion of atmospheric gases, rainfall inputs of water and nutrients, immigration of fauna, and anthropogenic perturbations.

The large number and diversity of springs in Florida represents a globally significant concentration of these ecosystems. It is likely that many of the larger springs ecosystems have been in existence for approximately 15,000 to 30,000 years, since the end of the last major ice age (Martin 1966, Munch *et al.* 2006). This extended time period has allowed the evolution of highly adapted plant and animal communities.

Springs represent an important resource for human utilization as well, both by indigenous peoples as supported by archeological evidence, and by present day populations who utilize them for a variety of recreational purposes (Scott *et al.* 2002). There is little doubt that the intrinsic aesthetics of clear, cool water vigorously emanating from the underground will continue to interest and fascinate humans. Many of Florida's oldest tourist attractions (*e.g.*, Weeki Wachee mermaids, Homosassa fish bowl, and Silver Springs glass bottom boats – see Figure 1) utilize spring ecosystems as their main draw. In addition, numerous spring boil areas have been modified to facilitate swimming, recreation, and even “health spas”. Today all of the largest springs in Florida, whether privately or publicly owned, are managed as recreational parks, which, in turn, attract a large number of visitors and generate many millions of dollars in revenue on an annual basis. Correspondingly, many springs have suffered declines (often unintentional) in their condition (*e.g.*, up-rooting of vegetation, bank erosion, litter, etc.) due to visitation by ever increasing numbers of people.

However, over the last two decades other more serious factors, with the potential to permanently alter Florida's spring ecosystems, have been increasingly recognized. Two of the most apparent anthropogenic factors that may be causing significant changes in spring ecosystems are: 1) the reduction in groundwater supply through consumptive human withdrawals; and 2) the simultaneous pollution of groundwater, principally with nitrate-nitrogen, resulting from human land use changes, cultural practices, and general population growth. The full spectrum of the combined effects associated with flow reductions and nutrient enrichment on spring ecosystems is not yet clear. However, there is justifiable concern for potential negative consequences due to the obvious degradation of other aquatic habitats worldwide subjected to declining flows and water levels, and increased nutrient loading. The potential consequences of nutrient enrichment in springs include an increase in opportunistic primary producers and organic matter deposition, an increase in nuisance algae species biomass, a decrease in plant and animal productivity and diversity, a reduction in water quality and not insignificantly, a reduction of the aesthetics these ecosystems have long provided. Clearly, an effort to synthesize the current state of knowledge concerning the effects of nutrient pollution on spring ecosystems is warranted. It is in this context that this project began.

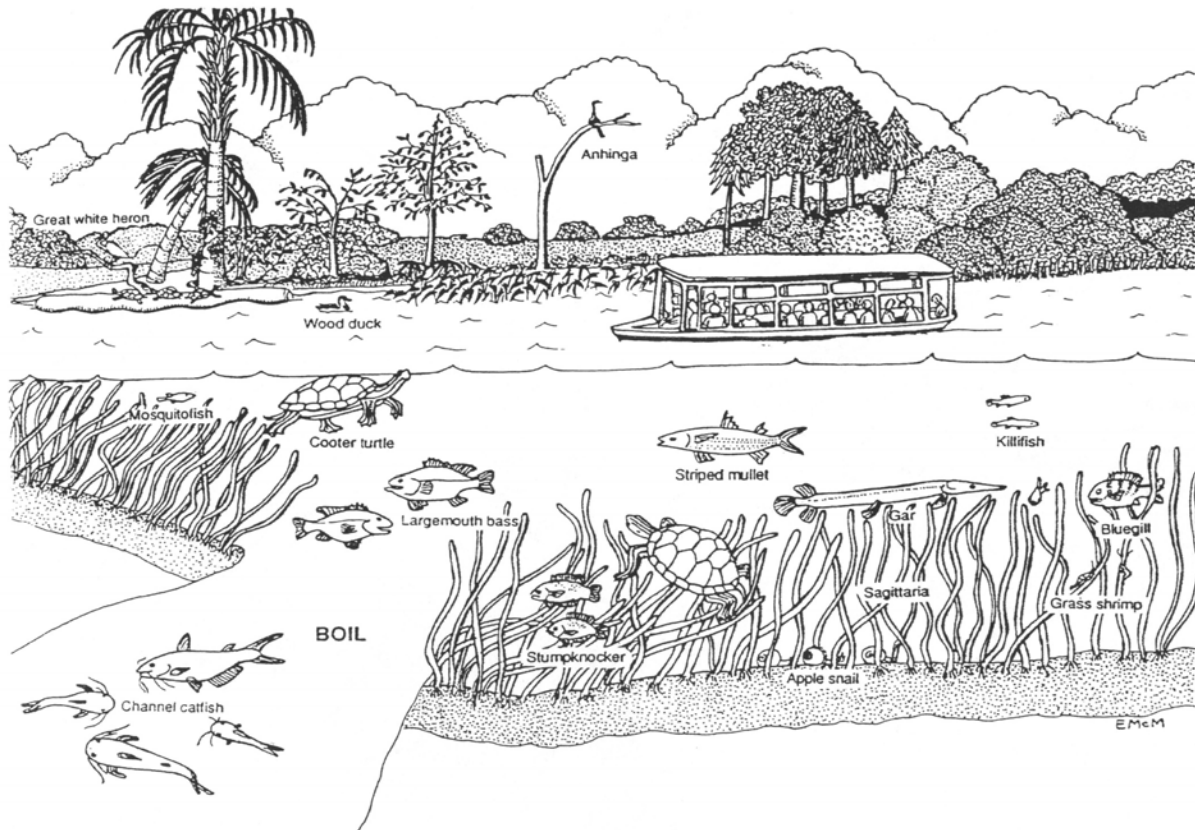


Figure 1 – An artist’s representation of life in Silver Springs at the time of H.T. Odum’s 1957 landmark study (illustration by Elizabeth A. McMahan, from Odum et al. 1998).

Springs as Ecosystem Laboratories

Spring ecosystems have been the focus of some notable ecological studies, due to their diverse flora and fauna, and because their stable environmental characteristics generate natural controlled settings suitable for general ecological research. Springs research is broad and varied, ranging from descriptive classifications based on water discharge and chemistry, to observations of endemic flora and fauna, to studies of community ecology through whole system measurements. Some attempt has been made to use the term “Crenobiology” (derived from *creno*, the Greek root for spring) as a banner for “the study of life in springs” (Botosaneanu 1998).

The study of community ecology generally follows one of two methodologies. The first, the “reductionist” method, in which single species and their associated ecological controls are studied, in turn may be combined with other species-centric studies to assemble a working community model. This approach is generally limited to the study of dominant species, and even if multiple components are quantified and combined, the resulting sum of the parts is unlikely to represent a functional community. The second method, the “holistic” or “systems-level” approach, attempts to study the community in its entirety. The major challenge to the holistic approach is the concern that not enough useful information is obtained concerning the fate of

individual species and resources that might be of greatest practical interest to managers and the public. Clearly, a comprehensive knowledge of ecosystems can only be obtained using both holistic and reductionist studies. A central thesis of this chapter is that our understanding of spring ecology and how to apply effective management and protection to spring ecosystems should be based on both types of studies together.

Spring ecosystems (or, simply springs), are highly suitable for the study of community ecology and ecosystem function at a holistic level. This is because the external forcing functions that determine spring structure and function are more stable than for many other aquatic ecosystems. This environmental stability, in turn, results in less temporal complexity in springs than in other aquatic ecosystems and more consistent food webs based on relatively stable groups of primary producers. In addition, springs offer a range of different community structures as a response to their differences in physical and chemical condition, creating a natural experiment with which to relate ecosystem function.

Another important reason to study spring ecosystems is that springs provide an opportunity to characterize the groundwater upon which humans are so dependent. A better understanding of land use changes and their resulting effects on groundwater quantity and quality changes has emerged through the study of springs (Munch *et al.* 2006; Cohen 2007). An appropriate analogy that supports the need for increased emphasis on springs monitoring and ecological research is that these environments are comparable to the “canary in the cage” used to warn coal miners of impending disaster. Florida needs a greater focus on ecological research and monitoring to gain a better understanding of just how much ecological risk already exists due to the nutrient enrichment and eutrophication of our formerly pristine springs.

Spring Stability and the Evolutionary Time Scale

The concept of springs as stable-state ecosystems likely originated during the early 1950s from observations made by collaborating naturalists from the University of Florida, including D.K. Caldwell, J.H. Davis, D. Natelson, H.T. Odum, W.C. Sloan, L.A. Whitford, and J.L. Yount. During this time, these and other researchers were intensively surveying the larger springs of Florida to describe the flora and fauna found there and in recognition that these ecosystems could serve as ideal sites for experimental studies. In a report summarizing work completed during 1953, H.T. Odum states that community metabolism, temperature, and major chemical constituents are “essentially constant” (Odum *et al.* 1953). The steady-state concept of springs was further expanded by Whitford (1956) in his observations that discharge, temperature, gas, and mineral content of spring waters were all relatively constant within individual spring ecosystems (although quite different between springs) and that only light varied greatly as a consequence of temperate latitudes. In his landmark paper ***Primary Production in Flowing Waters*** (1956) Odum uses the term “chemostatic” to describe Silver Springs and to propose that spring ecosystems can be studied as quasi steady-state systems. The stability of spring ecosystems must also be viewed in context of larger time scales, such as evolutionary or geologic time scales. The stability of Florida’s springs can extend only back in time to, at most, the last ice age (~ 15,000 to 30,000 years before present) when sea levels were dramatically lower. Yet, there are no other ecosystems outside of the tropics and the ocean that have had such a long period of relatively constant external forcing functions and resulting community adaptation.

As dynamic entities composed of physical, chemical, and biological components and fueled by a variety of external energy flows, springs and spring runs have all the qualifications required to be considered as “ecological systems” or ecosystems. Hence, this chapter provides an overview of Florida’s artesian springs and spring runs as ecosystems, with an emphasis on describing their system-level properties. This systems approach is in contrast to the more common descriptions of aquatic ecosystem structure as defined by individual water quality parameters or plant and animal species lists. When available, additional information from springs and spring run ecosystems from other localities in the United States and elsewhere is utilized to emphasize, enhance, or contrast information from Florida springs throughout this chapter.

SPRINGS ECOSYSTEM DIAGRAMS

Spring and spring run ecosystems are products of their environments and may be evaluated by considering their surroundings and their relationship with this environment. Appropriate scales for consideration of springs are global, regional, and local. Examples of how each of these scales affects spring ecosystems are provided below.

Global/Regional Scale

Florida’s springs are a part of the global and continental environment and economy. Their location between north latitudes 30.8 and 27 (decimal degrees) puts them in the southern temperate zone of North America, an area rich in rainfall and groundwater, influenced by moderate temperatures, and subject in more coastal areas to salt water influences. As global and national economies influence land use changes in this region of Florida, springs are affected. For example, agricultural products in the Suwannee River area of Florida include dairy products and row crops, both industries that are subject to regional market factors. These land uses, in turn, alter spring hydrology and water quality through their irrigation requirements and increased loads of nitrogen and other pollutants to underlying groundwater.

A second regional influence on spring ecology results from their unique aesthetic and recreational opportunities for humans. Several of Florida’s springs are economic engines, attracting a high rate of international and interstate visitation (5% and 31.5% of visitors, respectively, Bonn 2004). These visitors spend money that fuels local economies that have the potential to affect the springs’ ecologies through mechanisms such as groundwater pumping, increased surface water runoff pollutant transport, and the direct and indirect effects of recreational use and aquatic weed control.

Springshed Scale

The life-blood of Florida’s springs is groundwater, principally derived from the Floridan aquifer which is largely supplied by regional rainfall. The quantity and quality of this groundwater determines the basis for much of the aquatic ecology of Florida’s springs. Just as surface water features rely on a watershed, springs are dependant upon their “springshed”, the area of land that constitutes the majority of their source of water to the aquifer, and can also be called the capture zone, catchment basin, or contributory area.

Figure 2 illustrates the springshed delineations of many of Florida's largest spring ecosystems. These springshed delineations are held by the Florida Geological Survey (FGS) and were produced using multiple methods using many data sets including surface water and ground-water flows, potentiometric levels, subsurface conduit maps and dye trace studies and many other hydrogeologic information (FGS 2007). The inset portion of Figure 2 shows an image of the Ichetucknee Springs springshed located in north central Florida. A large number of anthropogenic activities within this springshed have the potential to affect the ecology of these springs.

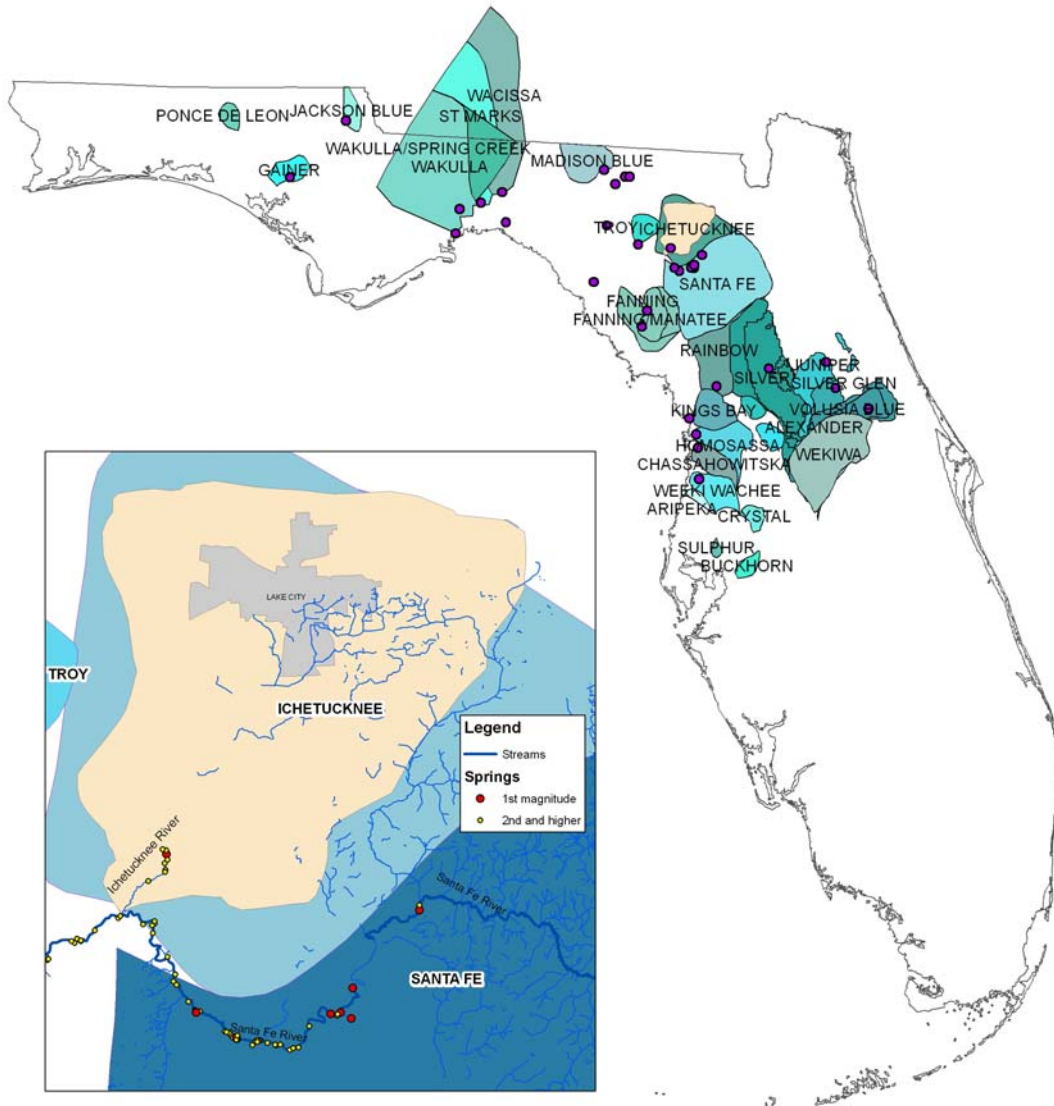


Figure 2 – Florida springshed delineations, with an inset of the Ichetucknee springshed in North Central Florida (FGS 2007).

The symbolic “energese” language of H.T. Odum is shown and briefly defined in Figure 3a, while Figure 3b represents a conceptual diagram that illustrates the linkage between terrestrial ecosystems, developed land uses, and groundwater within a Florida artesian spring at the

regional scale. The diagram includes the major forcing functions of sunlight, atmospheric inputs (wind, rain, and storms), with associated water and nutrients, and economic drivers (tourism, markets, and goods) interacting with developed land use changes. This conceptual energy diagram focuses on flows of nitrogen and energy, with counter flows of money for those pathways mediated by human activities. Variables in the diagram include: natural lands and low intensity land uses that do not receive significant inputs of nitrogen from anthropogenic uses; developed lands that include all other land uses; the water and nitrogen associated with the natural and developed lands; the artesian groundwater within the basin; and the physical and biological structure of a spring. Key system-level exports in the diagram include evapotranspiration, outflows of goods (recreational services), and downstream exports of water and organic material.

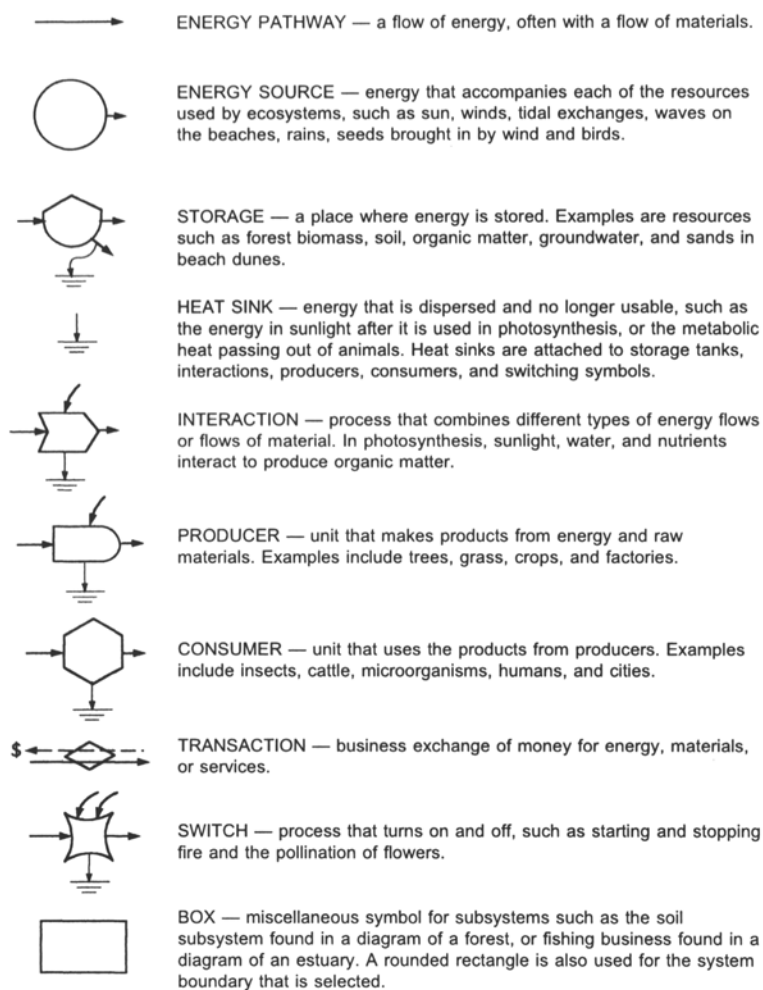


Figure 3a – Energy symbols in the “Energeses” model language, from Odum et al. (1998).

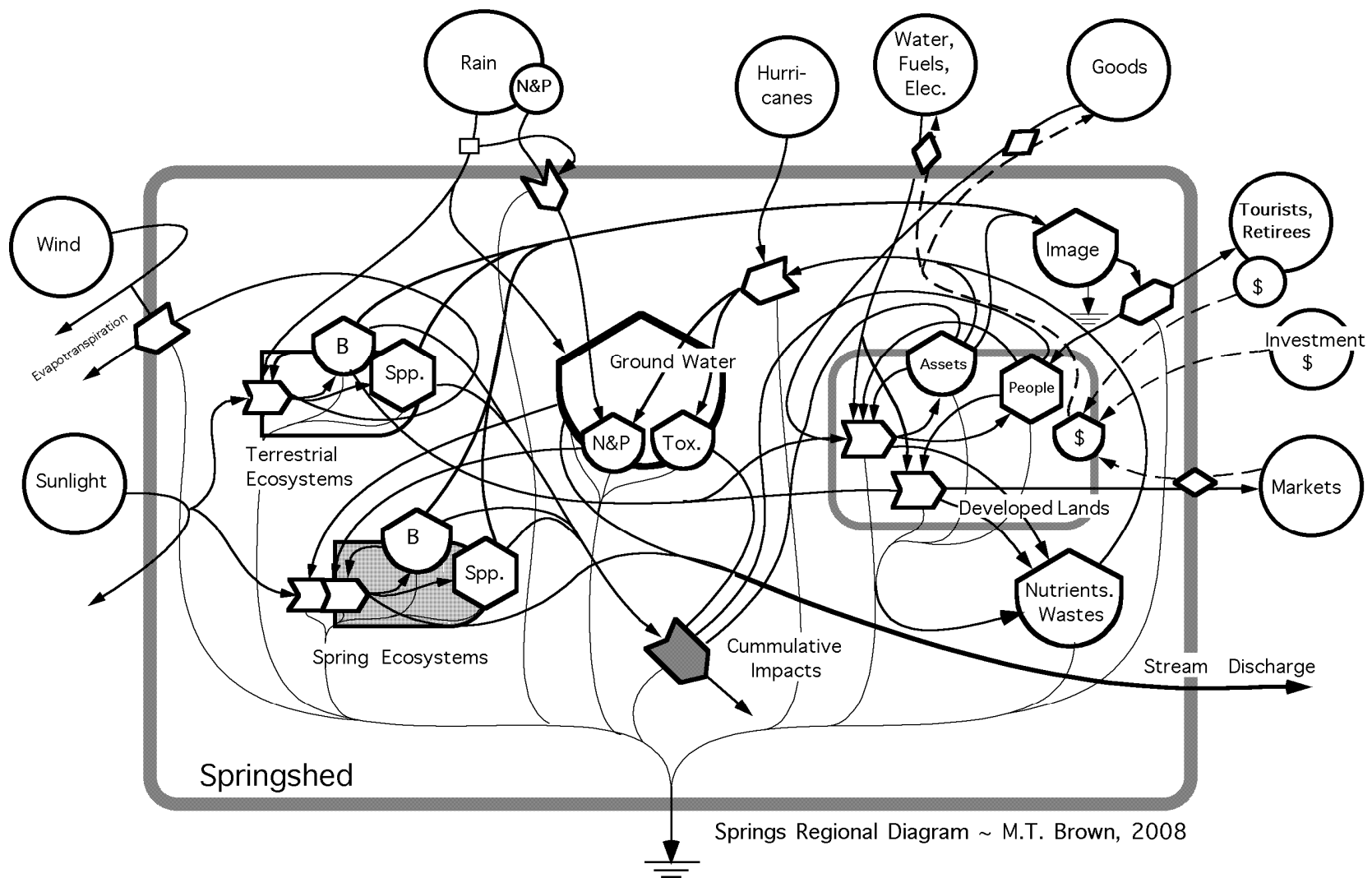


Figure 3b – Conceptual springs regional diagram (M.T. Brown 2008). Key forcing function at the regional scale include: sunlight, wind, precipitation, and associated nutrients, hurricanes, and human goods and services. Springsheds are in turn influenced and modified by their associated undeveloped and developed terrestrial environments with fertilizer and waste nutrient inputs and cumulative synergistic impacts resulting from consumptive water uses, recreation, and various resource management activities.

Documentation of the effects of regional land use changes in springshed basins on water quality changes in major springs (especially nitrate concentrations) has substantially improved in the past five years (Munch *et al.* 2006; Cohen 2007). Munch *et al.* (2006) conducted a detailed evaluation of land use changes in a five-mile radius around Silver Springs and nitrate concentrations in the Silver Springs system. This analysis found that approximately 75% of the water discharging from Silver Springs originates within a two-year capture zone contained in a 6.4 km (4-mile) radius around the spring covering about 135 square km (52 square miles). Analysis of aerial photos taken during the past fifty years suggests that land cover within the two-year capture zone has changed from a predominantly natural landscape to a mostly urban/agricultural area. This change corresponds to increased nitrogen loading, principally as a result of increased groundwater nitrate concentrations. Figure 4 provides another example of the observed correlation between increases in human population and increases in nitrate concentration of the ground water discharging from Weeki Wachee Spring in Hernando County.

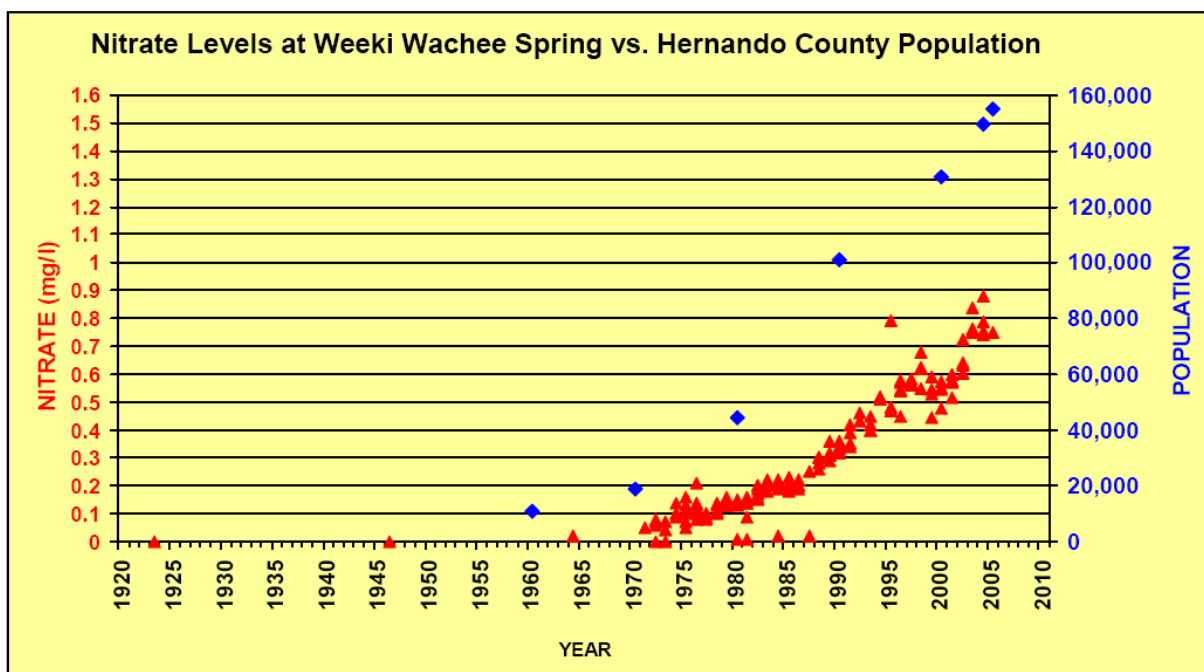


Figure 4 – Population growth (diamonds) in Hernando County, Florida and nitrate nitrogen concentration (triangles) at Weeki Wachee Spring from 1923 to 2006 (from DEP 2006).

Spring Scale

Springs in Florida occur where the underlying aquifer is at or near the surface allowing groundwater with net positive head pressure to be discharged. Springs are also found where surface water features have incised into the underlying karst geological formations. Many of Florida's springs are found along the banks or the bottom of streams, and are therefore integral components of larger stream systems.

A typical spring ecosystem exhibits a large amount of physical, chemical, and biological complexity. The proximal external factors affecting this complexity are sunlight, artesian

groundwater inputs, biological exchanges, and human activities. In general, a spring ecosystem includes all the internal abiotic and biotic components typical of most aquatic ecosystems including: aquatic macrophytes (higher plants) that support a diverse assemblage of attached algae (periphyton, benthic algae, and pseudo-plankton), detritus (dead plant and animal material generally associated with benthic organic sediments), associated animals feeding on detritus, and a faunal food web of herbivores, omnivores, and carnivores. Because of their continuous discharge, springs commonly serve as headwaters for streams, rivers, and sometimes lakes and ultimately contribute a great deal of freshwater to downstream inland and coastal aquatic ecosystems.

Figure 5 provides a systems diagram illustrating some of the immense complexity inherent in a relatively unaltered Florida artesian spring ecosystem. This model provides a summary of the major external forcing functions, internal energy storages and processes, and interactions between the spring ecology and the human economy. Functional groups within trophic levels illustrate the potential complexity of a spring ecosystem and the multiple interactive linkages.

Figure 6 provides an aggregated diagram of a spring ecosystem modified by human activities. Aggregation of functional groups is useful for the sake of combining elements of like structure and function into larger wholes. At this level of diagram aggregation illustrated forcing functions include: sunlight, atmospheric inputs of water and nutrients, groundwater inputs of water and nutrients, sediment derived inputs of nutrients, and anthropogenic inputs such as management actions, goods, services, and people. Aggregated outflows in the diagram include evapotranspiration, surface water discharges with downstream particulate matter and nutrient export. The spring ecosystem diagram illustrated in Figure 6 is entirely included within the springshed landscape diagram illustrated above in Figure 3.

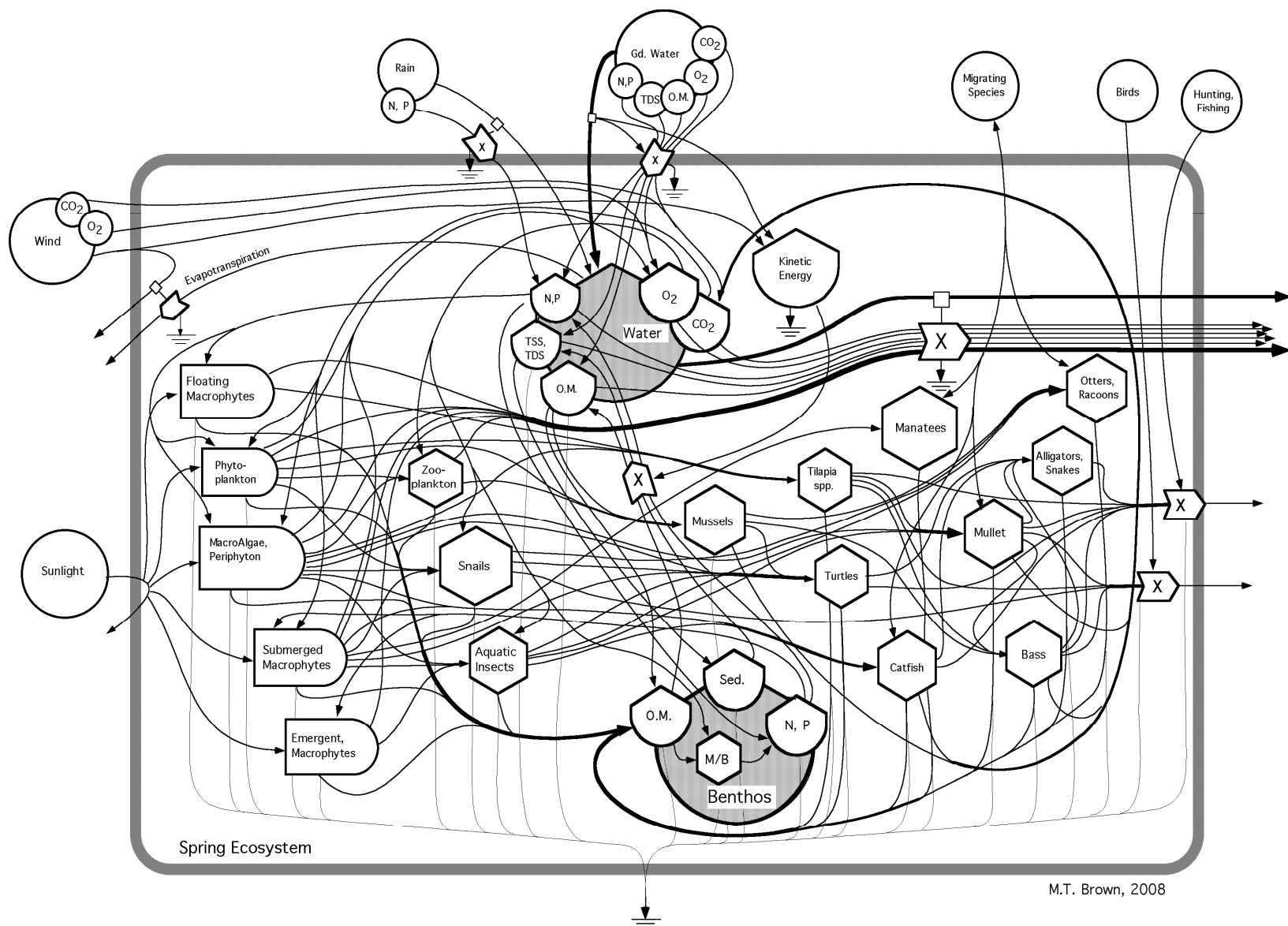


Figure 5 – Detailed conceptual diagram of a Florida artesian spring ecosystem (M.T. Brown 2008).

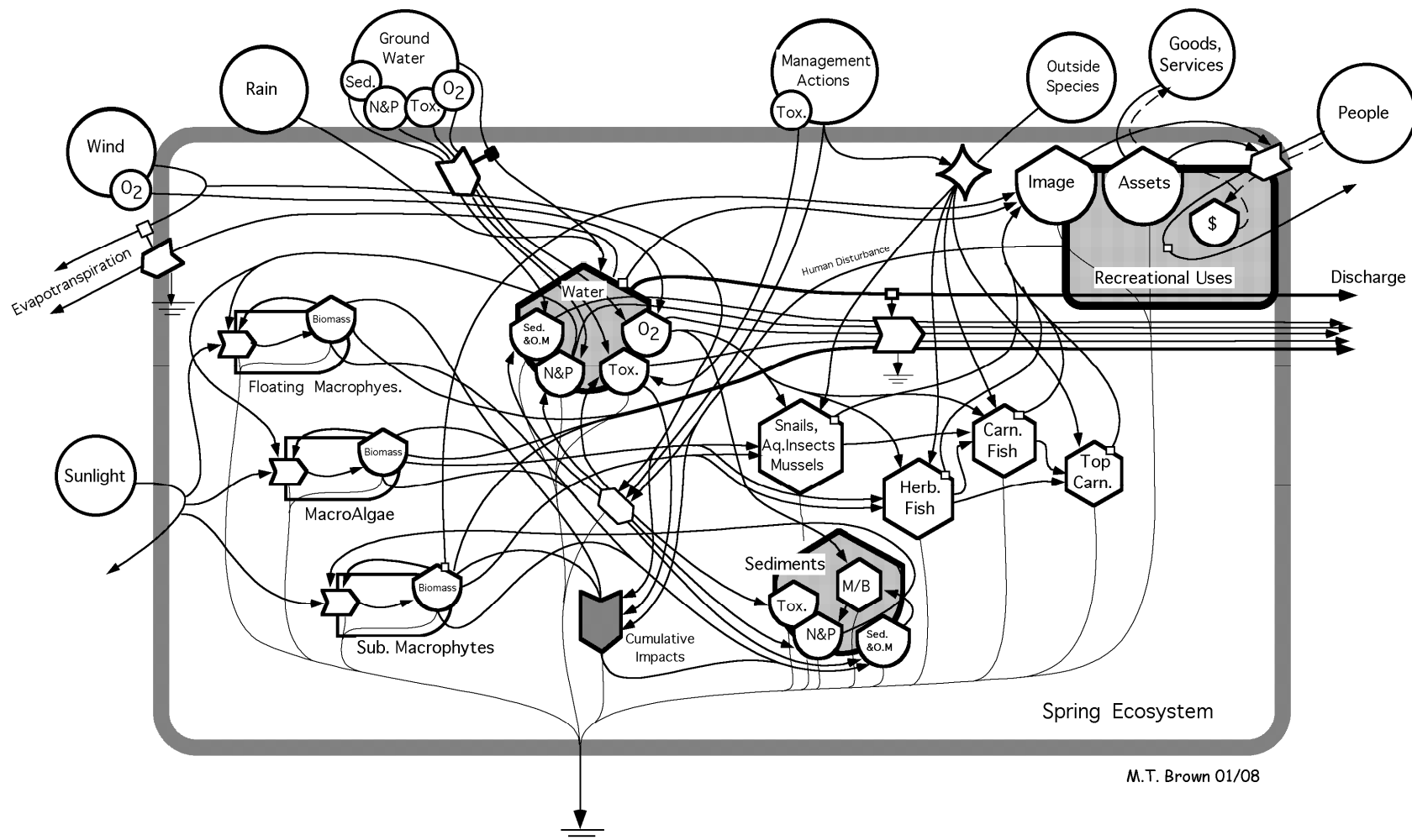


Figure 6 – Aggregated spring ecosystem diagram that incorporates human recreation and management activities (M.T. Brown 2008).

ENVIRONMENTAL FORCING FUNCTIONS

Solar Inputs

Solar inputs comprise the largest portion of the total external energy delivered to natural communities, and, in turn, are converted by photosynthesis into organic matter and other forms of potential energy, with the entropy of heat losses equally balancing inputs. The conceptual model of energy flow through a natural community, described and quantified by Odum (1956, 1957a, 1957b) in his work at Silver Springs, Florida, documented that only a fraction (24%) of the total solar energy (insolation) delivered to the system was absorbed by primary producers, which subsequently converted only about 5% of this energy into gross primary production (Figure 7). While numerically low, this conversion of solar energy to useful plant sugars (also called photosynthetic efficiency) is high compared to most natural and human-cultivated plant-based systems.

As noted earlier, the majority of springs in Florida are located between 30.8 and 27 degrees north latitude, and are subject to seasonal variation in incident light due to the orientation of the sun. Maximal solar inputs occur during the spring and summer and minimal solar inputs occur during winter, with corresponding patterns in daylight length. Solar inputs occur across much of the range of the electromagnetic spectrum (< 200 to 5,000 nm) but only certain portions of that spectrum are readily utilized by photosynthetic organisms for primary production. This portion of the spectrum, spanning the range of 400 to 700 nm wavelengths, commonly referred to as photosynthetically active radiation (PAR), is typically measured with a quantum sensor and expressed in units of $\mu\text{moles of photons per square meter per second}$ (Kirk 1994). Figure 8 illustrates a typical annual cycle for insolation as well as the PAR portion of that insolation.

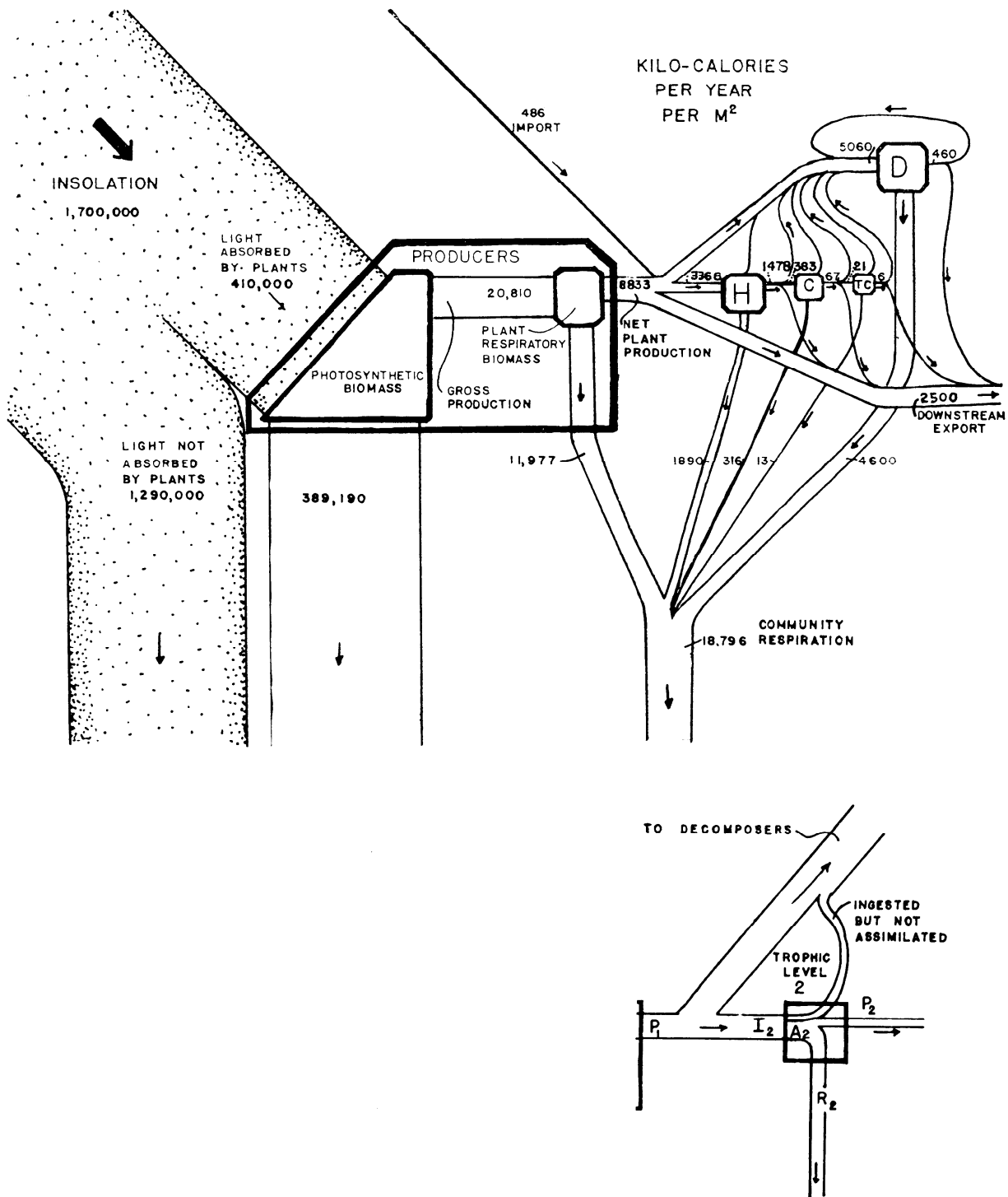


Figure 7 - Estimated energy flow diagram for Silver Springs, Florida, with all units in kilocalories per square meter per year (from Odum 1957b).

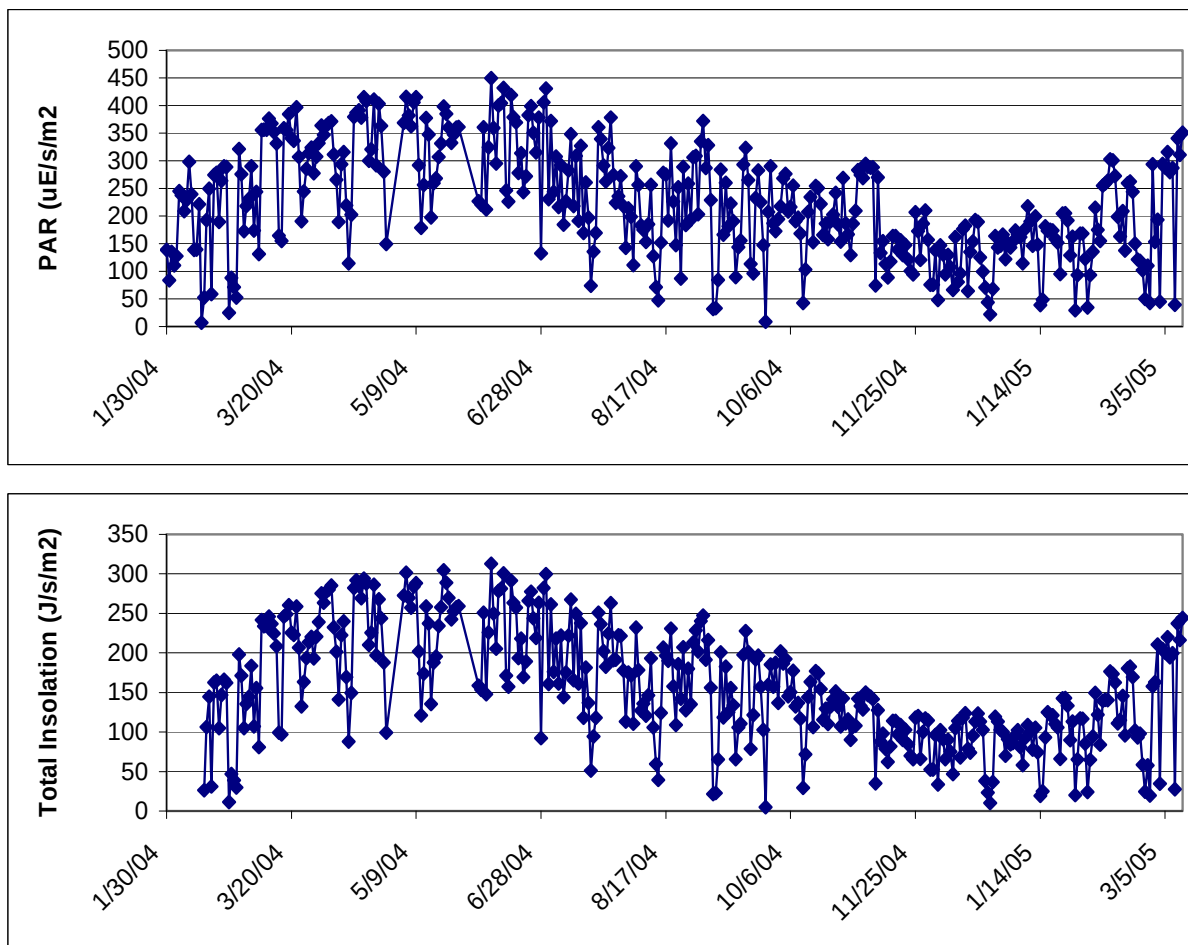


Figure 8 – Annual cycle of daily insolation and photosynthetically active radiation data recorded at Silver Springs, Marion County, Florida (from Munch et al. 2006).

Atmospheric Forcing Functions

Broadly, atmospheric inputs include both wetfall (precipitation and associated dissolved and particulate substances contained within precipitation) as well as dryfall (dry particulate matter carried by the wind). Average annual precipitation (USGS records from 1951 to 1980) for mainland Florida range from more than 64 inches in the panhandle to less than 48 inches near Tampa Bay. Most of Florida's springsheds receive between 52 and 60 inches of rainfall on an annual average basis (Miller 1997). The majority (~ 80%) of this precipitation is lost to evapotranspiration, a portion goes to surface runoff or shallow aquifers where it is delivered to streams and lakes (14%), and the balance (6%) percolates downward to recharge deeper groundwater aquifers (Fernald and Purdum 1998).

Springs receive atmospheric nutrient inputs directly on their water surface area and indirectly through their groundwater inputs and surface water runoff. Nitrogen, phosphorus, and numerous other elements and compounds are deposited on the surface of the land and water via the atmosphere. Due to their relatively small open water areas, springs and spring runs derive the

majority of their water and nutrient inputs from groundwater; direct atmospheric inputs are generally negligible.

Atmospheric nitrogen can be delivered to the environment as inorganic forms dissolved in rainwater or as particulate organic and/or mineralized forms. Atmospheric nitrogen exists primarily in the form of inert nitrogen gas (N_2), but inorganic nitrogen reaches the atmosphere through volatilized ammonia from industrial emissions, liquid ammonia fertilizers, and organic wastes. Emissions of oxides of nitrogen (NO_x) to the atmosphere occur through denitrification, the incomplete combustion of fossil fuels and industrial processes.

Because atmospheric nitrogen deposition occurs over the entire springshed, the cumulative load of nutrients to a spring via atmospheric inputs can be substantial. Measurements of total inorganic nitrogen (nitrate and ammonium) atmospheric deposition are obtained from monitoring stations managed by the National Atmospheric Deposition Program (see website for information and data: <http://nadp.sws.uiuc.edu/>, accessed December 2007). Detailed descriptions of the magnitudes of common sources and sinks for nutrients in springsheds are described in Chapter 2, and as demonstrated, the atmospheric deposition loading to springsheds can represent substantial inputs. Mitigating factors that may reduce the impact of atmospheric deposition on spring nutrient concentrations include low concentration per unit area, low daily input, and the likelihood of uptake by plants.

In springs, the gas exchange of oxygen and carbon dioxide between air and water is critically important (Matson and Harriss 1995). Due to their subsurface water source, springs frequently have low concentrations (and percent saturation) of dissolved oxygen in their upstream reaches. Atmospheric oxygen is the primary driving force to bring dissolved oxygen levels to saturation, with some input of dissolved oxygen being supplied by primary production. Carbon dioxide is an essential nutrient for plant growth in springs and other aquatic ecosystems. Hence, the atmospheric supply of this gas (about 3.5% by volume) is a component in replenishing the supply of inorganic carbon in many spring runs, although spring waters can initially be supersaturated in dissolved carbon dioxide due to their groundwater source (Duarte *et al.* 2007).

Other important atmospheric forcing functions include the effect of wind on mixing of waters and the transport of seeds and reproductive propagules. Many algal and plant species are highly motile in their resting and reproductive stages (Gurevitch *et al.* 2002). Those species with propagules that are carried by wind easily colonize spring heads, which are otherwise inaccessible to floating propagules. Atmospheric forcing functions may also be broadly interpreted to include invertebrate and vertebrate air borne inputs. The adult forms of aquatic invertebrates commonly occurring in springs (especially midges, stoneflies, and aquatic moths) depend upon flying skills to propagate in and re-colonize head spring areas. A large variety of aquatic and wetland dependent birds are very active in spring ecosystems and regularly migrate into and out of these systems. (Hoyer *et al.* 2006).

Groundwater Inputs

Groundwater inputs are the major hydrological, elemental, and mineral forcing functions for the artesian spring ecosystems of Florida. The groundwater supplies of Florida are derived from

precipitation, primarily within the state's boundaries, although some groundwater is derived from Alabama and Georgia precipitation (Fernald and Purdum 1998).

Florida has five principle aquifer systems. From largest to smallest they are: the Floridan, Biscayne, Surficial, Intermediate, and the Sand and Gravel aquifers (Miller 1997), each of which has corresponding importance as a source of freshwater for human usage. The largest aquifer in Florida and the one that is of primary importance to artesian springs is the Floridan (Figure 9). Key points of importance related to an understanding of the relationship between groundwater and springs in Florida are that:

- rainfall is the principal forcing function for groundwater recharge in Florida and is relatively independent (for practical purposes) of human control;
- artesian aquifers are the primary source of water for Florida's springs;
- artesian aquifers are also the primary source of water used in the state by humans; and
- as rainfall percolates into aquifers, its chemical characteristics are largely determined by the natural and anthropogenic uses of the overlying lands.

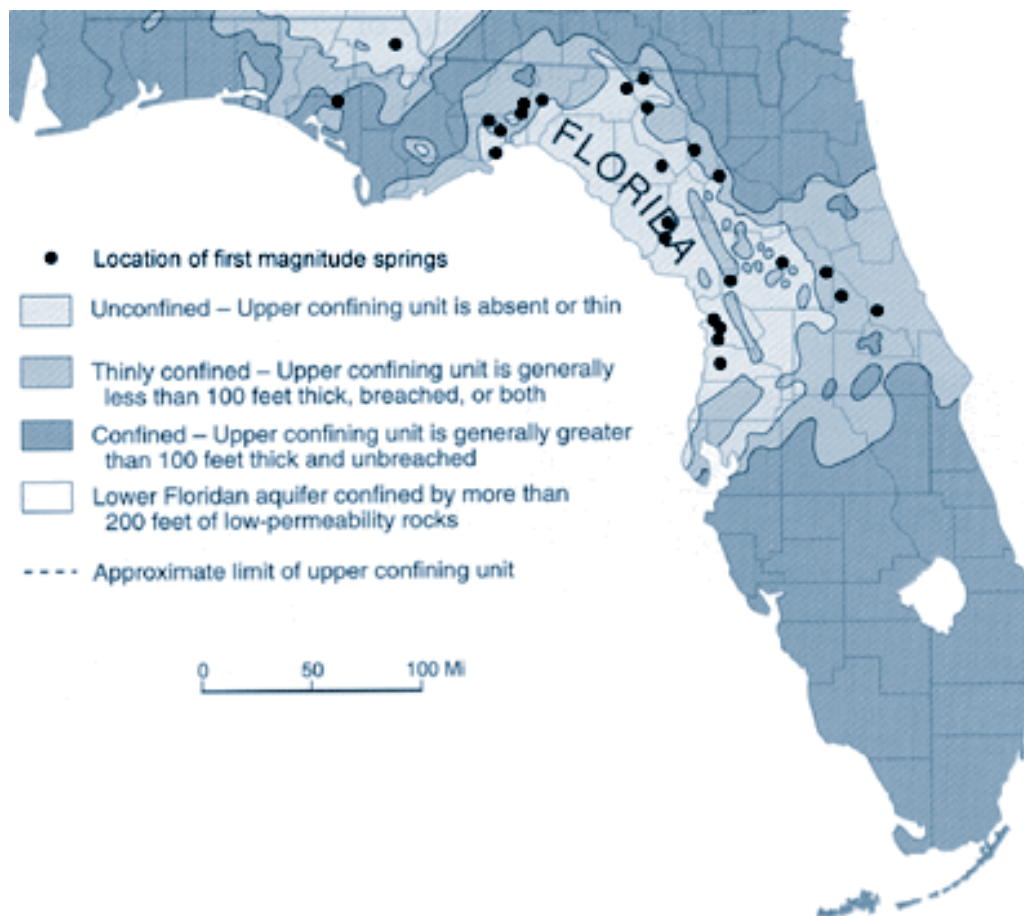


Figure 9 – General map of the extent of the confines of the Florida aquifer and the locations of the principal artesian first magnitude springs in Florida (from Fernald and Purdum 1998).

These points result in two principal connections between humans and the quality and quantity of water in Florida's aquifers: the first is that human consumptive use draws from aquifer storage and has lowered potentiometric head (the forcing function for spring discharge); the second is that cultural land use activities may result in increased quantities of nutrients and other chemical constituents in water delivered to the aquifers. Human-induced changes in groundwater quantity and quality have an indirect, but potentially significant effect on spring aquatic habitats, which obviously are aquifer dependent.

Evidence of the relation between groundwater withdrawals by humans and spring discharge is illustrated by long-term data for Rock and Wekiwa Springs groups near Orlando (WSI 2007a). Figure 10 depicts measured and modeled discharge from Wekiwa Springs for the period from 1959 to 2005. The measured spring discharge data show a general decline in spring discharge, apparently resulting from a combination of increased consumptive use (withdrawals) and declining rainfall totals over the corresponding time period (Intera 2006). The dashed line in Figure 10 corresponds to the minimum annual mean discharge for Wekiwa Springs as adopted by the St. Johns River Water Management District in 1991.

Evidence for the impact that land use activity has on aquifer water quality has been documented as well (Katz *et al.* 1999, Munch *et al.* 2006; Cohen 2007). Of primary consideration for this study are nutrients, principally nitrogen in the form of the compound nitrate. Nitrate is a naturally occurring component of aquatic ecosystems, and nitrogen is one of the essential elements for plant life. However, nitrate is readily utilized by aquatic plants and algae, and in excess can lead to the development of nuisance aquatic plant problems (Rabalais 2002; see Chapter 4). Table 1 provides an example of this type of land use analysis for Silver Springs in which modeled and actual data for springshed nitrogen loads and loads appearing at the spring boil show fairly good agreement. Other studies have "fingerprinted" specific nitrogen sources (animal waste, inorganic fertilizer, septic tank, etc.) based on ratios of stable nitrogen isotopes appearing in the spring vents (Phelps 2004; Toth 2003).

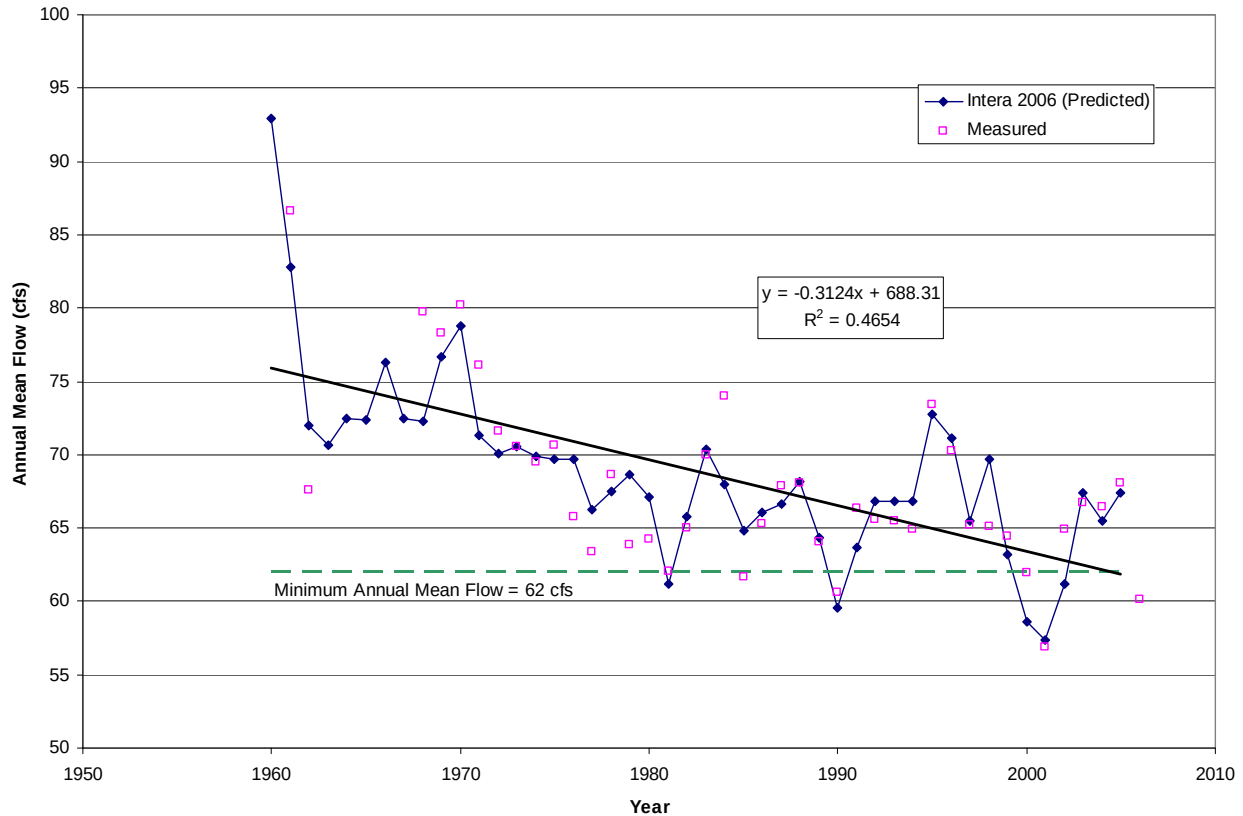


Figure 10 – Time series plot of annual average flows (measured and modeled) at Wekiwa Spring compared to the existing St. Johns River Water Management District minimum annual mean spring flow of 62 cfs established in 1991 (from WSI 2007a).

Concentrations of nitrate vary widely among the different springs and sometimes even amongst vents within large spring groups, but in a large percentage of springs, current measurements indicate nitrate concentrations are significantly elevated over those observed in springs contained in undeveloped springsheds (Champion 2001, Munch *et al.* 2006). This correlation between developed land use in a springshed and nitrate concentration of groundwater contained therein suggests a cause and effect relationship (Jones *et al.* 1997, Katz *et al.* 1999, Cohen 2007). Katz *et al.* (1999) utilized isotopic analyses to show that substantial portions of nitrate nitrogen found in the Upper Floridan Aquifer and in spring discharges are derived from anthropogenic activities such as fertilizer application for agriculture and residential uses, livestock waste, and human waste.

Table 1. Observed and simulated spring flows and nitrogen loads at Silver Springs, Florida, for the period from 1957 through 2055 based on land use/land cover analysis from historic aerial photographs and estimated loads and resulting spring boil total nitrogen concentration based on 2055 projected land uses (Munch *et al.* 2006).

Year	Observed Spring Flow	MODFLOW Simulated Spring Flow	Observed Nitrogen Load (lbs/yr)	Land Use / Land Cover Model Est. N Load (lbs/yr)	Observed Spring Nitrogen Concentration (mg/L)	Land Use / Land Cover Model Estimated N Concentration (mg/L)
1957	640.0	716.5	94,416.0	399,054.10	0.10	0.38
1979	778.0	710.8	814,898.6	802,633.06	0.71	0.76
1995	720.0	708.3	955,962.0	1,036,198.93	0.90	0.99
2005	680.0	687.6	1,057,606.7	1,120,813.63	1.07	1.10
2055	N/A	687.6	N/A	1,760,000.00	N/A	2.02

Similar work has been reported for Silver Springs (Phelps 1994, 2004), Rainbow Springs (Water and Air Research 1991), Wekiwa Springs (MACTEC 2007), and Wakulla Springs (Chelette *et al.* 2002). Figure 11 illustrates estimates of the contributory nitrogen sources for two spring systems, Wakulla Springs south of Tallahassee and Wekiwa Springs near Orlando. In the Wakulla springshed, human-derived wastewater sources (Tallahassee sprayfield, on-site septic tank systems, and wastewater residuals disposal) are estimated to contribute about 61% of the total nitrogen load at Wakulla Springs (Chelette *et al.* 2002). While atmospheric sources are estimated to provide 26% of the load to the springs, other research has found that those contributions are elevated when humans clear forest land and replace it with pasture and grass covered land uses (MACTEC 2007). For the Wekiwa springshed, residential fertilizer applications (20%), agricultural fertilizer applications (26%), and septic tanks (22%) represent the largest input categories, while atmospheric deposition was estimated to contribute 2% of nitrogen loading (MACTEC 2007). These two examples illustrate the variable nature of the source of nitrogen loading by springshed.

Anthropogenic Forcing Functions

As the discussion above reveals, indirect anthropogenic inputs to springs can be measured from the influence they have on nutrient delivery via atmospheric deposition and groundwater supply. Indirect anthropogenic impacts on springs may also result from changing downstream conditions through construction of dams and weirs, stream channelization and sedimentation, and harvesting or otherwise manipulating fish and other wildlife populations that normally include the spring and spring run in their home range.

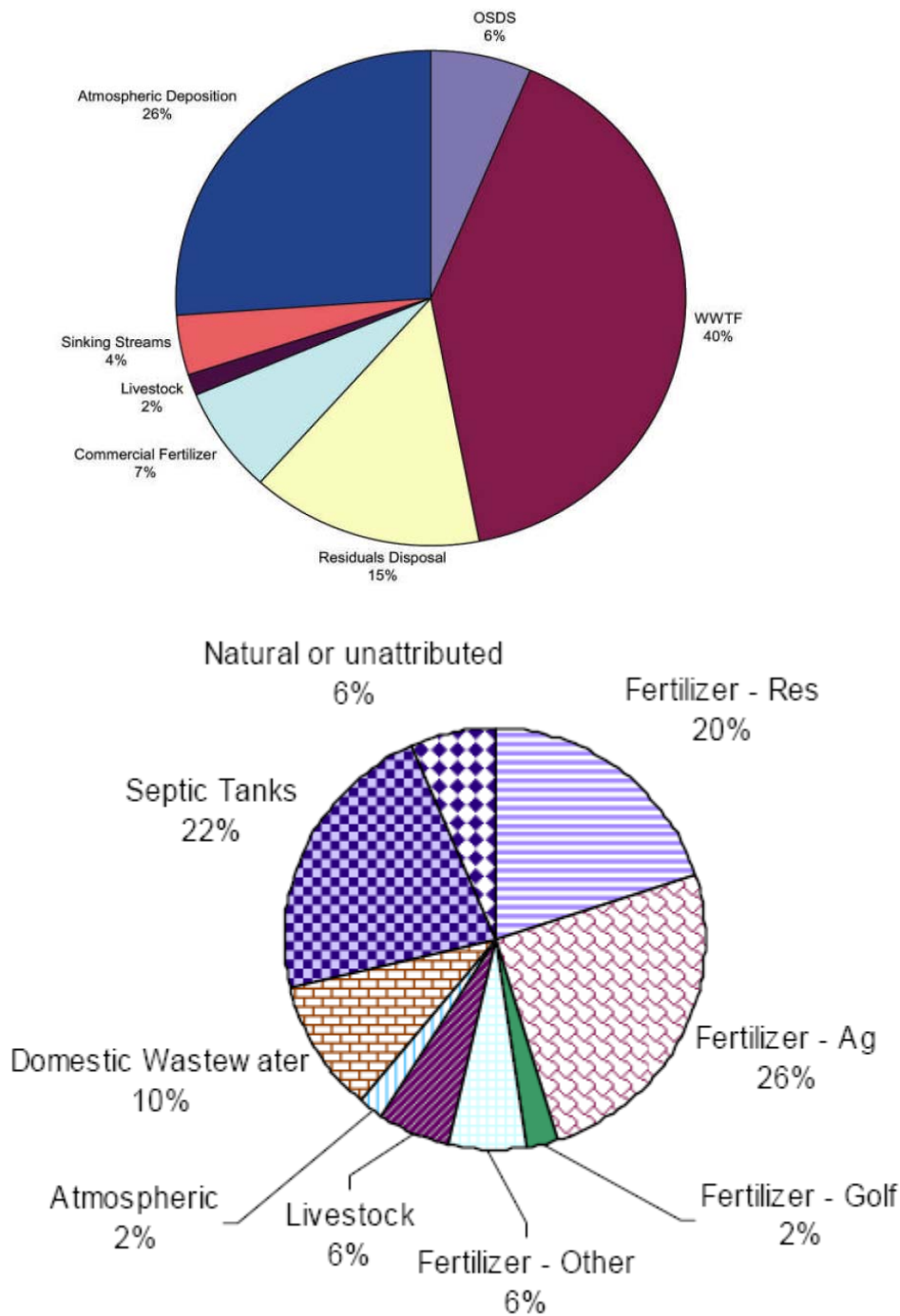


Figure 11 – Top pie chart illustrates the relative contribution of total nitrogen load to the springshed of Wakulla Springs for the period from 1990-1999 (Chelette et al. 2002); bottom pie chart illustrates the relative contribution of total nitrogen load to the springshed of Wekiwa Springs for 2004 (MACTEC 2007).

Direct anthropogenic inputs or forcing functions to Florida's artesian springs include: recreational activities that trample or dislodge sediments and submersed aquatic vegetation; aquatic plant management activities (principally in the form of physical, chemical, or biological

control of non-indigenous or “undesirable” plant and animal species); modification of spring habitats by construction that reduces connectivity (bulkheads, shoreline modifications, dams, or weirs); and general modifications to food webs by introduction of non-indigenous species and reductions in top level consumers through hunting, fishing, and habitat alteration.

Nutrient loads to the groundwater represent an indirect anthropogenic forcing function at the regional level while nutrient loads delivered via stormwater runoff to springs are an indirect factor at the local scale.

ENERGY/MATERIAL STORAGES IN SPRINGS

Spring Basin/Spring Run

Spring basins (and their various analogues: boil or pool) and spring runs are lotic aquatic habitats whose size corresponds to the volume of groundwater being discharged. Typical spring basins are round or oval, as is commonly observed with solution features in karst geology areas and are connected to their associated spring run. Springs have been classified based upon geomorphic features, and can be further subdivided as springs, sinks, river rises, or karst windows (Wilson and Skiles 1989). As karst features, spring pools (or vents) may initially form through catastrophic collapse, but their overall genesis may require millennia. Exceptions include springs discharging from karst fissures which underlie surface drainage rivers such as the Suwannee or Santa Fe Rivers. The smallest spring basins can be less than 3 m (~ 10 ft) in diameter while the largest spring groups (*e.g.*, Wakulla, Rainbow, Silver) have basins approaching 90 m (~ 300 ft) in diameter. The bathymetric profiles of spring basins are variable, but a typical spring basin has gradually sloping sides which descend to the vent/s like a funnel. Because of this sloped gradient, spring basins are susceptible to the deposition of sediments from upland erosion. Depths of spring basins rarely exceed 15 m (~ 50 ft) and are commonly less than 5 m (~ 16 ft), although the vent/s of the springs often connect to a network of underwater caves, tunnels, and passages which can reach depths greater than 100 m (~330 ft). The underwater structure of many of Florida’s largest spring systems have been explored and mapped, none more extensively than Wakulla Springs (Figure 12).

Spring runs begin as a direct extension of a spring basin, drain according to surface elevation gradients, and typically join with other surface water features. Spring runs can be defined as streams which derive 50% or more of their base-flow from groundwater sources (Scott *et al.* 2004). In the karst-rich portion of Florida, many streams receive substantial base flow from springs. The size of spring runs corresponds to the volume of water they discharge, ranging from a few meters to 100 m (~330 ft) in width, while lengths range from tens of meters to tens of kilometers for the largest spring runs (*e.g.*, Silver, Rainbow, Wakulla, Wekiva).

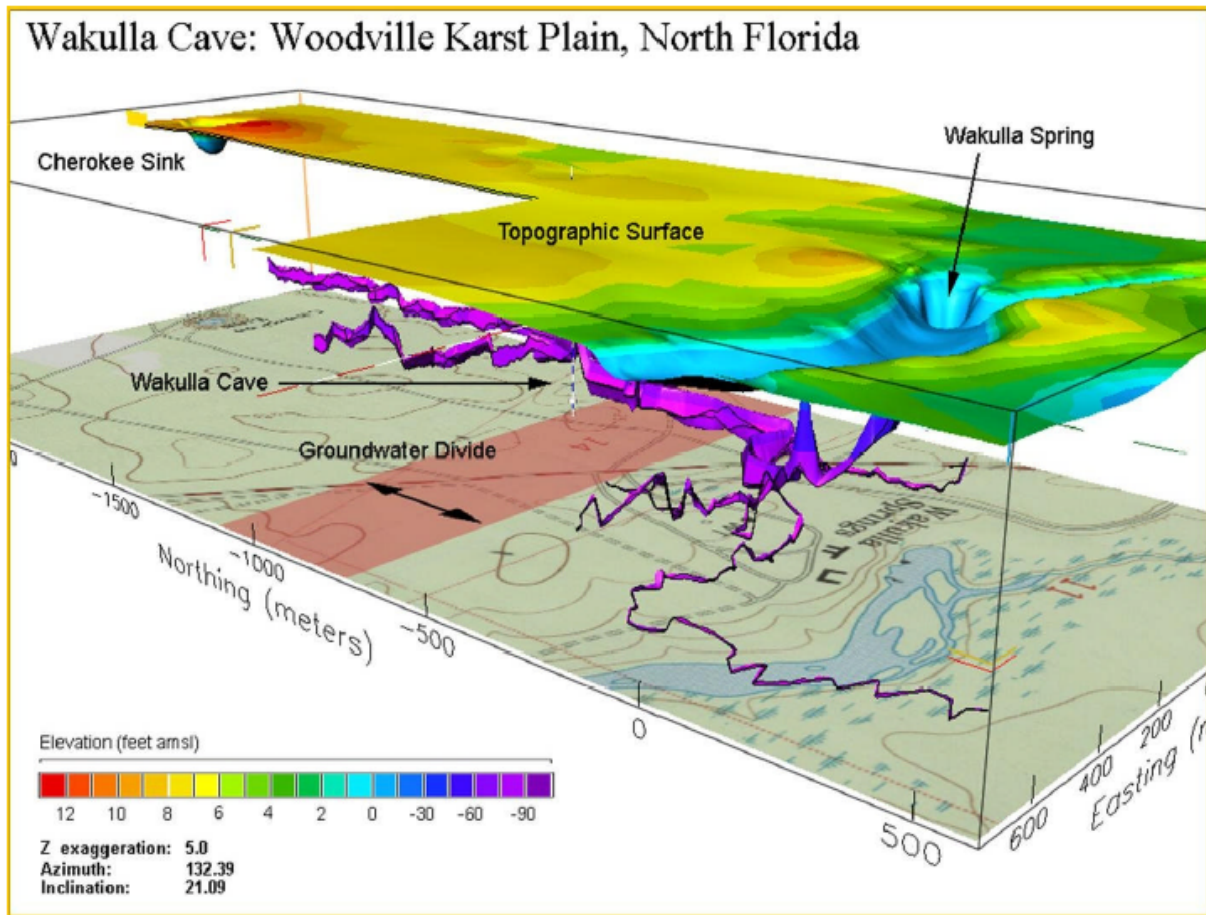


Figure 12 – Three-dimensional diagram of the Wakulla Cave and Spring System in Wakulla County, Florida (from Loper et al. 2005).

Spring flows are created by a difference in potentiometric head between the groundwater and the receiving water. A portion of the potential energy contained in this water is converted to kinetic energy as water discharges from a spring vent, determining the discharge rate and the resulting flow velocity. Given that the size of a spring run corresponds to the quantity of water it discharges, water residence times are typically short, in the range of hours, and preclude the development of measurable plankton abundance (Hynes 1970).

Spring flow can expel floating macrophytes such as water lettuce (*Pistia stratiotes*) and water hyacinth (*Eichhornia crassipes*) that might otherwise block the light essential for photosynthesis in submersed primary producers. Uninterrupted spring flow provides a nearly continuous source of essential elements (e.g., oxygen, carbon, hydrogen, nitrogen, phosphorus, potassium) and lessens boundary layer effects that might otherwise limit critical gas exchanges (Westlake 1967).

Stream velocity is also related to sediment composition (Butcher 1933, Hynes 1970; see Chapter 4). Favorable sediments for macrophyte growth, such as sandy clays (Power 1996) may be scoured away at velocities > 0.30 m/s (Hynes 1970) and sand substrates begin to give way to gravel and large rocks at stream velocities of 0.60 m/s or greater (Butcher 1933). When spring

flow is reduced by natural or anthropogenic factors, scouring velocities are not maintained and spring basins have been observed to fill with coarse and fine sediments (Scott *et al.* 2004). Re-establishment of spring basin morphology may require considerable time if spring flows are restored.

High water clarity often facilitates littoral zones that include the entire spring and spring run, although other factors including human recreation, herbivore grazing, stream velocity, sedimentation, and riparian shading commonly influence the distribution and abundance of plant life (see Chapter 4).

Water and Dissolved Constituents

Arguably the most important structural component of a spring (other than its basin morphometry) is its water. In a flowing spring system, there is a continual supply of inorganic and organic materials in both dissolved and particulate forms. This is beneficial to many forms of life, both autotrophic and heterotrophic, and provides the basis for the observation that some springs have been found to be among the most productive ecosystems on the earth (Odum 1971). Water discharged from artesian springs associated with the Floridan Aquifer typically has slightly basic pH, is commonly under-saturated in dissolved oxygen and over-saturated with dissolved carbon dioxide, and contains a variety of elements in trace amounts. Spring water is typically low in inorganic particulate matter as well as colored dissolved organic matter, with the exceptions of *river rises*, whose discharges are principally composed of surface waters re-emerging after their entry in a sinkhole or swallet (Butt *et al.* 2007). Water is a natural solvent and through its movement, provides a mechanism of transporting substances. Consequently, nitrate produced by natural processes or deposited by anthropogenic activities on surface lands and waters can be transported to groundwater and subsequently discharged to spring ecosystems.

The first and most commonly utilized classification for Florida springs is based on magnitude of discharge as initially described by Meinzer (1927), subsequently utilized by Rosenau *et al.* (1977), and continues to be used today (Table 2).

Table 2. Spring classification by magnitude of discharge (after Meinzer 1927).

Magnitude	Average Discharge
First	100 cfs (64.6 mgd) or more
Second	10 to 100 cfs (6.46 to 64.6 mgd)
Third	1 to 10 cfs (0.646 to 6.46 mgd)
Fourth	100 gpm to 1 cfs (448 gpm)
Fifth	10 to 100 gpm
Sixth	1 to 10 gpm
Seventh	1 pm to 1 gpm
Eighth	Less than 1 gpm

cfs = cubic feet per second; mgd = million gallons per day; gpm = gallons per minute;
pm = pints per minute; 1 ft³ = 0.0283 m³; 1 gal = 3.785 liter; 1 pint = 0.473 liter

Because the groundwater discharged from springs is qualitatively influenced by surrounding geology, soils, and land surface activities, the resulting differences in water chemistry have allowed springs to be classified and grouped based on their predominant ions (Whitford 1956, Slack and Rosenau 1979, Woodruff 1993). Using cluster analysis of the six predominant ion (calcium, bicarbonate, magnesium, sulfate, sodium, and chloride) concentrations for 170 springs, Woodruff (1993) arrived at four distinct spring types and their percent occurrence): calcium-bicarbonate springs (76%), sodium-chloride (salt) springs (12%), mixed calcium/salt springs (8%), and low ion (softwater) springs (4%, Table 3).

Table 3. Ranges of ion concentrations for the six most predominant ions (calcium, bicarbonate, magnesium, sulfate, sodium, and chloride) from 170 Florida springs which were utilized to create four distinct springs groupings via cluster analysis (from Woodruff 1993).

Spring Group	Ca ⁺² (mg/L)	HCO ₃ ⁻ (mg/L)	Mg ⁺² (mg/L)	SO ₄ ⁻ (mg/L)	Na ⁺ (mg/L)	Cl ⁻ (mg/L)
Low-ion	0.7 – 4.8	1 – 20	0.2 – 2.6	0.3 – 7.6	0.8 – 8.2	1 – 15
Calcium bicarbonate	1 – 74	1 – 255	0.2 – 20	0.2 – 78	1 – 17	1 – 21
Mixed	32 – 167	13 – 396	10 – 77	12 – 477	6 – 127	10 – 235
Salt	40 – 600	76 – 205	20 – 546	43 – 1683	160 – 4400	240 – 9400

Data sources: USGS, SRWMD, and SJRWMD

Primary Producers

Primary production in spring ecosystems is dominated by photoautotrophic life forms which use energy derived from sunlight to fix organic matter from inorganic compounds. Chemoautotrophic bacteria are also capable of generating organic material from inorganic sources, and may exist in anaerobic springs, but their ecology or relative importance is unknown. Additional sources of organic chemical energy to spring ecosystems are largely derived from litter fall from surrounding riparian vegetation. The amount of these allochthonous inputs varies widely, depending on site specific conditions and seasonal cycles. The variability of these organic matter inputs must be considered in regard to the trophic structure and food webs supplemented by these inputs.

The relative clarity of spring water facilitates the primary productivity and growth of autotrophic organisms at a variety of scales, from microscopic attached algae to macroscopic vascular plants. Most visible in many of Florida's springs are the macrophytes, a grouping that includes vascular plants, bryophytes, and macroscopic and colonial algae. The vascular aquatic plants have internal transport structures (xylem and tracheids), are principally angiosperms (flowering plants with enclosed seeds) evolved from land plants, and are comprised of relatively few species (< 1%) in comparison to the diversity of terrestrial vascular plants (Sculthorpe 1985). Bryophytes lack xylem and true roots and are represented by mosses and liverworts (Stream Bryophyte Group 1999), with native Florida spring genera including *Brachelyma* and *Fontinalis*.

Aquatic macrophytes can be further subdivided by their growth habits as submersed, floating, or emergent. Common native aquatic vascular plant species include strap-leaf sagittaria (*Sagittaria kurziana*), tapegrass or wild celery (*Vallisneria americana*), southern naiad (*Najas guadalupensis*), coontail (*Ceratophyllum demersum*), a variety of pondweeds (*Potamogeton* spp.), and fanwort (*Cabomba caroliniana*). Non-indigenous aquatic vascular plant species are present in many Florida spring ecosystems and include hydrilla (*Hydrilla verticillata*), Eurasian milfoil (*Myriophyllum spicatum*), Brazilian water weed (*Egeria densa*) water hyacinth (*Eichhornia crassipes*), and water lettuce (*Pistia stratiotes*).

The macroalgae are distinct in that they lack a vascular system or true roots, and are composed of individual cells that are independent and undifferentiated. Macroalgae that occur in springs and spring runs include the genera *Chara* and *Nitella* which have vascular plant like appearances, as well as filamentous genera principally from the green and cyanobacteria groups of algae such as *Cladophora*, *Enteromorpha*, *Lyngbya*, and *Vaucheria*. A survey of 29 Florida springs by Stevenson *et al.* (2007) found that almost all springs had macroalgae growing in them, with an average of 50% of the spring bottoms covered by macroalgae; many algal mats achieved thickness greater than 0.5 m, with seasonal variation in macroalgae biomass largely related to turbidity and sedimentation from flood events. (Stevenson *et al.* 2007). Although the two most common reported taxa of macroalgae were *Lyngbya wollei* and *Vaucheria* spp., 23 different macroalgal taxa were observed in the spring survey.

Collectively, macrophytes provide a physical structure upon which smaller primary producers can attach, thereby preventing their downstream export and facilitating access to a better light environment. These epiphytic communities consist of a myriad of microalgae, diatoms, cyanobacteria, and microbes that have variously been labeled as biofilms, periphyton, or as *aufwuchs* (German for growth) and Mattson *et al.* (1995) reported that spring run periphyton communities are typically dominated by epiphytic diatoms. This epiphytic community has high rates of primary production which can eclipse the productivity of macrophytes. Odum's (1957b) quantification of the trophic structure of Silver Springs observed that approximately two-thirds of the primary production was derived from the epiphytic community, even though the strap-leaf sagittaria (*Sagittaria kurziana*) macrophyte community represented about three quarters of the standing biomass.

Productivity of submersed vascular plants in spring ecosystems can be high as well. The annual cycle of biomass and productivity of wild celery (*Vallisneria americana*) was studied in Kings Bay, (Citrus Co.), using a modified hole-punching technique and applied to shoot density data to obtain estimates of production (Hauxwell *et al.* 2007). Areal leaf production ranged between 3.6 and 23.0 g/m²/d of dry biomass, with highest productivity observed in late spring/summer, with an annual total leaf production estimate of 2.7 kg/m²; placing the productivity of *Vallisneria* in Kings Bay above most literature values for other *Vallisneria* populations as well as global averages for seagrasses (Hauxwell *et al.* 2007). Examples such as these demonstrate the high levels of primary production in clear-water spring ecosystems.

The lotic nature of spring ecosystems would appear to preclude the formation of a self-sustaining phytoplankton community. However, stream and spring run waters can contain autotrophic

material made up of protists, algae, and cyanobacteria which have originated from the sloughing of benthic or epiphytic growths (Odum 1957; Allan 1995; Munch *et al.* 2006). This observation was supported by Swanson and Bachmann's research (1976) in Iowa streams, which reported that the average daily amount of chlorophyll exported downstream in the summer was highly correlated ($r > 0.9$) with the total standing crop of chlorophyll on the stream bottom, as well as with the bottom surface area upstream of the sampling point. A similar pattern was observed in three Florida spring-fed streams, with an increase in chlorophyll concentration with distance downstream, likely the result of cumulative increases in benthic supply of autotrophic material (Frazer *et al.* 2006). Within Florida spring runs and streams, pseudo-plankton (also known as tychoplankton) appears to derive largely from sloughing of periphytic and benthic autotrophic communities, and, as a result, the species composition is likely to be similar. Although perhaps not a true phytoplankton community, this autotrophic material represents a steady downstream export of chlorophyll and primary production available to primary consumers.

Primary Consumers

Primary consumers in spring ecosystems are represented by herbivores and omnivores. Vascular aquatic plants are directly consumed by manatees and turtles like the herbivorous Florida cooter (*Pseudemys floridana*) and the omnivorous yellow-bellied slider (*Trachemys scripta*). Snails are also important primary consumers, with larger species such as the Florida applesnail (*Pomacea paludosa*) consuming vascular plants and smaller species such as members of the *Elimia* genus consuming periphyton. As noted in the previous section, the highest rates of primary productivity are derived from the epiphytic community, which, in turn, supports a diversity of aquatic macroinvertebrate primary consumers. Invertebrate densities in spring ecosystems can be substantial (Table 4), with important orders being shrimp-like crustaceans (Amphipoda), midges (Chironomids), aquatic worms (Oligochaeta), larval flies (Diptera), snails (Gastropoda), mayflies (Ephemeroptera), caddisflies (Trichoptera), and aquatic beetle larvae (Coleoptera). Mattson *et al.* (1995) reported that macroinvertebrate communities are typically dominated by chironomids, ephemeropterans, and trichopterans. Observations made by Munch *et al.* (2006) found chironomids, trichopterans, and lepidopterans dominated collections made from Silver Springs and suggested that the daily chironomid emergence is correlated with dominance of strap-leaf sagittaria (*Sagittaria kurziana*) and much lower in areas dominated by filamentous attached and benthic algae.

Other primary consumers include freshwater mussels which are found in Florida springs, but not at the diversity or abundance observed state wide, perhaps a function of lower plankton availability in spring runs. A survey of 16 major Florida springs documented 18 species of freshwater mussels, of which the most commonly occurring was the non-indigenous Asiatic clam, *Corbicula fluminea* (Walsh and Williams 2003). In that study, a general increase in the abundance of mussels downstream of the spring vent was observed. As noted earlier, there is often a pattern of increasing pseudo-plankton (tychoplankton) downstream in spring runs, and together these observations suggest that suspended material may limit the abundance and distribution of filter feeders in these ecosystems.

Table 4. The mean number (and std. dev.) of organisms collected from vegetated substrate in Mill Pond Spring, a feeder spring of the Ichetucknee River (from Woodruff 1993).

Subclass / Order	Number of Organisms (average #/m ²)	Standard Deviation
Oligochaeta	1,051	1,135
Hirudinea	584	903
Diptera	633	573
Ephemeroptera	24	73
Odonata	195	230
Lepidoptera	24	73
Trichoptera	925	1,132
Coleoptera	97	292
Amphipoda	26,767	17,540
Isopoda	2,360	3,332

Spring ecosystems, which have a navigable connection to coastal waters, are utilized by manatees as a place to feed and as a thermal refuge during cold seasons. Manatees are obligate herbivores whose annual average feeding rates have been estimated at 33.2 kg (73 lb, fresh weight) of vascular plants per day (Bengtson 1983), although consumption rates are likely influenced by animal size and reproductive status. Manatees have been observed feeding on a variety of submersed and floating vascular plant species, but do not appear to select for or measurably feed upon filamentous algae.

Although aquatic plants have co-evolved with herbivores and should be able to recover from cropping by herbivores, when consumption by herbivores continually exceeds vegetation production rates, overgrazing and loss of vegetation can result. Non-indigenous snails may cause overgrazing, with possible destructive avenues being diverse feeding abilities such as those possessed by the channeled applesnail (*Pomacea canaliculata*), or due to the very high densities observed in smaller species, *i.e.* 10,000 *Melanoides tuberculatus* per square meter in the St. Johns River (Thompson 2004). Seasonal loss of submersed vascular plants appears to have occurred in some spring ecosystems due to grazing by manatees (Jacoby *et al.* 2007); particularly during winter seasons when manatee densities are highest and reduced light levels correspond to lower plant productivity. Major reductions in the abundance of submersed vascular plants and a shift from vascular plants to non-grazed filamentous algae has been reported as a result of manatee feeding at Kings Bay, a spring group which forms the headwaters of Crystal River in Citrus County, Florida (Hauxwell *et al.* 2004).

Obligate herbivorous fish are rare in Florida springs as most species which consume plant material are also general omnivores and are likely ingesting a mix of detritus and invertebrates. Mullet (*Mugil* spp.) is a good example of an omnivorous fish common to Florida spring systems linked by navigable connection to marine waters. Other largely herbivorous species include the non-indigenous sailfin catfish (*Pterygoplichthys multiradiatus* and *P. disjunctivus*), the sucker

mouth catfish (*Hypostomus* sp.), and blue tilapia (*Oreochromis aurea*), which have become common in several spring systems, including Rock, Wekiwa, Volusia Blue, and others in the St. Johns River drainage. These non-indigenous fish species are undergoing a range expansion following their introduction from a variety of accidental and purposeful events in state waters beginning in the 1960's. While non-indigenous fish can also be found in stream and lake systems, the thermal refuge provided within spring ecosystems may facilitate their expansion northward in Florida. Sailfin or suckermouth (*Pterygoplichthys* and *Hypostomus* spp.) catfish were not observed in a 1992 survey of fish fauna from seven springs contained in St. Johns River drainage basin (Woodruff 1993), but have been observed in several of these same springs since at least 2005 (Davis and Herring 2005, author's observations).

Higher-Level Consumers

Faunal studies of Florida springs are perhaps best represented by fish collections, many of which are maintained by the Florida Museum of Natural History. In a review of museum data for occurrence of fishes in Florida springs, Walsh and Williams (2003) documented more than twenty thousand fish specimens collected from Florida springs representing no less than 99 species from 65 springs. These species represent approximately three quarters of the 126 native fishes that occur in Florida freshwaters and illustrate the collective importance of spring ecosystems as fisheries habitat (Gilbert 1987). Within individual springs, fish diversity is influenced by spring size and its connectivity with other drainages. Silver Springs, which appears to have the best historic fishery records available, has relatively stable fish species diversity, as evidenced by the following: Hubbs and Allen (1943) reported thirty-five species in the 1940s, Walsh and Williams collected twenty-nine species in 2002, while Munch *et al.* (2006) observed thirty-three species in 2004-05. Munch *et al.* (2006) pointed out that while the number of fish species utilizing Silver Springs was similar to historical observations, the loss of channel catfish and mullet, presumably as a consequence of the downstream construction of the Kirkpatrick/Rodman Dam, has resulted in a major decline in overall fish biomass.

Other higher consumers found at variable population densities, but relatively unknown importance in springs include: a variety of bird species (*e.g.*, ibis, herons, egrets, cormorants, wood ducks, osprey, hawks, owls, and bald eagles), reptiles such as water snakes and alligators, and mammals such as otters, raccoons, and of course, humans.

Decomposers

Detritus and dissolved organic matter (DOM) from macrophytes and allochthonous material forms an important reduced chemical energy pool available for consumption by a range of invertebrate detritivores and microbial decomposers. The recycling of energy and matter in spring ecosystems is complemented by the detrital pathway. Bacteria and fungi are two broad functional groups which utilize organic detritus as a primary energy source.

Spring Biomass Pyramid

H.T. Odum was the first published researcher to apply general system ecology principles from aquatic to spring ecosystems (Odum 1957b, Kemp and Boynton 2004). During his multi-year project researching over 20 Florida artesian springs, Odum noted that the biomass of spring trophic levels (*i.e.*, producers, primary consumers, secondary consumers, etc.) forms a classic “pyramid”, with lower biomass and numbers of living organisms at the higher trophic levels (Figure 13). This figure illustrates the predominance of strap-leaf sagittaria (*S. lorata* = *S. kurziana*) and associated periphytic algae as the biological flywheel of the Silver Springs ecosystem. Average standing stock (dry weight biomass) of these plants was estimated by Odum as about 809 g/m². Herbivores, including turtles, midges, snails, and the herbivorous fish mullet (*Mugil cephalus*) are the next step up on the biomass pyramid with an estimated average biomass of only 37 g/m². Higher trophic levels include primary and secondary consumers such as carnivorous fish, alligators, and numerous fish-eating birds such as the double-crested cormorant (*Phalacrocorax auritus*), anhinga (*Anhinga anhinga*), herons and egrets (Ciconiiformes). The biomass of the primary consumers was estimated as 11 g/m² while the top consumers had an estimated biomass of only 1.5 g/m². An important parallel metabolic track occurs in the detrital food chain that includes decomposer organisms such as bacteria, aquatic insects, and crayfish. Continuing work by Odum and other researchers in general systems studies found this relationship to be the typical at all scales for adapted systems (Odum 1983).

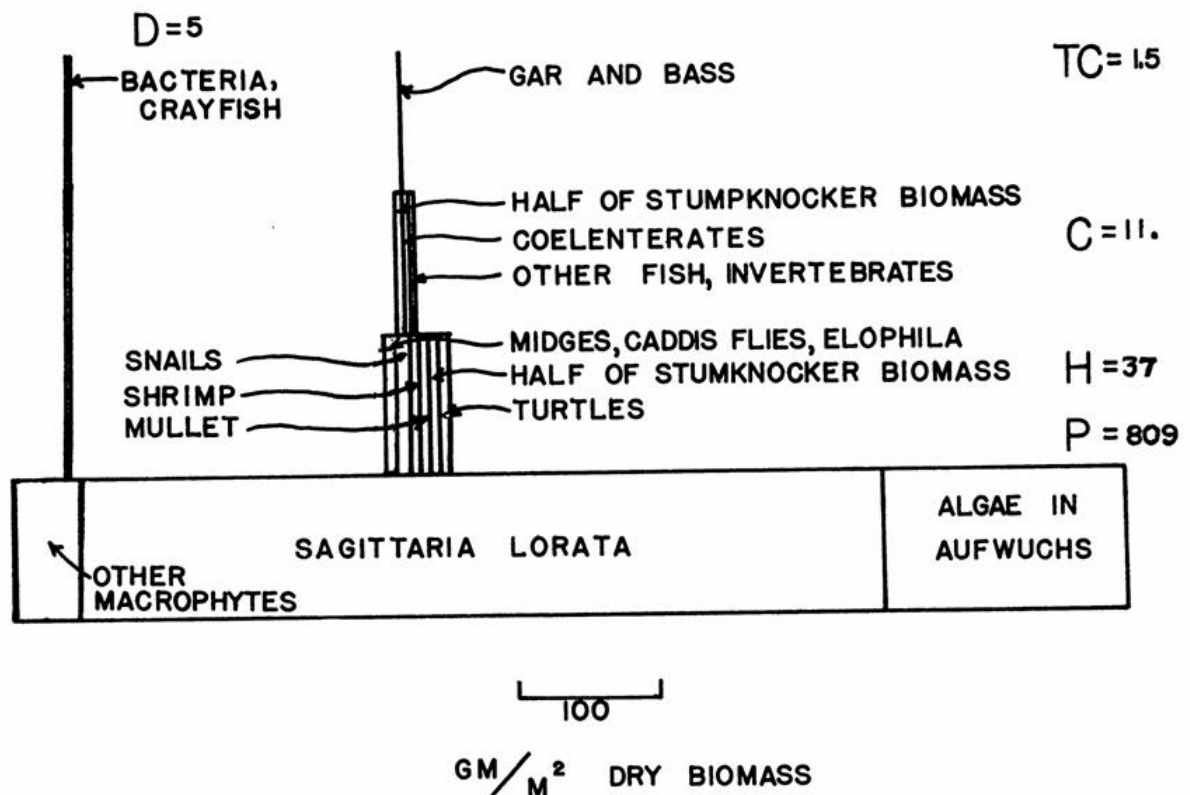


Figure 13 – An example of the pyramid of biomass for the Silver Springs community (from Odum 1957b).

ECOSYSTEM-LEVEL PROCESSES

The utilization of measured dissolved oxygen changes to estimate whole ecosystem metabolism in flowing aquatic ecosystems has been implemented in only a limited number of Florida springs by Odum (1956, 1957a, 1957b), although current data for several spring systems have recently become available (Munch *et al.* 2006, WSI 2006, 2007b), as well as metabolism estimates from a variety of interstate and international streams (*e.g.* Naiman 1983, Marzolf *et al.* 1994, Young and Huryn 1999, Mulholland *et al.* 2001).

Community metabolism can be conveniently and rapidly assessed for entire spring ecosystems by measuring the mass of dissolved oxygen at upstream and downstream stations. The availability of data sondes that collect and store *in situ* measurements of dissolved oxygen and temperature, as well as quantum sensors to do the same for photosynthetically available radiation has greatly improved the ability of researchers to generate unattended single or multiple station data for the estimation of community metabolism. A suitable spring run segment is identified and equipped to provide a record of hourly dissolved oxygen concentration, percent saturation, and temperature conditions. Diffusion is estimated from knowledge of percent saturation and average flow velocity. Oxygen mass transport and rate-of-change are calculated from continuous flow records, hydraulic residence time, and dissolved oxygen concentration changes. Five components of community metabolism can be estimated using this methodology:

- Gross primary productivity (GPP), the total primary productivity of the entire submersed photosynthetic community, including all algae and macrophytes;
- Net primary productivity (NPP), the net difference between gross primary production and community respiration equal to the organic (fixed) carbon available at the base of the aquatic food web;
- Community respiration (CR), the dark respiration or oxygen consumption of the entire aquatic community, including microbial populations, algae, macrophytes and fauna;
- P/R ratio, ratio between gross primary production and community respiration, indicating autotrophic vs. heterotrophic status of the aquatic ecosystem;
- Photosynthetic (or GPP) efficiency, the conversion efficiency of useable PAR to gross primary production.

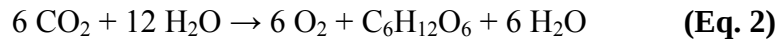
Primary Productivity

Primary productivity can be defined as the rate of formation of organic material from inorganic carbon by photosynthetic activity and through the photosynthetic generation of oxygen, can be measured as a rate value representing the conversion of solar energy to reduced chemical energy (Bott 2007). In the process of creating this organic material, some energy is lost through respiration (R_a), while the resulting formation of organic material is often defined as net primary productivity (NPP), and the combination represents gross primary productivity (GPP). This can be represented as:

$$GPP = NPP + R_a \quad (\text{Eq. 1})$$

Gross primary productivity (GPP) is the total primary productivity of the entire submersed plant community, including all algae and macrophytes, and typically expressed in terms of the amount of oxygen produced per unit area and unit time, (*i.e.*, g O₂/m²/d). Net primary productivity (NPP) is the net difference between gross primary production and community respiration and is equal to the organic carbon available at the base of the aquatic food web. Daily dissolved oxygen rate of change measurements integrate a number of ecological functions and are readily convertible to units of energy (Reeder and Binion 2001).

While there are primary producer bacteria which generate organic mater without solar inputs (*i.e.* chemoautotrophs), they do not generate oxygen and their importance in Florida spring ecosystems is unknown but believed to be minor. Therefore the measurement of primary production in spring ecosystems is based on the equation describing photosynthesis:



The rate of photosynthesis can be measured via changes in dissolved oxygen (or alternatively carbon dioxide) typically in units of mass per area per time, such as g O₂/m²/d. The utilization of dissolved oxygen changes to measure community metabolism in streams was pioneered by Odum (1956) in his study of Florida springs. It was based on the theoretical considerations that oxygen is introduced into the water as a result of photosynthetic primary production during the daylight hours; oxygen is consumed by living organisms (bacteria, animals, and sometimes chemical oxidation); oxygen is diffused into air or water depending on the saturation gradient; there can be a potential influx of oxygen through accrual of groundwater and surface drainage inputs (see Figure 14). Therefore, changes in dissolved oxygen concentrations (C) are a function of photosynthesis (P), community respiration (R), atmospheric diffusion (D), and corrected for the accrual (if needed) from discrete water inputs from surface or groundwater inputs:

$$C_{\text{oxygen}} = P - R \pm D + A \quad \text{(Eq. 3)}$$

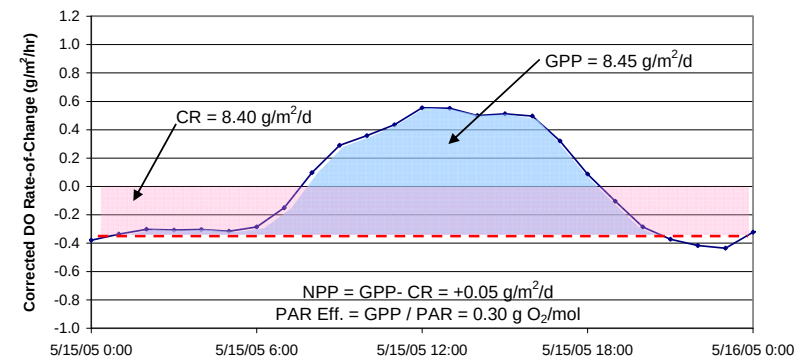
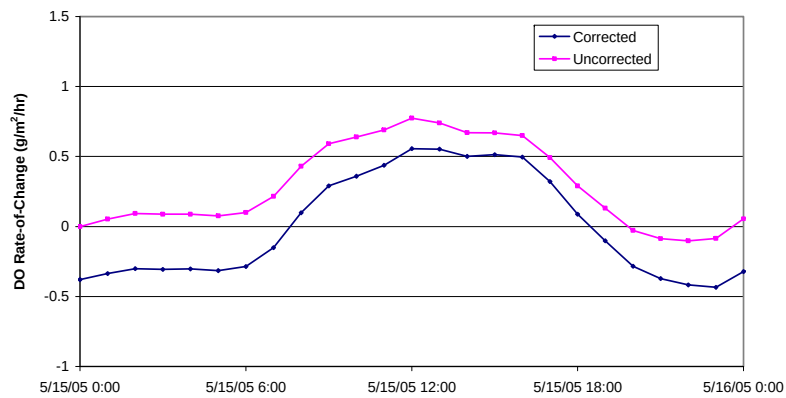
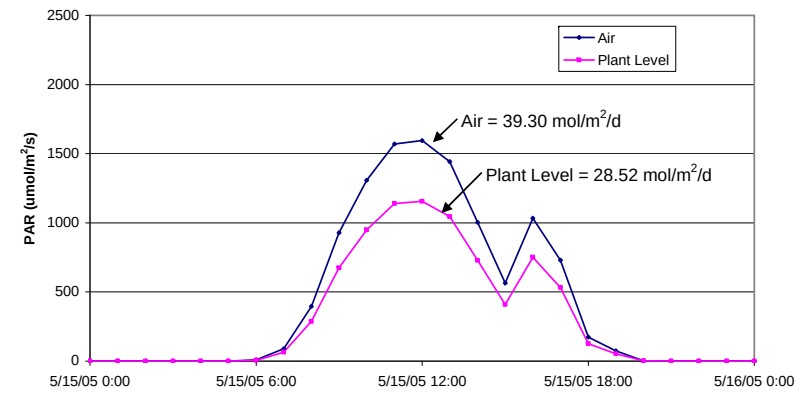
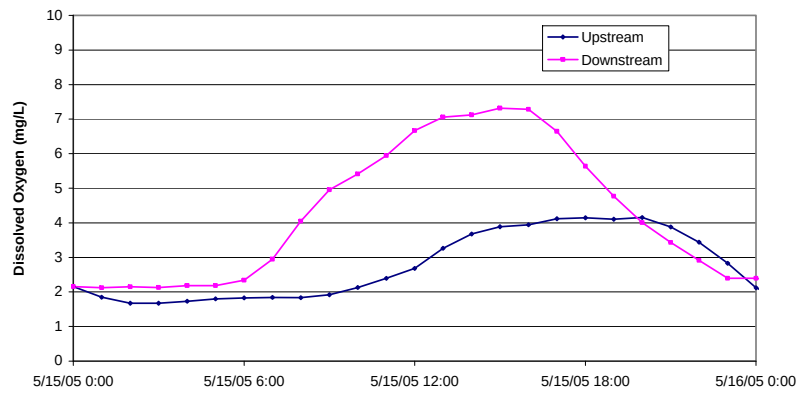


Figure 14 – Example determination of ecosystem metabolism based on upstream-downstream dissolved oxygen data from Silver Springs (from WSI 2007b).

Community Respiration

Community respiration (CR) is the oxygen consumption of the entire aquatic community (ecosystem), including microbial, floral and faunal populations. Respiration is reported as community respiration because there is no practical way to differentiate between the metabolism of heterotrophs, such as microbes, invertebrates, and fish; and that of autotrophs. Community respiration occurs throughout day and night periods and it is assumed that nighttime CR equals daytime CR. Community respiration can be strongly affected by the biogeochemical oxygen demand of the microbial community, which can rapidly increase following inputs of organic matter such as riparian litterfall or aquatic plant detritus following herbicide applications (WSI 2006).

Because respiration can not practically be differentiated between autotrophs or heterotrophs, it is collectively termed community respiration and is commonly expressed on a daily basis as CR₂₄, and which adds some uncertainty in the estimation of GPP and NPP (see equation 1). Hence, net primary production (NPP) may be more accurately termed net daily metabolism (NDM, or net ecosystem productivity or net community productivity) or the net change in oxygen concentration through biological activity, thus:

$$\text{NDM} = \text{GPP} - \text{CR}_{24} \quad (\text{Eq. 4})$$

Productivity/Respiration Ratio

The ratio of gross primary production to community respiration (P/R) was introduced by Odum (1956) as a simple index of the relative dominance (or balance) of autotrophic and heterotrophic metabolism in stream ecosystems. As such, the P/R ratio was intended to classify ecosystems as either autotrophic (P/R > 1) or heterotrophic (P/R < 1) depending on whether ecosystems were net producers or net consumers of organic matter. Heterotrophic state (community respiration) and autotrophic state (gross primary production) are related (Dodds 2006, as an ecosystem with high autotrophic activity will likely have high heterotrophic activity and certainly have high community respiration; however, an ecosystem with more heterotrophic activity will not necessarily have more autotrophic activity (*e.g.*, the condition obtained with high biological oxygen demand loading). An asset of P/R ratios is that they provide for consideration of enrichment by organic carbon in addition to nitrogen and phosphorus, while recognizing that stream food webs can be based on autotrophic or heterotrophic organisms (Dodds 2006).

Photosynthetic Efficiency

Photosynthetic (or gross primary productivity, GPP) efficiency represents the efficiency of conversion of light energy to organic matter through the photosynthetic activity of primary producers. Photosynthetic efficiency considers the light energy that primary producers can utilize, commonly referred to as photosynthetically active radiation (PAR), which has wave lengths between 400 and 700 nm (Kirk 1994) and expressed in units of light (quanta, moles, or Einsteins) per unit area and time. As gross primary production is typically expressed in terms of

the amount of oxygen produced per unit area and unit time, (*i.e.*, g O₂/m²/d), the resulting photosynthetic efficiency term can be expressed as g O₂/mol of PAR.

Community Export

Community export refers to downstream losses of organic carbon from the spring system. Plant matter (algae and macrophyte biomass) is typically lost from attached plant communities and flows downstream, partially forming the basis for downstream food webs. This downstream export can be readily estimated by sampling two components (WSI 2006, 2007b):

- Floating macrophytic and algal/plant materials
- Fine particulate export of microscopic plant and algal materials.

Pollutant (Nutrient) Assimilation

Flowing aquatic ecosystems are highly productive (Odum 1956), and hence have tremendous potential to productively assimilate nutrients and other pollutants within definable concentration ranges. Effectively assimilated nutrients are either used by the aquatic ecosystem to enhance its own productivity and food-chain support functions, are permanently buried in sediments, or are lost to the atmosphere (nitrogen only). Net nutrient assimilation rate can be estimated based on upstream and downstream nutrient concentrations, discharge rates, and effective volume and surface area of the aquatic system (WSI 2006, 2007b). Detailed process studies are essential to understand and quantify gross nutrient flux in aquatic systems (see Chapter 3).

Ecosystem-level metrics of spring (and stream or aquatic) ecosystems may provide essential methods for assessing impairment of designated beneficial uses. Three different but interrelated measures of the whole ecosystem function for spring (and stream) ecosystems are: community metabolism; community export; and nutrient assimilation rates. When quantified, they can be compared to reference sites and have been found to be sensitive to perturbations and pollutants.

Secondary Productivity

Consumers convert the chemical energy contained in their food into their own biomass in a process called secondary productivity and the efficiency of this transfer of energy up trophic levels has been termed ecological efficiency (Lindemann 1942). In other words, ecological efficiency is a measure of the amount of energy in the biomass that is produced by one trophic level and subsequently incorporated into the biomass produced by a higher trophic level; on average only 10 percent of energy is transferred with the balance lost through respiration and heat loss (Ricklefs 1990).

Based primarily on his research at Silver Springs and other Florida springs, H.T. Odum (1983) hypothesized that community metabolism as measured by gross primary productivity or by total community respiration is maximized in adapted ecosystems. Odum's hypothesis was named the "Maximum Power Principle" and its importance becomes increasingly clear as researchers attempt to explain the complex cause and effect relationships of multiple stressors in spring

ecosystems. Knight (1980) tested this hypothesis at Silver Springs and found that the *in situ* periphyton productivity of mesocosms in Silver Springs was in fact maximized when consumer densities were approximately the same as those that naturally occur in the spring ecosystem. Ecosystem productivity was found to be lower when consumer densities were lower and higher than this apparent optimum.

In his metabolism measurements at eleven Florida springs, Odum (1957a) found that most were operating at similar ecological efficiencies, or in other words, their abilities to effectively utilize solar inputs to fix carbon (*i.e.*, primary producer biomass) were approximately equal. Until proven otherwise, it may reasonably be assumed that spring ecosystems cannot consistently exceed these observed ecological efficiencies. This assumption is borne out by observation that the gross primary productivity values measured in relatively unaltered springs are at the same approximate level as gross primary productivity documented in other highly adapted and subsidized ecosystems (*e.g.*, coral reefs, tropical rain forests, fertilized agricultural operations, etc.).

The importance of the Maximum Power Principle for assessing nutrient effects in spring ecosystems cannot be overstated. All significant biological activity in a typical spring ecosystem is dependent upon autochthonous productivity. Ultimately the number and secondary productivity of macroinvertebrates, amphibians, reptiles, fish, birds, and mammals is dependent on the efficiency of the conversion of sunlight to reduced carbon by photosynthetic plants living in the spring flow. If in their natural state, springs are indeed already adapted to run at optimal efficiency, then any perturbation that upsets the natural balance of the system will reduce the gross primary productivity (power) of the spring flora and thereby lower the life-support capacity of the spring. Work by Knight (1980) confirmed that this general principle (also known as the “subsidy-stress hypothesis”, [E. P. Odum *et al.* 1979]) operates in Silver Springs *in situ* mesocosms when densities of primary consumers (snails) and secondary consumers (small fish) were altered from their normal, adapted levels. Chapter 6 pursues this line of reasoning further in evaluation of the proximal and ultimate effects of nutrient increases on spring ecology.

HUMAN AND AESTHETIC USES

The use of springs by humans has always been important, although their primary uses have likely changed over time. In prehistoric times, springs would have represented important locations for high quality drinking water and as areas that would have attracted prey resources. Based on these attributes, some early human settlements were associated with springs. The use of springs for drinking water supply still continues, commonly as a source for bottled water.

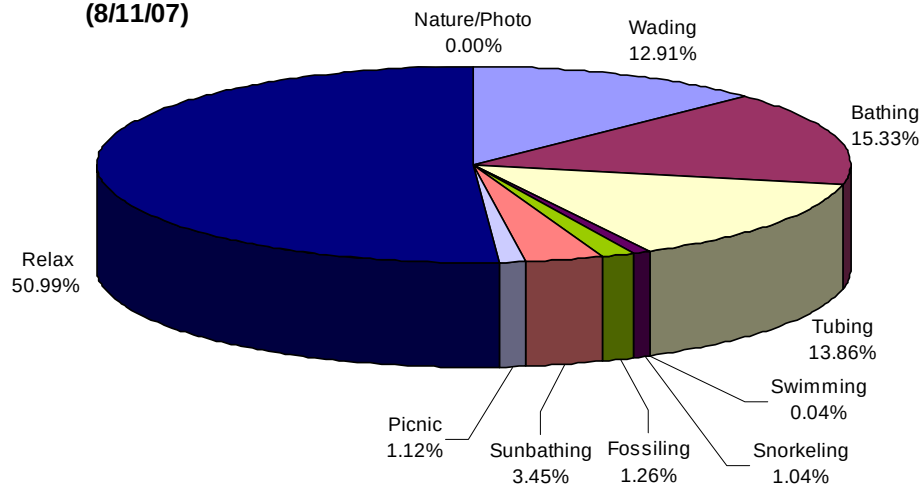
Human usage and the resulting direct impacts are often critical in the health of spring ecosystems. Important components of human usage include: the total number of visitors, the number of visitors actually entering the springs and spring runs for water dependent activities (wading, tubing, kayaking, canoeing, swimming, scuba diving, or snorkeling), and number of visitors for other non-water dependent activities (picnicking, hiking, and bird watching). The human component includes the inputs of money spent to visit and utilize springs for recreation and aesthetic purposes. In one perspective, maintaining and protecting spring ecosystems from degradation ensures that monetary inputs are not diminished. Unfortunately, human recreation can alter spring ecosystems by direct damage to primary producers through erosion, trampling,

cutting, and uprooting of macrophytes resulting from wading, power boat propellers, and boat anchors. Indirect human effects include changes in the quality and quantity of groundwater supplying spring ecosystems from land use changes and population increases around springs. Ironically, it may be the aesthetic attraction that springs hold for human beings which leads to their subsequent recreational over exploitation.

Recreational Uses

During the last century, Florida's springs have been utilized for recreational activities and, consequently, many springs have been physically modified for this purpose. Physical modifications found at a number of springs include the following: seawalls, rip rap, dams and weirs, deposition of beach sand, boardwalks and docks, concrete-lined swimming pools, and large covered facilities for boats and people. Broadly speaking, springs attract users who will be engaged in two types of outdoor recreation, those that are water dependent (*i.e.* water contact) such as swimming, snorkeling, wading, bathing, tubing, or canoeing, and those that are non-water dependent but focus upon the spring's aesthetics; these include sunbathing, picnicking, hiking, bird and people watching, or camping. As Figure 15 illustrates, detailed summer weekend counts at Rock and Wekiwa Springs in Orange County, Florida, found that there was an approximately even distribution between water contact and non-contact activities, as well as a demonstration that recreational activities vary by spring due to site-specific characteristics such as water depth and flow velocity. Unique recreational or tourism features exist at many springs as well; Silver Springs is noted for its glass bottomed boat tours, Homosassa Springs its underwater "fish bowl" viewing chamber, Ichetucknee Springs is a noted tubing destination, and Volusia Blue Springs is noted for winter time viewing of manatees. The one generalization that can be made concerning springs today is that all of the larger springs (first magnitude) are managed as parks, either by private or public entity.

**ROCK SPRINGS (KELLY PARK)
(8/11/07)**



**WEKIWA SPRINGS
(8/12/07)**

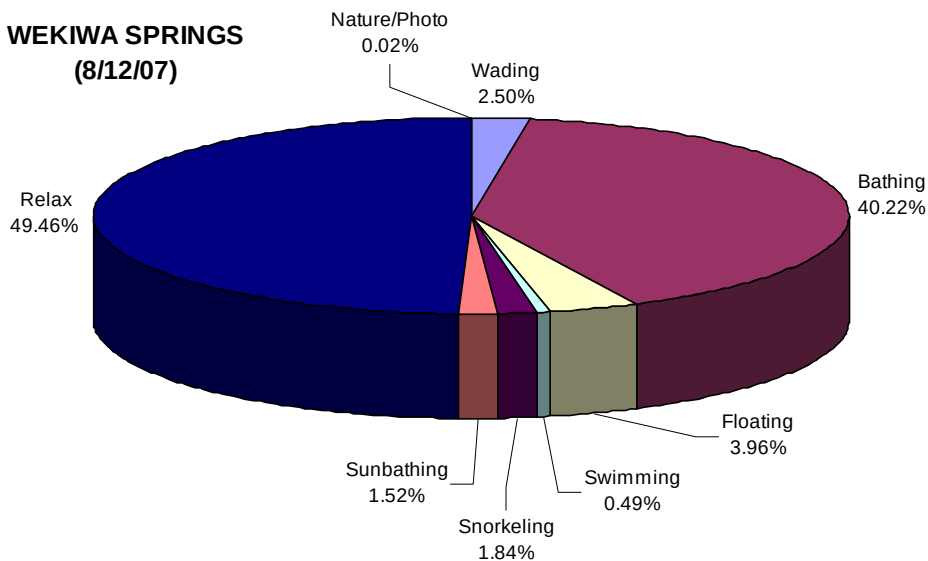


Figure 15 – *Water dependant recreational activity by category for Rock Springs (Kelly Park) and Wekiwa Springs State Park on August 11th and 12th, 2007 (WSI 2007a).*

Visitation Seasonality

Visitation has seasonal characteristics, as most water dependent recreation takes place during the warmer seasons when spring waters can provide a refreshing experience. One study of eight springs (Silver Glenn, Silver, Alexander, Apopka, Bugg, Ponce de Leon, Gemini, and Green) in the St. Johns River Water Management District of Florida documented that these springs

experienced peak use in spring (Apr-Jun) and summer periods (Jul-Sep) (Bonn 2004). Comparisons of human use at two springs with very different seasonal patterns are illustrated in Figure 16. The influence of non-contact water recreation can be detected in the results of a study of spring visitation in four springs located in Florida state parks: Ichetucknee, Wakulla, Homosassa, and Volusia Blue. Peak attendance for these springs occurred from spring through summer for Ichetucknee and Wakulla, where in-water activities are the dominant forms of recreation and from winter through spring for Homosassa and Volusia Blue (which had a July peak also), reflecting the influence of non-contact recreation using winter tourism, fish observation, and manatee watching (Bonn and Bell 2003). Seasonal recreational shifts are observed at Volusia Blue Spring State Park, where in-water activities are prohibited in the fall and winter when large numbers of manatees are present; but are offset by the great number of visitors which come to the park during these time periods for manatee observation. Patterns in the weekly usage were reported in a comprehensive study of Rainbow Springs river recreation (Holland and Cichra 1994), in which weekend use levels were twice or more the use levels of the total for the weekdays.

Visitation Numbers

In-water recreation use numbers in springs are dependent on time of year, day of week, and weather, with highest use during summer holiday weekends (Memorial Day, Fourth of July, and Labor Day). Estimates of annual numbers of Rainbow River users yielded about 33,000 people recreating on the river in 1994 (Holland and Cichra 1994). This relatively low number is an estimate of just those persons engaged in water dependent recreation on the Rainbow River (mostly tubers floating downstream) and did not include persons recreating at the headsprings and associated park where annual visitation is substantially higher. Another study of water dependent recreational users was conducted on Silver Glenn Spring (Pandion Systems, Inc. 2003) in which the main types of recreation observed were swimming, fishing, and boating. Swimmers utilized both the park's recreation area and boats to gain access to the spring, but all fishing was done from boats ranging in types and sizes from small runabouts less than 5 m to houseboats approaching 20 m in length, and many of the larger vessels stayed in the spring run for multiple days at a time. During summer holiday events, as many as 200 boats could be found in the Silver Glenn Spring run, an area of approximately 6.1 ha (15.2 ac).

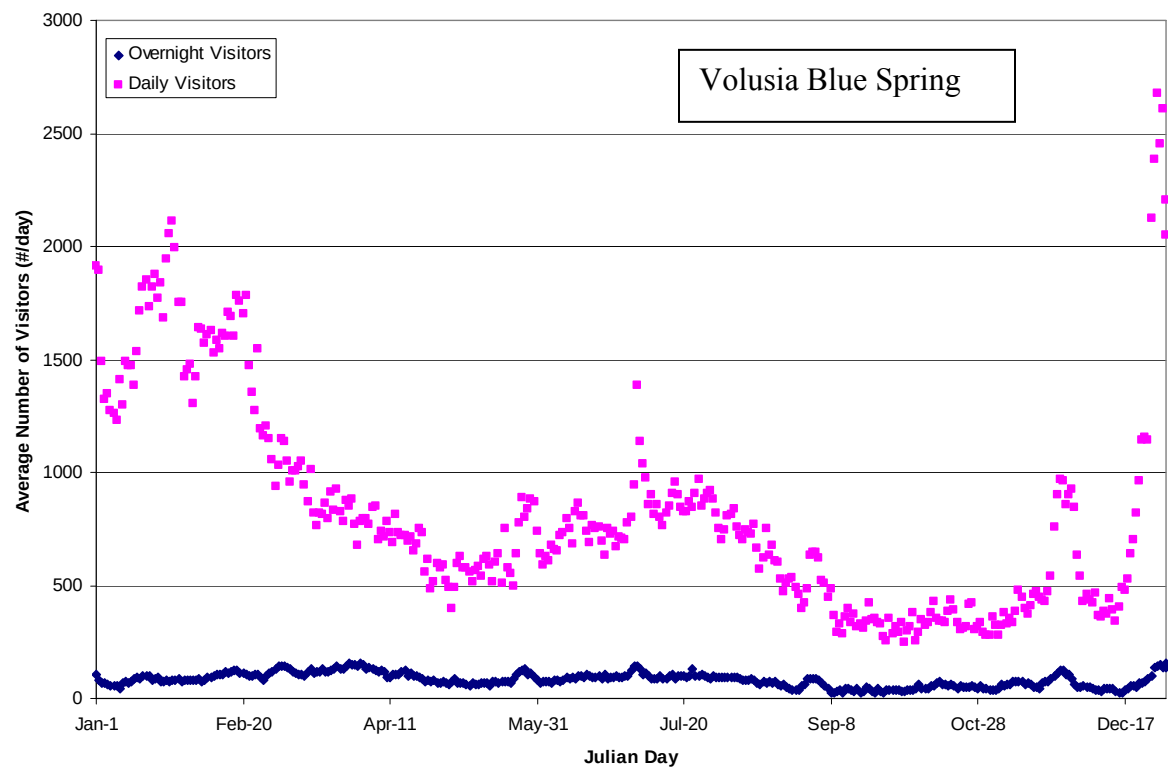
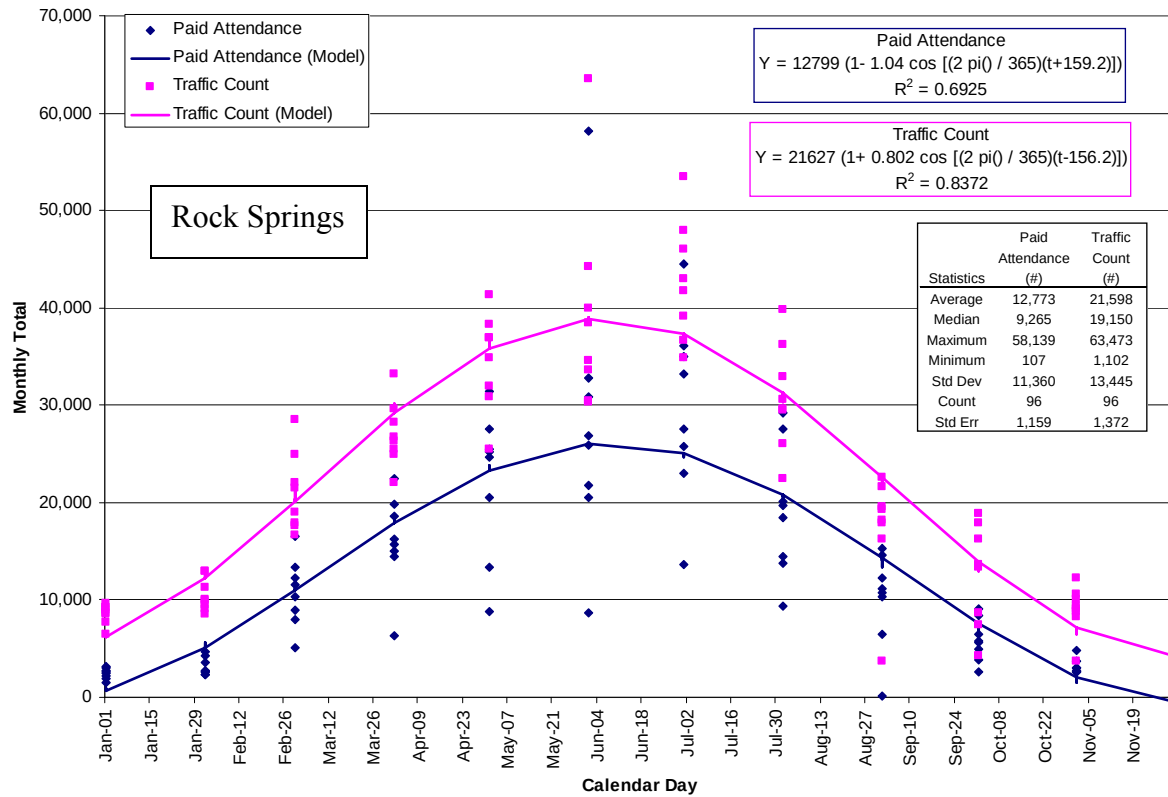


Figure 16 – Comparison of human use seasonality at Rock Springs and Volusia Blue Springs (from WSI 2007a and WSI 2003 respectively).

Visitation numbers are influenced by the unique features of the spring, as well as other factors such as adequate parking and regulations (*i.e.*, no alcoholic beverages allowed at state parks). The number of people utilizing a representative sample of Florida's springs is available in two detailed socioeconomic reports (Bonn and Bell 2003, Bonn 2004). Bonn and Bell 2003 examined attendance records from 1992-2002 for four springs-focused state parks each with large numbers of human utilization. Over this 11 year period of record, annual attendance to the Ichetucknee Springs State Park increased from 134,000 people to nearly 189,000 people (41% increase), Wakulla Springs annual visitor attendance increased from 163,000 to 184,000 (13% increase), Homosassa Springs State Park annual visitor attendance increased from over 200,000 to nearly 266,000 (33% increase), and Volusia Blue Spring State Park annual visitor attendance decreased from 360,000 to 337,000 (6.4% decline).

In Bonn 2004, visitation numbers for eight different Florida springs in Marion, Lake, and Volusia Counties of Florida were estimated using 2002/2003 data with annual attendance estimates for the smaller spring ecosystems being 5,776 for Apopka, 2,888 for Bugg, 14,439 for Green, and for the larger springs, 77,233 for Alexander, 57,755 for Gemini, 259,000 for Ponce de Leon, 1,096,000 for Silver, and 39,235 visitors a year for Silver Glenn Springs.

Between these two studies which used data from the years 2002 and 2003, total attendance for the six first magnitude springs (Silver Springs excluded) was approximately 1,092,468 persons, representing an average annual attendance of approximately 182,000 persons per first magnitude spring. Silver Springs was not included in this average value because as many people visited this one spring as the other six first magnitude springs combined, which would have skewed the calculated average visitation statistics.

Excluding river rises and karst windows, Florida has 24 first magnitude springs/ spring groups, the majority of which provide public recreation (Scott *et al.* 2002); multiplying this number by the average number of visitors calculated above results in over 4.4 million potential visitors and when combined with the approximate 1.1 million visitors to Silver Springs alone, results in 5.5 million visitors per year in 2002/2003 numbers. The Bonn and Bell (2003) data suggest an annual average increase of 1.26% in visitation, which if applied to the previous estimate, results in over 5.7 million visitors to first magnitude springs per year during 2006/2007. Smaller springs (2nd and 3rd magnitude) also attract numerous visitors, sometimes as many or more than larger springs. For example, Ponce de Leon Spring (Holmes County), attracted an estimated 259,000 visitors in 2002, although visitation numbers for smaller springs are probably in the thousands to tens of thousands per year (Bonn 2004).

The estimate used above of applying the average attendance figures from six first magnitude springs to total number of statewide first magnitude springs is simplified and certainly an approximation. As the detailed studies by Bonn and Bell (2003) and Bonn (2004) illustrate, there is much variation from spring to spring, both in visitation numbers (and economic impact) due to the unique characteristics of each spring and the recreational opportunities it presents. Nevertheless, this estimate of the potential number of visitors has value as it quantifies this likely significant ecological effect, namely the number of visitors (greater than five million per year), that may be utilizing Florida's springs for recreation.

Economic Impacts

Bonn and Bell (2003) report direct economic impacts for four major springs-related Florida state parks estimated by visitor spending in 2002, which ranged from nearly \$23 million at Ichetucknee Springs to \$10 million at Blue Spring. Individually, the Ichetucknee Springs and Wakulla Springs had similar estimates of overall spending for the two parks (approximately \$22 million). Although Ichetucknee Springs attracts more visitors from outside the area, Wakulla Springs' visitors spend more than those visiting Ichetucknee Springs; on average \$89 a person per day is spent at Wakulla Springs and \$34 at Ichetucknee Springs (2003 dollars). At the lower end of economic impact were Homosassa Springs and Volusia Blue Spring with total spending estimates of \$13.6 million and \$10 million respectively in 2002. These estimates were the result of these parks being heavily attended by visitors from outside the county with relatively low spending per visitor. In terms of wages and salaries, Ichetucknee Springs generated the highest wages at \$5.09 million and Wakulla Springs generated the most employment at 347 jobs (Bonn and Bell 2003).

The Bonn (2004) study of eight different springs revealed that total annual direct spending by visitors accounted for over \$65 million, generated over \$13 million in wages, and created over 1,100 jobs. Average daily spending was estimated by category and varied widely between parks; however, four park average spending by category was 22.9% for restaurants, 19.9% for admission fees, 14.8% for groceries, 13.8% for shopping, 13.5% for lodging, 6.4% for evening entertainment, 4.3% for transportation, and 4.3% for all other spending. Silver Springs, which has a large theme park associated with the natural springs' environment, accounted for 94% of the total economic impact, while the remainder of the springs contributed only 6%. This illustrates that the revenues, jobs, and economic impacts generated by Silver Springs has more to do with its development as a tourist site (with commensurate gate fees and retail purchase opportunities) rather than simply being one of Florida's largest springs, and that the economic impact generated by the Silver Springs attraction cannot be directly applied to other springs. This may be especially true considering springs- focused parks operated by governmental agencies that do not have a profit-focused business plan. Nevertheless, based on the examples where economic impacts have been estimated, it can be suggested that Florida's major springs make substantial economic contributions.

Effects of Recreation on Spring Ecosystems

A study of Silver Glenn Spring observed the majority of the spring run (6.1 ha) showed impacts from recreation, with direct or indirect mechanical damage from boat propellers and anchors (Pandion Systems, Inc. 2003). While swimming generally caused little impact on submersed aquatic vegetation, wading caused trampling and areas near the spring boil where visitors accessed the water were devoid of submersed aquatic vegetation, as was the western part of the run where boaters preferred to anchor (Pandion Systems, Inc. 2003). The Holland and Cichra (1994) study also characterized the effects of recreation on the submersed aquatic vegetation in Rainbow River. During periods of low recreational use, the quantity of uprooted and cut drifting plants did not increase as recreation activity increased throughout the day, but during periods of high use, the quantity of drifting plants did increase with increased recreational activity. It was also noted that very few areas throughout the river appeared to be devoid of vegetation due to

recreational activity, instead appearing to be influenced more by natural factors, such as water depth and substrate. Shallow areas were prone to propeller damage; because recreational activity of several different user groups (*i.e.* tubers, boats, canoes) occurred at the same time, it was difficult to determine which user group was responsible for the observed plant damage. However, observational evidence suggested that the majority of the damage to submersed aquatic vegetation was due to power boats. The findings of these two studies (Holland and Cichra 1994, Pandion Systems, Inc. 2003) suggest that the type of recreation strongly influences the effect on vegetation and that power boats have the most potential to cause harm. Personal observations indicate that people wading in shallow areas result in the near total absence of submersed vascular plants, while filamentous and attached macroalgae can remain and appear substantially more resistant to damage from trampling.

Perhaps the most influential study to gauge the impact of recreational use (largely tubers) on the submersed aquatic vegetation and benthic habitats was conducted on the Ichetucknee River (Dutoit 1979). This study demonstrated a linkage between recreational activities and damage to the ecology of the spring run, primarily through physical disturbance in the form of trampling, uprooting, breakage, and generalized destruction of submersed and emergent aquatic vegetation. Recognizing that the aquatic vegetation stabilizes sediments and forms the basis for the food web of this spring system, park management adopted limits to the number of recreationalists on the Ichetucknee River. Subsequent management changes to the number and frequency of recreational tubers using the river were implemented to minimize damage to the submersed aquatic vegetation. This entailed setting the daily number of tubers to 750 in the upper river and 2,250 at the midpoint tube launch, as well as closing the shallow upper section from September through May following the peak summer use period; such limitations allowed for aquatic plant re-growth (Florida Department of Environmental Protection 2000).

Human Use Carrying Capacity

The concept of carrying capacity has been applied to outdoor recreation as a technique to manage the impact of human use on natural resources. Various facets of carrying capacity as applied to springs in public use areas include: the physical amount of space needed to accommodate recreation; visitors needs such as parking or restrooms; the ecological impacts of recreation on air, water, soil, plant, or animal resources; and the social carrying capacity defined as the level of human use above which the quality of recreation would be diminished (Billington 1995). Thus recreational carrying capacity has two components, ecological and social, with ecological relating to environmental damage and social relating to the visitor (Shelby and Herblein 1986).

Published case studies of the carrying capacity of Florida's spring ecosystems have been conducted on the Rainbow and Ichetucknee Rivers and relied on the visitor surveys to characterize maximum usage levels. Generally, perceptions of increased crowding resulted in decreased satisfaction among users. According to Holland and Cichra (1994) visitors' perceptions of crowding on the Rainbow River indicated that 65% of weekend users rated the river "slightly" to "moderately" crowded, and 8% reported "extremely" crowded, while 83% of weekday river users reported the river as "not at all" to "slightly" crowded and 2% reported "extremely" crowded. Perceptions of crowding by visitors were correlated with self-reported

levels of satisfaction of their springs experience by Holland and Cichra (1994), with 52% of weekend users and 49% of weekday users rating their trip as "perfect" or "excellent", and only 5% of weekend users and 4% of weekday users rated their trip as fair or poor. A subsequent study of visitor tolerance for crowding was made in an effort to better gauge social carrying capacity through the perceptions and experiences of 464 recreational visitors utilizing the Rainbow River between May and September 1994 (Billington 1995). This study treated perceptions of social carrying capacity as a function of crowding among three user groups: tubers, motorized boaters, and non-motorized boaters. Results suggest that perceived crowding was highest among motorized boaters and lowest among tubers, while satisfaction levels were highest for non-motorized boaters and lowest among tubers. The relation between crowding and satisfaction suggests that the social carrying capacity for tubers may be approached during heavy use days, but overall, insufficient evidence exists to conclude that social carrying capacity has been exceeded for the majority of river users at the Rainbow River (Billington 1995).

A final study examining the social carrying capacity was provided by Paulauskas' (2001) research examining the experience of recreationalists using the Ichetucknee River in relation to perceptions of crowding. Results were derived from 320 respondent surveys conducted on site between May and June 2000. The author reported that if respondents encountered fewer than expected recreationists, they rated their experience as "highly satisfying" and that respondents with no expectations or who encountered as many as expected, also rated their experience as "highly satisfying". However, perceptions of crowding did appear to influence overall satisfaction levels of river recreationists and the study revealed an inverse relationship with crowding on overall satisfaction ratings, in that as perceptions of crowding increased, satisfaction levels decreased (Paulauskas 2001). The results from this study indicate that despite heavy weekend use, when between 50% and 65% of the respondents rated the river as crowded, perceptions of social carrying capacity did not appear to be exceeded. This suggests that for Ichetucknee Springs State Park, a good balance between the need to meet recreational use demands and the need to limit recreational numbers for ecosystem protection has been achieved.

DISCUSSION

Spring and spring runs are complex aquatic ecosystems with a variety of forcing functions, energy storage structures, and ecosystem processes. These ecosystems are entirely dependent upon the amount and nature of the energies and materials they receive from local, regional, and even global systems in which they are embedded. Far too often, the study of these spring ecosystems has focused on select forcing functions or individual structural components with inadequate consideration of the whole. While these species or process-level observations contribute towards our knowledge of spring ecosystems, their interpretation and applicability is likely to be limited to the spring from which they were gathered and provide little insight into the generalized responses of springs to anthropogenic impacts.

As evidenced throughout this report, dozens of research and monitoring projects have been conducted in Florida's springs over the past decade. While our knowledge about specific indicator organisms or limited trophic groups in springs has increased as a result of these studies, they have pointed more to the factors that are different between springs rather than to their underlying similarities. Quantification and comparison of multiple forcing functions, entire

trophic level structure, and ecosystem-level processes such as gross primary productivity and community respiration provides a more holistic view of springs and holds promise for developing commonalities among the hundreds of different springs that occur in Florida.

Chapter 6 of this report provides an in-depth review of examples of holistic studies in spring ecosystems, as well as conclusions from that research and recommendations for future research. Increased nutrient inputs in many of Florida's springs are an observed fact, as described above and in the following chapters. Nutrient inflows to springs are one ecological forcing function that has the potential to significantly alter the form and function of the impacted spring ecosystems. However, for improved understanding and management of springs as natural resources, elevated spring nutrient concentrations must be placed into the context of the overall spring ecosystem, including the numerous additional external forcing functions described in this chapter. A holistic approach to providing some quantification or estimation of all of the principal forcing functions and key details of spring structure and function should be considered in future spring studies.

REFERENCES

- Allan, J.D. 1995. Stream Ecology, Structure and function of running waters. Chapman and Hall. 388 pp.
- Bengtson, J.L. 1983. Estimating Food Consumption of Free-Ranging Manatees in Florida. The Journal of Wildlife Management 47(4): 1186-1192.
- Billington, H.E. 1995. Use Levels, Encounters, Satisfaction and Perceived Crowding among Recreation Visitors to the Rainbow River. M.S. Thesis. University of Florida. 90 pp.
- Bonn, M.A. 2004. Visitor profiles, economic impacts and recreational aesthetic values associated with eight priority Florida springs located in the St. Johns River Water Management District. Special Publication SJ2004-SP35.
- Bonn, M.A. and F.W. Bell. 2003. Economic Impact of Selected Florida Springs on Surrounding Local Areas. Report prepared for the Florida Department of Environmental Protection. Tallahassee, FL.
- Botosaneanu, L. (Ed.). 1998. Studies in Crenobiology. The Biology of Springs and Springbrooks. Backhuys Publishers, Leiden, The Netherlands. 261 pp.
- Bott, T.L. 2007. Primary productivity and community respiration. *In*: Hauer, F.R. and G.A. Lamberti (Eds.). Methods in stream ecology, 2nd Edition. Academic Press. 877 pp.
- Brown, M.T. 2008. Original conceptual springs regional diagrams used in Figures 3a, 5, and 6. Department of Environmental Engineering Sciences. University of Florida. Gainesville, FL.
- Butcher, R.W. 1933. Studies on the ecology of rivers. I. On the distribution of macrophytic vegetation in the rivers of Britain. Journal of Ecology 21: 58-91.
- Butt, P.L., T.L. Morris, and W.C. Skiles. 2007. Swallet/Resurgence Relationships on the Lower Santa Fe River, Florida. Karst Environmental Services, Inc. High Springs, Florida. Prepared for Water Resource Associates, Inc. Tampa, Florida.
- Champion, K.M. 2001. Chemical characteristics of selected springs in the Southwest Florida Water Management District. Final Report. 107 pp.
- Chelette A., T.R. Pratt, and B.G. Katz. 2002. Nitrate loading as an indicator of nonpoint source pollution in the lower St. Marks-Wakulla Rivers watershed. Northwest Florida Water Management District. Water Resources Special Report 02-1. <http://www.nwfwmd.state.fl.us/pubs/nitrate/wrsp02-1.htm>
- Cohen, M.J. 2007. Sources, transport and transformations of nitrate-N in the Florida environment. Final Report. St. Johns River Water Management District. SJ2007-SP10.

- Davis, A. and B. Herring. 2005. Inventory of rare and endemic plant and animal species of Ponce DeLeon, Gemini, and Green Springs. Florida Natural Areas Inventory. Tallahassee, FL. Final Report for the St. Johns River Water Management District. Special Publication SJ2006-SP8.
- Dodds, W.K. 2006. Eutrophication and trophic state in rivers and streams. *Limnology and Oceanography* 51(1, part 2): 671 - 680.
- Duarte, C., Y. Prairie, T. Frazer, M. Hoyer, S. Notestein, D. Canfield, Jr., and R. Martinez. 2007. Abstract: High CO₂ flux from Florida springs. 30th Congress of the International Association of Theoretical and Applied Limnology. Montreal, Canada.
- DuToit, C.H. 1979. The carrying capacity of the Ichetucknee Springs and River. M.S. Thesis. University of Florida. Gainesville, FL. 176 pp.
- Fernald, E.A. and E.D. Purdum (*Eds.*). 1998. Water Resources Atlas of Florida. Institute of Science and Public Affairs. Tallahassee, Florida.
- Florida Department of Environmental Protection (DEP). 2000. Ichetucknee Springs State Park Approved Unit Management Plan. Division of Recreation and Parks, Florida Department of Environmental Protection. Tallahassee, FL. 148 pp.
- Florida Department of Environmental Protection (DEP). 2006. Florida's Springs Strategies for Protection and Restoration. Prepared by The Florida Springs Task Force. 185 pp.
- Florida Geological Survey (FGS). 2007. Florida Springsheds. Geographical information system data file. Department of Environmental Protection / Florida Geological Survey. Tallahassee, FL.
- Frazer, T.K., S.K. Notestein, and W.E. Pine, Jr. 2006. Changes in the Physical, Chemical and Vegetative Characteristics of the Homosassa, Chassahowitzka and Weeki Wachee Rivers. Final Report. Prepared for the Southwest Florida Water Management District. Brooksville, FL. 174 pp.
- Gilbert, C.R. 1987. Zoogeography of the freshwater fish fauna of southern Georgia and peninsular Florida. *Brimleyana* 13: 25-54.
- Gurevitch, J., S.M. Scheiner, and G.A. Fox. 2002. The ecology of plants. Sinauer Associates, Inc. Sunderland, MA. 523 pp.
- Hauxwell, J.A., C.W. Osenberg, and T.K. Frazer. 2004. Conflicting Management Goals: Manatees and Invasive Competitors Inhibit Restoration of a Native Macrophyte. *Ecological Applications* 14(2): 571-586.
- Hauxwell, J.A., T.K. Frazer, and C.W. Osenberg. 2007. An annual cycle of biomass and productivity of *Vallisneria americana* in a subtropical spring-fed estuary. *Aquatic Botany* 87: 61-68.

- Holland, S.M. and C.E. Cichra. 1994. Human and environmental dimensions of the recreational use of Blue Run and Rainbow Springs State Park, Dunnellon, Florida. Final Report. Submitted to the Florida Department of Natural Resources, Division of Recreation and Parks. 275 pp.
- Hoyer, M.V., Notestein, S.K., Frazer, T.K., Canfield Jr., D.E. 2006. A comparison between aquatic birds of lakes and coastal rivers in Florida. *Hydrobiologia* 567: 5-18.
- Hubbs, C.L. and E.R. Allen. 1943. Fishes of Silver Springs. *Proceedings of the Florida Academy of Sciences* 6: 110-130.
- Hynes, H.B.N. 1970. The ecology of running waters. University of Toronto Press.
- Intera. 2006. Statistical Modeling of Spring Discharge at Rock and Wekiwa Springs in Orange County, Florida. Final Report. Prepared for the St. Johns River Water Management District, Palatka, FL.
- Jacoby, C.A., T.K. Frazer, S.R. Keller, and S.K. Notestein. 2007. Final Report. Kings Bay Submersed Aquatic Vegetation 2004 to 2006. Prepared for the Southwest Florida Water Management District. Brooksville, FL.
- Jones, G.W., S.B. Upchurch, K.M. Champion, and D.J. Dewitt. 1997. Water-quality and Hydrology of the Homosassa, Chassahowitzka, Weeki Wachee, and Aripuka Spring Complexes, Citrus and Hernando Counties, Florida (Origin of Increasing Nitrate Concentrations). Ambient Ground-Water Quality Monitoring Program. Southwest Florida Water Management District. 167 pp.
- Katz, B.G., H.D. Hornsby, J.F. Bohlke, and M.F. Mokay. 1999. Sources and chronology of nitrate contamination in spring waters, Suwannee River basin, Florida. *Water-Resources Investigations Report*: 99-4252.
- Kemp, W.M. and W.R. Boynton. 2004. Productivity, trophic structure, and energy flow in the steady-state ecosystems of Silver Springs, Florida. *Ecological Modeling* 178: 43-49.
- Kirk, J.T.O. 1994. Light and photosynthesis in Aquatic ecosystems. 2nd Edition. Cambridge University Press. Great Britain.
- Knight, R.L. 1980. Energy Basis of Control in Aquatic Ecosystems. Ph.D. Dissertation. University of Florida. 200 pp.
- Lindemann, R.L. 1942. The Trophic-Dynamic Aspect of Ecology. *Ecology* 23(4): 399-417.
- Loper, D.E., W.M. Landing, C.D. Pullman, A.B. Chan Hilton. 2005. Degradation of Water Quality at Wakulla Springs: Assessment and Recommendations. Report of the Peer Review Committee on the Workshop Solving Water Pollution Problems in the Wakulla Springshed of North Florida. 84 pp.

- MACTEC. 2007. Phase 1 Report Wekiva River Basin Nitrate Sourcing Study. Prepared for St. Johns River Water Management District and Florida Department of Environmental Protection. 183 pp.
- Martin, R.A. 1966. *Eternal Spring: Man's 10,000 Years of History at Florida's Silver Springs*. Great Outdoors Press, Inc., St. Petersburg, FL.
- Marzolf, E.R., P.J. Mulholland, and A.D. Steinman. 1994. Improvements to the diurnal upstream-downstream dissolved oxygen change technique for determining whole-stream metabolism in small streams. *Canadian Journal of Fisheries and Aquatic Sciences* 51: 1591-1599.
- Matson, P.A. and R.C. Harriss. 1995. *Biogenic Trace Gases: Measuring Emissions from Soil and Water (Ecological Methods and Concepts)*. Blackwell Science. Cambridge, MA. 394 pp.
- Mattson, R.A., J.H. Epler, and M.K. Hein. 1995. Description of benthic communities in karst, springfed streams of north central Florida. *Journal of the Kansas Entomological Society* 68(2): 18-41.
- Meinzer, O.E. 1927. Large springs in the United States. U.S.G.S. Water Supply Paper 557. 94pp.
- Miller, J.A. 1997. Hydrogeology of Florida. Ch. 6 *In* A.F. Randazzo and D.S. Jones (Eds.). *The Geology of Florida*. University Press of Florida. Gainesville, FL.
- Munch, D.A., D.J. Toth, C. Huang, J.B. Davis, C.M. Fortich, W.L. Osburn, E.J. Philips, E.L. Quinlan, M.S. Allen, M.J. Woods, P. Cooney, R.L. Knight, R.A. Clarke, S.L. Knight. 2006. Fifty-year retrospective study of the ecology of Silver Springs, Florida. Publication Number: SJ2007-SP4. St. Johns River Water Management District, Palatka, FL.
- Mulholland, P.J., C.S. Fellows, J.L. Tank, N.B. Grimm, J.R. Webster, S.K. Hamilton, E. Martí, L. Ashkenas, W.B. Bowden, W.K. Dodds, W.H. McDowell, M.J. Paul, and B.J. Peterson. 2001. Inter-biome comparison of factors controlling stream metabolism. *Freshwater Biology* 46: 1503-1517.
- Naiman, R.J. 1983. The annual pattern and spatial distribution of aquatic oxygen metabolism in boreal forest watersheds. *Ecological Monographs* 53: 73-94.
- National Atmospheric Deposition Program (NADP). 2007. Information and data available from web site: <http://nadp.sws.uiuc.edu/>. Accessed December 2007.
- Odum, E.P. 1971. *Fundamentals of Ecology*. Third Edition. W.B. Saunders Co., Philadelphia, PA.
- Odum, E.P., J.T. Finn, and E.H. Franz. 1979. Perturbation theory and the subsidy-stress gradient. *BioScience* 29: 349-352.

- Odum, H.T. 1956. Primary Production in Flowing Waters. *Limnology and Oceanography* 1: 102-117.
- Odum, H.T. 1957a. Primary Production Measurements in Eleven Florida Springs and a Marine Turtle-Grass Community. *Limnology and Oceanography* 2: 85-97.
- Odum, H.T. 1957b. Trophic structure and productivity of Silver Springs, Florida. *Ecological Monographs* 27(1): 55-112.
- Odum, H.T. 1983. *Systems Ecology: an Introduction*. John Wiley & Sons, New York, NY.
- Odum, H.T., Galindo, O., Parrish, B., Pinkerton, R., Sloan, W.C., and Whitford, L.A. 1953. Productivity of Florida Springs Factors controlling marine invasion in Florida fresh waters. Third semi-annual report to the Biology Division, Office of Naval Research 3: 134-156.
- Odum, H.T., E.C. Odum, and M.T. Brown. 1998. *Environment and Society in Florida*. Lewis Publishers. Boca Raton, FL.
- Pandion Systems, Inc. 2003. Carrying Capacity Study of Silver Glen Spring and Run. Prepared for the Florida Department of Environmental Protection. Tallahassee, Florida. 86 pp.
- Paulauskas, G. 2001. Factors Associated with Satisfaction of Recreational Users on the Ichetucknee River. M.S. Thesis. University of Florida. Gainesville, FL. 83 pp.
- Phelps, G.G. 1994. Hydrogeology, water quality, and potential for contamination of the upper Floridan Aquifer in the Silver Springs ground-water basin, central Marion County, Florida. USGS Water Resources Investigations Report 92-4159.
- Phelps, G.G. 2004. Chemistry of ground water in the Silver Springs Basin, Florida, with an emphasis on nitrate. Scientific Investigations Report 2004-5144. Denver, CO.
- Power, P. 1996. Effects of current velocity and substrate composition on growth of Texas wildrice (*Zizania texana*). *Aquatic Botany* 55(3): 199-204.
- Rabalais, N. 2002. Nitrogen in aquatic ecosystems. *Ambio* 31: 102-112.
- Reeder, B.C. and B.M. Binion. 2001. Comparison of methods to assess water column primary production in wetlands. *Ecological Engineering* 17: 445-449.
- Ricklefs, R.E. 1990. *Ecology*. 3rd Edition. W.H. Freeman and Company. New York, NY.
- Rosenau, J.C., G.L. Faulkner, C.W. Hendry Jr., and R.W. Hull. 1977. Springs of Florida. Bulletin 31 (revised). Division of Resource Management, Bureau of Geology, Florida Department of Natural Resources. Tallahassee, Florida. 461 pp.
- Scott, T.M., G.H. Means, R.C. Means, and R.P. Meegan. 2002. First magnitude springs of Florida. Florida Geological Survey. Open File Report No. 85. Tallahassee, Fl. 138 pp.

- Scott, T.M., G.H. Means, R.P. Meegan, R.C. Means, S.B. Upchurch, R.E. Copeland, J. Jones, T. Roberts, and A. Willet. 2004. Springs of Florida. Bulletin No, 66. Florida Geological Survey. Tallahassee, FL. 677 pp.
- Sculthorpe, C.D. 1985. The biology of aquatic vascular plants. Koeltz Scientific Books. Konigstein, Germany. 610 pp.
- Shelby, B., and T. Heberlein. 1986. Carrying capacity in recreation settings. Oregon State University Press. Corvallis, OR.
- Slack, L.J. and J.C. Rosenau. 1979. Water quality of Florida Springs. Florida Geological Survey, map series 96.
- Stevenson, R.J., A. Pinowska, A. Albertin, and J.O. Sickman. 2007. Ecological condition of algae and nutrients in Florida springs: The Synthesis Report. Prepared for the Florida Department of Environmental Protection. Tallahassee, FL. 58 pp.
- Stream Bryophyte Group. 1999. Roles of bryophytes in stream ecosystems. Journal of the North American Benthological Society 18(2): 151-184.
- Swanson, C.D. and R.W. Bachmann. 1976. A model of algal exports in some Iowa streams. Ecology 57: 1076-1080.
- Thompson, F.G. 2004. An identification manual for the freshwater snails of Florida. Florida Museum of Natural History. University of Florida. Gainesville, FL. Accessed December 2007 at: <http://www.flmnh.ufl.edu/malacology/fl-snail/snails1.htm>
- Toth, D.J. 2003. Water quality and isotope concentrations from selected springs in the St. Johns River Water Management District. Technical Publication SJ2003-1. Palatka, FL: St. Johns River Water Management District.
- Walsh, S.J. and J.D. Williams. 2003. Inventory of Fishes and Mussels in Springs and Spring Effluents of North-Central Florida State parks. Final Report submitted to the Florida Park Service. Prepared by the U.S. Geological Survey, Gainesville, Florida. 94 pp.
- Water and Air Research (WAR). 1991. Diagnostic Studies of the Rainbow River. Report prepared for Southwest Florida Water Management District, Brooksville, FL. Pp. variously numbered.
- Westlake, D.F. 1967. Some effects of low-velocity currents on the metabolism of aquatic macrophytes. Journal of Experimental Botany 18(2): 187-205.
- Wetland Solutions, Inc (WSI). 2003. Human Use and Ecological Evaluation of the Recommended Minimum Flow Regime for Blue Spring and Blue Spring Run, Volusia County. Report prepared for the St. Johns River Water Management District, Palatka, FL. pp. variously numbered.

- Wetland Solutions, Inc. (WSI). 2006. Phase 2 Final Report. Pollutant Load Reduction Goal (PLRG) Analysis for the Wekiva River and Rock Springs Run, Florida. Report prepared for the St. Johns River Water Management District, Palatka, FL. 269 pp.
- Wetland Solutions, Inc. (WSI). 2007a. Human Use and Ecological Water Resource Values Assessments of Rock and Wekiwa Springs (Orange County, Florida) Minimum Flows and Levels. St. Johns River Water Management District Special Publication SJ2008-SP-2, Palatka, FL. 192 pp.
- Wetland Solutions, Inc. (WSI). 2007b. Phase 3 Final Report. Pollutant Load Reduction Goal (PLRG) Analysis for the Wekiva River and Rock Springs Run, Florida. Report prepared for the St. Johns River Water Management District, Palatka, FL. 418 pp.
- Whitford, L.A. 1956. The communities of algae in the springs and spring streams of Florida. *Ecology* 37(3): 433-442.
- Wilson, W.L. and W.C. Skiles. 1989. Partial reclassification of first-magnitude springs in Florida. pp. 65-72 *in* B.F. Beck (*Ed.*). Engineering and environmental impacts of sinkholes and karst. Florida Sinkhole Research Institute, University of Central Florida, Orlando, FL.
- Woodruff, A. 1993. Florida Springs Chemical Classification and Aquatic Biological Communities. M.S. Thesis. University of Florida. Gainesville, FL. 117 pp.
- Young, R.G. and Huryn A.D. 1999. Effects of land use on stream metabolism and organic matter turnover. *Ecological Applications* 9: 1359-1376.

Springshed Nutrient Loading, Transport and Transformations

Matthew J. Cohen
School of Forest Resources and Conservation
University of Florida

Summary

A discussion of the effects of nutrients on springs biota and ecosystems of necessity requires an understanding of the manner and mechanism of nutrient delivery. Moreover, as evidence accumulates for particular consequences of nutrient and contaminant loading, understanding how those loads can be attenuated is crucial. This chapter focuses on nutrient loading to springsheds, with an emphasis on processes of transport and attenuation that are germane to their delivery to springs. It starts by describing the flowpaths and hydrogeology of Florida's karst systems, with an emphasis on intrinsic vulnerabilities to nitrogen loading in particular. A discussion about land use and land cover change, and the sources of nutrient pollution, follows. Nitrogen loading is by far the most well studied spring contaminant, but examination of other changes that have occurred in springs, including changes in flow, dissolved oxygen, hardness and conductivity that have been documented within and across springs is informative. Attention is also set on the future of nutrient loading, including the potential saturation of phosphorus along subsurface flowpaths, with important implications for the timeline of nutrient load reduction. Finally, the state of our understanding of springsheds as closed systems of water and solutes is examined, with an emphasis on areas of uncertainty that are relevant questions for future research.

The Literature: What is Known

From this review of the existing literature on nutrient loading there are four essential areas for which managers can proceed with relative certainty:

- *Complex flowpaths and a wide distribution of residence times characterize the hydrogeology of the Floridan Aquifer.* The timeline and source area of water delivered to springs is of critical importance to springshed management, but these physical attributes are poorly constrained in karst systems. The presence of large conduits, uneven limestone porosity, complex potentiometric gradients and shallow relief make the delineation of springsheds an area of active research.
- *Karst landscapes are vulnerable to pollutants from anthropogenic activities at the surface.* The implications of this are profound for land use planning. In particular, it is clear that the risks of aquifer contamination are greatly attenuated in regions of the state and springshed where regional confining layers (e.g., Hawthorn Formation) limit the rate of interaction between surface and Floridan Aquifer waters. Nitrogen (in nitrate form) is particularly problematic because it is effectively inert, and therefore readily transported,

in the low organic matter, relatively high dissolved oxygen environment of the upper Floridan.

- *Water quality is changing in dramatic ways.* Because of the intrinsic vulnerability of Florida's karst geology to contaminant transport, this fact is well documented. What is perhaps not as well documented is the uneven manner in which water quality is declining. Much emphasis on nitrogen (in nitrate form) enrichment has ensued from as much as 350-fold increases above background concentrations in some springs; overall, spring nitrate concentrations appear to have increased by a factor of 10. In contrast, phosphorus concentrations have not markedly increased, presumably due to high exchange capacity with the limestone matrix. Other water quality parameters have also changed; hardness appears to have increased systematically since the 1970's, perhaps a signal of changing subsurface flowpaths that deliver increasingly old groundwater. Similarly, dissolved oxygen concentrations have declined since the 1970's, in many cases crossing ecologically significant thresholds (~ 1.0 mg/L); this cause for this decline is unknown, but may also be related to the age of the water emerging at spring vents. Finally, regular observation of trace quantities of pharmaceuticals and other chemical by-products of modern society (e.g., DEET, caffeine) illustrate the degree of connectivity between the groundwater and nearby human activities.
- *The preponderance of N pollution appears to be from fertilizer sources.* There are several reasons to treat this finding as an over-generalization, but most of the accumulated evidence from mass balance computations and isotopic tracer studies suggests that mineral fertilizers, and therefore not septic tanks and wastewater sprayfields, are the principal sources of N pollution. One key caveat discussed, is that the isotope method is relatively poorly constrained for subsurface flowpaths, which may lead to interpretive errors. More importantly, the source determination for each spring needs to be considered unique; management of those sources must therefore be calibrated to local conditions.

The Literature: What is Not Known, with Emphasis on Future Research Directions

- *What are the temporal dynamics of water age?* It is clear from the literature that there remain large uncertainties about the age mixture of water discharging from spring vents. Given significant discord between observed dye tracer residence times (days to weeks) and nominal ages (decades), a research program to better understand water age over time seems critical. Decomposition, auto-correlation and cross-correlation analyses of resulting time series should enable improved understanding of flow regimes and also links with other water quality variables that are strongly relevant to springs ecology (nutrients, salts, dissolved oxygen). Specifically, if binary mixing models are useful simplifications of spring vent hydrology, time series will allow decomposition of flows into two components, with insight into the relative importance of each, and changes in mixing with regional climatic trends. These methods need to be applied cognizant that different springs are likely to have different hydrogeologic properties, and inference from one spring may not apply in others. This uncertainty has key implications on pollutant delivery in karst systems, which can be highly variable. Pulses of nutrients and other water quality parameters (dissolved oxygen, salts, toxins) have been invoked for

catastrophic shifts in other systems, particularly when ecosystem drivers have broadly changed. The presence of such pulses (even long duration anomalies might be considered pulses) in spring systems is unknown, and the implications on springs ecology equally uncertain.

- *What is the natural variability in spring flow, and how vulnerable is this to human appropriation?* Ongoing efforts to set minimum flows and levels (MFLs) should consider the role of flow in what are generally considered to be water quality response variables. For example, changes in nitrate that are implicated in springs ecological change have occurred along with changes in fish access, vent discharge, and salinity, among other things. Moreover, in advective systems, flux is often a better predictor of ecological enrichment than is concentration, and with declining flows, fluxes are affected. Understanding the role of flow both directly and indirectly in spring ecosystems, and linking that to how water has been appropriate is likely to be high value research.
- *What are the sources of N in springsheds?* While there is accumulating evidence (see above) that the source of N is principally mineral fertilizer, there remains significant uncertainty about the interpretation of bulk stable isotope measurements in complex karst hydrologic systems. First, there is a broad omission of N fixation from N budgets (which would tend to lighten the isotopic ratio of overall N delivery). Second, nitrification processes are poorly understood: since that process results in large kinetic fractionation (lightning) and denitrification is negligible in the aquifer, the potential impact on the overall N isotope ratio is both unknown and of crucial importance for understanding flow paths. This is also relevant for questions beyond nitrogen delivery, since there is a plausible connection between loading of organic wastes and declines in dissolved oxygen. Constraining the isotopic kinetics in springsheds by observations along flowpaths will likely improve understanding of water and pollutant sources.
- *What are the causes and effects of water quality changes beyond elevated nitrate?* The synthesis of the literature on springs is dominated by information about nitrogen, but essentially devoid of similarly detailed studies of other water quality parameters. Where surveys have been done across a broad-spectrum of water quality attributes (Stevenson *et al.* 2004, for example), attributes such as salinity, flow, dissolved oxygen and phosphorus were at least as predictive of ecosystem change as nitrogen, despite the dramatic enrichment of N that has been observed. There is a clear and present need to understand how variability in these attributes occurs, and the extent to which that variability is in response to anthropogenic activities. For example, significant negative correlation between DO and algal cover exists (Stevenson *et al.* 2004); there are myriad mechanisms (water age, increased BOD loading) that might lead to reduced DO concentrations in the Upper Floridan, but these remain critically understudied. Septic tanks, animal waste disposal systems and sprayfields generate enormous quantities of biological and nitrogenous oxygen demand if discharged unoxygenated into the groundwater. Since dissolved oxygen concentrations are strongly spatially variable, have significantly declined across a broad spectrum of springs (Scott *et al.* 2004), and were predictive of algal cover, understanding the roles of hydrogeologic and anthropogenic processes in low DO at spring vents is a first-order research unknown.

- *What is the assimilative capacity of the landscape and aquifer for nutrients and other contaminants?* Efforts similar to the springshed nutrient budgeting for watersheds in the northeastern US yield an estimate of 20% for the fraction of terrestrial N load that is transported by rivers to the sea. In a karst environment where N movement is essentially unimpeded, conservative estimates of landscape attenuation are as high or higher (70-90%), without accounting for N fixation. Even where efforts were made to estimate the load reaching the aquifer (MACTEC 2007), those estimates are 6 fold higher than what emerges at the spring vent. Elaborating the reasons for this discordance, and how it might be affected by development and enhanced by management, should be a research priority. Issues that will need to be dealt with are response lags due to aquifer residence times, and the relative importance of surface vs. vadose zone vs. aquifer processes. Moreover, as land development increases, there may be loading thresholds that exceed the assimilative capacity of the landscape and lead to elevated load breakthrough. The potential for observing this effect is low for nitrogen pollution, but may be high for phosphorus. Ensuring that P saturation fronts are not advancing towards spring vents is important for forecasting.
- *How responsive are springsheds to management interventions?* As we begin to understand the links between springshed activities and declining water quality in spring ecosystems, evaluating the extent to which parameters are management-sensitive is relevant to both timelines for recovery and prioritization of management efforts. This is relatively well understood for N (see Obreza 2002 for an assessment of BMPs on N delivery), but not at all for other water quality metrics in springsheds. If other parameters (P, DO, salts, flow) figure prominently in holistic springshed management, understanding how to best manage them is a clear priority.

INTRODUCTION

The objective of this chapter is to synthesize literature on nutrient loads, transformations and sinks in springsheds, emphasizing processes occurring prior to spring water emergence at the boil. After a brief background on nutrient cycles and karst hydrogeology, the chapter discusses sources (loading models, water and nutrient source tracing, temporal dynamics, spatial dynamics) and then transformations and sinks (abiotic attenuation, biotic attenuation, management-inducible attenuation). The chapter will close with a synthesis of the knowledge stores relevant to springshed management, and the gaps that should be targets for future research.

Nutrient enrichment is a water quality problem with global scope; the effects of nutrients on the primary productivity of freshwater (lotic and lentic), estuarine and marine environments has been widely discussed and demonstrated (Hutchinson 1957, Schindler 1977, Carpenter *et al.* 1998a, Rabalais 2002). Moreover, broad scale nutrient enrichment - principally resulting from the use of modern inorganic fertilizers but also from fossil fuel combustion and land use change - has dramatically altered global biogeochemical cycles (e.g., doubling the rate of global N cycling - Vitousek *et al.* 1997) and watershed loading above what is predicted as background levels (Omernik 1977). For nitrogen (N), anthropogenic influence is particularly pronounced; commercial fertilizer use worldwide now accounts for 140 Tg (10^{12} g) of N yr⁻¹, a figure that exceeds the upper estimate of the quantity fixed naturally in terrestrial ecosystems (Vitousek *et al.* 1997). N delivery to freshwater and marine ecosystems is principally via riverine transport (Boyer *et al.* 2002) accounting for ca. 25% of watershed load in Northeastern rivers (Figure 1).

The addition of nutrients is responsible in many cases for changes in the rate of primary production, and therefore indirectly on the composition of primary producers as competition constraints are altered (Smith *et al.* 1999). For example, non-linear shifts in lake primary producers moving from rooted aquatic plants to phytoplankton have been broadly attributed to P enrichment (Vollenweider 1976, Canfield and Bachman 1981, Wetzel 1983, Carpenter *et al.* 1998b), with important implications for how the P loading to these lakes is managed. Cascading effects of nutrient enrichment typically include changes in oxygen and light dynamics of aquatic systems, with deleterious effects on animals adapted to pre-enrichment conditions (Hynes 1970), and on whole system metabolic processes (Dodds 2006). Generally, nitrogen (N), phosphorus (P) or both (Elser *et al.* 2007) limit ecosystem productivity, and as such, the focus of nutrient attenuation efforts.

While the discussion of eutrophication in lake systems is relatively mature (e.g., Schindler 1977), the hydraulic circumstances in flowing water systems, such as constant advection to maintain diffusion gradients and turbulent mixing, make generalization about eutrophication in all aquatic systems from lake models alone problematic. A new synthesis of eutrophication in lotic systems has begun to emerge (Tank and Dodds 2003, Dodds 2006, Hilton *et al.* 2006) with important but often subtle variations from lentic eutrophication, particularly with regard to alternative mechanisms for changes in primary productivity (Caraco *et al.* 2006). As such, while phosphorus may be the limiting nutrient in lakes (Carpenter *et al.* 1998a), and nitrogen most frequently the limiting nutrient in marine systems (Smith 2006), the influence of nutrients on flowing water ecosystems

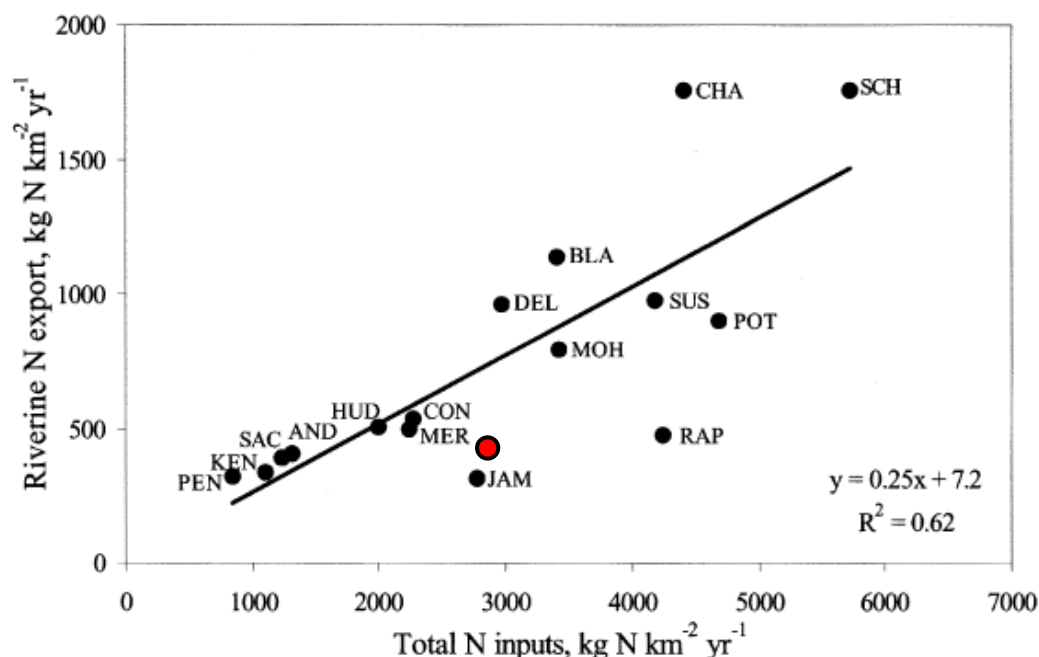


Figure 1 – N inputs ($\text{kg m}^{-2} \text{yr}^{-1}$) vs. riverine delivery (Boyer *et al.* 2002; see reference for three-letter codes). Loads have increased ~ 20 fold since the mid-1800's. SE USA (red dot) falls near line defined by rivers from NE USA; a global model was identical (Vitousek *et al.* 1997).

may be more ambiguous (alternating co-limitation or no limitation – Smith *et al.* 1999, Elser *et al.* 2007). Consequently, management of both N and P from anthropogenic sources is a critical priority for managers, regulators and scientists worldwide. Aggressive management schemes that limit the quantity or improve timing and uptake of fertilizer applications, enhance or restore the landscape assimilative capacity, reduce the load from fossil fuel combustion, and decouple human waste from waterways are needed globally. Evidence has shown that these efforts can work, but the probability of success in managing the problem is maximized by understanding stores, fluxes and transformations intrinsic to the system being managed.

Addressing the observed eutrophication (principally overgrowth of filamentous algae) in spring ecosystems in Florida requires attention to the myriad mechanisms and potentially complex dynamics of nutrient loading and processing. As such, a synthesis of nutrient effects in Florida's springs starts with a discussion of the source and chronology of nutrient loading. The mechanisms and temporal dynamics of nutrient loading to spring vents are relevant to their effect. Perhaps as importantly, a synthesis of nutrient loads to springs at the same time as consideration of the effects, allows risks and opportunities for future management to be linked. For example, a role of phosphorus in the decline in spring biological condition has been suggested. Because phosphorus concentration in spring discharges has, in general, not increased through time, it has been essentially neglected in the literature on springshed management (a point to which this review will return in depth). The implicit assumption for why P has not increased along with N appears to be that the carbonate aquifer matrix has sufficiently high sorption capacity to attenuate anthropogenic loads. This particular assumption is being tested as part of the loading literature (Nair *et al.* 2004), but has direct relevance to synthesis of ecological effects if, as those authors predict, P saturation and breakthrough can occur.

Emphasis on N loading vis-à-vis other water quality parameters has occurred within the scientific and regulatory communities due to strong evidence for anthropogenic N enrichment in the karst environment of North Florida; evidence for contemporaneous P enrichment is absent. Karst is vulnerable to nitrate-N transport; indeed Katz *et al.* (2005) and Phelps (2004), among others, use N_2 partial pressure in spring-vent water to conclude that denitrification is negligible, and nitrate behaves like a conservative solute. As such, increasing human development in karst regions inexorably leads to increased N loads without major efforts to manage sources.

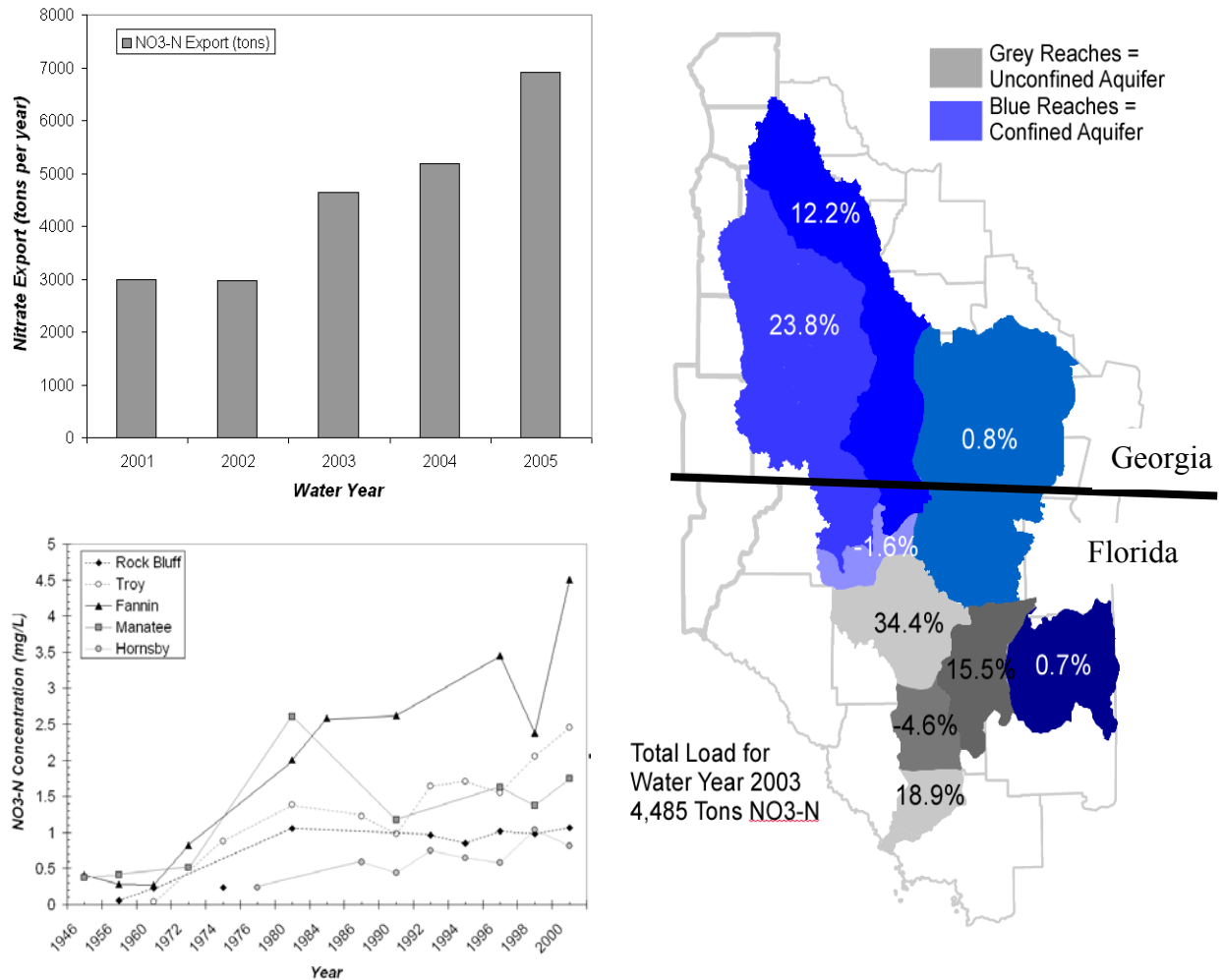


Figure 2 - Nitrate load to the Gulf of Mexico from the Suwannee River: a) changes in loads between 2001 and 2005 (driven by changes in water flows), b) time series nitrate concentrations at 5th magnitude springs along the Suwannee, and c) estimates of nitrate load by sub-basin. Basins where a regional aquitard is absent (shown in grey) are 25% of the area, but contribute 65% of the load. (Hornsby *et al.* 2002, 2003, 2004, 2005; Mirti and Mantini 2006).

For example, Figure 2 summarizes recent trends in N loading to the Suwannee River over time; these trends, replicated nearly ubiquitously where springsheds include intensive human land uses (Scott *et al.* 2004), are the principal motivating force behind this chapter. Clear upward trends in load are evident, as is spatial identification of sources (i.e., sub-basins shaded grey,

representing 25% of the area and 65% of the load). Observed increases in N loads to the Suwannee River are principally attributed to springs and diffuse groundwater (Hornsby and Mattson 1997, Pittman *et al.* 1997). Nitrate-N concentrations of springs, which discharge directly from the upper Floridan Aquifer, have increased substantially from near background concentrations (≤ 0.1 mg/L) (Katz 1992, Maddox *et al.* 1992) to > 5 mg/L at present (Katz *et al.* 1999).

In general, consideration of nutrient loading requires an accounting effort. The goal is to tabulate accurately the inputs and outputs of a key nutrient for comparisons across catchments or through time. Van Breeman *et al.* (2002) present an approach for 16 watersheds in the Northeastern United States; for N, they tabulate the important sources and sinks and arrive at nominal relationships between loading and export that are useful for understanding the magnitude and vulnerability of sinks, the importance of land use and the key areas of uncertainty. Their methodology, and examples of similar efforts for the more complex and confounded environments of karst springsheds, are an important component of this report.

Landscape loading and subsurface transport/transformations of nutrients are the most well studied aspect of springs, at least with respect to nitrogen. Indeed, while links between nutrients and ecological effects may remain somewhat ambiguous (e.g., Stevenson *et al.* 2004), the collective understanding of nutrient loading, temporal nutrient delivery trends, travel times of water and nutrients, principal sources of loads, and subsurface transformations is relatively mature. By way of example, the current synthesis effort identified key literature sources in each of several categories within the general framework of nutrients and Florida's springs. Figure 3 summarizes the distribution in the number of references compiled, illustrating the significant focus on sources, and more limited focus on downstream effects.

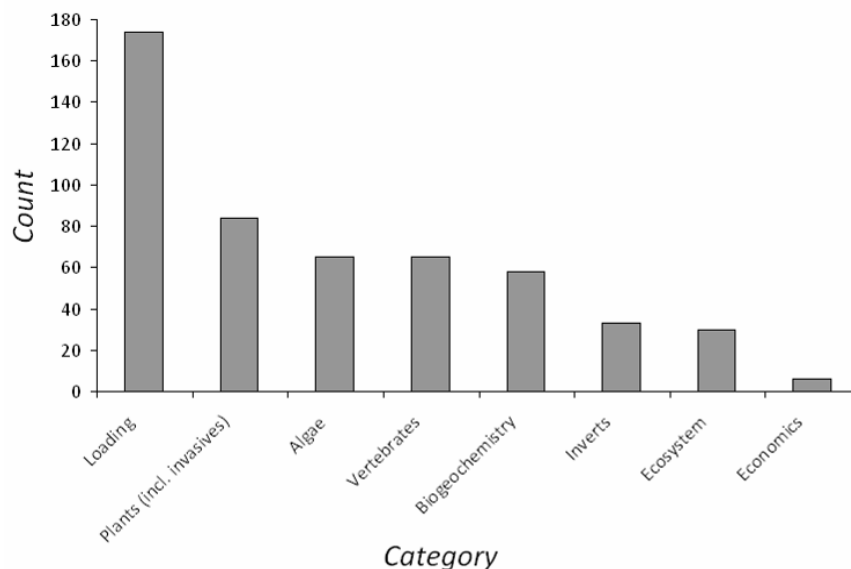


Figure 3 – Number of publication on each of a variety of topics germane to nutrient effects in springs identified for this study. This result highlights important knowledge stores and gaps.

HYDROGEOLOGY

Hydrology in a Karst Environment

Hydrology in Florida is complicated by two aspects of its geological setting (Berndt *et al.* 1996). First, the State is flat, leading to anastomosing flow paths, long residence times, closed surface basins (isolated wetlands, swallets), and dominance of inter-flow (i.e., instead of surface runoff). Second, the geologic basement of Florida is limestone, leading to a karst landscape (defined here as the presence of a self-organizing aquifer, in this case made of carbonate). Champion and Starks (2001) suggest that an understanding of karst is a prerequisite to understanding the hydrology and water quality of springs. Ewers (2006) suggests that failure to appreciate the complexity of karst aquifers (predominantly by assuming isotropy in hydrogeologic modeling) has led to poor decision making, and wasteful spending on poorly predictive models. The dissolution processes that characterize the development of karst lead to subsurface flow conduits, massive groundwater flow anisotropy, and numerous sinkhole and swallet features that link surface flows (streams and rivers) to the groundwater matrix and conduits (Kincaid *et al.* 2004, Ewers 2006). The resulting complexity of subsurface flowpaths means attribution of hydrologic and pollutant loads to particular areas is less clear than for surface drainage networks.

The principal deep aquifer system in the State is the Floridan Aquifer (Figure 4), which covers the entire state, and portions of South Carolina, Georgia, Alabama and Mississippi. This carbonate aquifer is among the most transmissive karst aquifers in the world, making it an ideal water source, and consequently, the source of water for over 93% of Florida's population (Fernald and Purdum 1998). Protecting the quality and quantity of this resource is of paramount policy importance, and nutrient pollution to the aquifer is one of a constellation of stressors that are already deleteriously affecting it. While affects on the Floridan Aquifer exist throughout the state, springs do not. The vast majority of springs occur in North and Central Florida, principally because of the proximity of the Floridan to the surface in areas and greater landscape relief.

Several features particular to Florida karst (eogenetic or not deeply buried; Florea and Vascher 2007) are relevant to nutrient loading to springs. First, eogenetic karst has high matrix porosity (Martin and Dean 2001), which leads to highly accessible storage; the result is that spring discharge is very weakly responsive to short-term weather, a condition quite different from the karst regions of Kentucky, Missouri, Texas and elsewhere around the globe where the karst is more deeply buried. Indeed, an analysis of flow flashiness in 12 Florida springs (Florea and Vascher 2007) suggests that peak flows are less than 5 times minimum flows over 90% of the time, a homeostasis typical of basalt aquifer springs, not karst. The reservoir from which spring flow derives is extremely large, and as such nominal residence times are long; the importance of this for the time domain of nutrient delivery is extremely important, and will be discussed in detail later. A second peculiarity of the Floridan Aquifer karst is that flow through the matrix and conduits is a dynamic interplay driven by hydrologic conditions. Martin and Dean (2001) have observed in the Santa Fe sink-rise system that during low flow, matrix and secondary conduit contributions are high, but that at high flow, major conduits dominate. This has implications for nutrient delivery to springs; during periods of high flow, primary short-term



Figure 4 – Extent and confinement of the Floridan Aquifer. The Floridan is among the world's most productive karst aquifers and source of most of Florida's drinking water (Miller 1990).

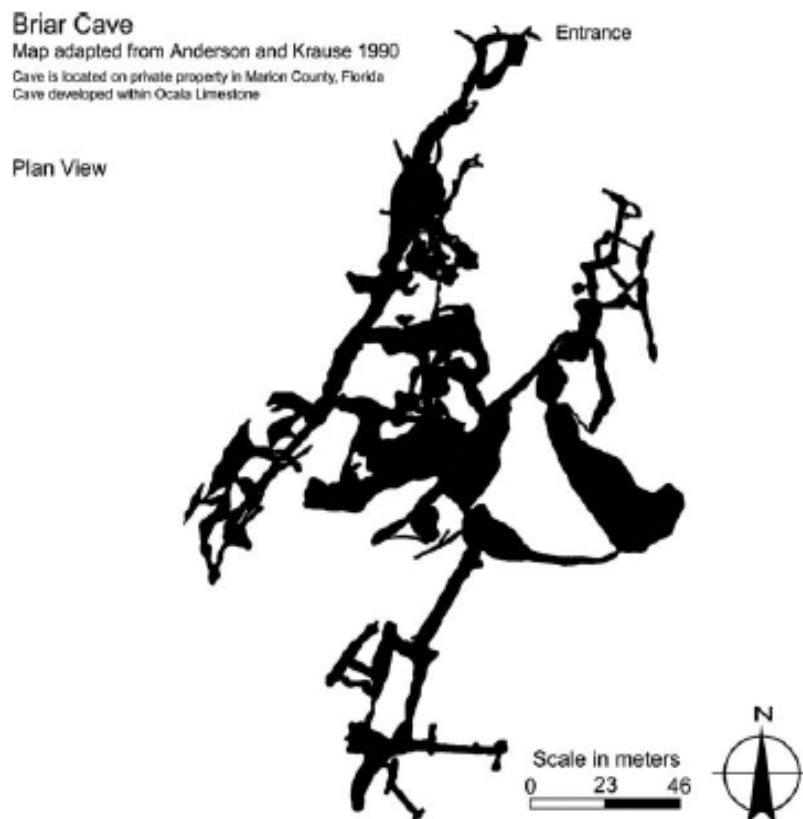


Figure 5 – Plan view of Briar Cave (Marion County) showing complex anastomosing channels that generally follow matrix fractures (NE-SW), but include caves and lateral connections (Florea and Vascher 2007).

recharge areas are likely to be the dominant source where surface water loads via a swallet or sinkhole. At low stage, matrix flow is more important, and dispersed nutrient loading across the unconfined region is likely to be more predictive of what emerges from the spring vent.

The matrix that contains the Floridan is not uniform, leading to significant anisotropy in flows. Vertically, limestone deposits of different ages have different properties, and harbor water with different chemistry. For instance, in the Silver Springs region, Suwannee and Ocala are the shallowest and Oldsmar and Cedar Keys are the deepest; corresponding differences in salinity and ion profiles exist. The Upper Floridan Aquifer (UFA) refers to water in the Ocala formation which ranges in thickness between 0 and 180 feet; it may be exposed or buried beneath Miocene clay and Plio/Pleistocene sand deposits. Laterally, anisotropy of aquifer properties is extreme, with high fracture porosity (Martin and Dean 2001), and complex anastomosing networks of large and small conduits that move water through the subsurface in predictable (Werner 2000)

SYSTEM	SERIES	STRATIGRAPHIC UNIT	APPROXIMATE THICKNESS (FEET)	LITHOLOGY	HYDROGEOLOGIC UNIT	
QUATERNARY	Pleistocene to Holocene	Undifferentiated post-Miocene deposits	0 - 100+	Marine quartz sand. Also fluvial and lacustrine sand, clay, marl, and peat deposits.	SURFICIAL AQUIFER SYSTEM	
	Pliocene	Undifferentiated Pliocene deposits	0 - 100	Nonmarine clayey sands, red and yellow, fine to coarse-grained to pebbly, kaolinitic, crossbedded.		
TERTIARY	UNCONFORMITY					
	Upper Miocene to Pliocene (?)	Undifferentiated Upper Miocene-Pliocene deposits	0 - 100+	Marine sands, argillaceous, carbonaceous; sandy shell marl; some phosphatic limestone. Also terrestrial-deltaic (?) interbedded deposits of clay, sand, and sand clay. Phosphatic, including a rubble of phosphate rock and silicified limestone residuum in a gray and green phosphatic matrix.	INTERMEDIATE CONFINING UNIT	
	UNCONFORMITY					
	Middle and Lower Miocene	Hawthorn Group	0 - 140	Marine interbedded sand, cream, white, and gray, phosphatic, often clay, green to gray and white, phosphatic, often sandy; dolomite, cream to white and gray, phosphatic, sandy, clayey; and some limestone, hard, dense, in part sandy and phosphatic.		
	UNCONFORMITY					
	Upper Eocene	Ocala Limestone	0 - 180	Marine limestone, white to cream to tan and brown, granular, soft to firm, porous, highly fossiliferous, cherty in places. Lower part at places is dolomite, gray and brown, crystalline, porous.	FLORIDAN AQUIFER SYSTEM	UPPER FLORIDAN AQUIFER
	UNCONFORMITY					
	Middle Eocene	Avon Park Formation	800 - 1,100	Marine limestone, light brown to brown, finely fragmental, low to high porosity, highly fossiliferous (mostly foraminifers); and dolomite brown to dark brown, firm to very hard, low to moderate porosity, crystalline, saccharoidal; both limestone and dolomite are fractured. Carbonaceous or peaty; gypsum present in small amounts.		MIDDLE SEMI-CONFINING UNIT
	Lower Eocene	Oldsmar Formation	500 - 650	Marine limestone, light brown to chalky white, porous, fossiliferous, with interbedded brown, porous, crystalline dolomite; minor amounts of anhydrite and gypsum.		LOWER FLORIDAN AQUIFER
	UNCONFORMITY					
	Paleocene	Cedar Keys Formation	400 - 700	Marine dolomite, light gray, hard, slightly porous to porous, crystalline, in part fossiliferous, with considerable anhydrite and gypsum, some limestone.	SUB-FLORIDAN CONFINING UNIT	

Figure 6 - Hydrogeologic units in the Silver Springs basin (after Phelps 2004, Scott et al. 2004).

but still massively complex ways (Kincaid *et al.* 2004, Florea and Vascher 2007 – see Figure 5). Cave diving experience (e.g., Fisk and Exley 1976) visually confirms the complexity and anisotropy of the matrix.

The presence of the Miocene confining unit (the interbedded marine sands and phosphatic clays of the Hawthorn Group) significantly affects the connectivity between surface and groundwater (Scott *et al.* 2004). Where that confining unit is thick and intact, hydrologic and nutrient processes almost exclusively occur in the surface sediments and the surficial aquifer; nutrient migration into the aquifer is expected to be slow. Where the Hawthorn has, over time, been eroded away via surface water action, the Ocala limestone has been exposed, along with the UFA within it. Figure 4 shows the extent of that exposure (areas in brown are unconfined). The zone of active erosion of the Hawthorn is known as the Cody Escarpment (Cody Scarp), and this divide is hydrogeologically critical (Figure 6).

The importance of the Cody Scarp for hydrologic processes is enormous. At and below the scarp, strong groundwater-surfacewater interactions lead to unique features such as the Santa Fe River Sink at O'Leno State Park where the river is captured in its entirety by a sinkhole, emerging 5 km downstream. Below the Scarp where the limestone is exposed, prevalence of surface water features (wetlands, stream channels, lakes) drops dramatically and are replaced by spring vents and karst windows where the potentiometric surface of the Floridan intersects the land surface. Springs and spring runs are therefore surface expressions of the level and quality of the aquifer.

Similarly, the importance of the Cody Escarpment in delineating zones with distinct biogeochemical processes is also difficult to overstate. As observed by Hornsby (2007), above the scarp where the Miocene Hawthorn Formation precludes surface water percolation to the Florida, the surface waters and the surficial aquifer are generally elevated in dissolved organic carbon (DOC), and depleted in N, presumably because large wetland areas and areas with terrestrial soils that have high water tables, leads to rapid rates of denitrification, and variably enriched with P; indeed N:P ratios in these headwater areas where the Hawthorn is intact and land use intensity is low may be less than 1.0. In groundwater near the scarp, P levels climb dramatically due to interactions with the phosphatic clays of the Hawthorn, but then decline due to sorptive processes occurring between the phosphate and the CaCO₃ aquifer matrix. However, it should be noted that some springs have naturally high levels of P (to be discussed at length later) suggesting that P sorption may not be uniformly high. Nitrate concentrations are generally low until water from the upper Floridan Aquifer (UFA) that has been enriched with nitrates (i.e., near areas of intensive human land use) becomes an important component of river flow. Figure 2 illustrates this trend, with loading occurring in areas shaded grey in the unconfined region.

These confined, transitional and unconfined hydrologic zones (Figure 7) and associated expected nutrient conditions (moderate P/low N, high P/low N, low P/high N, respectively – Hornsby 2007) underscore why spring nutrient enrichment has focused on nitrogen. Reasons for intrinsic vulnerability of unconfined landscapes to N enrichment will be described later, but first it is relevant to address how the contributing areas for spring flow have been defined.

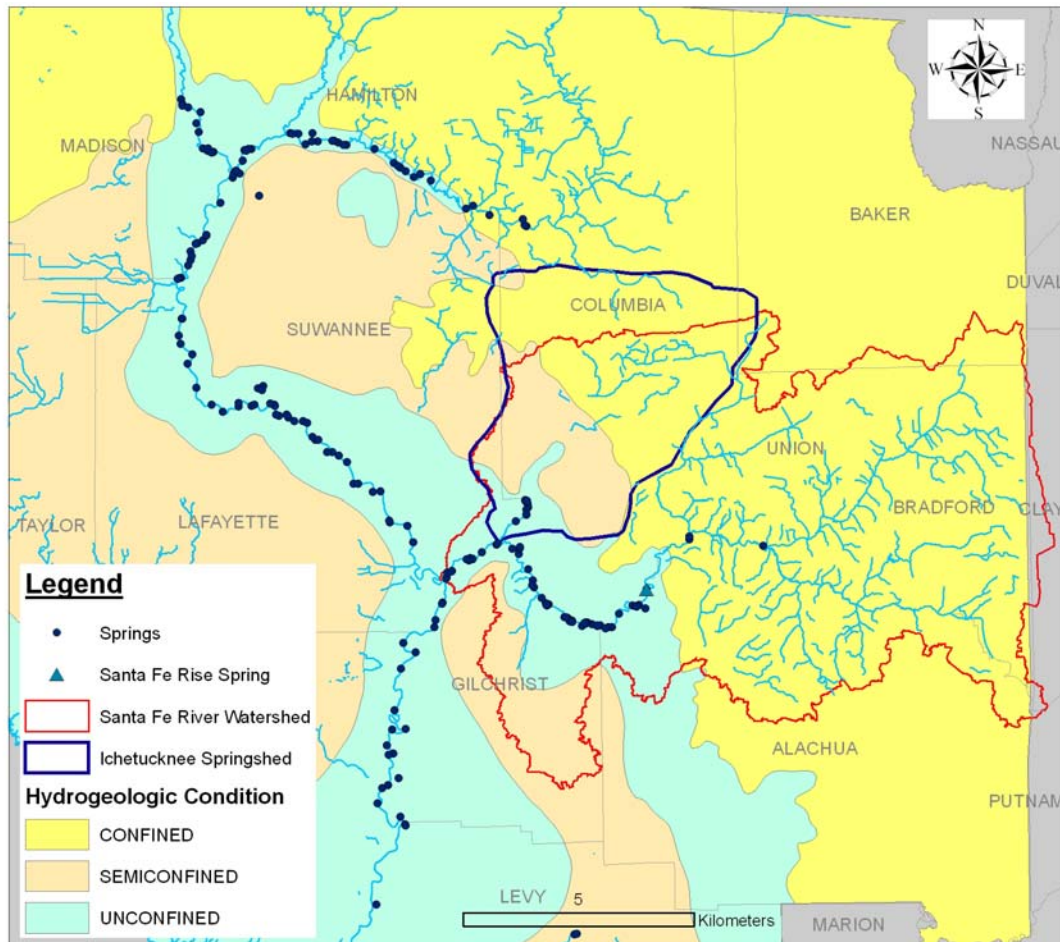


Figure 7 – Spatial survey of hydrogeologic zones in the eastern part of the Suwannee River Water Management District (after Upchurch *et al.* 2007). The Cody Escarpment defines the boundary between where the Floridan is confined and unconfined. Springs (blue dots) and surface streams (blue lines) are shown.

Typology of Florida's Springs

Karst springs (i.e., not water table seeps – Scott *et al.* 2004) occur where the potentiometric surface of the Floridan Aquifer intersects the ground surface. They are categorized according to median discharge (Figure 8a from Scott *et al.* 2004 and Rosenau *et al.* 1977, after Meinzer 1927). The logarithmic partitioning of discharge into magnitudes partially obscures the dramatic differences in flow between for example a 1st magnitude (> 65 million gallons per day) and 3rd magnitude (< 6.5 million gallons per day) spring. Comparison of hydraulic and ecological processes between springs of such differing size is potentially problematic, and scaling relationships for generalizing process-level measurements made at a spring of a particular size are clearly required. Examples of factors expected to be different for varying spring magnitude are light regime, depth, flow velocity, recreational impacts, and densities of large herbivores.

Springs occur most prevalently below the Cody Escarpment where the UFA is suddenly unconfined by the Hawthorn Formation aquitard (Wakulla, Ichetucknee and Silver form in this manner), and near the channels of major rivers (e.g., Santa Fe, Suwannee, Ocklawaha) traversing

a)

Magnitude	Average Flow (Discharge)
1	100 cfs or more (64.6 mgd or more)
2	10 to 100 cfs (6.46 to 64.6 mgd)
3	1 to 10 cfs (0.646 to 6.46 mgd)
4	100 gpm to 1 cfs (448 gpm)
5	10 to 100 gpm
6	1 to 10 gpm
7	1 pint to 1 gpm
8	Less than 1 pint/min

b)

SPRING		
	Onshore	Offshore
Vent	<u>Onshore Vent</u> Examples: Karst spring Resurgence (River Rise) Estavelle (intermittent resurgence or exsurgence) Subaqueous riverine vent Subaqueous lacustrine vent Sand boil	<u>Offshore Vent</u> Examples: Offshore karst spring Unnamed offshore vent Offshore estavelle vent
Seep	<u>Onshore Seep</u> Examples: Subaerial riverine seep Subaqueous lacustrine seep	<u>Offshore Seep</u> Examples: Unnamed offshore seep Offshore estavelle seep

Figure 8 – a) Nomenclature for spring magnitude; cfs = cubic feet/ second, mgd = million gallons/day, gpm = gallons/minute). There are 720 springs (39 1st, 191, 2nd, 151 3rd magnitude). b) Nomenclature for spring types based on where and how water is discharged.

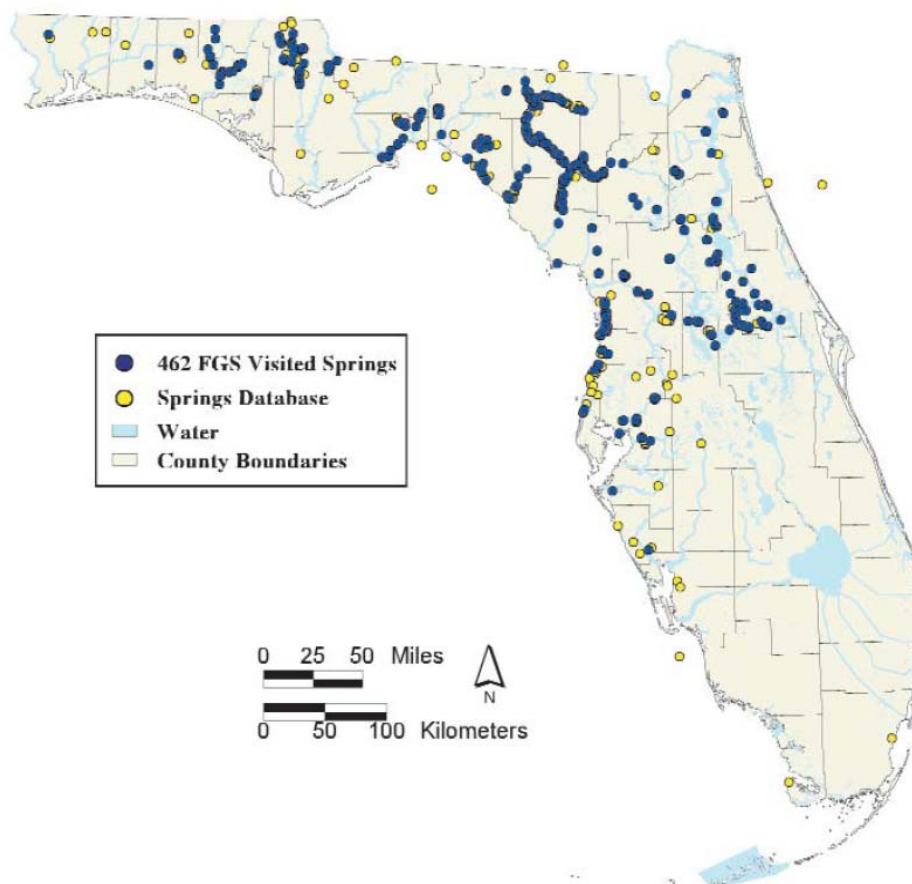


Figure 9 – Locations of Florida's > 700 springs, including those visited by Scott et al. (2004).

the unconfined karst region. Figure 9 shows the location of the springs; the sweep of the Suwannee River is clearly evident from the tremendous density of springs that discharge in that region. Numerous springs also occur at the coast, where the land surface dips and intersects the Floridan; Homossassa springs, Kings Bay, Chassahowitzka, Weeki Wachee springs among many others are formed in this manner. Tidal effects (Yobbi 1992) can complicate the flow and nutrient dynamics of these systems.

There is also a preponderance of sub-aqueous springs, including Blue Springs (currently inundated by Rodman Reservoir), Apopka Springs (discharging to Lake Apopka) and numerous submarine vents (Lambert and Burnett 2003, Slomp and van Capellen 2004). Nutrient effects at the locations of submarine groundwater discharge sites can be important for estuarine ecology (Sigua and Tweeddale 2003, Paytan *et al.* 2006) including the incidence of red tide (Hu *et al.* 2006). Other springs occur where riverine flows reemerge after sinkhole capture and passage through subsurface conduits (e.g., Santa Fe River Rise); while varying amounts of water emerging in these systems is river water, and Wilson and Skiles (1989) argue that they should not be categorized as springs, Martin and Dean (2001) demonstrate that there is indeed substantial flow-dependent mixing with groundwater. A typology of springs based on where they occur (Copeland 2003) is presented in Figure 8b.

Springshed Delineation

A springshed is defined as the area over which water falling at the surface (but ultimately traveling through the subsurface) will collect at a particular spring vent (Upchurch *et al.* 2004b). More often than not, the contributing area for a particular vent or small isolated spring cannot be delineated from catchment areas delineated for a spring complex. For example, the springs of the Ichetucknee complex are fed by water from different parts of the springshed, but only the springshed delineation for their aggregate catchment is possible given existing potentiometric surface data.

A springshed is most often delineated in the same manner as a surface watershed, with the exception that the terrain boundaries are based on the elevation of the groundwater potentiometric surface (Shoemaker *et al.* 2004). This presents several challenges. First and foremost is that the “terrain” that defines boundaries (i.e., groundwater levels) is extremely flat, and delineating edges without exceedingly dense well stage data is impossible. Second, the potentiometric surface that is the groundwater terrain is dynamic, depending on rainfall and recharge rates. As such, the boundaries of springsheds tend to be fuzzier to accommodate the interannual variability. Third, the measurement of the “terrain” by groundwater wells is less frequent and of lower spatial resolution than would be true for a surface drainage system (i.e., a digital elevation model), so the precision of the delineation is lower. A schematic of a springshed (Figure 10 – after Upchurch and Champion 2004) shows the various focal points of springshed delineation and protection. Loper *et al.* (2005) use similar terminology (primary, secondary and tertiary protection zones) for the level of nutrient management recommended to reduce loads to Wakulla Springs. The combined inputs of surface water and subsurface drainage are extremely important to parse for purposes of understanding nutrient loads arriving at the spring vent (Figure 10).

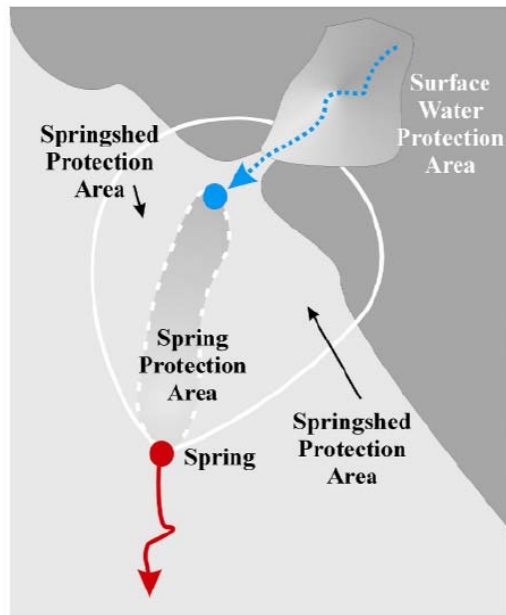


Figure 10 – Schematic of springshed with surface water drainage in the confined region, a sinkhole (blue dot) capturing flow after passage into the semi- and un-confined regions, a historic stream channel that is the presumed flow course of the karst conduit (“trace”), and the spring. Priority areas for water quality protection are shown (Upchurch and Champion 2004).

By way of example, Figure 11 shows the delineated springshed for the Ichetucknee complex in the Suwannee River Water Management District (SRWMD) (SRWMD 2002). The dashed line delineates areas where, over some time frame, water in the subsurface moves towards Ichetucknee Springs; this boundary was for 2002, and would be expected to vary year to year, depending upon rainfall patterns. The presence of confining units (Hawthorn Group) in the northern watershed leads to surface water drainage networks that clearly diverge from the groundwater basin. For example, the headwaters of Rose Creek (the main tributary draining south from Lake City), Olustee Creek (which drains via surface channels to the east, and out of the springshed) and Falling Creek (a tributary of the Suwannee, draining via surface channels to the north) are in the springshed, but dominant flowpaths for the latter two are not to the Ichetucknee. This complicates the process of developing a hydrologic budget, which also complicates the ability to construct a nutrient budget. Moreover, much of the characterization of subsurface flow boundaries is predicated on model assumptions; the size and geography of springsheds appears to be strongly sensitive to these assumptions (Shoemaker *et al.* 2004), with as little as 40% spatial concordance between different models of the springshed area.

Another mechanism for delineating springsheds is the use of major ion chemistry via a process named hydrochemical facies analysis (Champion and Upchurch 2003, Upchurch *et al.* 2004a). The central premise of this approach is that pools of water in the subsurface have major ion chemistry profiles, and since most of these ions are conservative (i.e., don’t react, at least in the subsurface), similarities in major ion chemistry between two disparate locations can be used to infer flow linkages between them. Use of discriminant and principal components analyses on well water samples is then used to identify regions with generally similar and generally distinct hydrochemistry. Hydrochemical facies have been used to delineate flow paths in the

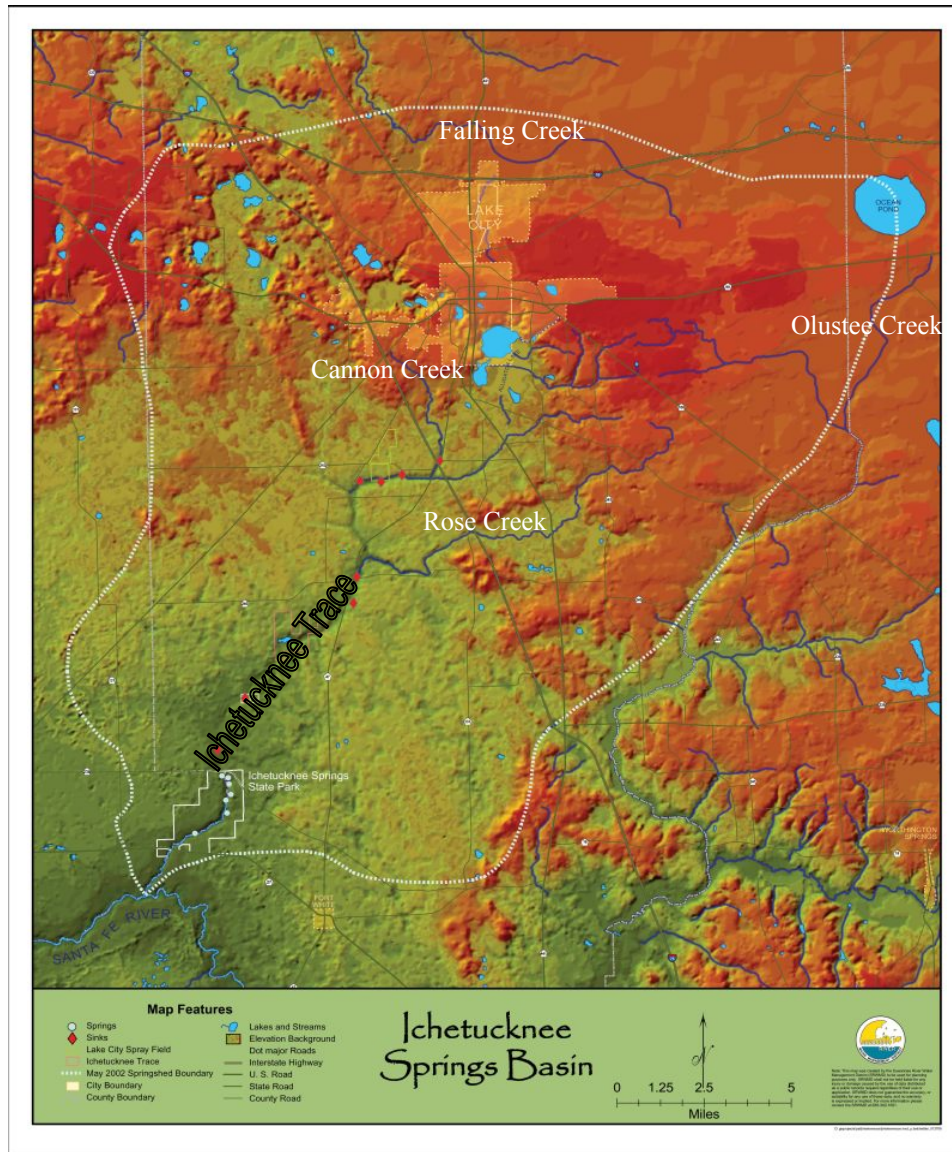


Figure 11 – Delineation of the Ichetucknee springshed in May 2002, including Lake City. Note the disappearing streams (red dots are sinks), the historic stream channel (the Ichetucknee Trace) and the movement of surface water from the northern springshed into Olustee Creek to the east and Suwannee River tributaries to the north (SRWMD 2002).

Ichetucknee springshed (Upchurch and Champion 2004 – Figure 12), springs typology in the Southwest Florida Water Management District (Champion 2001), and broad groundwater basins in the Suwannee River Water Management District (Hornsby 2007). The two principal benefits of this method are 1) confirmatory (i.e., vis-à-vis the potentiometric delineation) and 2) discriminatory at a scale that the potentiometric method is not. Figure 12 shows the ion profiles for water from various springs in the Ichetucknee complex, and up-gradient wells; concordance between springs and certain wells suggests a hydrologic connection. The inference is that there are two distinct catchments (1: Ichetucknee Head, Cedar Head, Blue Hole; 2: Mission, Mill Pond, Devils Eye). Similar research from the St. Marks system (Barrios and DeFosset 2006) suggest that four groundwater flow components comprise the St. Marks Rise.

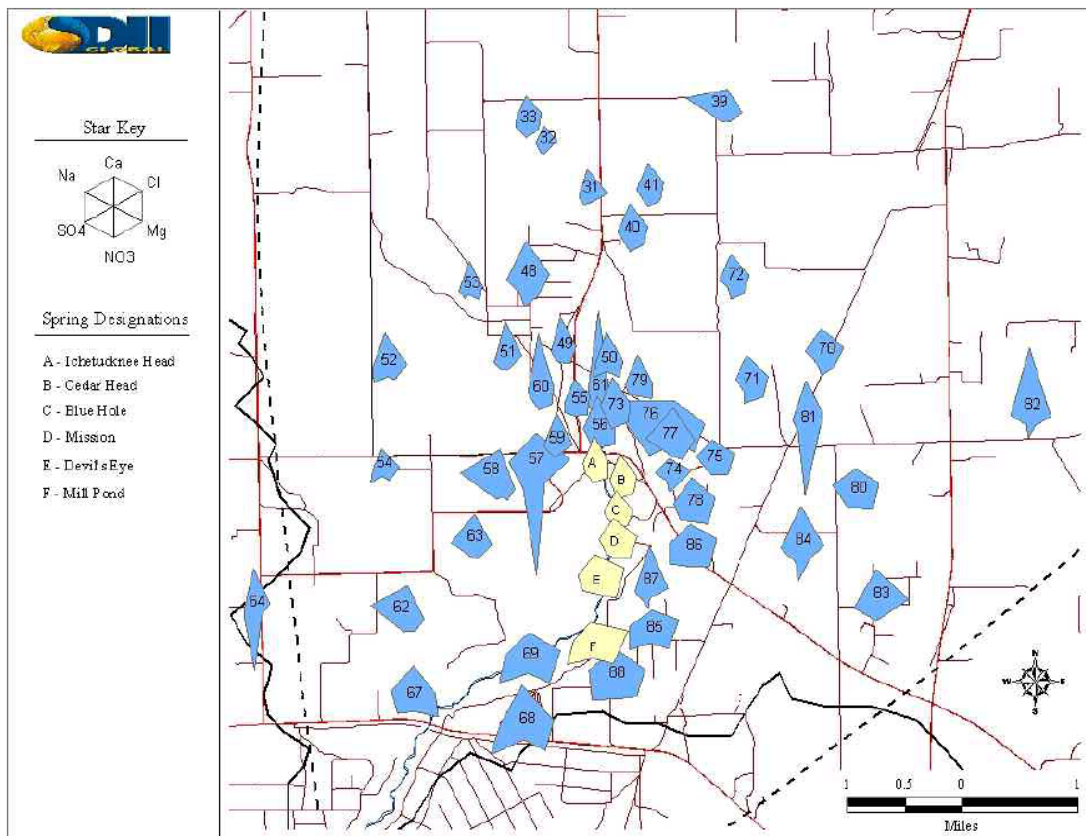


Figure 12 – Use of major ion chemistry to delineate the flowpaths and source areas for particular springs in the Ichetucknee complex (A, B, C, D, E, F). The shape of the “star” represents the relative concentration of various ions, and concordance between a spring vent star and well samples upstream (blue stars) suggests a hydrologic connection. Clear groupings appear to be A/B/C and D/E/F. These springs are notably different in their nitrate concentration, among other water quality parameters.

Delineation of springsheds has utility for developing budgets of water and nutrients for springs. However, several important caveats about delineated boundaries should be made clear. First, as already mentioned, certainty about flowpaths of rainfall in the geographic bounds of a delineated springshed is complicated by surface water drainage that may transport water elsewhere.

Second, where there is a predominance of conduit flow for moving water through the aquifer, some of the water (and therefore nutrients) delivered to the springshed may be transported in conduits that emerge outside the springshed. For example, Toth and Fortich (2002) speculate for the Wekiva that some of the springshed conduits bypass the spring completely, discharging directly or diffusely to the St. Johns River. Anisotropic flowpaths, possibly orthogonal to contemporary potentiometric gradients, might lead to this unusual circumstance.

Another example of the complex nature of the conduit system comes from dye trace studies on the springs of the Ichetucknee River. Despite the convergence of water to the river from 9 springs, the conduit systems are not the same for each. A regional conduit system from the Ichetucknee Trace (see Figure 11) appears to load to Blue Hole, while a more local conduit

system loads to Mission, Mill Pond and Devils Eye springs. The latter system apparently moves water to Devils Eye spring (on the west side of the river) from a conduit that also discharges to Mission and Mill Pond (on the east side of the river). As such, delineation of the Ichetucknee springshed is actually a composite of smaller springsheds, each with different hydrochemical

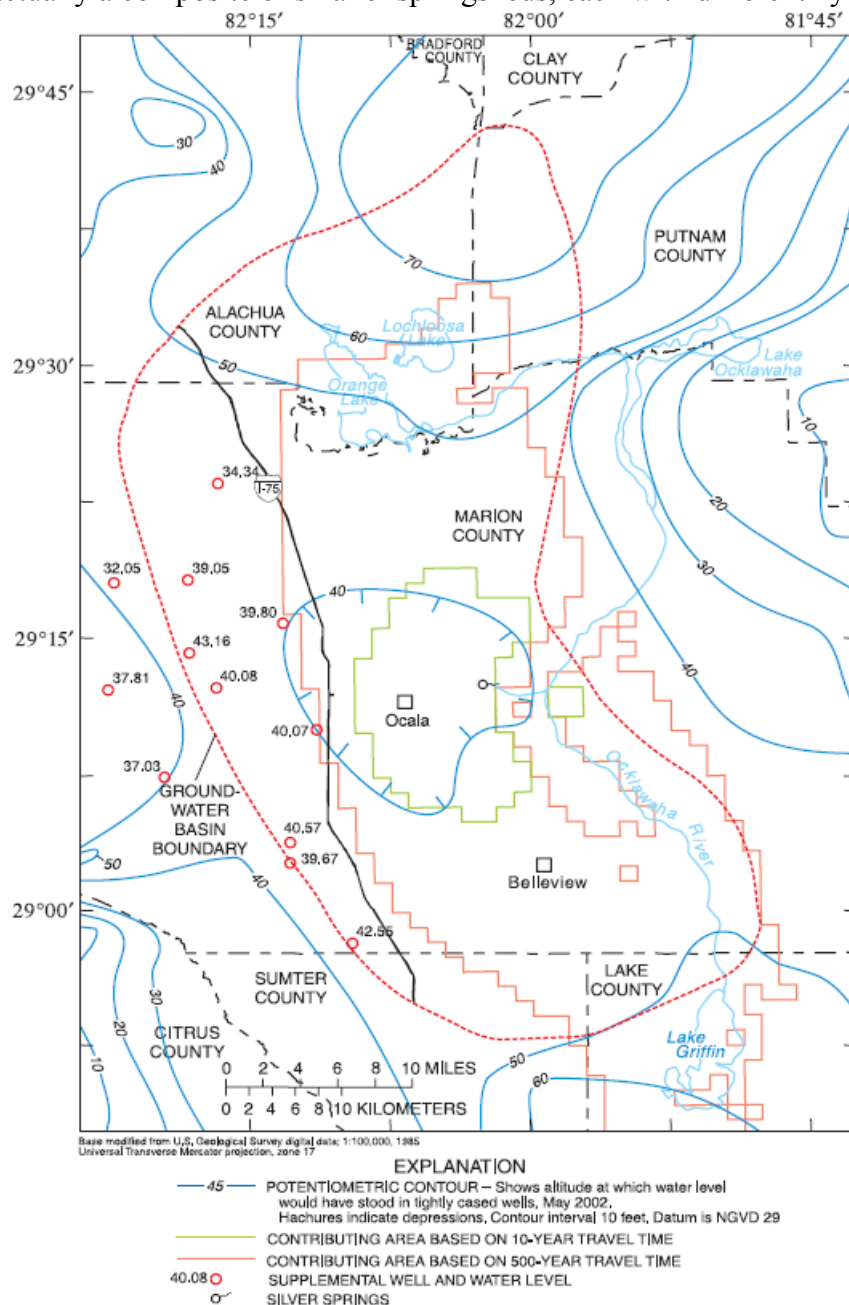


Figure 13 - Delineation of springshed (red dashed line) and capture zones (500 year travel time – pink line, 10 year travel time - green line) for the Silver Springs springshed (Phelps 2004).

properties, conduit maturity, depth and nominal residence times. Understanding the hydrogeologic setting for a given candidate spring is likely to be extremely important in understanding the potential impacts of nutrients.

Finally, while springsheds do delineate flow direction, they do not imply flow velocity. Shallow potentiometric gradients, flow anisotropy and extremely variable recharge rates lead to the condition where the time of concentration (i.e., time required for a molecule of water to move from precipitation to a particular gaged location, in this case, the spring vent) can vary from hours to millennia. This leads to strongly incongruous evidence about the residence times and transit velocities of water and nutrients in the subsurface. For example, Karst Environmental Services (1997) reports, rapid transit times (nominally 8 days) for water moving from Rose Creek (Figure 11) sink to Ichetucknee springs. In contrast, age dating techniques for the water (Katz *et al.* 2001, Katz *et al.* 2004, Katz *et al.* 2005) indicate recharge ages of 20-25 years. The implications are quite significant: if the water is uniformly 20 years old (i.e., piston flow model), then the nutrients and other contaminants emerging today are the signal of loading that occurred in the mid-1980's. More likely, however, is that the water at the spring vent is a binary mixture of young (days to years) and old (decades to millennia); nutrients, calcite undersaturation, and oxygen are all associated with the younger water (Toth and Katz 2006). Moreover, there is evidence of mixing with Lower Floridan Aquifer (LFA) water at sites near the St. Johns River (Knowles *et al.* 2002), which may explain spatial variability in nitrates, dissolved oxygen, salinity and calcite saturation (Toth and Katz 2006). Understanding the time domain of loading is important for interpreting current loads, anticipating load reduction response times, and determining the influence of drought and flood conditions on spring ecology. While efforts to implement dye tracing (Karst Environmental Services 1997, DeFosset 2003, Moore and Martin 2005) are expensive and provide incomplete pictures of groundwater movement, they are critical.

Given this uncertainty, a key refinement in springshed delineation is the definition of time-specific capture zones. This technique relies on modeling and makes potentially problematic assumptions about subsurface flow, but the resulting map product is of considerable utility for regional planning. Phelps (2004) produced a map (Figure 13) that shows 10-year and 500-year capture zones for Silver Springs; the proximity of these boundaries underscores the uncertainty associated with the approach. Upchurch and Champion (2004) define priority protection areas for springs water quality in this way; Figure 14 shows this delineation for Ichetucknee Springs.

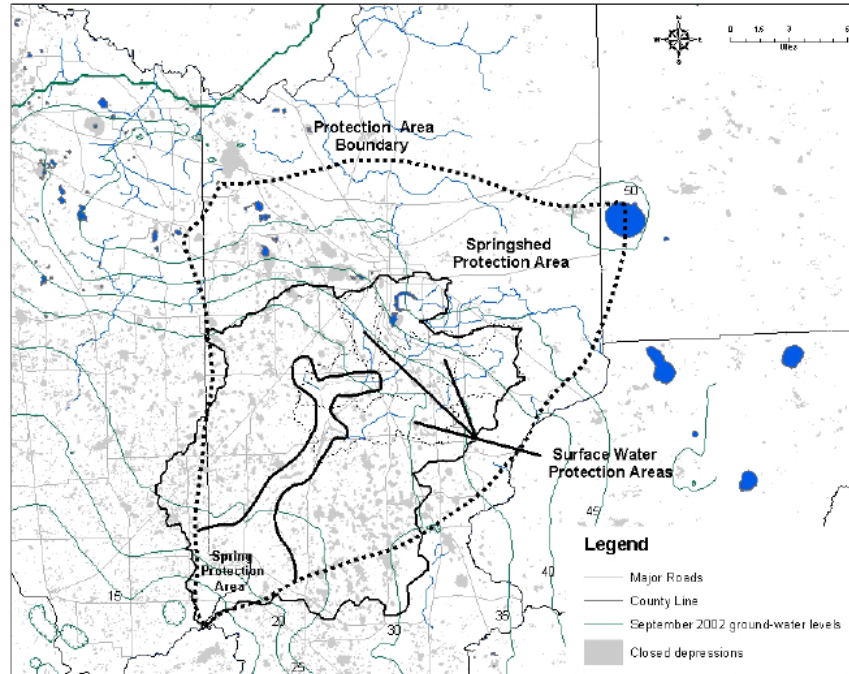


Figure 14 – Ichetucknee Springshed’s low, medium and high priority areas for water quality management. Ichetucknee Trace (Spring Protection Area) has highest priority due to short capture times and highly pervious soils. Surface Water Protection Area delineates areas that drain to surface features captured by sinkholes (e.g., Rose/Cannon Creek sinks) feeding spring conduit systems. Lowest priority is the Springshed Protection Area, where aquifer confinement and surface drainage minimize risk to spring water quality (Upchurch and Champion 2004).

Hydrogeology and Nutrient Loading

The importance of hydrogeology on nitrate loading to surface water is exemplified in the Santa Fe River basin, which has the contrasting hydrogeology of confined and unconfined regions. Specifically, the aquifer in an 820 mi² area of the upper basin is confined and surface water dominates transport, while the aquifer in a 546 mi² area in the lower basin is unconfined and the primary transport is via the Floridan. Loads by reach (Table 1) indicate that although the lower basin occupies only 41% of the watershed, it generated roughly 98% of the load over the last 5 years (see Figure 2 for spatial partitioning). While land use activities (crops and improved pasture) and animal activities (chicken and dairy farms, improved pastures), which are the likely sources of nitrate (Lamsal *et al.* 2006) are expected to load at similar rates in both areas, the intrinsic capacity of the landscape to denitrify is dramatically different, resulting in a massively elevated contamination risk in unconfined aquifer regions.

Table 1. Nitrate-N loads (kg/km²/yr) generated by the two reaches of the Santa Fe River watershed during the years 2001-2005 (Data sources: Hornsby *et al.* 2002, 2003, 2004, 2005; Mirti and Mantini 2006).

Santa Fe River	2001	2002	2003	2004	2005
Upper Basin (confined)	4	3	29.6	15	56
Lower Basin (unconfined)	475	581	696	1128	1302

Assessing Aquifer Vulnerability

In a setting like the karst landscape of North Florida, water quality vulnerability is far from uniform; the example from the Santa Fe River basin underscores the role of geology in regulating contamination risk from nitrogen. Across all contaminants, the degree of confinement, the rate of recharge, the amount of rainfall, the position of conduits, the proximity to springs, the intensity of land use, and the efficacy of management controls figure prominently in understanding the mass and rate of delivery to the aquifer and springs. This has necessitated the use of predictive models to help prioritize hot-spots. Hot-spots in Florida conform with areas where the aquifer is unconfined and land use is intensive. It is important to note that the model was not developed with sufficient density of karstic calibration sites to be of predictive utility. However, this map underscores the sorts of methods used to understand the spatial distribution of risk and therefore guide management.

To account for both known multiple causes of aquifer water quality decline, and inherent lack of understanding of karst flowpaths, the Florida Geological Survey (FGS) developed the Floridan Aquifer Vulnerability Assessment (FAVA) based on a weight-of-evidence synthesis of risk factors (Arthur *et al.* 2007). Among the key drivers of that model are hydrogeology and confinement; the resulting map product (Figure 15) conforms closely to environmental geology. Similar local efforts (e.g., Wekiva Aquifer Vulnerability Assessment – Cichon *et al.* 2005) refine these maps for local planning purposes.

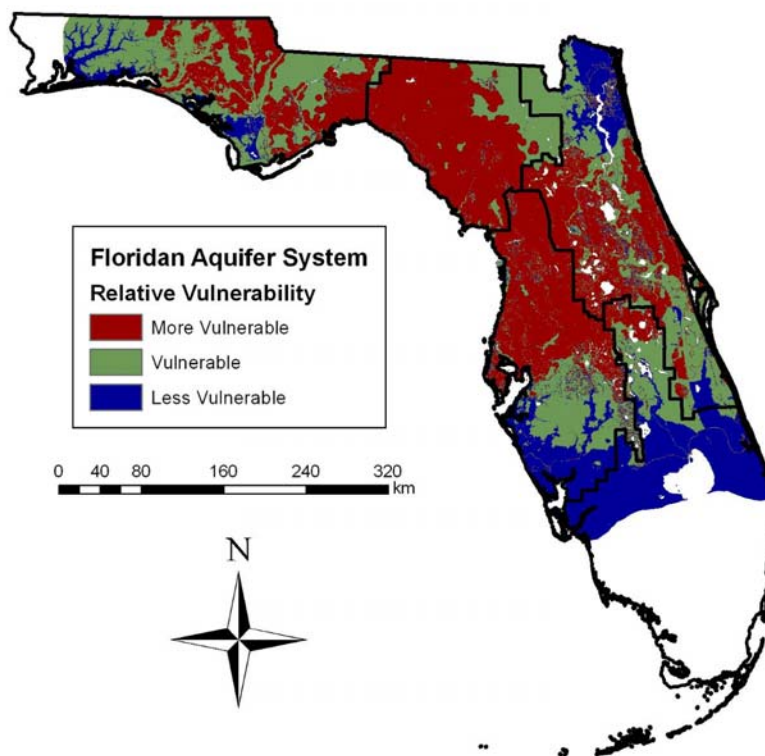


Figure 15 – Relative vulnerability of the Floridan Aquifer System to pollution from overlying land uses (from Arthur *et al.* 2007). Areas in white are outside the study bounds.

Timescales of Water and Nutrient Fluxes

Times of flux between recharge and emergence at a spring vent represent a source of significant and important uncertainty, with direct relevance to understanding current and predicting future nutrient concentrations observed in springs. Because the drainage network consists of sub-surface pathways through stores with unknown effective volume, it is generally not possible to use conventional hydrograph techniques to determine watershed convergence properties. Moreover, the reported times of concentration based on modeling and dye trace studies (e.g., Phelps 2004, Karst Environmental Services 1997) vary over 5 orders of magnitude (days to centuries) within a given springshed. Phelps (2004) further reports two estimates of water age from the same spring made 3 months apart that are 1-5 years and >50 years associated with large observed shifts in spring discharge. Katz *et al.* (2004) suggested that recharge of recent origin coming from shorter groundwater flow paths and/or from features that are hydraulically connected to the upper Floridan Aquifer (e.g., sinkhole) could contribute a larger fraction of total spring discharge during high flow conditions.

There are two complimentary lines of evidence that are widely used to determine the time-domain of connectivity between particular points in the landscape and the outflow of spring vents. The first is an aggregated method based on the concentration of chronometric tracers; typically these are gases whose concentration has varied in well described ways in the atmosphere (Figure 16). Assuming these gases are unreactive, and that no gas exchange occurs once water has recharged, concentrations of these gases in water is indicative of the time at which it was recharged (Katz *et al.* 2001). When this technique is implemented, numerous tracers are used because they represent different time scales (e.g., ^{14}C has been used for long-term age dating – Toth and Katz 2006), or checks in event of contamination. Probably the most promising technique is the combined measurement of ^3He and ^3H (the daughter product), both based on nuclear bomb-testing that peaked in the early 1960's. The concentrations of the various tracers then need to be interpreted in terms of how water flows through the system; that is, the computed nominal age of the water varies based on whether piston flow (limited mixing, water moves through the system with other water recharged at the same time), binary mixing (two water sources at various fractions) or exponential mixing (mixing of multiple water ages) is assumed (Katz *et al.* 2001). Evidence varies for which of these flow models is most plausible. Katz *et al.* (2001) show evidence supporting a piston flow model, while Toth and Katz (2006) working in some of the same systems, argue for a binary mixing model of moderately old water (pre-1940) and young water (ca. 1990). Moreover, the various tracers disagree to a significant extent (see Figure 17), at least with respect to the placement of water age within a fairly well defined range. There is no intrinsic reason to expect springs to behave uniformly with regard to hydrogeology, but site-specific uncertainties arising from unknown flowpaths, residence times and mixing dynamics significantly affect management strategies and expectations.

The general picture that emerges from the aging measurements is water that, on average, has spent between 10 and 30 years in the subsurface. This estimate emerges regardless of which hydrologic flow model is invoked (Katz *et al.* 2001). However, if a binary mixing model holds (for which Toth and Katz 2006 provide evidence, and for which nitrogen delivery dynamics are further supportive), then the results from among the earliest efforts to characterize spring water age (Katz *et al.* 2001) suggest that between 30 and 70% (and in some cases more) of the water at 12 springs was from water with residence times less than 4 years.

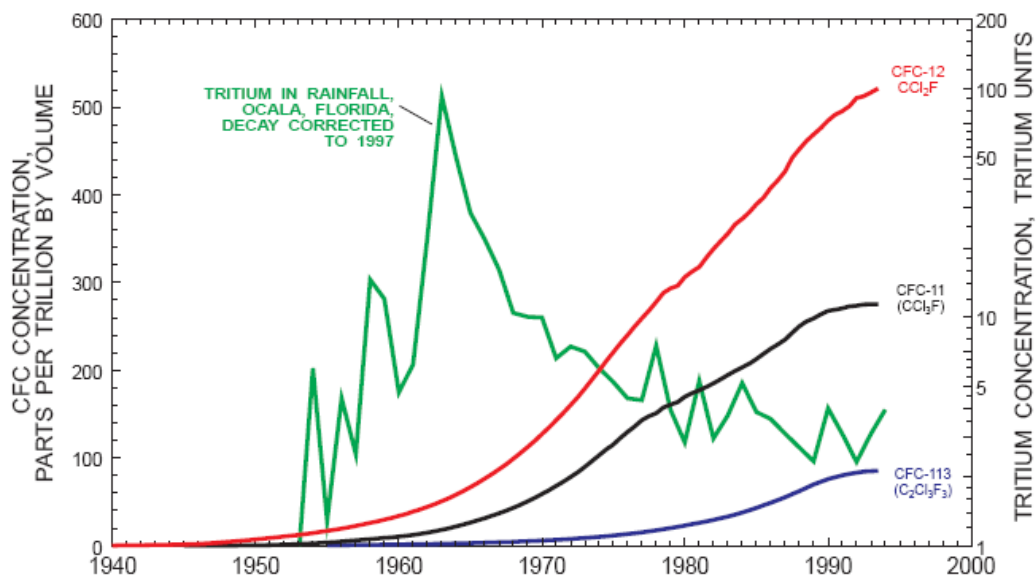


Figure 16 – Concentrations of various tracers (decay corrected) of groundwater age as a function of time. Water recharged prior to 1950 is considered tracer free (after Katz et al. 2000).

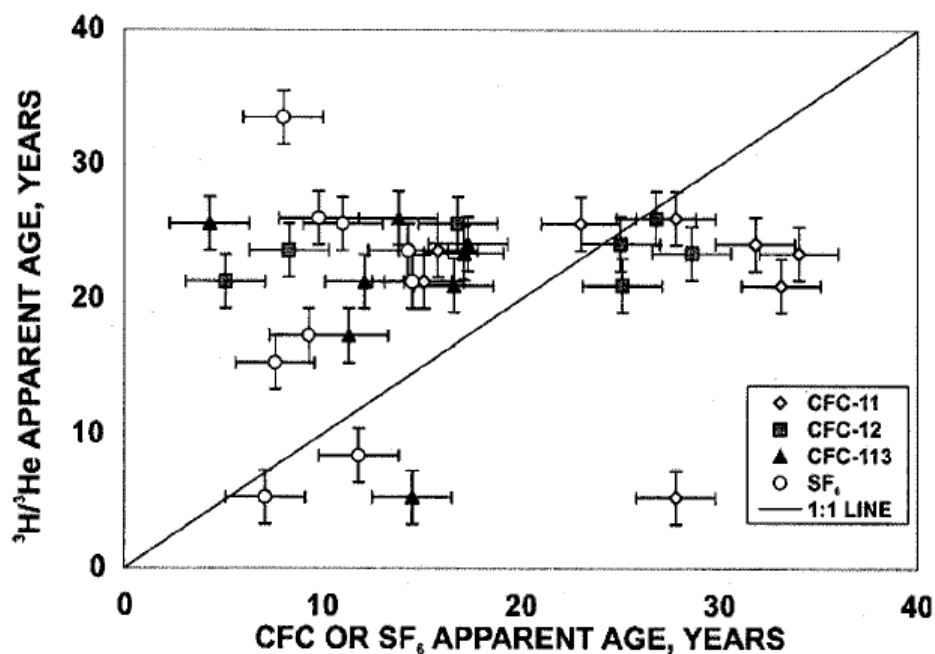


Figure 17 - Estimated water ages for Florida springs (Katz et al. 2001) using multiple dating techniques. While the measures are generally poorly correlated, they are consistently suggestive of recharge dates between 5 and 35 years before present.

Another method for assessing flow connectivity and rate between surface locations via subsurface pathways is the use of injected fluorescent dye (Karst Environmental Services 1997, Butt and Murphy 2003, DeFosset 2003, Kincaid *et al.* 2004, Moore and Martin 2005). In general, while some dye injections are never recovered over the period of observation, the travel

times of dye plugs suggest much more rapid flux of water in conduits; for example, a transit time of 8 days was observed between surface flows into Rose Creek sink and outflows at Ichetucknee Springs (Karst Environmental Services 1997). This discordance in time domains for subsurface pathways is strongly suggestive that a piston flow model is not appropriate, calling into question the utility of the nominal water age for management purposes. Indeed, if, as demonstrated in Toth and Katz (2006), there is strong negative covariance between nutrient, dissolved oxygen (Katz *et al.* 1999), and ionic saturation deficits of water and its age, then it is plausible that short-residence time flowpaths dominate nutrient delivery. This generates dramatically different expectations regarding the time domain of responses to changes in land use or management practices.

TRENDS IN WATER QUANTITY AND QUALITY

Water Quantity

Flows in springs are generated at a rate of roughly 1 cfs of flow per square mile of delineated springshed area (Upchurch and Champion 2004). Strong correlations in spring discharge with climatic forcing are observed (Knockenmus and Yobbi 2001), but the time domain of correlation is apparently over 3-years (that is, flow is correlated with rainfall over the last three years). Chelette *et al.* (2002) report remarkable variability (5-28 cm/s) in flow velocities over 6 months of observations in Wakulla Springs; the responsiveness of spring hydraulics to antecedent rainfall conditions is an area of needed research. Interestingly, only a small fraction (6-23%) of the incident rainfall on the entire springshed (both confined and unconfined areas) can be accounted for in spring flow; since evapotranspiration (ET) accounts for only 67% of rainfall on a landscape basis, a significant fraction of flow (as much as 25%) leaves the land via unknown pathways, presumably diffuse groundwater flow or submarine discharges. It is important to reiterate here that the uncertainties related to springshed delineation/size and surface runoff routing make closure of springshed water budgets highly problematic.

Flow matters in springs for a variety of demonstrated and hypothetical reasons. Clearly, as flows change, fluxes of contaminants dissolved in the water also change. Hilton *et al.* (2006) argue for flux rather than concentration as the predictor of biological response. Moreover, the classical evolution of eutrophication in response to nutrient enrichment so well described for lakes (Wetzel 1983) is not as clear in running waters (Hynes 1969, Dodds 2006) where biological access to nutrients is constrained in part by residence times. Residence time clearly plays a role in the degree to which lakes respond to P enrichment (Vollenweider 1976, Schindler 1977), and Hilton *et al.* (2006) invoke residence time as a critical regulator of phytoplankton responses in rivers. As flow declines, residence times in the sub-surfaces would be expected to increase (perhaps non-linearly) which may alter the degree to which nutrient effects can be observed in springs. It is worth noting that residence times in nearly all of the major springs are extremely short, despite some evidence for flow reductions (e.g., Munch *et al.* 2006 in Silver Springs).

Declines in flow can affect both the load and the residence times of nutrients in spring runs, and can also be expected to indirectly affect biota by changing the hydraulic environment in which they live. Indeed, Whitford (1956) speculates on the role of flow in the spatial distribution of epiphytes in Silver Springs. The most obvious and alarming change in spring ecosystem primary

production is increases in filamentous algal growth, and algal attachment has been shown to respond to shear stresses induced by advection (Wade *et al.* 2002). Effects of flow velocity on animals (e.g., gastropods) are also likely; as flow volumes decline, flow velocities generally decline commensurately. Animals (and indeed plants) for which the hydraulic environment is critical for life history are likely to be affected by such changes, with unknown ecological consequences.

Evidence for flow declines are subject to some uncertainty because of climatic variability and a poor understanding of time lags between rainfall inputs and spring discharges. However, long term statistically significant downward trends have been observed at several springs (Silver and Ponce de Leon) and weaker trends observed at Wekiva and Rock springs (German 2003). Notably, however, several springs with significant algal problems near the vent (Silver Glen, Alexander) showed no decline in flow with time. Chelette *et al.* (2002) provide some evidence that current flows at Wakulla Springs (~350 cfs) are markedly lower than historic values, which were over 600 cfs. Champion and Starks (2001) report dramatic declines in Crystal (Figure 18), Sulphur and Lithia springs between 1937 and 1997, preceding the major drought effects of the last decade; some evidence of decline at Rainbow Springs, among the largest springs in the state, is also evident. Garman and Garey (2005) report on declines in a submarine spring discharge to the point where, since 1961, no discharge has been observed at all at Jewfish Sink (a submarine spring). Kissingen Springs in the Peace River basin, historically a 2nd magnitude spring, is another example where discharge ceased in the 1950's. The cause of this lack of flow due to changes in the aquifer surface has been ascribed to climatic effects, and extraction for municipal and agricultural uses (e.g., weak statistical effects of consumptive use on flow in Knockenmus and Yobbi 2001, strong effects in Weber and Perry 2004). Odum (1957) speculates that the fate of Kissingen is possible for other springs if judicious use of water resources is not made a high priority. While it is clear that such a fate has not been widely realized despite significant pressure on the UFA for agricultural and municipal supply, it is also clear that flow regulates all processes in springs, and continued vigilance to protect flow rates by avoiding excessive aquifer drawdown is essential.

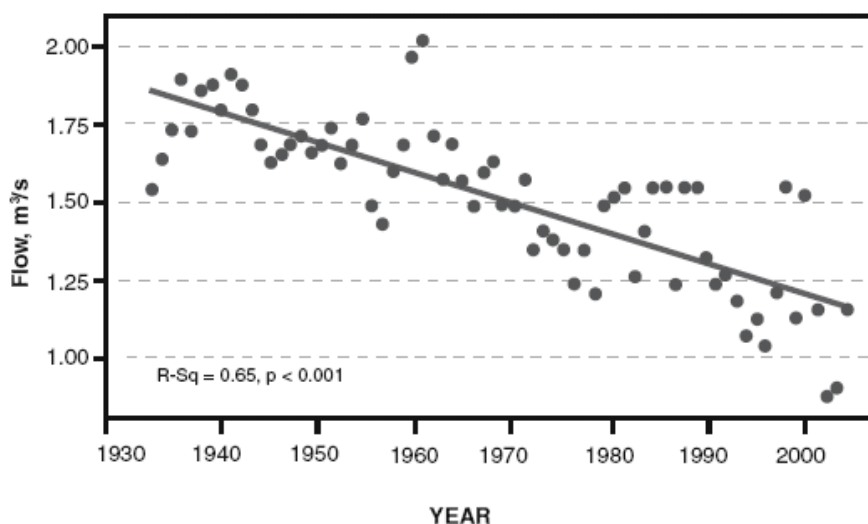


Figure 18 – Flow at Crystal Springs, Hillsborough County since 1933 (Weber and Perry 2006).

Nitrogen

The nitrogen cycle is shown in Figure 19. Excellent summaries of the behavior of N in the environment exist (Bowden 1986, Rabalais 2002). In all, it is estimated that human-derived sources contribute between 60% and 80% of the global N deposited on land annually, and that nearly 50% of the N transported in the world's rivers ($\sim 36 \times 10^{12}$ g N/yr) is of anthropogenic origin (Galloway *et al.* 2004). Key facets for understanding N fate and transport in Florida are: 1) high assimilatory (plant uptake) and dissimilatory (denitrification) potential in regions with high water table (e.g., confined regions), and 2) negligible sorption and denitrification potential once nitrate is in the karst aquifer (Katz *et al.* 2004). To understand why N enrichment in springs is occurring requires understanding the spatial concordance between intensive land uses (e.g., dairies, row crops, poultry houses) and regions where the Floridan Aquifer is unconfined. Water enriched with mineral fertilizers and organic N spends very little time in the root zone (where plant uptake can occur) and encounters conditions unfavorable for dissimilatory removal in the shallow UFA, which is generally oxic (limiting the potential to use nitrate (NO_3) as a terminal electron acceptor) and low in available carbon (the electron donor for microbial respiration).

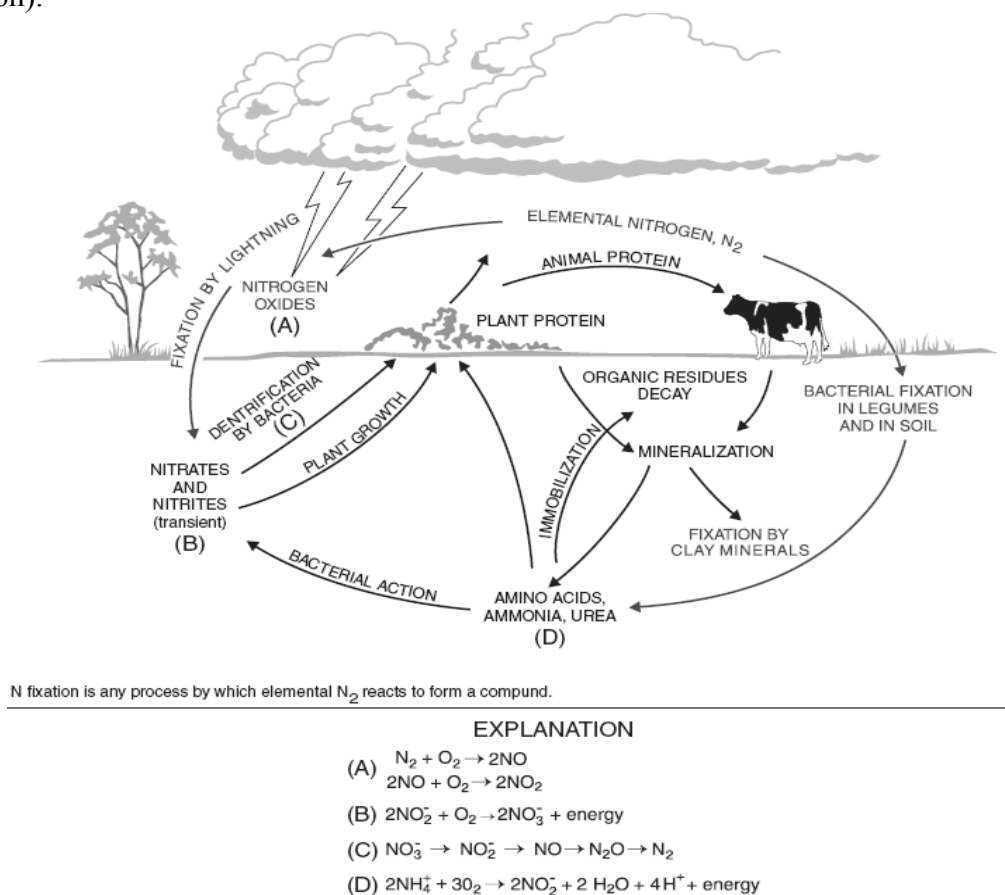


Figure 19 – Schematic of N biogeochemical cycling between various pools (Bowden 1986).

Nitrogen is, by far, the most well studied nutrient in springsheds. Of the 174 references on nutrient loading to springs synthesized for this chapter over 50% dealt principally with sources

and fate of N. Most of the rest address flowpaths (dye trace studies, springshed delineation). With the exception of reports that provide reconnaissance data on numerous water quality parameters (e.g., Scott *et al.* 2004, Stevenson *et al.* 2004), only 5 reports address possible effects of other nutrients, so the discussion that follows focuses predominantly on N load (and the nitrate species of N in particular).

Nitrogen has several forms in an aqueous environment; these include two oxidized inorganic ions (nitrate – NO_3^- , and nitrite – NO_2^-), reduced inorganic species (ammonium – NH_4^+), dissolved gases (nitrogen gas – N_2 and nitrous oxide – N_2O), and myriad organic species of varying lability (collectively referred to as dissolved organic N – DON and particulate organic N – PON). While all species can be found in spring rivers, nitrate dominates delivery of N at spring vents (Figure 21). A small number of springs (Beecher, Santa Fe in Columbia County, Columbia, Treehouse springs and Holton Creek Rise) are dominated by ammonium and DON. However, most springs, particularly those that are severely enriched, are dominated by nitrate. Temporal trends in other forms of N are unknown. Several properties of the nitrate ion make it particularly problematic as a groundwater pollutant. First, it is highly soluble (saturation of nitrate in water occurs at ~300 g/l) and extremely mobile, moving rapidly through soil profiles, due to low anion exchange capacity and low affinity for nitrate; this rapid leaching leads to contaminated groundwater. Second, once nitrate has passed out of the soil/vadose zone, the absence of electron acceptors and anion binding sites in the mineral matrix of aquifers (karst or otherwise) markedly slows nitrate reactivity; in fact, some authors have shown that nitrate reactivity in groundwater is so slowed ($0.013 \mu\text{mol N L}^{-1} \text{d}^{-1}$) that its transport was comparable to a bromide tracer (Smith *et al.* 2004), and that nitrite production rates ($0.036 \mu\text{mol N L}^{-1} \text{d}^{-1}$) more than compensated for this attenuation rate. Others have documented enhanced nitrification of dissolved organic nitrogen (DON) and ammonia in shallow groundwater (where oxygen is present) (Miller *et al.* 1999), with important implications for N isotopic fractionation (if the process is rate limiting and incomplete) and also for dissolved oxygen dynamics.

The reason for the high emphasis on N is that observed trends in nitrate-N are nearly ubiquitous in areas where anthropogenic loading to the springshed land surface has occurred. For example, water quality monitoring of the major rivers in the Suwannee River Basin over two decades has indicated a statistically significant increasing trend in the concentrations of nitrate-N (Ham and Hatzell 1996), which is primarily attributed to groundwater discharges in the Middle and Lower Suwannee reaches (Pittman *et al.* 1997). Similar trends have been observed for the Ocklawaha River, particularly where that system interacts most closely with groundwater (Mytyk and Delfino 2004). Figure 20 shows nitrate concentration trends for springs in the Suwannee Valley. Figure 21 shows a similar synthesis across a total of 69 springs (Strong 2004). The x-axis is N concentration in the 1970s and the y-axis is contemporary concentration. Note that these data are principally 2nd and 3rd magnitude springs; upward trends for 1st magnitude are well established in Katz *et al.* (1999), Champion and Starks (2001), Chelette *et al.* (2002), Scott *et al.* (2004), Munch *et al.* (2006), Upchurch *et al.* (2007), among numerous others. Points above the 1:1 line have seen enrichment; the mean increase was 0.46 mg/L to 1.04 mg/L as N, but clearly there were some sites at which the increase was far greater, and some where concentrations declined. Indeed, Strong (2004) reports a trend of generally unknown cause where several springs increase through 1998 (Figure 21) and then decline to current concentrations (e.g., Hornsby springs – Figure 22).

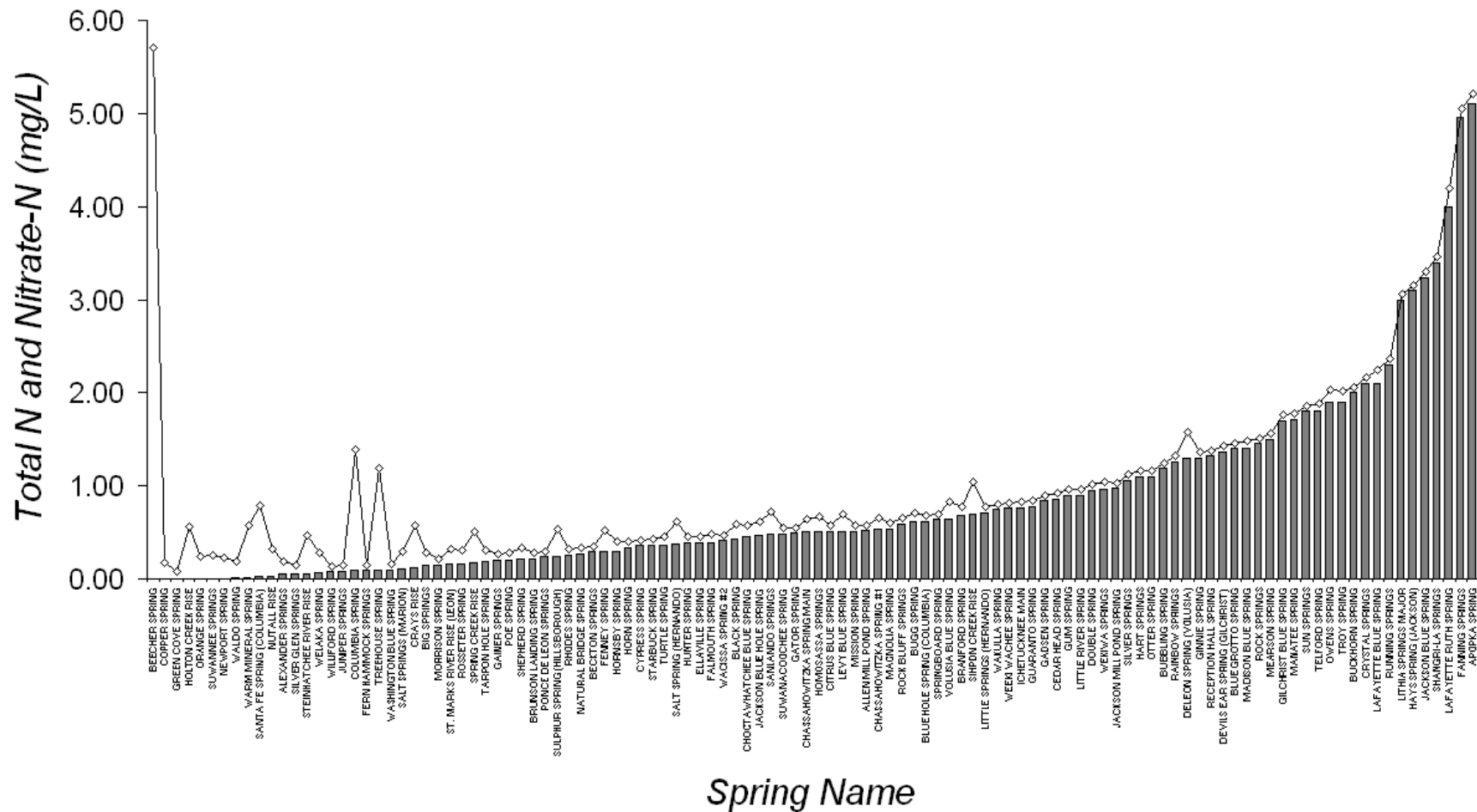


Figure 20 – Nitrogen loading to major springs of Florida; shown are both nitrate and total N load. Note that for most springs, most of the N (>75%) arrives as nitrate, but ammonia is important for some that have low nitrate concentrations.

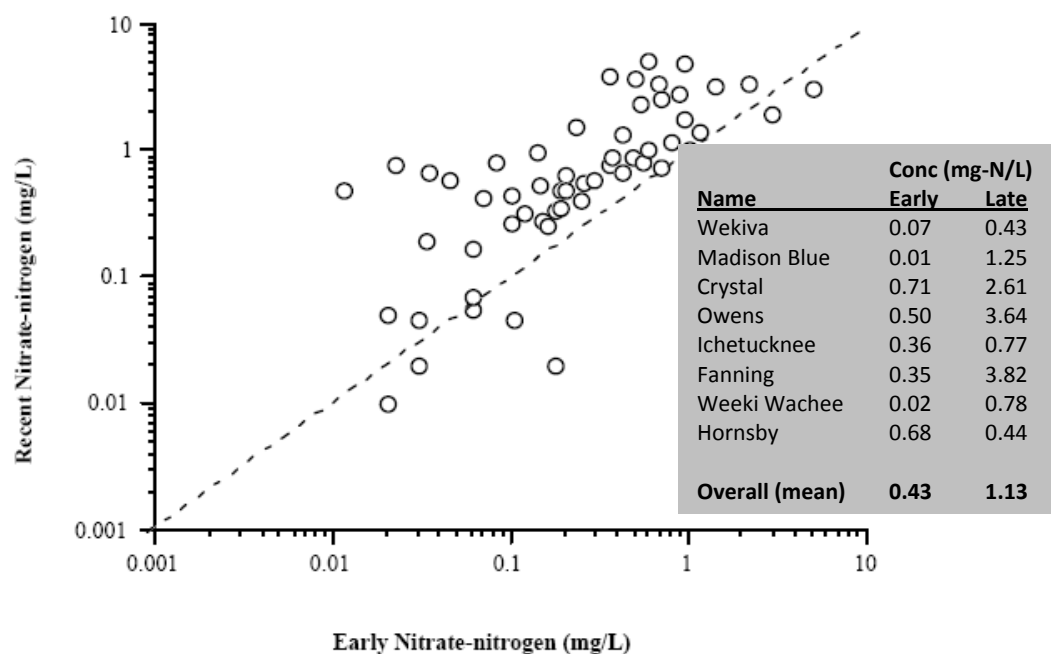


Figure 21 – Relationship between early time period (1907-1979) nitrate-nitrogen and recent time period (1990-2003) nitrate-nitrogen, with a 1:1 line (- -), for 69 Florida springs (Strong 2004).

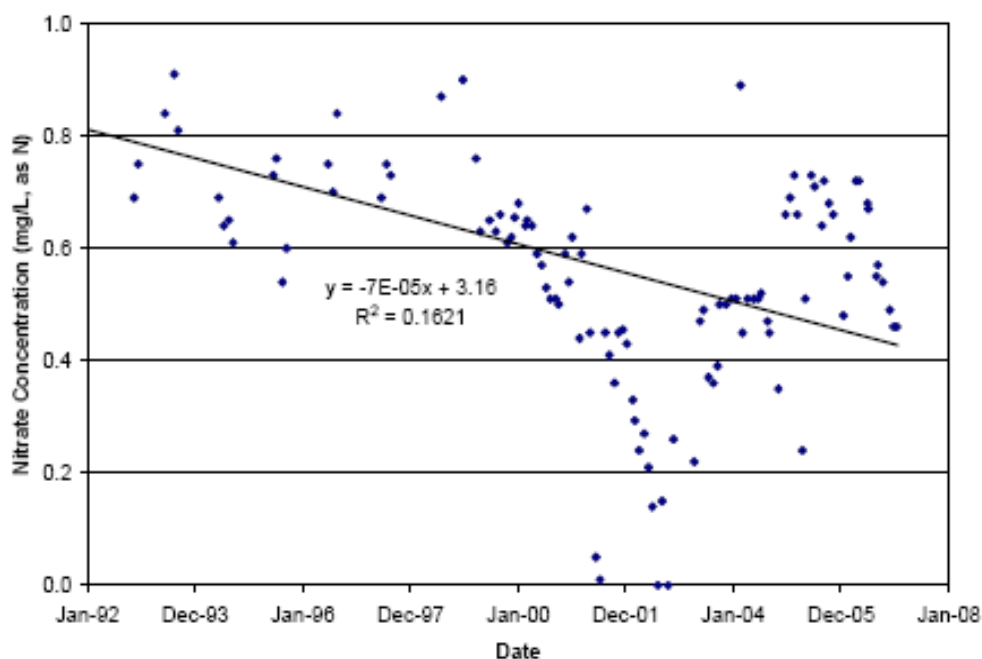


Figure 22 – Nitrate trends in Hornsby Springs (Alachua County) since 1992 illustrating declines since 1998.

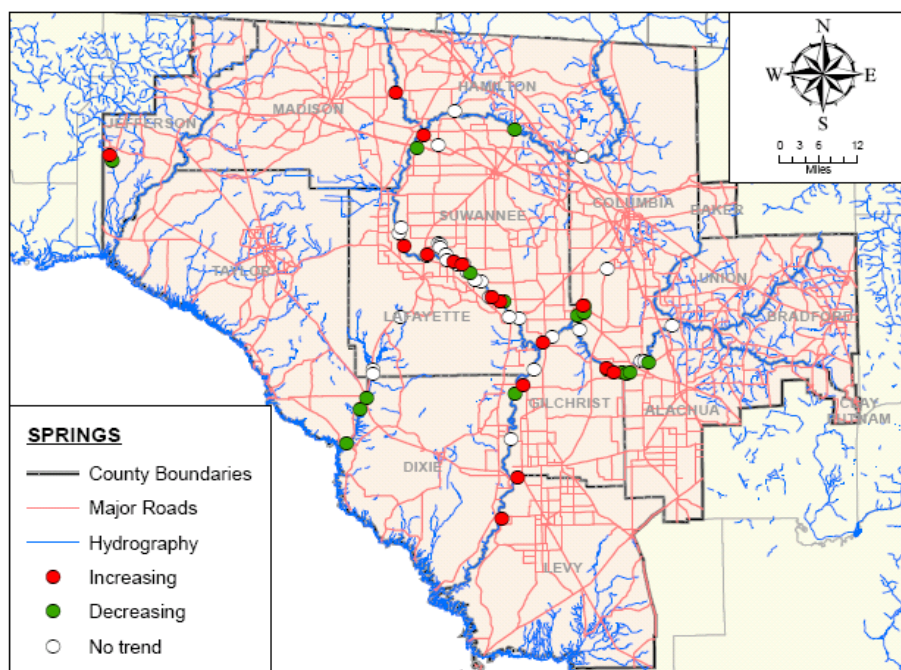


Figure 23 – Trends in nitrate concentrations in springs of the SRWMD (Upchurch *et al.* 2007).

A synthesis of recent (1989-2006) records for springs ($n = 68$) in the SRWMD (Upchurch *et al.* 2007) suggests that significant trends occur in both directions (positive = 55% and negative = 25%), with some springs exhibiting no trend (20%); these are reported spatially in Figure 23. The picture that emerges is complex, and suggests that recent control efforts may be working in some places and not others. The prevalence of negative trends may also be driven hydrologically (see Figure 22) with recent drought and flood conditions clearly manifest in the signal at Hornsby Springs. Toth and Katz (2006) observed a negative trend between nitrate concentrations and age, suggesting that as spring vent flow became older (i.e., deeper source water during low flow conditions) nitrate concentrations declined; Einsiedel and Meyer (2006) observed the identical inverse relationship for karst springs in Germany. This formal link between discharge and age is an important research need because of its implications for regulatory minimum flows and levels.

Analysis of the concordance between nutrient loading and flow may be confounded by hysteretic (i.e., path dependent) behavior in the delivery mechanisms. Van Herpe and Troch (2000) observed counter-clockwise hysteresis in flow vs. nitrate concentration relationships in a Belgian river (Figure 24), suggesting that nitrates arrive during the recessional phase of the storm hydrograph. Current monitoring data are insufficient to determine if similar patterns are observed in Florida springs; autocorrelation length in nitrate concentrations is apparently less than the sampling interval for both springs and rivers (Cohen, unpublished data). As such, the prevalence and incidence of occurrence and effect of pulses due to storm flows like those observed for dissolved organic carbon by Katz *et al.* (2004) in Wakulla Springs are unknown. Moreover, potentially non-linear ecosystem effects due to pulsed nutrient delivery are possible if storm flows are missed by current sampling frequency.

What is clear from the time series record, at least at Wekiva Springs, is a strong cross-correlation of discharge and concentration with essentially no evidence of lag. This observation (Figure 25) confounds interpretation of water age dating techniques that assume a piston flow model. While flow could reasonably be expected to respond to up-gradient climatically-driven changes in potentiometric surfaces due to nearly instantaneous transmission of potentiometric pressure (Martin and Dean 2001), the concordant arrival of nitrates with extremely short lag means that travel times need to be far shorter than the years-to-decades estimates widely published (Katz *et al.* 2004). A binary mixture of young and old water with a nominal age of 20-25 years, but comprised of flow with markedly shorter residence times (Toth and Katz 2006) is more likely, and, as discussed above, supported by evidence from dye trace studies. The amplitude of the variability suggests that young water carries the bulk of the nitrate, an observation partially confirmed by negative covariance between age and nitrate concentrations (Katz *et al.* 1999). It is also plausible that the positive cross-correlation between flow and nitrate concentration is due to proximate sources only; if this is true, the amplitude of variability in Figure 25 would imply that these sources are a large fraction of the total load. Frydenborg (2006) observed that most of the load arriving at the Ichetucknee was entrained by the sinkholes that capture confined region flow. Chelette *et al.* (2002) report concentrations in the Wakulla System, where nitrate concentrations increase dramatically between Middle River Sink (one of several key conduits to the vent) and the spring. Indeed, upward trends clearly observed in the concentrations at Wakulla are not matched by those in the sink, suggesting that either the nitrate is delivered from diffuse sources between the sink and the spring, or that the vast majority of the nitrates are from other smaller conduits. Loper *et al.* (2005) cite that the load from the confined to the unconfined portion of the Wakulla springshed is 73,000 kg N (of which some may be attenuated), compared with 270,000 kg N at the spring vent; this supports the contention that most of the N is introduced in the karstic short-time capture zones.

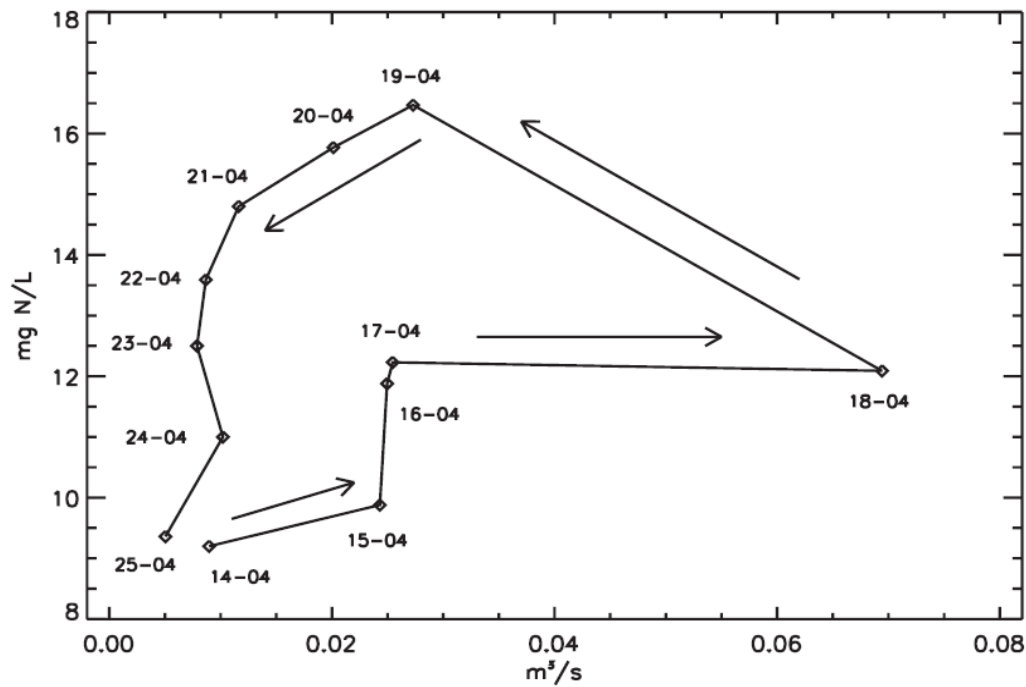


Figure 24 - Flow vs. nitrate hysteresis (van Herpe and Troch 2000).

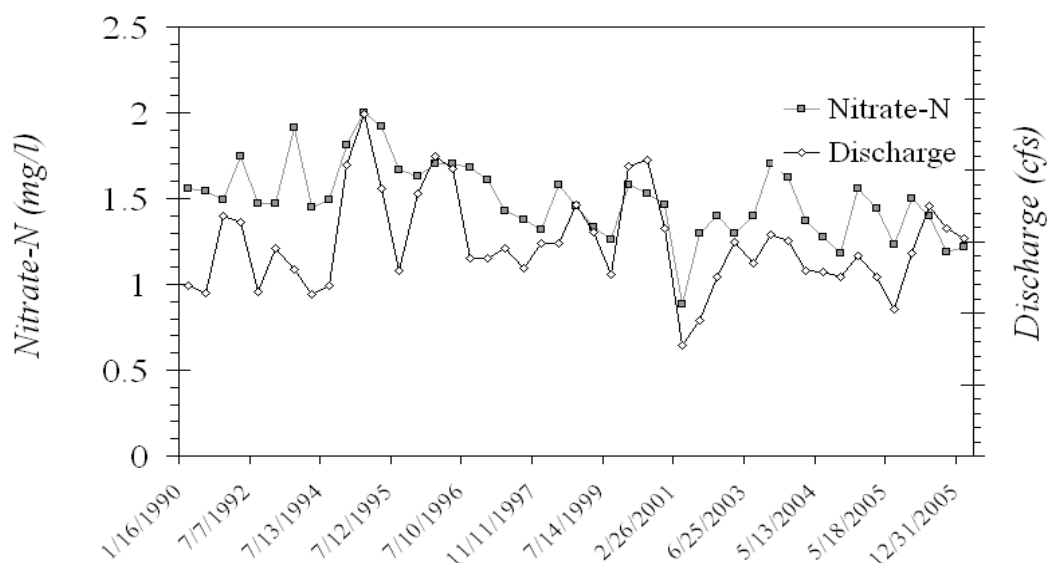


Figure 25 - Time series measurements of $\text{NO}_3\text{-N}$ and discharge in the Wekiva Springs.

Given the potential for disproportionate importance of local sources, the observation (Upchurch and Champion 2003) in the Ichetucknee springshed of nearly monotonic increases in NO_3 concentrations with proximity to the trace and springs is important. In that study, distinct areas, mostly near the spring and tracer, were geostatistically characterized as having UFA nitrate concentrations in excess of 2 mg/L, which is markedly higher than levels observed in any of the springs in that complex.

Phosphorus

In most freshwater systems, P is limiting. Indeed Hutchinson (1957) suggested that for examining the impacts of nutrients on lakes, ecologists should focus efforts on understanding P. That prediction has been prescient across a wide array of aquatic systems, but most notably for lakes (Vollenweider 1976, Carpenter *et al.* 1998b). Odum (1957) found no association between P levels in springs and their primary production, concluding that the mechanisms that lead to P limitation in lakes (Schindler 1977) are not present in flowing water systems like springs. The same conclusion regarding eutrophication in flowing waters was arrived at regarding nitrates (Odum 1957, Duarte and Canfield 1980), suggesting that nitrogen may not have significant ecological effects in springs; this represents probably the most important unknown in springs ecosystems ecology.

The phosphorus cycle (Figure 26) is in some ways simpler than N (no gaseous phase, few valence states), but is made complex by the numerous geochemical reactions that involve phosphates. The principal source of P in the modern landscape, both in Florida and elsewhere, is mineral fertilizer. Notably, however, the source of P fertilizer is generally geologic, including the vast Hawthorn Formation deposits in Florida (e.g., Bone Valley deposits in central Florida supply ~30% of the world's P). The presence of this massive and concentrated geologic source of P means that many ecological systems receiving Floridan Aquifer water are loaded heavily with P. Indeed the nominal concentrations of P in springs are between 50 and 100 ppb, which

suggests that historic N:P ratios (molar basis) were less than 1:1. Note, however, that N:P ratios in advective (flowing water systems) are only informative regarding nutrient limitation if some other input (e.g., light) is not limiting.

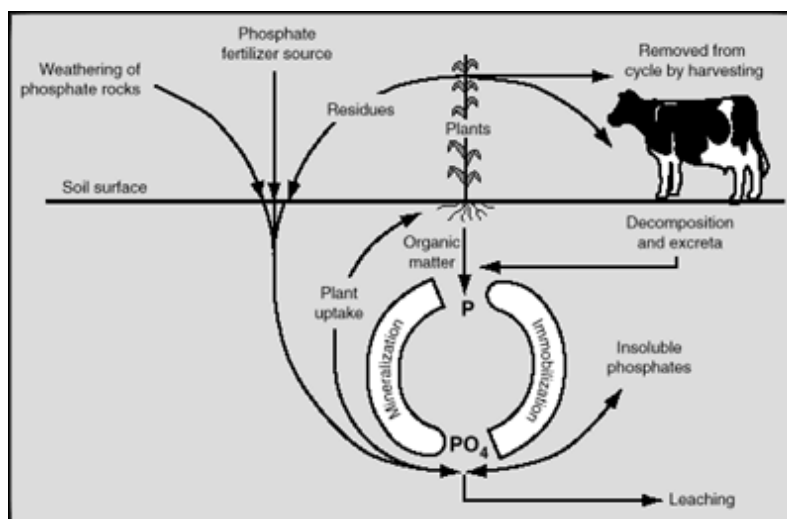


Figure 26 – Generic P cycle. The P cycle in Florida is characterized by low sorption in the Plio-Pleistocene sediments of the confined region, massive stores of geologic P in the Hawthorn Formation, and almost inexhaustible sorption capacity in the carbonate aquifer matrix.

There are several reasons related to loading that explain why P limitation may not persist in springs. First is the presence of apatite ($CaPO_4$) in the Hawthorn Formation which weathers relatively easily. P weathering is expected to be most pronounced at the Cody Escarpment, and streams flowing over the scarp and then into the Floridan are generally P enriched (Hornsby 2007). The concentration of total P reaching Ichetucknee springs (60-80 ppb) is markedly less than the concentration in Rose Creek Sink (200-600 ppb), one of several principal accumulation points for runoff from the confined region of the springshed (Frydenbourg 2006). This suggests that most of the P is sorbed during passage through the Floridan Aquifer towards the spring, and that the P in the fertilizer applied to lands overlying the unconfined aquifer is not reaching the springs. The presence of geologic P somewhere along the flowpath is the likely explanation for the relatively high P levels observed in several springs compared, for example, with lakes and wetlands (Figure 27). Toth and Katz (2006) observed a significant negative relationship between water age and phosphate concentration, consistent with P enrichment by surface waters interacting with the Hawthorn and then following shallow flow paths to the spring vent.

A second factor regulating P loading to the springs is the strong chemical sorption potential of the aquifer matrix for mineral P. While P breakthrough is expected to occur under extreme P loading (Nair *et al.* 2004), the enormous sorption capacity of the calcitic soils and the carbonate aquifer are likely responsible for P loading trends that are starkly different than comparative N loading. Indeed, at many springs with strong upward trends of nitrate, the TP trends are stationary (Figure 28).

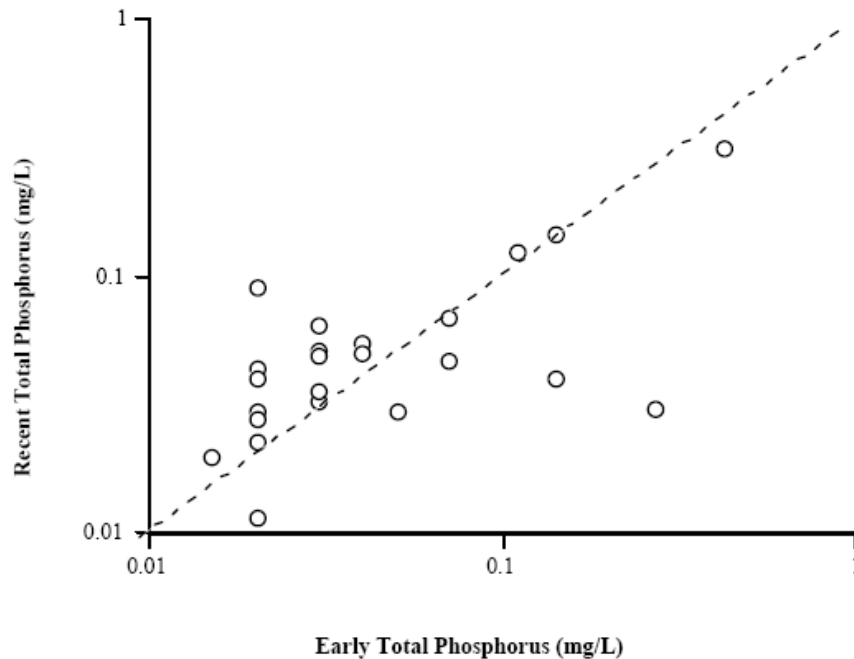


Figure 27 – Summary of trends and nominal concentrations in 23 springs comparing observations in the 1907-1979 period and observations in 1990-2003. Nominal concentrations are low (~50 ppb) and no significant trend is observed (Strong 2004).

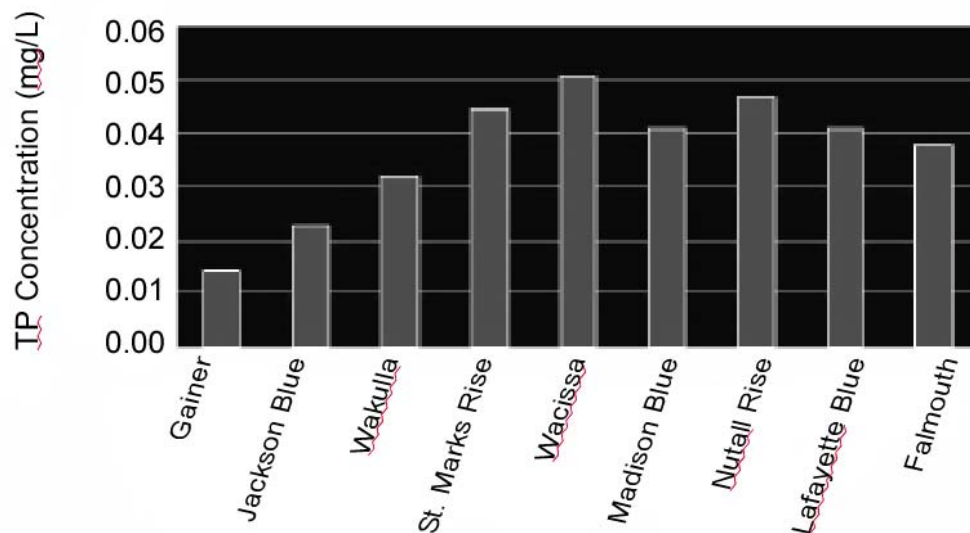


Figure 28 – Summary of TP concentrations in some of Florida's 1st magnitude springs, many of which have seen significant recent increases in nitrate concentrations. TP concentrations are, in general, low and unchanged. (Data from Scott et al. 2004; figure from Loper et al. 2005)

Carbon

Organic matter dynamics in the subsurface are outside the scope of this review, but several key observations should be made. First, as in surface streams, microbial processing and trophic

concentration of energy occur; Simon (2000) showed interesting similarities between surface stream organic matter processing and the processing that takes place in karst conduits, noting among the several differences the relative absence of nutrient limitation, presumably because of the ratio of flux to production. In addition to subsurface heterotrophic respiration which mineralizes both particulate and dissolved organic carbon, there are geochemical processes that result in abiotic attenuation. It is worth pointing out that the self-organizing character of the karst solution conduits occurs in part because of interactions between surface sources of organic acidity and carbonate dissolution.

The carbon emerging in spring waters is, with few exceptions, almost exclusively inorganic. Nominal organic carbon concentrations across a broad survey of well samples in the Silver Springs springshed (Katz *et al.* 2001, Phelps 2004) are nearly below detection limit (~1 mg/L), though there is evidence of episodic breakthrough of dissolved organic carbon in Wakulla Springs during periods of storm flow (Chelette *et al.* 2002, Katz *et al.* 2004). BOD levels are also extremely low; Phelps *et al.* (2006) are among the only studies to report this quantity, and observed no BOD levels higher than 1.2 mg/L, with most less than 0.5 mg/L. As such, any BOD introduced into the aquifer from wastewater sources is metabolized or geochemically bound during passage, so no trend in enrichment has been observed. If BOD loads to the aquifer are significant, it will be manifest as DO changes.

The result of organic mineralization (biotic or abiotic) is increases in solution of carbonates. Consequently, inorganic carbon levels are uniformly high; dissolved CO₂ levels in 5 springs were between 9 and 12 mg/L (Phelps *et al.* 2006), and alkalinity levels are usually extremely high (50-150 mg/L). There is evidence that hardness (a proxy for dissolved inorganic carbon in a carbonate system) has increased significantly ($p < 0.05$) since the 1970's (Strong 2004), with nominal increases of 25% (Figure 29). One speculative explanation for this is that as groundwater levels have declined with time due to drought and pumping, water emerging at the spring vent is older; longer subsurface residence times would affect the degree of calcite or dolomite saturation, and might also affect other water quality parameters (e.g., salts, dissolved oxygen and nitrate concentrations) that are ecologically relevant. Declines in rainfall pH with time might also be factors in these observed changes.

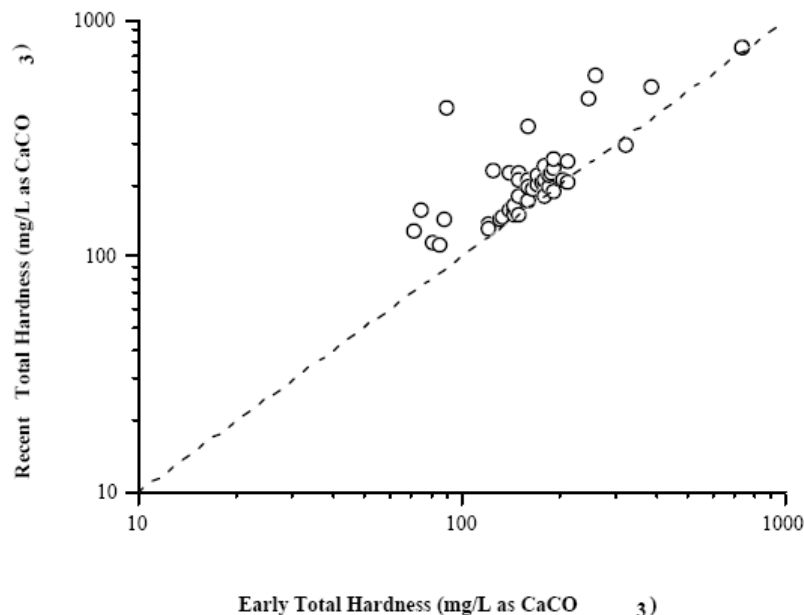


Figure 29 – Relationship between early time period (1907-1979) total hardness and recent time period (1990-2003) total hardness, with a 1:1 line (---), for 49 Florida springs (Strong 2004).

Other Water Quality Parameters

The role of nutrients in spring ecosystems is the subject of this work, but nutrient effects can be confounded by other water quality parameters. For example, many of the same effects of eutrophication on fauna (i.e., oxygen stress) can be observed in areas where dissolved oxygen is naturally low. There is strong evidence of spatial variability in dissolved oxygen (DO) levels in springs (Phelps 2004 – Figure 30), and also strong evidence of temporal declines (Scott *et al.* 2004 – Figure 31); effects of this variability are unknown. Of note is the observation (Andrews 2000) that DO concentrations in most shallow wells, even in the vicinity of dairy farms, were high, which suggests both short residence times and ultimately favors the process of nitrification of organic and ammonia N. Barrios and DeFosset (2006) also report high levels of DO (> 3.5 mg/L) in the Upper Floridan, and a significant positive association ($r = 0.5$) between nitrates and DO, supporting the notion that shallow, short-residence time flow paths are the dominant conveyance of both. Stevenson *et al.* (2004) observed that DO in the vent is the only variable significantly associated with algal cover (the preferred metric of algal dominance – Quinlan *et al. in review*); increased algal cover was correlated with lower DO. Munch *et al.* (2006) report declines in DO in the Silver Springs system, and conclude that they are ecologically significant.

Identifying whether spatial and temporal variability of DO is implicated in ecological change, and, if so, whether it responds to anthropogenic stressors and management is a topic of future inquiry of immediate relevance to springs. Moreover, if declines in DO are in some way related to increased algal dominance, low DO levels within algal mats due to microbial respiration may constitute a positive feedback that constrains a system within an algal steady state even after the stressor that led to algal dominance in the first place is removed (Dodds 2003). It is worth pointing out also that high rates of P mineralization are observed in anoxic environments

(Chambers and Odum 1990); consequently, declining DO in spring vents could make more P available for fueling plant or algal productivity.

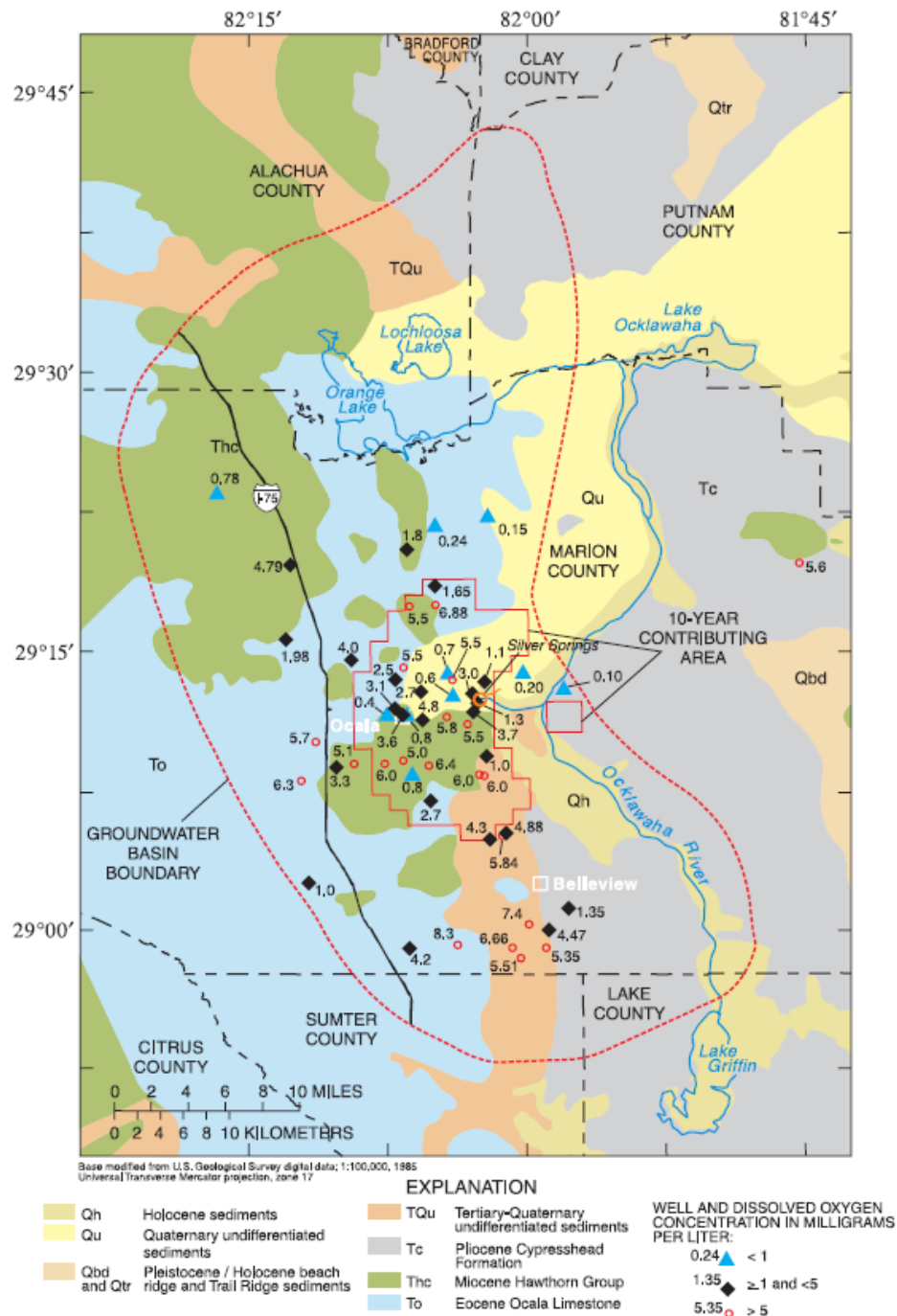


Figure 30 – Map showing the significant variability in Upper Floridan Aquifer DO concentrations, with trend towards anoxic conditions closer to the springs. Underlying the points are the Silver Springs springshed and the geologic regions (Phelps 2004).

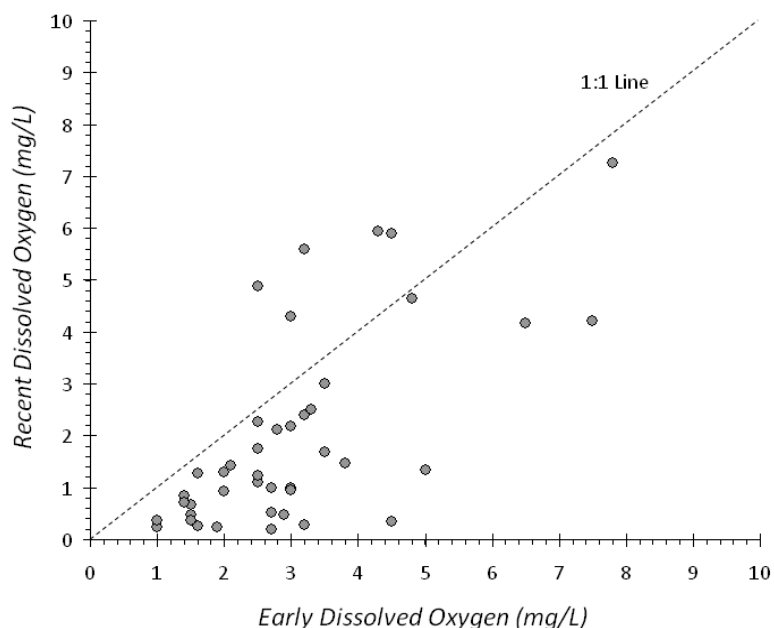


Figure 31 – Historic (1972) vs. recent (2002) dissolved oxygen levels measured in the vents of 42 springs showing strongly significant declines ($p < 0.001$) (synthesized from Scott et al. 2004).

Other water quality metrics have also been discussed as possibly playing a role in ecological changes in springs. Among the numerous confounders of the nitrate-algae relationship in springs is the presence of abundant algae at Silver Glen and Alexander springs, both of which have nitrate concentrations at background levels (~30 ppb). However, both have comparatively high specific conductance ($> 1000 \mu\text{S}/\text{cm}$); Florida Geological Survey scientists (H. Means, personal communication) have reasoned that salinity changes due to flow declines may have precipitated algal blooms. Cowell and Botts (1994) observed that conductivity and alkalinity were the best predictors of algal abundance, while nitrate provided no predictive power. Formal survey and experimental consideration of this possibility should be among research activities improving understanding of spring ecosystems.

Temperature of water is also often reported when examining trends in water quality in springs. Despite the relatively minor variation of water temperature with time, temperature has been used as a metric of subsurface residence times and even more broadly as an indicator of source (Champion 2001, Martin and Dean 2001). Temperature changes may be particularly relevant as a tracer of local source runoff.

Finally, there is evidence of contamination from the class of chemicals widely referred to as emerging contaminants (industrial chemicals, personal care products, pharmaceuticals, etc.). Phelps *et al.* (2006) report results from wells and springs in the St. Johns River Water Management District in which they examined concentrations of non-traditional contaminants (e.g., benzene, bisphenol A, caffeine, DEET, naphthalene, atrazine, many others). The results are important, though not suggestive at this time, of a strong toxicity risk. Phelps (2004) found DEET in all 3 spring vents at Silver Springs, and in 27 of 35 wells; geology appeared to play a role in where it was found, with all sites where DEET was not observed at locations where Ocala limestone is covered by younger sediments. Other compounds that were found frequently

include bisphenol-A (polycarbonate resin), phenols (disinfectant), and triclosan (disinfectant common in antimicrobial soaps). None were measured in sufficient concentrations to pose known ecological or health risks. Few observations of caffeine, a relatively short-lived tracer of human contamination, suggests either long residence times or low loads from septic/wastewater.

SOURCES OF NUTRIENTS

Nitrogen

The vast preponderance of attention that has been paid to nitrate loading has resulted in a relatively mature understanding of the sources of N to the landscape, with several notable exceptions. Delineating sources is made markedly less complex than it might be for P because there is no geologic store of N. As such, all of the nitrogen emerging in spring vents was deposited on the land surface.

The list of presumed loads is long, and includes atmospheric deposition (wetfall and dryfall), imported fertilizer, imported food (for people and livestock) which result in domestic wastewater discharges (centralized systems and septic tanks), and biological N fixation by plants, an often overlooked component of regional N budgets. Figure 32 shows a summary of source importance for watersheds in the northeastern US (Boyer *et al.* 2002, van Breeman *et al.* 2002), illustrating the kinds of results delivered for springsheds. On the omission of fixation from springshed source budgets, it is worth pointing out that under pre-development conditions biological N fixation represented over 90% of the terrestrial N budget, and is estimated to represent 30-35% of the contemporary budget; its omission leads to potentially enormous underestimation of the springshed nitrogen mass loading. The magnitude of the contemporary contribution in the sandy soils of Florida's springshed is totally unknown.

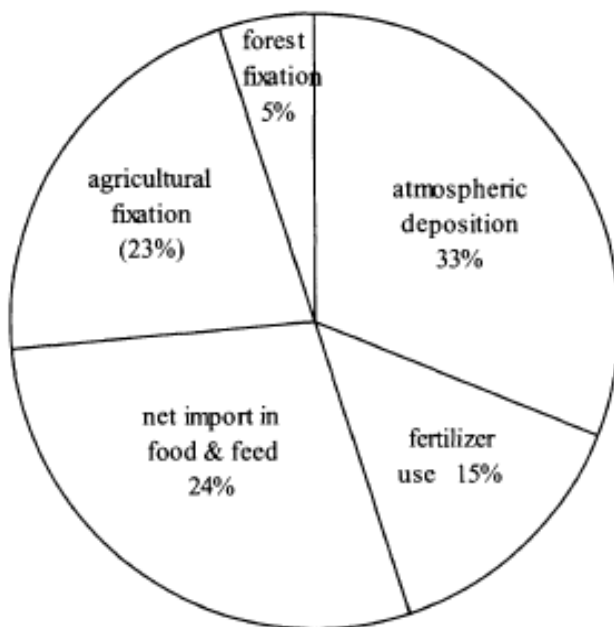


Figure 32 – Summary of the nominal fractional importance of various N inputs to 16 watersheds in the northeastern US (van Breeman *et al.* 2002)

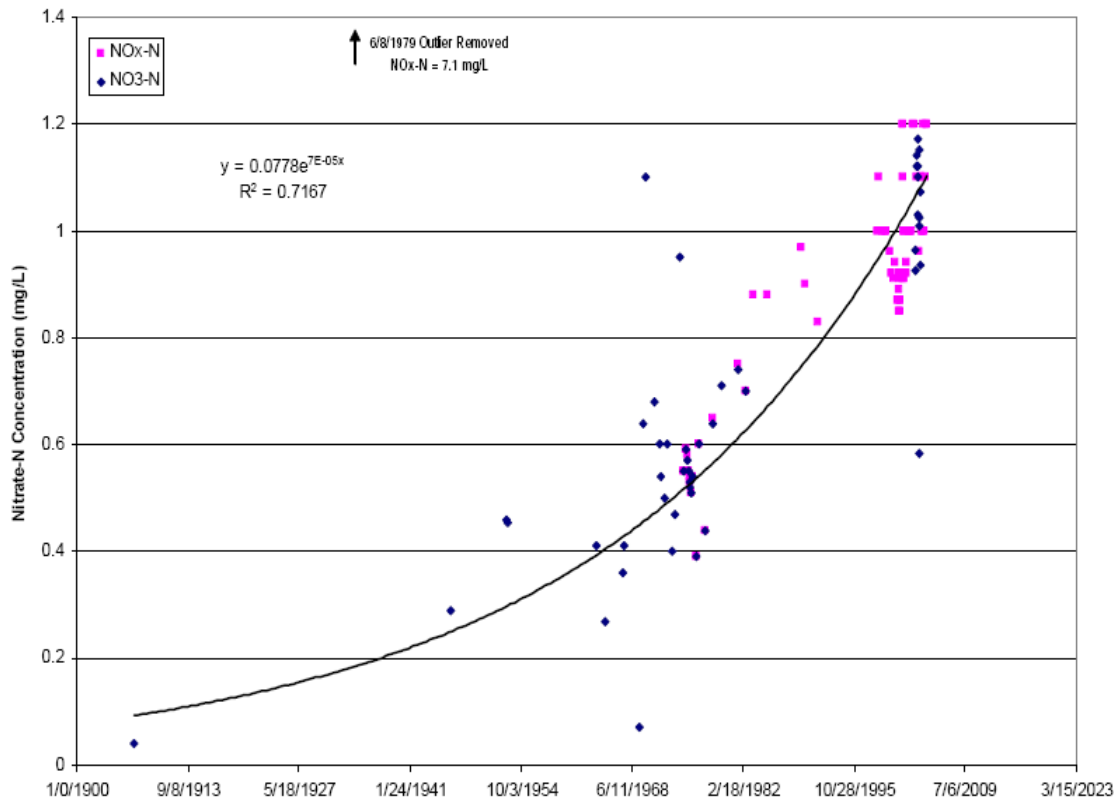
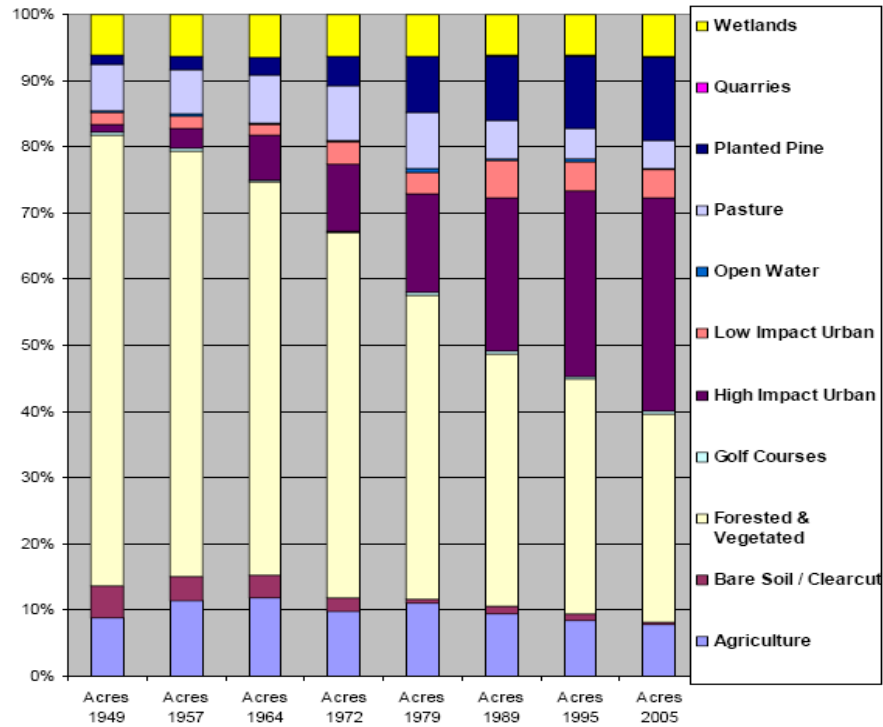


Figure 33 – Concordance between springshed development and observed $\text{NO}_3\text{-N}$ concentrations in Silver Springs (Munch et al. 2006). The strongest signal appears to be from urbanization since agricultural lands decline in importance over the period of record.

What is clear from the data is that land use is principally responsible for increases in nitrate loads. Munch *et al.* (2006) report changes in land use in the Silver Springs watershed that are coincident with observed increases in nitrate concentrations emerging from the spring (Figure 33), and Stevenson *et al.* (2004) found a strong correlation between the quality of the local buffer and nitrate concentrations.

Natural Sources

Atmospheric deposition from wet and dry fall is estimated from long-term monitoring locations (National Atmospheric Deposition Program), of which there are several in Florida. The longest term site in North Florida is Bradford Forest, where wet fall measurements have been collected since 1977; other sites are used based on proximity to the springshed in question. Interestingly, trends vary quite substantially among sites; Bradford Forest has been relatively steady or slightly upwards for both ammonia and nitrate over the last 20 years, while other stations (MACTEC 2007) have shown marked declines in nitrate, presumably in response to improved regional air quality. Spatial variability in atmospheric load is high, with urban areas exhibiting particularly high deposition rates. Wet fall measurement alone is used to represent deposition because dryfall measurement (i.e., dust) is often confounded by sample contamination (bird droppings, dead insects); standard practice is to take wet fall measurements (Figure 34) and multiply them by 2 to estimate total atmospheric load. Most studies do not make this correction, and therefore likely underestimate atmospheric load.

Another source of N in springsheds is biological N fixation (BNF), a quantity rarely estimated in the efforts to understand catchment scale N budgets. Estimates of BNF for temperate environments are 100-200 kg N/ha/yr (Vitousek *et al.* 2002, Hubbell and Kidder 2003), and are regulated in part by availability of N in soils, and the prevalence of epiphytic cyanobacterial colonization of soil surfaces, tree trunks and leaves (Vitousek *et al.* 2002). Overall, BNF appears to be ubiquitous, and, though sensitive to pH, drought, temperature and inter-species competition, of enormous importance with respect to the overall magnitude of N fluxes. In an assessment of 16 northeastern watersheds, van Breeman *et al.* (2002) compute that fixation in forest and agricultural lands represents 28% of the total N budget; for some basins, agricultural fixation ($\sim 2300\text{--}4500\text{ kg/km}^2\text{/yr}$) is larger than fertilization. These values are 5-fold the expected total atmospheric deposition ($\sim 500\text{ kg/km}^2\text{/yr}$), which in some areas is a significant albeit diffuse source (e.g., Phelps 2004, Katz *et al.* 1999). While few studies quantify BNF for Florida landscapes, Hiers *et al.* (2003) report that native legumes in the understory of longleaf pine savannas exhibit high though variable levels of BNF, as expected for fire adapted ecosystems.

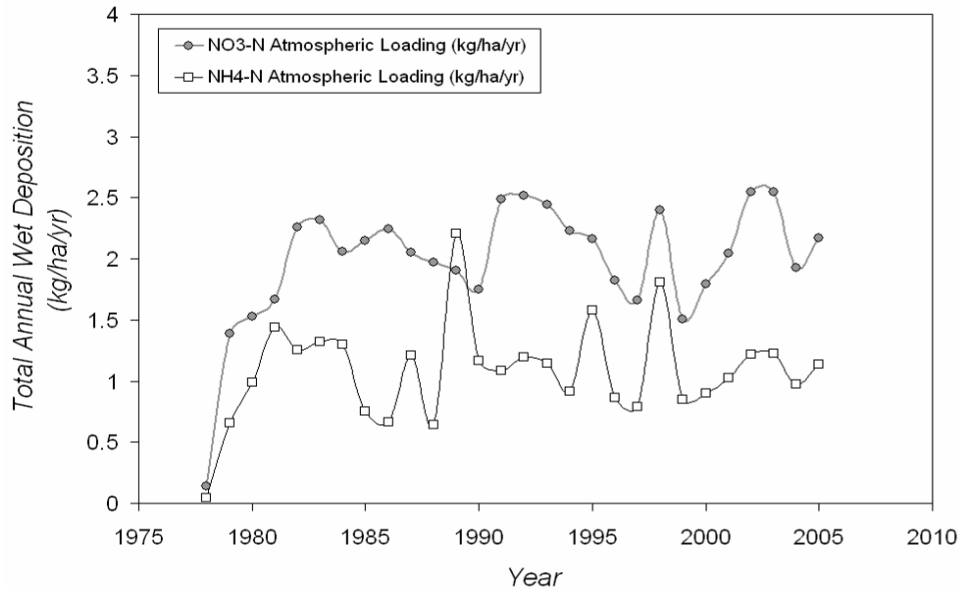


Figure 34 – Time series of annual wet deposition in $\text{kg ha}^{-1} \text{yr}^{-1}$ for ammonium (NH_4) and nitrate (NO_3) from Bradford Forest, North Central Florida between 1978 and 2005 (from National Atmospheric Deposition Program location at Bradford Forest <http://nadp.sws.uiuc.edu/sites>). For load estimation both ammonium and nitrate should be included because of nitrification.

Fixation of nitrogen is an energetically expensive process that requires either strong electrical gradients (as made possible in lightning and in the Haber-Bosch process via which humans fix nearly all the mineral N used in fertilizer) or substantial biological energy. While it is frequently noted that only certain plants are capable of fixing N from the atmosphere, in fact it is certain prokaryotes, such as microbial symbionts (e.g., genus *Rhizobium*), free-living bacteria (e.g., genera *Clostridium* and *Azotobacter*), and blue-green algae (e.g., genera *Anabaena* and *Microcystis*) that make this process possible. The reason that so few organisms can perform this process is that conditions under which it can occur are highly reducing, a setting created symbiotically in root nodules of N-fixing plants and in the cells of blue-green algae. Diazotrophs (microbes that fix N) use the enzyme nitrogenase, which is strongly sensitive to oxygen, and 8 moles of ATP (cellular energy carrier) per mole of ammonia fixed to overcome the strong triple-bonds that make atmospheric N biologically unavailable. The ammonia resulting from fixation is rapidly incorporated into certain amino acids, such as glutamine or alanine, which can be transferred to other N-containing compounds by a variety of commonly occurring amino-acid transfer reactions.

Inorganic Sources

Fertilizers are the most important anthropogenic source of nitrates on a mass loading basis (i.e., in contrast to the amount that actually reaches the UFA and the spring, which is discussed below) in nearly all N budget cases for springsheds. Assembling credible data for fertilizer inputs is relatively easy, but requires several assumptions. Authors that take the approach of using fertilizer sales for estimating fertilizer inputs to springsheds (e.g., Katz *et al.* 1999) are forced to make assumptions about loads when county boundaries (for which sales data are compiled) do not correspond with springshed boundaries. Some authors (MACTEC 2007) use recommended

fertilizer application rates (e.g., from UF/IFAS: www.edis.ifas.ufl.edu – Table 2) coupled with a detailed land use map to estimate fertilizer applied to the land. One problem with both method is that attenuation is unaccounted for; that is, as N is absorbed by plants or denitrified within the field boundary, it will limit the loading rate to the aquifer. The rate of uptake is not well known, and is expected to be quite variable as a function of soil type, crop phenology, season, etc. The standard practice in springshed nutrient budgets (e.g., Jones *et al.* 1996, Katz *et al.* 1999, Chelette *et al.* 2002, MACTEC 2007) is to assume a land use loading rate. The values, summarized in Tables 3 and 4 are derived from a) long term stormwater data or b) model output.

Land use loading is an inexact measure of loading; in Obreza (2002), N loading rates by land use in Florida are synthesized (Tables 3 and 4). Moreover, the effects of BMPs on attenuation of N pollution is weak; Currens (2002) reports an increase in the median N load after implementation in the deeper karst aquifers in Kentucky. The data in Table 4 are more specific to loading rates

Table 2. Recommended fertilizer application rates for Florida (UF-IFAS EDIS publications)

Crop/Land Cover	N Application Rates (kg N / ha / yr)	Source	Notes
Residential Lawns	80 - 240	Trenholm <i>et al.</i> 2002	
Landscape Plants	80 - 160	Trenholm <i>et al.</i> 2002	
Athletic fields	200 - 280	Miller and Cisar 2005	for bermudagrass fields est. from recommended monthly application rates
Dairy cow pastures	240 - 360	Sollenberger 2006	
Hay production	140 - 300	Staples <i>et al.</i> 2003	
Corn Silage	50 - 300	Staples <i>et al.</i> 2003	
Sorghum silage	60 - 300	Staples <i>et al.</i> 2003	
Vegetable production	180 - 200	Cockx & Simonne 2003,	
Corn	150/210	Mylavarapu <i>et al.</i> 2002	Irrigated/non-irrigated
Sugarcane	90	Mylavarapu <i>et al.</i> 2002	
Wheat	80	Mylavarapu <i>et al.</i> 2002	
Legumes (soy, peanut, alfalfa)	0	Mylavarapu <i>et al.</i> 2002	
Deciduous fruit trees	140-200/200-400	Crocker and Rose 1999	mature fruit trees/mature nut trees, respectively
Citrus	140 - 200	Morgan and Hanlon 2006	
Plantation Forests (young)	45 - 55	Jokela and Long 1999	in the first year
Plantation Forests (established)	160 - 220	Jokela and Long 1999	Applied every 6-8 years

than are the Event Mean Concentration estimates more widely used (Table 3), and they address one of the principal shortcomings of estimating applied load only (Table 2), which is that some of that applied load is harvested and only a fraction of the load reaches waterbodies (surface or subsurface). Several observations can be made regarding this synthesis. First, the ranges of applied fertilizer are enormous (e.g., see range for urban land uses) which introduces some uncertainty when a single number is used; the reality is that these rates are unverifiable on a case by case basis, so it is hard to improve accuracy. Second, N export ranges are, in many cases, unknown. Finally, and most importantly, estimated vs. observed rates of actual surface water body loading (right-most column) are in dramatic disagreement (e.g., see row crops and pine tree nurseries) and the difference between imports and exports+loss is suggestive of massive denitrification (e.g., recreational areas, corn, improved pasture). Further disagreement can be

observed between estimates of row-crop loads and observed concentrations in Table 4 and in Albert (2002), where UFA nitrate levels were up to 130 mg/L.

Both methods (fertilizer application rates and generic land use loading parameters) are questionable for high-recharge low-reactivity karst landscapes and may dramatically underestimate the loads. By way of example, Table 5 summarizes the concentrations in wells in the Silver Springs springshed (Phelps 2004), which indicate strong impacts of overlying land use on nitrate concentrations in the UFA, but at levels far higher than expected by stormwater data in

Table 3. Summary of annual land use loads and event-mean concentrations nationally and in Florida. Data are for total N load, total N concentrations and nitrate concentrations. (after Harmel *et al.* 2006)

		Land use						
	Location	Urban – Low Intensity	Urban – Med Intensity	Urban – High Intensity	Pasture	Row Crops	Citrus	Prod. Forests
Total N Loading (kg/ha)	Nationally	9	11	7.8	8.7	16.1	-	2.9
	Reference	Omeric	Omeric	Omeric	Reckhow	Reckhow	-	Reckhow
	Florida	11.6	16.6	32.1	11.2	6.9	7.2	3.75
	Reference	Harper	Harper	Harper	Harper	Harper	Harper	Korhnak
Total N Conc. (mg/L)	National	2.64	1.85	1.75	4.13	7.06	-	2.73
	Reference	multiple [†]	multiple [†]	multiple [†]	multiple [†]	multiple [†]	multiple [†]	multiple [†]
	Florida	2.29	1.8	2.83	1.97	2.28	1.71	1.31
	Reference	Harper	Harper	Harper	Harper/Graves	Harper/Graves	Harper/Graves	Korhnak
Nitrate Conc. (mg/L)	National	0.72	0.56	0.57	0.81	4.71	-	0.32
	Reference	multiple [†]	multiple [†]	multiple [†]	multiple [†]	multiple [†]	multiple [†]	Binkley
	Florida	0.28	0.68	0.19	0.80 [†]	0.80 [†]	0.80 [†]	0.08
	Reference	McConnell	McConnell	McConnell	McConnell	McConnell	McConnell	Korhnak

[†] - mixed land use.

[‡] - References include Reckhow *et al.* (1980), Tarabe *et al.* (1997), McConnell *et al.* (1999), L.V. Kohnak (unpublished data), Harper (no date), Graves *et al.* (2004), Binkley *et al.* (2004)

Table 4. Summary land use loads and harvest exports for Florida (after Obreza 2002)

Land use	N import (lbs/acre/yr unless specified)	N export (lbs/acre/yr unless specified)	Loss in Runoff/Leaching Measured Modeled (lbs/acre/yr)
Low Density Residential	0-264	0	6.4 19
High Density Residential	0-264	0	10.4 66
Commercial	0-264	0	28.7 -
Recreation Areas	87-220	0	2.4 11
Golf Courses	87-348	0	18.8 -
Improved Pasture	120-160	10-41	9.9 -
Bahiagrass Pasture	50-180	8-27	9.9 11
Unimproved Pasture	0	0	2.4 -
Native Range	0	0	2.4 -
Corn	210	0.8 per bushel	6.2 38
Sorghum	150	1.7 per cwt	6.2 38
Cotton	60	0.03 per lb	6.2 38
Wheat	80	1.2 per bushel	6.2 38
Tobacco	80	1.7 per cwt	6.2 38
Peanuts/Soybeans	0	80 per ton	7.9 38
Tomato/Pepper	200	4 per ton	7.9 38
Beans	60-100	0.1 per bushel	7.9 38
Cucumbers/Melons	150	0.026 per cwt	7.9 38
Citrus	50-240	0.13 per box	6.4 36
Peaches	80-100	2.4 per ton	6.4 36
Cattle Feedlot	125 per 1000 lb cow	unknown	- 62
Dairy	250 per 1400 lb cow	unknown	- 62
Laying Hens	1.0 per 4 lb animal	unknown	- 43
Broiler Chickens	0.9 per 2 lb animal	unknown	- 43
St. Augustine grass sod	260	unknown	- 16
Bahiagrass sod	180	unknown	- 16
Leatherleaf ferns	100-350	52-164	- 188
Vineyards	100	2.2 per ton	- 157
Pine tree nursery	200	125	7.9 157
Pine plantation†	200-250	19	4.9 -

† - This level of fertilization is typically over a 20 year rotation, not each year.

Florida (Table 4). Andrews (1994, 2000) reports concentrations downgradient from row-crops and dairies in the Suwannee Valley that regularly exceed the 10 mg/L standard applied by the USEPA for protection of drinking water; notably, despite some wells with nearly 130 mg/L NO₃-N, no evidence of phosphorus enrichment was observed. Such high levels of NO₃ contamination are emblematic of the intrinsic vulnerability of karst areas to over-fertilization. The presence of abundant dissolved oxygen and essentially no organic carbon suggest that opportunities for denitrification along the flow paths to the regional springs (Blue, Telford, Convict springs, all with dramatically elevated concentrations) are minimal.

Clearly, as nutrient budgeting matures as a science, actual observations of vadose zone fluxes within different land uses are required to constrain estimates of load. Studies of residential fertilization (e.g., Cisar *et al.* 2004) have shown strong covariance between applied loads and

resulting leachate concentrations (Morton *et al.* 1988), but with peak observed nitrate concentrations of 2.6 mg/L at nearly 250 kg/ha/yr application rates. Confounding factors in estimating loads are irrigation rate, which varies widely for urban lawns, and the quantity of soil organic matter (Park 2006). Park (2006) found only weak differences in loading between standard mineral fertilizers and slow release varieties, contrary to findings in Cisar *et al.* (2001). Similar work in row crop fields (e.g., Hubbard and Sheridan (1989) for the SE Coastal Plain) supports the elevated concentrations predicted by the modeling output in Table 4. Tree crops (peaches, citrus, pecans) have been studied for groundwater nutrient enrichment. Concentrations range from 5 to 16 mg/L downgradient of citrus farms (McNeal *et al.* 1995, Lamb *et al.* 1999, Crandall 2000), with relatively rapid declines in concentration with depth.

Table 5. Nitrate-N concentration (mg/L) in ground-water samples grouped by land use at well locations in the Silver Springs springshed (From: Phelps 2004).

Land use	N	Minimum	Maximum	Median
Urban	29	<0.02	5.9	1.15
Agriculture	13	0.05	12	1.7
Rangeland & forest	11	<0.02	2.2	0.09
Transportation and utilities	3	0.88	4.0	1.57

Organic Sources

Nitrate loads from organic sources (i.e., human and animal wastes wherein the organic and ammonia N has been nitrified) are also extremely important, and methods for estimation of loads are relatively well-developed. Most often, the assumption is that all of the load from septic tanks and wastewater sprayfields is recharged directly to the Floridan Aquifer; MACTEC (2007) and Chelette *et al.* (2002) make the assumption that 30% of the load is attenuated; verification of this level of attenuation, and comparable attenuation rates for fertilizer loads, is a research need.

Embedded in Table 4 is an estimate of the loading derived from confined animal operations, a source of significant nitrogen, BOD and other water quality concerns. Andrews (1994) reports on concentrations in the groundwater downgradient of dairy operations, and observes nitrate concentrations averaging 26 mg/L and exceeding 100 mg/L in some cases. Woodard *et al.* (2002) also observe massive enrichment downgradient of a dairy farm, with concentrations as high as 68 mg/L and averaging 18 mg/L in soil solutions; the relationship between soil solution chemistry and groundwater concentration is unknown, but in karst areas with limited denitrification and rapid porewater turnover, a strong correspondence is likely. Poultry operations (Hatzell 1995) are similarly significant sources of N (mean groundwater concentrations of 13 mg/L), and have been shown to be sources of aerosolized ammonia as well (Lopez-Zamora *et al.* 2007).

The authors of Table 4 do not report whether the confined animal operations data in Table 4 are nitrate loads or total N, but assuming the latter, most of that N will be as ammonium or organic N. That form of N is far less mobile in the environment than nitrate and thus is not observed in spring vents at concentrations of concern. However, the microbially mediated nitrification process converts ammonium to nitrate, using oxygen as the terminal electron acceptor. As such,

high loads of dairy waste can be converted to nitrate within the oxic conditions persistent within the upper Floridan Aquifer. Associated effects on dissolved oxygen will be discussed below.

Also embedded in Table 4 is an estimate of N loads from septic tanks. The typical number for a standard On Site Treatment and Disposal System (OSTDS) is that it yields 3-4 kg N per person per year; assuming that 70% (Anderson and Otis 2000) of that N reaches the groundwater, a typical household is expected to discharge 5-7 kg $\text{NO}_3\text{-N/yr}$. Modern performance-based treatment systems can reduce N loads by 75%, which, despite the costs, is widely considered essential because of the intrinsic vulnerability of the Floridan Aquifer to nitrate enrichment.

Septic tank loads to aquifers are problems ubiquitous to areas with strong surface-groundwater connectivity. Reay (2004) presents data from the coastal zone in Virginia that may provide some parallel to the Florida experience (Figure 35). In particular, that work shows that drainfield concentrations of both N and P are extremely high (3-4 orders of magnitude higher than ambient

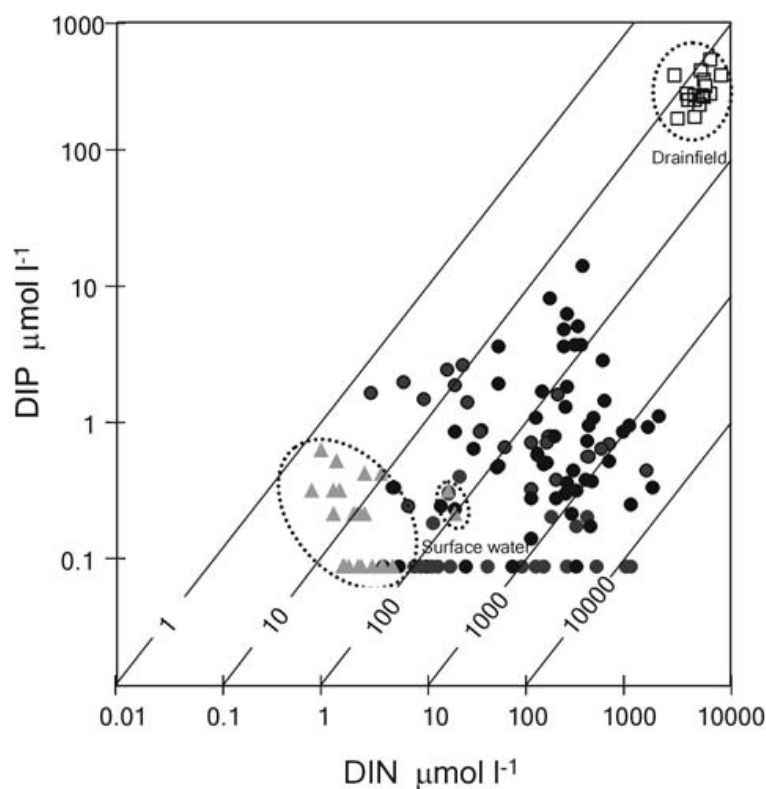


Figure 3. DIN vs. DIP concentrations for drainfield ($\square$), shoreline ground water ($\bullet$), and surface water samples ($\blacktriangle$). DIN:DIP isolines are presented as diagonals. DIP values below MDL were assigned a value of $0.08 \mu\text{mol/L}$.

Figure 35 – Relation between nutrient load to groundwater from septic tanks (after Reay 2004).

environment conditions) and that P and N attenuation rates are markedly different. Moreover, the N:P ratio of the leachate and environment are roughly the same ($\sim 10:1$). During passage from the drainfield to the sites where groundwater discharges to the surface there is typically a 2-3 log (2 to 3 orders of magnitude) decline in dissolved inorganic P (DIP), and typically much

more; the majority of samples along the flow path are within a factor of 10 of ambient concentrations (i.e., 3-log reduction). In contrast, flow path attenuation of N is smaller, as indicated by the 1-2 log reduction in concentrations of dissolved inorganic N and this results in an N:P ratio of ~50-5000:1.

Not included in Table 4 is an estimate of wastewater discharges from centralized facilities (point source exports), which have been the subject of close scrutiny in areas like Lake City and Tallahassee. Loper *et al.* (2005) reviewed the evidence for nitrate enrichment from the Tallahassee wastewater sprayfield at Wakulla Springs, and concluded that it was the most significant (as high as 70% of the total load – Chelette *et al.* 2002) and most manageable of the various springshed sources. That sprayfield discharges approximately 20 million gallons per day to the land surface in the region of the springshed known as the Woodville Karst Plain where the aquifer is unconfined. Rapid and unattenuated movement of water and nitrates into the groundwater is assumed in the sandy unconfined soils of the karst plain.

Isotope Tracing of N Sources

The identification of multiple sources of N leads to the management-relevant question of which sources are most important for meeting load reduction objectives. Whole springshed budgeting is relevant in this regard, since it allows comparison of bulk loads, but the substantial uncertainty about the fraction of load that actually reaches the aquifer has led researchers to use the ratio of stable nitrogen isotopes (^{14}N and ^{15}N) in a sample to deduce the source (Hornsby 1994, Panno *et al.* 2001). This method has a long history of being used in surface flow tracing, and has been carefully explicated, including several important caveats, in Kendall (1998). The central premise is that animals preferentially excrete the lighter isotope in urine, resulting in enrichment in organic wastes; nitrification followed by denitrification during storage (e.g., pipes, septic tanks and waste lagoons) and transport (through soil and aquifer) further fractionates organic N with resulting waste stream nitrate-enriched with ^{15}N (10-20‰). Since fertilizer has an isotopic ratio close to atmospheric (defined as 0‰), usually 3-5‰, the isotopic ratio of nitrate-enriched source water will signal the principal source: low (3-8‰) for fertilizers and high (10-15‰) for organic sources (Figure 36 – Phelps 2004).

Bacchus and Barile (2005) used isotopes to conclude that loading of N to Alexander Springs was from on-site sewage disposal; while high ^{15}N enrichment in the vegetation (~8-12‰; note that vegetation incorporation is typically a *lightening* process) is suggestive of unusual isotope loading, differences in flow between sewage (est. < 2 cfs) and the spring vent (> 100 cfs) suggest the need for further study before concluding that septic tank loads are important in Alexander Springs. This inference is further complicated by not having a reference value for the isotopic composition of the vent water. What is clear is that isotopic ratio alone (i.e., without an associated concentration signal) is not an indicator of pollution, since nitrate concentrations downstream of the main vent (after mixing with septic tank effluent in the groundwater prior to emergence at the spring) are still very low (~ 40 ppb, Mattson *et al.* 2006).

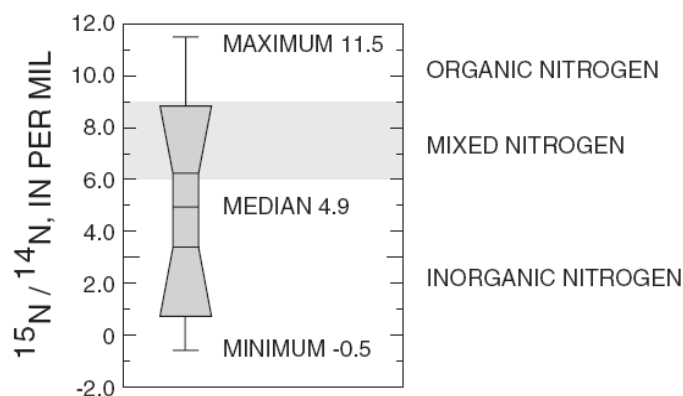


Figure 36 – Summary of N isotopic measurements for groundwater samples in Silver Springs springshed (Phelps 2004), and their interpretation. Spring samples were generally higher (4-9‰) and strongly variable in time.

This technique has been widely used for tracing N sources in springs (e.g., Toth 1999, Champion and Starks 2001), and the results suggest that, in the vast majority of cases, fertilizer sources are of principal importance (Figure 37 and Table 6). In some cases, however, wells and springs have been measured with isotopic ratios strongly indicative of organic sources: Lafayette County wells/Poe Springs – Katz *et al.* (1999), Alexander Springs – Bacchus *et al.* (2003), DeLeon Springs – Phelps *et al.* (2006).

Table 6. Comparison of $\delta^{15}\text{N}$ values measured in springs and groundwater basin

Location	N	$\delta^{15}\text{N}$ values			Nitrate sources	References
		Min	Max	Median		
Rainbow springshed	19	0.5	7.7	2.4	Inorganic fertilizers	Jones <i>et al.</i> (1996)
Wekiwa springshed	9	3.6	11.2	4.8	Inorganic fertilizers, organic sources	Toth and Fortich (2002)
Woodville Karst Plain	13	1.7	13.8	6.8	Inorganic fertilizers, organic sources	Katz <i>et al.</i> (2004)
Wakulla Springs (subset of the Woodville Plain)	3	5.3	6.1	5.8	Inorganic fertilizers	Katz <i>et al.</i> (2004)
Suwannee Basin springs	26	2.7	10.6	5.4	Inorganic, organic sources	Katz <i>et al.</i> (1999)

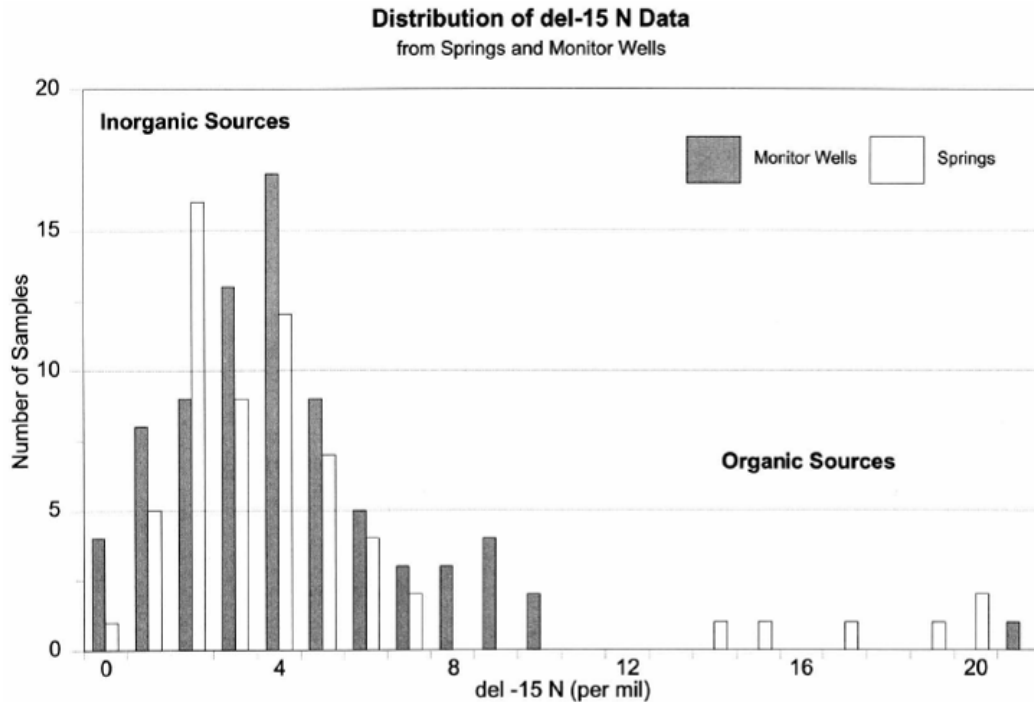


Figure 37 - Distribution of $\delta^{15}\text{N}$ values from SWFWMD spring (Champion and Starks 2001).

It is also important to note that one of the arguments posited against the importance of animal wastes as a source is the isotopic composition of the nitrate that is discharged from the springs, which is comparatively light and therefore indicative of inorganic sources. This neglects fractionation of N isotopes during nitrification of organic and ammonia N to nitrate; during this process, the heavy isotope is preferentially excluded, so the resulting nitrate is lighter. This will tend to mask the influence of organic sources unless the nitrifying bacteria oxidize all of the available Kjeldahl N.

Another confounder of isotopic inference relates to the omission of biological nitrogen fixation (BNF) among the sources. Generally speaking, the fixation of N_2 gas (defined as 0‰) from the atmosphere induces some kinetic fractionation, preferentially uptaking the lighter (^{14}N) isotope. As such, the resulting fixed nitrogen will be -3‰. If this source is regionally significant, and there are few reasons to presume that it is not, then a mixture of nitrate sources from BNF and septic tanks may resemble nitrate of a fertilizer source. Because flowpaths delivering water to the springs are underground, and because they represent mixture sites for multiple nutrient sources, our mechanistic understanding of flowpath changes in ^{15}N and subsequent mixing needs to be improved before isotopic information is used with authority. Moreover, there is a significant need to understand the temporal variability of isotopic signals; Phelps (2004) reports values from Silver Springs that vary dramatically (~3‰ vs. 8‰) between observations 6 months apart. Quantifying time-series variability and mechanisms for it are important for improving our allocation of load responsibility, and are likely to yield insights into the mechanisms for delivery (e.g., as a function of flow).

There are several unexplained discrepancies in the tracing of sources that are likely fruitful areas for further inquiry. Principal among these is the observation based on loading estimates that the

Tallahassee sprayfield is responsible for over 70% of the total anthropogenic N enrichment in Wakulla Springs, while the nitrate isotopic measurements are consistent with fertilizer sources (6.3‰ – Chelette 2002). For reasons related to the complexity of nitrogen fractionation, even in the subsurface where denitrification is presumed to be negligible, it is relevant to ensure that isotopic measurements are being interpreted correctly. Given the strong fractionation associated with nitrification and the potential influence of biological N fixation on isotopic measurements of nitrates in the water mixtures at spring vents, there is some potential that our use of this binary inference about sources is incorrect. Careful tracing of isotopic fractionation from source to vent is necessary to establish the appropriate manner in which to interpret $\delta^{15}\text{N}$ data.

Synthesis of N Springshed Budgets

Most attention in springs protection has been on N, and most of the focus has been on identifying the sources of N to the spring ecosystems. This section selects a couple of key case studies.

Figure 38 shows the loads of N to groundwater after attenuation by soil in the Wekiva springshed, the most comprehensive and recent example of a detailed springshed N budget (MACTEC 2007), wherein they conclude that a) only a small fraction (~21%) of the N applied to the land surface actually reaches the groundwater or surfacewater, and b) that despite a strong urban springshed landscape with septic systems, fertilizer use dominate the load. Though septic tanks represent nearly 25% of the total load; the isotopic ratio of the spring is relatively low (~4.8‰ – Table 6). A local aquifer vulnerability assessment has been done for this area as well, allowing more formal evaluation of links between particular locations and dynamics of water quantity and quality (Cichon *et al.* 2005).

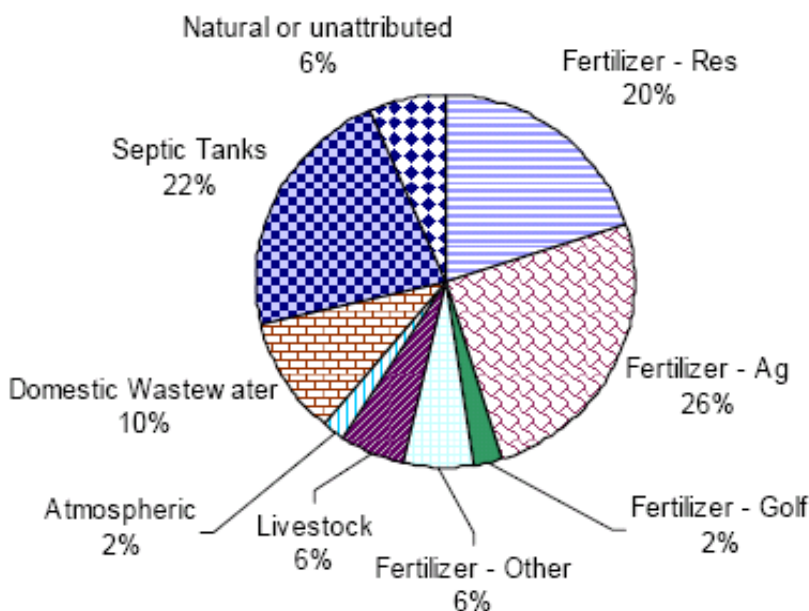


Figure 38 – Summary of N loads to groundwater for the Wekiva springshed (MACTEC 2007).

A similar study of the Rainbow Springs catchment yielded a similar conclusion about the principal source of N. Fertilizer, principally from improved pastures, was estimated to contribute almost 50% of the total load (Table 7 and Figure 39); horse farms and confined cattle operations

were responsible for an additional 30% of the load. Overall, atmospheric deposition was also important as a source (over 15% of the total load) while septic tanks and sewage discharges were considered negligible. This is somewhat consistent with the very low isotopic ratio (2.4‰).

Table 7. Total N loadings (tons/yr) into groundwater in Rainbow springshed (Jones *et al.* 1996)

Source	Regions			% of total loads
	Eastern	Central	Western	
Atmospheric	431	504	467	16.8
Septic tanks	22	17	24	0.7
Turf Fertilization	50	11	18	0.9
Golf courses	84	0	35	1.4
Sewage	13	3	1	0.2
Septage spreading	58	0	24	1.0
Row crops	0	0	44	0.5
Cattle production	410	439	407	14.7
Horse farms	991	510	< 1	17.5
Improve pasture	1,728	1,364	871	46.3

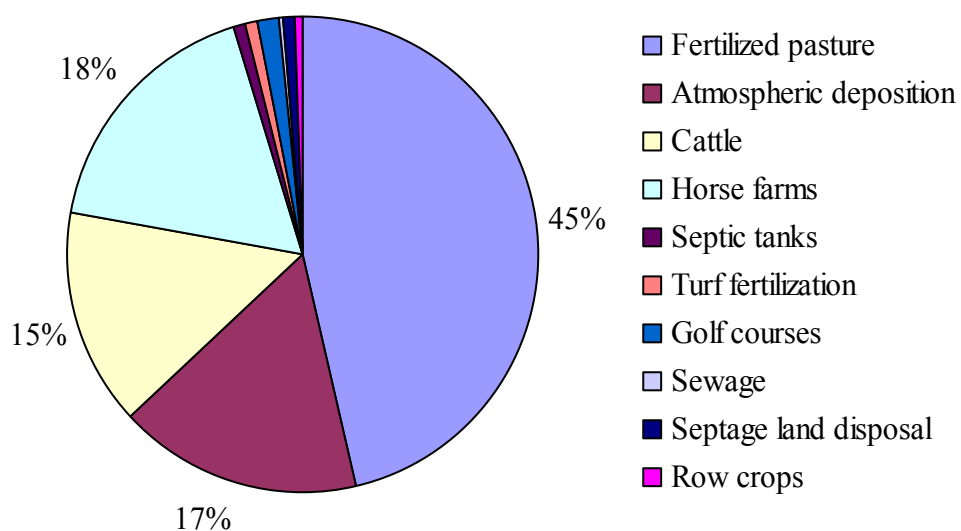
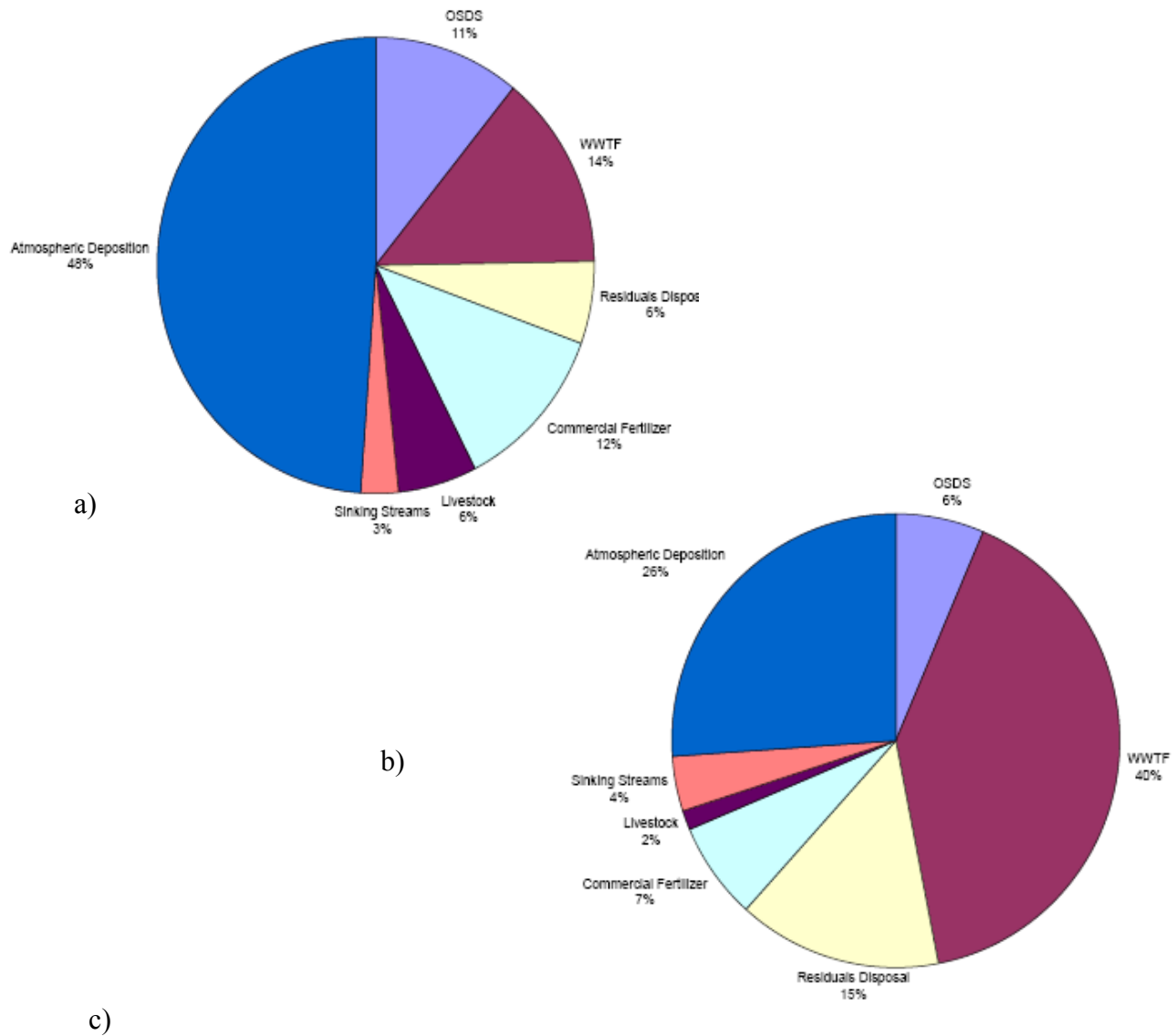


Figure 39 – Relative contribution of N loads different sources to the groundwater discharging from the Rainbow Springs (after Jones *et al.* 1996).



Source	Predominant form	Semi-confined (kg-N/yr)	Unconfined (kg-N/yr)	Total (kg-N/yr)
Atmospheric Deposition	IN	619,000	675,000	1,294,000
WWTF Effluent	IN	8,000	363,000	371,000
WWTF Residuals	indeterminate	0	154,000	154,000
OSDS*	IN	172,000	111,000	283,000
Commercial Fertilizer	IN	211,000	104,000	315,000
Livestock*	ON	124,000	33,000	157,000
Sinking Streams*	ON	0	72,000	72,000
Total		1,134,000	1,512,000	2,646,000

*1999 values.

Figure 40 – Estimates of a) surface loads to Wakulla Springs, b) annual delivery based on coarse hydrologic modeling, and c) actual loads by region. The 350 cfs of water at the vent (ca. 0.9 mg N/L) represents a flux of 273,000 kg, an attenuation of nearly 90% (Chelette *et al.* 2002).

Another effort in the Wakulla springshed (Chelette *et al.* 2002) where the Tallahassee sprayfield facility is in the unconfined region and demonstrably connected to the spring, suggests that the

spray field is uncharacteristically important (40%) as a source of N (Figure 40b). This estimated importance arises only after the transport and delivery is considered; when only direct loading is considered, atmospheric deposition dominates the load, and human wastes are but 25% of the load. It is also notable from this study that the consequences of loading on the confined region are a function of geologic regime, with nearly all the effluent loads occurring in the unconfined region, despite most of the fertilizer application occurring in the less vulnerable confined and semi-confined regions; part of this may be explained by sinkhole-conduit systems that link large regional loads (e.g., Tallahassee's sprayfield) to the spring. The observation that the nearly 1.15 million kg N/yr surface loading yields an observed load of only 73,000 kg/yr (Chelette *et al.* 2002) suggests the large attenuation potential of those parts of the state where surface water and high-carbon soils and sediments co-exist.

Foster (2008) concludes that atmospheric deposition is a large portion of the load in Ichetucknee (Figure 41); the fate of atmospheric N is unknown, and omission of biological N fixation further adds to the uncertainty. Moreover, because of how land use loading is computed, atmospheric deposition is very likely double counted.

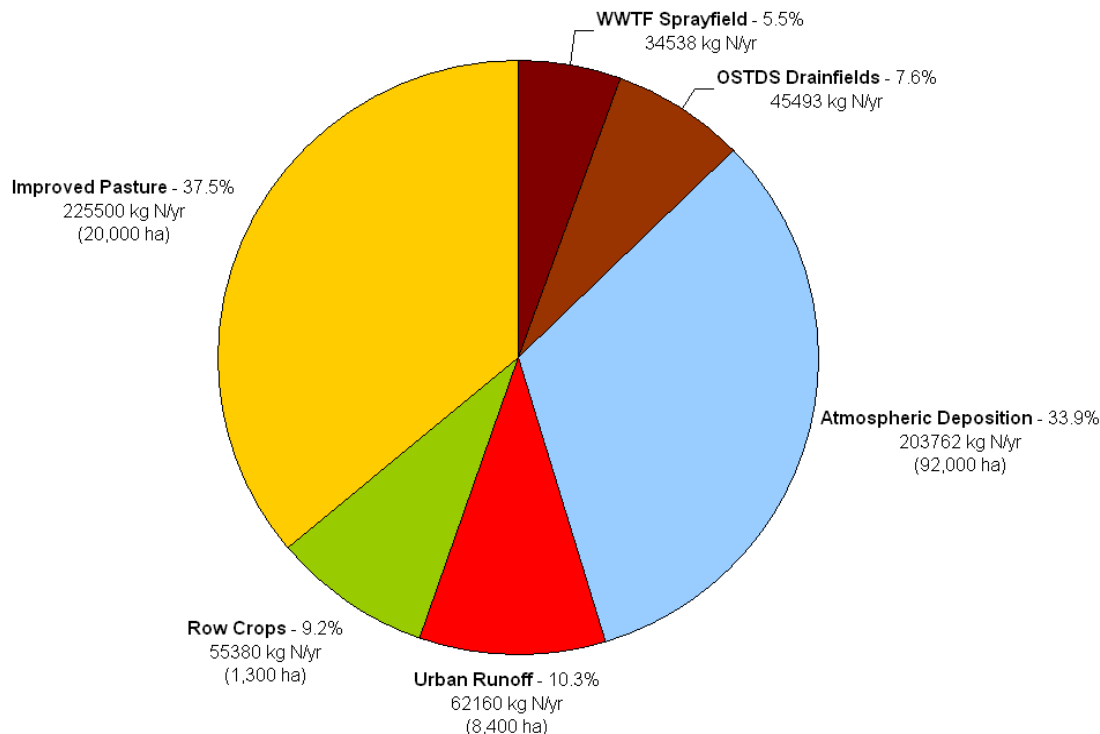


Figure 41 – Synthesis of sources for the Ichetucknee Springshed (Foster 2008).

Phosphorus

Comparatively little is known about the magnitude of P sources in springsheds. While there have been numerous studies of P loading from biosolid application (Graetz and Nair 1995), septic tanks (Reay 2004), wastewater sprayfields (Loper *et al.* 2005), and fertilizers, there is essentially no consolidated information on the relative magnitude of these sources in the fluxes observed at springs. Part of that is almost certainly because no significant changes in P loading have been observed (e.g., Figure 28, which shows springs with marked N enrichment exhibiting

P concentrations unchanged from inferred background levels). Moreover, most of the work on P loading in Florida has focused on areas where sandy soils and perched aquifers dominate (e.g., spodosols – Graetz and Nair 1995), and not where the carbonate sink is large and proximate to the load.

Loper *et al.* (2005) argue that this attention on N is warranted by two observations: 1) P loading is not increasing in any systematic way, so using it to explain recent ecological changes in springs is problematic, and 2) geology is the principal regulator of P loading, so loading is not management sensitive. Stevenson *et al.* (2007) echo this observation, suggesting that while modest correlations between algal abundance and P were observed, the ability to regulate P in springs was limited, warranting attention to N alone as a management objective.

In contrast, however, Sigua and Tweedale (2003) report large groundwater P loads to the Indian River Lagoon. Indeed, the N:P ratio in measured groundwater discharges was just over 3.4:1 (84,900 kg N vs. 24,300 kg P), suggesting high P mobility; this area is sandy and wet, so the generality of these results to springs more broadly may be confounded by characteristics of the flowpath. This finding is particularly surprising because surface water inputs are strongly dominated by N (i.e., N:P ~ 30:1 for atmospheric sources, and 8:1 for both point and non-point surface water discharges). Concordance between submarine groundwater discharge flowpaths and the karstic flowpaths to freshwater springs is unknown.

On the latter point regarding the geological controls on P there are two factors to consider, one pertaining to load generation and the other to load attenuation. Geologic loads of P are expected to be high (though variable) in this landscape because of the presence of the Miocene Hawthorn formation, previously described. Among the many important features of this interbedded clay/sand layer is the abundance of apatite minerals (CaPO_4) that are the basis of Florida's phosphate mining industry. Apatite is a highly weatherable material, and water percolating through, or more importantly running over the Hawthorn is expected to dissolve significant quantities of P. If this weathering/erosion process occurs proximate to the spring, it is quite likely that concentrations of P at the spring vent will be elevated. Indeed, Ichetucknee State Park contains a site historically used for mining phosphate, illustrating the potential significance of proximate P sources. No systematic effort to understand the links between geologic setting and P concentrations has been undertaken, but it is clear that substantial and unexplained variability in P concentrations exists. Among the hypotheses that might be tested are that P levels are high in springs with flowpaths that are sufficiently shallow to interact with the Hawthorn, or in close enough proximity to the Cody Escarpment where surface water weathering processes and subsequent sinkhole capture lead to P enrichment. Given weak but significant evidence of links between P concentrations and the dominance of *Vaucheria* spp. (one of the principal filamentous algal species of concern) (Stevenson *et al.* 2007), additional attention to P as a driver of springs ecology is warranted. As such, efforts to understand the degree to which P in springs is a management sensitive parameter are also relevant.

Carbon (BOD)

The role of organic carbon in spring systems is negligible in all measurements except those made during extreme events when either a) stormflows dominate via conduits and/or surface runoff,

bearing DOC, or b) tannin-stained water from downstream rivers creates a backwater event, also during extreme floods. The delivery of dissolved inorganic carbon, a necessary condition for driving high levels of submerged aquatic production, is clearly sufficient. Calcite saturation indices and alkalinity, both of which measure the degree of cation (Ca, Mg) saturation, but also reflect the carbonate concentrations in the water, support the inference that rock-water interactions in the aquifer maintain high levels of DIC. Katz *et al.* (2004) reports bicarbonate concentrations averaging nearly 200 mg/L for large springs, and others (Katz *et al.* 2001) report similar levels for smaller springs.

Despite the relative paucity of organic C in the spring vents, there are well-known sources of organic C in the springshed. Natural sources (DOC from wetlands and shallow-water table soils in the confined reaches) and anthropogenic sources (e.g., septic tanks, animal waste lagoons, waste water sprayfields) exist; given the potential BOD and NOD load from anthropogenic sources, it is notable that there is an inverse correlation between dissolved oxygen and $\delta^{15}\text{N}$ (a tracer of organic N) among the springs at Ichetucknee (Katz *et al.* 2004). For example, given a cBOD+NBOD load of 200 mg/L in septic tank leachate, and a flow rate of 400 L per day, one septic tank can deoxygenate over 6 million liters of aquifer water per year (assuming nominal DO of 5 mg/L) if the drainfield is in the groundwater. Modern systems (drainfields and sprayfields) allow greater oxygenation of the water, so calculations above are likely to be reasonable primarily for older or illegal septic system. The Ichetucknee springshed has over 2,000 septic tanks (Foster 2008), while nearly 30,000 exist in the springshed of the Wakulla (Chelette *et al.* 2002), and 65,000 in the springshed and surface water basin of the Wekiva (MACTEC 2007). By extrapolation, the potential DO impacts of septic tanks alone are high; understanding the role of DO in springs, and then how DO management might be improved, appear to be avenues for important research, all despite the relative unimportance of BOD at the spring boil.

Other Water Quality Parameters

Mechanisms for the variability in the delivery of salts are unknown. There appears to be both a hydroclimatic and geological basis (Phelps 2004, Scott *et al.* 2004, Toth and Katz 2006). For example, strong inverse correlation between conductivity and flow was observed at Wakulla Springs (Loper *et al.* 2005), suggesting spring vent water is a mixture of low conductivity water varying in discharge over short time scales, and high conductivity water delivered more evenly. Extrapolating that relationship suggests that, during periods of drought, conductivity levels rise. It is currently unknown what the implications of age-salinity relationships might have on springs, but episodic disturbance has been widely implicated in ecological transitions in lakes (Scheffer *et al.* 2001). The mechanisms for the role of salinity, for example, as a stressor of SAV or excluder of grazer populations that regulate filamentous algal population, is currently unknown and may require substantial research to clarify.

Similar uncertainty exists about mechanisms and importance of delivery of industrial contaminants (e.g., DEET). While it is clear that the source is human waste waters, the time domain for delivery, the hydrogeochemical controls on transport, and the ecological consequences are not so clear. Given the low concentrations generally observed (e.g., Phelps 2004), this is an area worthy of additional monitoring for temporal trends, but probably not yet

for detailed accounting of sources. Analysis of ecological impacts, on the other hand, is extremely important because of evidence of ecotoxicological consequences of even relatively low concentrations.

SINKS AND TRANSFORMATIONS OF NUTRIENTS

Typical nutrient sinks in watershed budgets include assimilation by biota (including harvest and export for crops, wood and animals), dissimilatory biotic removal (denitrification, sulfate reduction), and both physical and chemical abiotic sinks (e.g., sedimentation and sorption of P). Van Breeman *et al.* (2002) consider the main pathways for loss of N (plant uptake, crop removal, denitrification, riverine export) and conclude that denitrification represents 50% of estimated losses, and exports (food, wood and riverine) account for 31%; the remainder is estimated to be changes in storage (soil, biomass).

Nitrogen removal is characterized by particular “hot spots” and “hot moments” (*sensu* McClain *et al.* 2002; hot moments might be periods during which rivers flood and thus interact with organic rich riparian sediments) in the landscape. Wetlands in particular are well-known sites for both uptake/soil accretion and denitrification. Table 8 summarizes the rates of N removal in wetlands and riparian areas in the Southeast. Figure 42 summarizes the same N cycle processes illustrating both the enormous potential for removal and the significant heterogeneity in process rates.

Table 8. Nitrogen removal mechanisms in floodplain and wetland riparian forests in the southern United States (after Walbridge and Lockaby 1994)

Mechanism	Location	Rate (kg N / ha / yr)
Deposition	Maryland	11.0
	Louisiana	350.1
Denitrification (potential)	Little River, Georgia	31.5
	Coastal Plain, Georgia	224.0
Denitrification (mass balance observations)	Tar River, NC	130.0
	Maryland	47.7
	Coastal Plain, Georgia	1.5
NH ₄ ⁺ adsorption	Tar River, NC	64.2
	Maryland	0.8
Microbial Immobilization	Tar River, NC	16.2
	Coastal Plain, Georgia	87.0
Plant Uptake	Tar River, NC	15.5
	Little River, Georgia	51.8
	Maryland	15.0

Denitrification, the most important long-term sink for N, is principally constrained by the availability of carbon (denitrifying bacteria are heterotrophic) and the absence of oxygen (when O₂ is present it provides a thermodynamically favorable electron acceptor); the process may also be nitrate limited (in low concentration settings), but is rarely constrained by the presence of the microorganisms. Indeed, Andrews (2000) observed that, while all other conditions for denitrification were unfavorable, counts of denitrifying bacteria were frequently greater than 10,000 per 100 mL.

Reference	Rates		Conditions
	g N m ⁻² day ⁻¹	g N m ⁻² yr ⁻¹	
Wetlands			
Dieberg and Brezonik (1985)		28	Nutrient-enriched swamp (FL)
Koerselman et al. (1989)		6	Discharge fen, Netherlands
		20	Recharge fen, Netherlands
Johnston (1991)		0.002–0.34 (av. = 0.19)	Low-nutrient natural wetlands
		16–134 (av. = 60)	Nutrient-enriched wetland
Jørgensen (1994)		20–92	Wetlands, Denmark
Phipps and Crumpton (1994)		171	River-fed constructed wetlands (IL)
Kadlec and Knight (1996)		280	Treatment wetland, theoretical rate
Kadlec and Knight (1996)		801	Treatment wetland, based on I/O analyses
Comín et al. (1997)	0–3.46		Agricultural runoff, <i>Phragmites</i> marshes in Spain
Spieles and Mitsch (2000)		62–66 ¹	River-fed constructed wetlands (OH)
Lane et al. (1999)		10	Mississippi River diversion at Caernarvon (LA)
Riparian systems			
Peterjohn and Correll (1984)		4.5–6.0	Riparian forest, Chesapeake Bay (MD)
Groffman et al. (1991)	0.22		NO ₃ + glucose, buffer zones
	1.58		NO ₃ + glucose, grass strips
Hanson et al. (1994)		0.5–1.6	Riparian maple swamp (unenriched)
		2.0–3.6	Riparian maple swamp (enriched)
Lowrance et al. (1985)		6.9	Restored riparian wetland
		4.3	Young hardwood riparian forest
Groffman and Hanson (1997)	0.87–1.3 ²		Moderately well-drained soil
	2.6–24.4 ²		Very poorly drained soils
Groffman and Hanson (1997)		1.5–15.5 ²	Alluvial soil
		1.0–2.0 ²	Light till

Notes: Studies listed here do not generally include wetlands exposed to wastewater, except for Kadlec and Knight (1996); av., average.

Figure 42 – Summary of measured N loss rates from selected wetland and riparian zone studies (from Mitsch et al. 2001). To convert $\text{g N/m}^2/\text{yr}$ to kg N/ha/yr , multiply values in this table by 10.

Nutrient Sinks in Karst Landscapes

Nitrogen

As with non-karst regions, the two significant long-term sinks for N are in the stored organic matter and denitrification to the atmosphere. The former is expected to be finite, with mineralization eventually roughly balancing uptake (agricultural harvest being one exception). The latter is rate limited by the availability of sites in the landscape with the combination of anoxia and labile organic matter to drive heterotrophic microbial metabolism.

Evidence for denitrification once nitrate is in the groundwater is absent. Several lines of evidence appear to confirm that nitrates are effectively conservative once in the UFA. First, as reported in Katz *et al.* (2004) and Phelps (2004), the partial pressure of N_2 gas in the water that emerges from the spring vents is consistent with expected equilibrium at recharge (Figure 43). Denitrification would be expected to increase N_2 concentrations; this condition was observed at only one of 14 locations in Suwannee and Lafayette counties (Katz and Bohlke 2000). Second, the Rayleigh distillation model for isotopic kinetics (Kendall 1998) in a closed system predicts that processes in which fractionation occurs (i.e., preferential use of ^{14}N vs. ^{15}N during denitrification) would tend to increase the “heaviness” of the remaining nitrogen (Einsiedl and Meyer 2006). As such, with denitrification, we would expect to see $\delta^{15}N$ of the groundwater steadily increasing with age. While there is no study of that particular relationship, the large fractionation due to denitrification ($\sim 30\text{‰}$ – Kendall 1998) and generally low values of $\delta^{15}N$ in spring discharge indicates that this process is small in magnitude if it occurs at all. Finally, the UFA is characterized by oxic conditions (Barrios and DeFosset 2006) and low levels of DOC (Katz *et al.* 2001, Phelps 2004) which suggests an environment unconducive to denitrification.

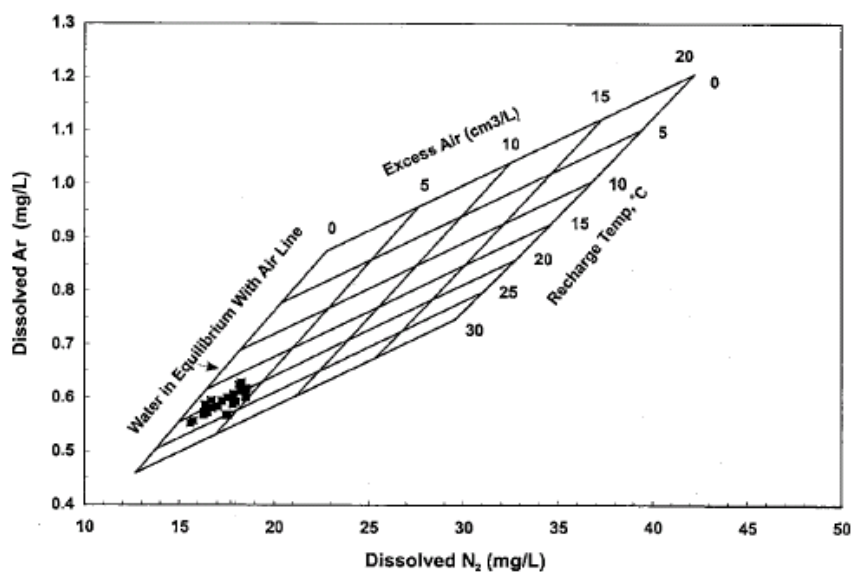


Figure 43 – Chart comparing concentration of N_2 and Ar gas dissolved in spring water (Katz *et al.* 2004). The fact that observations cluster near the air equilibrium line and at a position that indicates a 20-25 degree C recharge temperature suggests the absence of denitrification.

Given that N is likely to be nearly conservative in the subsurface, efforts to attenuate loads prior to transport through the soil to the aquifer are critical. Clearly, land use planning figures prominently in reducing loads (see sections above). Best management practices can also, in some cases, provide attenuation, but the degree of efficacy is likely to be a function of the extent to which water remains at or near the surface where BMPs can operate. In areas with rapid recharge (i.e., karst plains), opportunities to store and treat stormwater are limited. Some of the conventional treatments for managing diffuse loads of nitrogen (denitrification walls, lagoons,

treatment wetlands) are limited by hydrogeologic constraints on surface water storage and residence times; as such, managing/reducing sources is likely to be far more effective than managing/enhancing sinks. Some nitrate removal in the riparian/hyporheic zone after spring emergence is likely (Mattson *et al.* 2006) and sensitive to land use practices (Hearne and Howard-Williams 1988), but also largely unquantified, and generally irrelevant for protecting headwater areas.

Phosphorus

P sinks in carbonate landscapes are overwhelmingly dominated by mineral adsorption. While in other parts of Florida, movement of P through the sandy aquifer is rapid and largely unattenuated (Campbell *et al.* 1995), in the karst regions where carbonate sorption occurs, P breakthrough has not occurred. The magnitude of the carbonate sink is unknown. It is plausible, given strongly preferential flowpaths in the subsurface, that saturation of P sorption capacity can occur within management-relevant time spans (Wang *et al.* 1995). The implications for this saturation are potentially profound given a) the relatively stronger association of ecological change with P rather than N, and b) the time domain of water quality recovery after breakthrough (Mansell *et al.* 1995, Wang *et al.* 1995), even with complete reduction in loading. As such, this should be an area of active research, with the primary objective to determine the degree of sorption saturation along principal flowpaths, and the timing and implications of future breakthrough.

In a carbonate aquifer system in the Florida Keys, Dillon *et al.* (2003) used radio-labeled $^{32}\text{PO}_4$ to demonstrate rapid adsorption onto the Key Largo limestone. That research established an equilibrium phosphate concentration in solution after extended interaction with phosphate-rich water of $\sim 26 \mu\text{M}$, which is markedly higher than concentrations observed in springs. Desorption isotherms, during which the sample that had been exposed to high levels was exposed to phosphate-free water, showed convergence to the same concentration, suggesting that this is the equilibrium P concentration of that limestone substrate. While inference from this distant experiment is perilous, it does suggest that the capacity for limestone to sorb P is extremely large. The kinetics of this uptake is not well-known and is a key factor in understanding the functional capacity of the matrix to sorb P loaded from the landscape.

In a study of P loading in calcareous soils in South Florida, Jaber *et al.* (2006) report extremely low P levels (0.04 mg/L) in groundwater beneath lands to which organic amendments were added. These concentrations support the contention that P sorption is large; further results in that work underscore the differences observed with sandy soil where P concentrations were nearly two orders of magnitude higher under the same treatment. Reed *et al.* (2006) study on P movement in calcareous soils in South Florida suggests remarkably little transport despite high application rates.

Under reducing conditions, the mobility of P can be changed dramatically. Kroeger *et al.* (2007) observed high levels of phosphate in submarine groundwater discharge in the Tampa Bay area draining regions of high population density and under reducing conditions; the results of that study, however, are not applicable to most of the Floridan Aquifer where N is transported as nitrate and oxic conditions prevail.

Carbon

There is no sink in the subsurface for inorganic carbon except abiotic gas exchange. Since gas exchange is expected to be strongly limited in the Floridan Aquifer, most aquifer water is saturated to super-saturated with respect to CO₂, a condition that leads to considerable degassing of CO₂ at spring vents. One of the consequences of this is proximate declines in pH, and the super-saturation of groundwater with respect to calcite in spring river water (with important implications for karst channel development).

Aquifer flowpath attenuation of organic carbon is nearly complete, based on typical low DOC conditions observed in springs. While episodic pulses of DOC rich water stains the vent flow at Wakulla Springs, among others, DOC levels in spring vents are ~ 2 mg/L or less. Numerous pathways for organic carbon attenuation exist. Most prominent is bacterial respiration, a process made possible by high levels of dissolved oxygen in much of the Upper Floridan Aquifer and high bacterial counts throughout the aquifer porosity (see Simon 2000 for karst aquifers generally). Other possible sinks include abiotic processing (carbonate adsorption – Zimmerman *et al.* 2006), though the relative importance of this pathways is, as yet, poorly quantified; areas where surface water interacts most with groundwater are dominated by microbial processes, while areas with relatively lower levels of connectivity exhibit DOC breakdown products indicative of abiotic attenuation pathways. The relative importance of the different pathways is relevant to the karstification of the carbonate matrix.

Other Water Quality Parameters

Much of the literature on other water quality parameters focuses on the presence of emerging contaminants (e.g., DEET). Surprisingly little is published about sinks for DO, despite the obvious merits of understanding behavior in the subsurface. What can be inferred from existing data is that natural attenuation is small (high DO is observed over large areas of the UFA – e.g., Katz and Bohlke 2000), but the effects of anthropogenic oxygen-consuming wastes at the springshed-scale are unknown.

Work on Florida's karst suggests that some of the emerging contaminants may be attenuated via biotic mineralization and/or biotic sorption as a function of time spent in the subsurface (Phelps 2004) while others (e.g., DEET) appear more conservative. Overall, however, there is limited information on the extent of attenuation, nor on the factors that might lead to variability in attenuation rates.

Springshed nutrient budget – Synthesis of Sinks

Numerous springshed nitrogen budgets exist and, despite subtle differences in assumptions and data quality, offer an opportunity to synthesize conditions. The best exemplars of nitrogen budgeting work (Boyer 2002, Van Breeman *et al.* 2002) are for surface drainage basins in the northeast; in those efforts the sources (previously presented) and sinks are quantified with the metric of success being the degree to which the N budget can be closed. Figure 44 shows estimates of the mean importance of the key sink/transformation pathways across 16 watersheds, and illustrates a level of detail not matched in Florida's springshed examples. It is important to

note that Boyer *et al.*'s study sites are all surface water systems, and springs are subsurface basins; intrinsic differences in processing capacity and delivery rates may limit the general utility of the observed N partitioning. Moreover, in no cases that were reviewed for this document were exports in food or changes in storage considered explicitly; the principal reason for this is that the objective of the springshed examples is to identify key inputs for management, not close the N budget. However, future efforts to more explicitly account for N sources and sinks would aid in understanding some of the curious results obtained, particularly with regard to the degree to which N loads are attenuated in springsheds despite substantial agreement that N sinks are largely absent.

Most of the sinks are of variable interest. While it is likely important to close the N budget to know the magnitude of food exports and changes in storage, these may be less important when allocation of load reduction responsibility is the principal objective.

One striking thing about the N fate pie-chart (Figure 44) for surface water systems is the magnitude of riverine export. On average, rivers transport 20% of the N deposited on land to the sea; the range is from ~12% to more than 35%. Given the arguments that most Florida springshed budgets neglect the important contribution of biological N fixation, and, more importantly, that a karst landscape is intrinsically vulnerable to N transport, the expectation would be that springsheds deliver more N (i.e., >> 20%) than other watersheds where denitrification and storage potentials are higher.

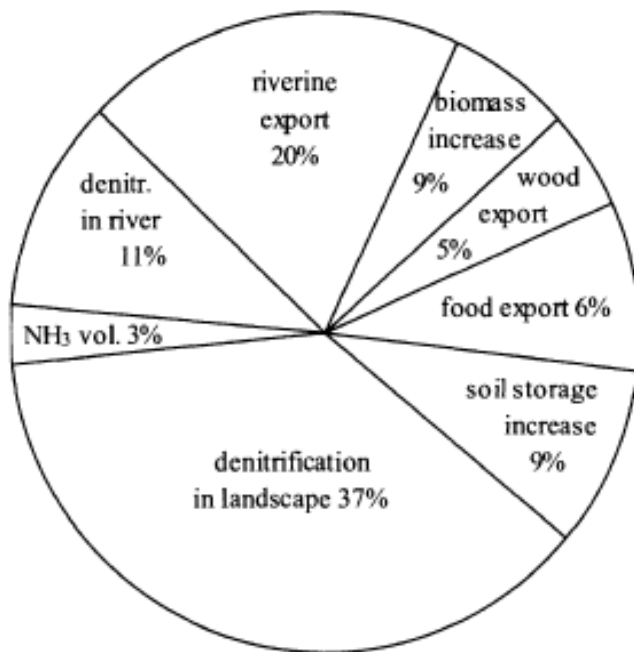


Figure 44 – Summary of the nominal fractional importance of various N outputs and sinks for 16 watersheds in the northeastern US (van Breeman *et al.* 2002).

A synthesis of 5 springshed loading budgets in Florida reveals the opposite result (Figure 45). For 4 of 5 springsheds (Ichetucknee is the exception), the spring discharges 10% or less of the total estimated load. In the Wekiva basin the load is 1,800 tons N/yr and spring discharge 230 tons N/yr. This result is after estimating the load attenuation between surface and groundwaters, estimated to be 7,600 tons N/yr (MACTEC 2007). In the Silver Springs system, the landscape attenuation is nearly 95% of the estimated load (Phelps 2004). Jones and Upchurch (1994) quantified the N load to the Kings Bay system, and observe large attenuation (2757 tons/yr load vs. 335 tons/yr spring flux); they suggest, based on a survey of wells, that proximate sources dominate the loading. They also posit that most of the N in that spring is of organic origin (e.g., wastewater sources) despite low $\delta^{15}\text{N}$ levels.

There are several plausible explanations for the observed attenuation in springsheds. First is that intrinsic time lags (Katz *et al.* 2001, Toth and Katz 2006) make comparison of contemporary spring fluxes with contemporary loadings problematic. That is, if water recharge occurred ca. 20 years before present, the nitrate concentrations in the spring vent are not representative of observed landscape loads. Water that has residence times longer than 50 years (expected to be as much as 70% of the flow – Toth and Katz 2006) would be expected to have concentrations near background, confounding budgeting efforts. While this is certainly possible, it is likely, as previously discussed, that most of the N is delivered via flowpaths with short residence times.

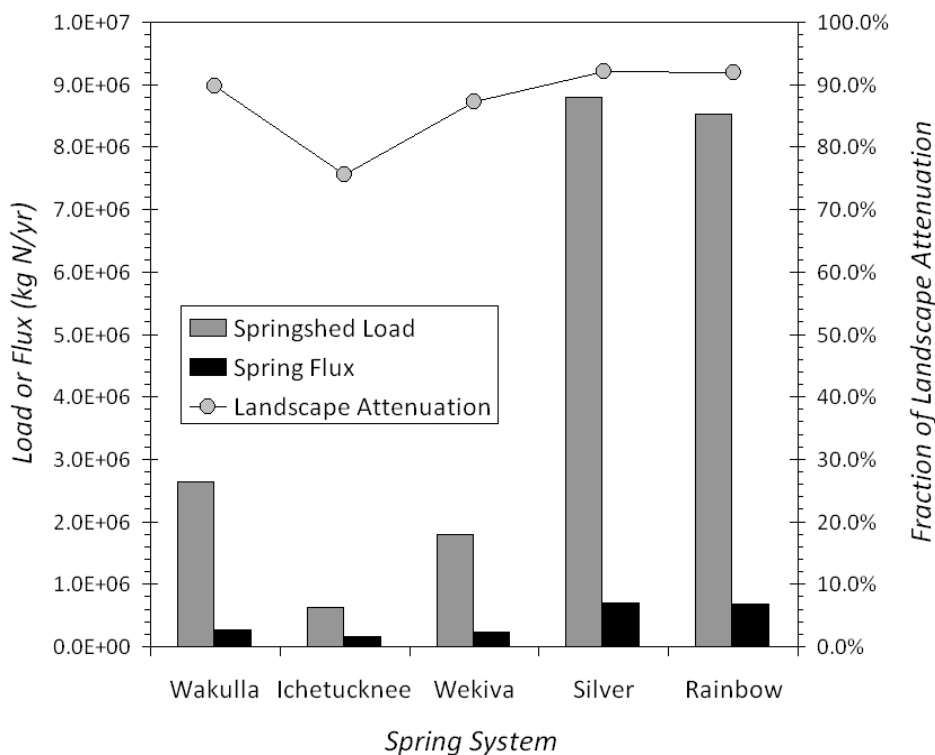


Figure 45 - Estimated N attenuation from budgeting work computed by comparing estimated landscape load to fluxes out of springs. (Chelette *et al.* 2002, Foster 2008, MACTEC 2007, Phelps 2004, Jones *et al.* 1996). Note: values reported for Wekiva are after estimated adjustment for load attenuation between the surface and subsurface; levels of total estimated attenuation are thus far higher.

In a similar argument, it is also plausible that the effective springshed is markedly smaller than the delineated boundary. Phelps (2004) provides 10-yr and 500-yr capture zones, both of which are substantially smaller than the delineated springshed; as such, the area over which active N loading occurs is likely small, and estimates of total springshed load are too high. Moreover, much of the delineated springshed for systems like Ichetucknee is within the confined region, and much of the water drains via surface flowpaths to other catchments. Developing nutrient and water budgets for effective springsheds is likely to yield a far clearer picture of source importance and help realistically target load reduction strategies.

It is further plausible that the subsurface conduit structure delivers only a portion of the water to the spring vent; Toth and Fortich (2002) speculate that this is occurring in the Wekiva system, with the remaining water (and nitrogen) delivered directly to the St. Johns River via subaqueous or diffuse discharge.

Finally, it is important to consider if the observed attenuation is the result of biological processes. While it would be surprising to observe accelerated denitrification in the karst regions, denitrification in the confined and semi-confined regions is clearly very rapid (Cohen *et al.* 2007). The general finding that most of the N loading occurs in the unconfined region and that denitrification in the subsurface is negligible suggest, however, that these levels of attenuation are confounded.

Regardless of the mechanism for the observed attenuation, it is clear that understanding why it occurs is relevant for management. If it is due to time lags, then forecasting changes in N loading due to contemporary management need to incorporate these lags. If it is due to differences between effective and delineated springshed size, then improving our understanding of N processes within the effective catchment are important. If it is due to flow by-pass, then larger scale N budgets (e.g., for the St. Johns) need to account for the displaced load. It is also worth pointing out that regardless of the water quality parameter of choice, understanding the springshed and flowpaths is a crucial baseline. Further work refining these concepts should remain a priority.

UNKNOWN AND RESEARCH PRIORITIES

The preceding synthesis of nutrient loading, and, perhaps more importantly, how load is affected by hydrogeologic processes, identifies several key research gaps that need to be addressed in the coming years. I have broken these by theme and offer a brief rationale for each.

Hydrologic and Geochemical

1. *Characterizing temporal dynamics of water age estimates.* It is clear from the literature on this topic (Katz *et al.* 2001, Toth and Katz 2006 to cite but a few examples) that there remain large uncertainties about the age mixture of water discharging from spring vents. Given the discordance between observed dye tracer residence times and nominal ages, a research program to better understand water age over time seems relevant. Decomposition, auto-correlation and cross-correlation analyses of resulting time series should enable improved understanding of flow regimes and also links with other water quality variables that are strongly relevant to springs ecology (nutrients, salts, dissolved oxygen). Specifically, if binary mixing models are useful simplifications of spring vent hydrology, time series will allow decomposition of flows into two components, with insight into the relative importance of each, and changes in mixing with regional climatic trends. These methods need to be applied cognizant that different springs are likely to have different hydrogeologic properties, and inference from one spring may not apply in others.
2. *Spring Flow variability and vulnerability.* Ongoing efforts to set minimum flows and levels (MFLs) should consider the role of flow in what are generally considered to be water quality response variables. For example, changes in nitrate that are implicated in springs ecological change have occurred along with changes in fish access, vent discharge, and salinity, among other things. Moreover, in advective systems, flux is often a better predictor of ecological enrichment than is concentration, and with declining flows, fluxes are affected. Understanding the role of flow both directly and indirectly in springs ecosystems, and linking that to how water has been managed in the springshed is likely to be high value research.

Nutrient Loading

1. *High resolution temporal dynamics* – Among the key implications of the literature is that pollutant delivery in karst systems can be highly variable, though less so in eogenetic karst. Pulses of nutrients and other water quality parameters (dissolved oxygen, salts, toxins) have been invoked for catastrophic shifts in other systems, particularly when ecosystem drivers have broadly changed. The presence of such pulses (even long duration anomalies might be considered pulses) in spring systems is unknown, and the implications on springs ecology equally uncertain.
2. *Improved N isotope tracing* – There is significant uncertainty about the interpretation of bulk stable isotope measurements in complex karst hydrologic systems. First, there is a

broad omission of N fixation from N budgets (which would tend to lighten the isotopic ratio of overall N delivery). Second, nitrification processes are poorly understood: since that process results in large kinetic fractionation (lightening) and denitrification is negligible in the aquifer, the potential impact on the overall N isotope ratio is both unknown and of crucial importance for understanding flow paths. This is also relevant for questions beyond nitrogen delivery, since there is a plausible connection between loading of organic wastes and declines in dissolved oxygen. Constraining the isotopic kinetics in springsheds by observations along flowpaths will likely improve understanding of water and pollutant sources.

3. *Water Quality beyond nitrogen.* The synthesis of the literature on springs is dominated by information about nitrogen, but essentially devoid of similarly detailed studies of other water quality parameters. Where surveys have been done across a broad-spectrum of water quality attributes (Stevenson *et al.* 2004, for example), attributes such as salinity, flow, dissolved oxygen and phosphorus were at least as predictive of ecosystem change as nitrogen, despite the dramatic enrichment of N that has been observed. There is a clear and present need to understand how variability in these attributes occurs, and the extent to which that variability is in response to anthropogenic activities.
4. *BOD Loading.* Septic tanks, animal waste disposal systems and sprayfields generate enormous quantities of biological and nitrogenous oxygen demand if discharged unoxygenated into the groundwater. Indeed, one septic tank emits enough BOD and NOD to deoxygenate over 6 million L of 5 ppm of dissolved oxygen in UFA water per year. Since dissolved oxygen concentrations are strongly spatially variable, have significantly declined across a broad spectrum of springs (Scott *et al.* 2004), and were the only parameter significantly associated with algal cover in Stevenson *et al.* (2004), understanding the roles of hydrogeologic and anthropogenic processes in low DO at spring vents is a first-order research unknown.

Subsurface Nutrient Processing

1. *Explanation of observed assimilative capacity.* Efforts analogous to the springshed nutrient budgeting for watersheds in the northeastern US yield an estimate of 20% for the fraction of terrestrial load that is transported by rivers to the sea. In a karst environment where N movement is essentially unimpeded, conservative estimates of landscape attenuation are as high or higher (70-90%), without accounting for N fixation. Even where efforts were made to estimate the load reaching the aquifer (MACTEC 2007), those estimates are 6 fold higher than what emerges at the spring vent. Elaborating the reasons for this discordance, and how it might be affected by development and enhanced by management, should be a first-order priority. Among the issues that will need to be dealt with are the intrinsic lags due to aquifer residence times, and the relative importance of surface vs. vadose zone vs. aquifer processes.
2. *Saturation of assimilative capacity.* As land development increases, there may be loading thresholds that exceed the assimilative capacity of the landscape and lead to elevated load

breakthrough. The potential for observing this effect is low for nitrogen pollution, but may be high for P. Ensuring that P saturation fronts are not advancing towards spring vents is important for forecasting.

3. *Management responsiveness* – As we begin to understand the links between springshed activities and responses in spring ecosystems, evaluating the extent to which parameters are management-sensitive is relevant. This is relatively well understood for N (see Obreza 2002 for an assessment of BMPs on N delivery), but not at all for other water quality metrics in springsheds. If other parameters (P, DO, salts, flow) figure prominently in holistic springshed management, understanding how to best manage them is a clear priority.

REFERENCES

- Albert, M.A. 2002. Monitoring and Modeling the Fate and Transport of Nitrate in the Vadose Zone Beneath a Suwannee River Basin Vegetable Farm. MS Thesis, University of Florida. Gainesville, FL.
- Anderson, D.L. and R.J. Otis. 2000. Integrated Wastewater Management in Growing Urban Environments. American Society of Agronomy, Crop Science Society of America, Soil Science Society of America. Agronomy Monograph No. 39.
- Andrews, W.J. 1994. Nitrate in Ground Water and Spring Water Near Four Dairy Farms in North Florida, 1990-93. U.S. Geological Survey Water-Resources Investigations Report 94-4162, 63 p. Reston, VA.
- Andrews, W.J. 2000. Time series sampling for nutrient and bacteria in ground water at four North Florida dairy farms and three springs along the Suwannee River, 1990-1993. U.S. Geological Survey Open File Report 00-0204, 61 p. Reston, VA.
- Arthur, J.D., A.E. Baker, J.R. Cichon, A.R. Wood, and A. Rudin. 2007. Florida Aquifer Vulnerability Assessment: Florida Geological Survey Bulletin 67, (3 plates) 150 p. Tallahassee, FL.
- Bacchus, S.T. and P.J. Barile. 2005. Discriminating Sources and Flowpaths of Anthropogenic Nitrogen Discharge to Florida Springs, Streams and Lakes. Environmental and Engineering Geoscience 11:347-369.
- Barrios, K. and K. DeFosset. 2006. Ground water chemical characterization of the St. Marks River Rise, Florida. Northwest Florida Water Management District Water Resources Special Report 06-01. Havana, FL.
- Berndt, M.P., E.T. Oaksford, M.R. Darst and R.L. Marella. 1996. Environmental setting and factors that affect water quality in the Georgia-Florida Coastal Plain study unit. U. S. Geological Survey Water Resources Investigations Report 95-4268. Reston, VA.
- Binkley, D. , G. G. Ice, J. Kaye, and C. A. Williams. 2004. Nitrogen and phosphorus concentrations in forest streams of the United States. Journal of the American Water Resources Association 40(5):1277-1291.
- Bowden, W. D. 1986. The biogeochemistry of N in freshwater wetlands. Biogeochemistry 4: 313-348.
- Boyer E.W., C.L. Goodale, N.A. Jaworski & R.W. Howarth. 2002. Anthropogenic nitrogen sources and relationships to riverine nitrogen export in the northeastern USA. Biogeochemistry, 57:137-169.

- Butt, P.L. and G.J. Murphy. 2003. Dyal and Black Sink dye trace studies, Columbia County Florida, May-September 2003. Karst Environmental Services for Florida Department of Environmental Protection. Tallahassee, FL.
- Campbell, K.L., J.C. Capece and T.K. Tremwel. 1995. Surface/subsurface hydrology and phosphorus transport in the Kissimmee River Basin, Florida. *Ecological Engineering* 5:301-330.
- Canfield D.E. and R.W. Bachmann. 1981. Prediction of total phosphorus concentrations, chlorophyll a, and Secchi depths in natural and artificial lakes. *Can. J. Fish. Aquat. Sci.* 38: 414-423.
- Caraco, N.F., J.J. Cole and D.L. Strayer. 2006. Top-down control from the bottom: Regulation of eutrophication in a large river by benthic grazing. *Limnology and Oceanography* 51:664-670.
- Carpenter, S.R., N.F. Caraco, D.L. Correll, R.W. Howarth, A.N. Sharpley and V.H. Smith. 1998a. Nonpoint Pollution of Surface Waters with Phosphorus and Nitrogen. *Ecological Applications* 8:559-568.
- Carpenter, S.R., J.J. Cole, J.E. Kitchella, and M.L. Pace. 1998b. Impact of dissolved organic carbon, phosphorus and grazing on phytoplankton biomass and production in experimental lakes. *Limnol. Oceanogr.* 43: 73-80.
- Chambers, R.M. and W.E. Odum. 1990. Pore water oxidation, dissolved phosphate and the iron curtain. *Biogeochemistry* 10:37-52.
- Champion, K.M. 2001. Hydrology and water quality of select springs in the SWFWMD. Southwest Florida Water Management District. Brooksville, FL.
- Champion, K. M. and R. Starks. 2001. The hydrology and water quality of select springs in Southwest Florida Water Management District. Water Quality Monitoring Program, Southwest Florida Water Management District. Brooksville, FL.
- Champion, K.M. and S.B. Upchurch. 2003. Delineation of Spring-Water Source Areas in the Ichetucknee Springshed. Florida Department of Environmental Protection. Tallahassee, FL.
- Chelette, A., T. R. Pratt, and B. G. Katz. 2002. Nitrate loading as an indicator of nonpoint source pollution in the Lower St. Marks-Wakulla Rivers watershed. Water Resources Special Report 02-1. Northwest Florida Water Management District. Havana, FL.
- Cichon, J.R., A.E. Baker, A.R. Wood, and J.D. Arthur. 2005. Wekiva Aquifer Vulnerability Assessment. Florida Geological Survey Report of Investigation 104, 36 p.
- Cisar, J.L., J.E. Erickson, G.H. Snyder, J.J. Haydu, and J.C. Volin. 2004. Documenting nitrogen leaching and runoff losses from urban landscapes. p. 266-269 *In* Environmental impact of

- fertilizer on soil and water. ed. W. L. Hall and W.P. Robarge. Oxford University Press. Cary, NC.
- Cisar, J.L., G.H. Snyder, J.J. Haydu, and K.E. Williams. 2001. Turf response to coated-urea fertilizers. *Proc. Fla. State Hort. Soc.* 114:254-258.2001.
- Cockx, E.M. and E.H. Simonne. 2003. Reduction of the Impact of Fertilization and Irrigation On Processes in the Nitrogen Cycle in Vegetable Fields with BMPs. University of Florida EDIS Publication #HS948. Gainesville, FL.
- Cohen, M.J., S. Lamsal and L.V. Korhnak. 2007. Sources, Transport and Transformations of Nitrate-N in the Florida Environment. St. Johns River Water Management District SJ2007-SP10. 125 pp. Palatka, FL.
- Copeland, R. 2003. Florida Spring Classification System and spring glossary: Florida Geological Survey, Special Publication No. 52, 18 p., Tallahassee FL
- Cowell, B. C., and P. S. Botts. 1994. Factors Influencing the Distribution, Abundance and Growth of *Lyngbya wollei* in Central Florida. *Aquatic Botany* 49:1-17.
- Crandall, C.A. 2000. Distribution, Movement, and Fate of Nitrate in the Surficial Aquifer Beneath Citrus Groves, Indian River, Martin, and St. Lucie Counties, Florida. U.S. Geological Survey Water-Resources Investigations Report 00-4057, 69 p. Reston, VA.
- Crocker, T.E. and A.J. Rose. 1999. Deciduous fruit for Central Florida. University of Florida EDIS Publication #CIR1221. Gainesville, FL.
- Currens, J. 2002. Changes in groundwater quality in a conduit flow dominated karst aquifer following BMP implementation. *Environmental Geology* 42:525-537.
- DeFosset, K. 2003. Preliminary Ground Water Basin Delineation for the Spring Lake Spring Group, Jackson County, Florida. Northwest Florida Water Management District, Water Resources Special Report 03-02.
- Dillon, K., W. Burnett, G. Kim, J. Chanton, D.R. Corbett, K. Elliott and L. Kump. 2003. Groundwater flow and phosphate dynamics surrounding a high discharge wastewater disposal well in the Florida Keys. *Journal of Hydrology* 284:193-210.
- Dodds, W.K. 2003. The role of periphyton in phosphorus retention in shallow freshwater aquatic systems. *J. Phycol.* 39:840-849.
- Dodds, W.K. 2006. Eutrophication and trophic state in rivers and streams. *Limnology and Oceanography* 51:671-680.
- Duarte, C. M., and D. E. Canfield. 1980. Macrophyte Standing Crop and Primary Productivity in Some Florida Spring-Runs. *Water Resources Bulletin* 26:927-934.

- Einsiedl, F. and B. Mayer. 2006. Hydrodynamic and Microbial Processes Controlling Nitrate in a Fissured-Porous Karst Aquifer of the Franconian Alb, Southern Germany. *Environmental Science and Technology* 40:6697-6702.
- Elser, J.J., M.E.S. Bracken, E.W. Cleland, D.S. Gruner, W.S. Harpole, H. Hillebrand, J.T. Ngai, E.W. Seabloom, J.B. Shurin and J.E. Smith. 2007. Global analysis of nitrogen and phosphorus limitation in freshwater, marine and terrestrial ecosystems. *Ecology Letters* 10:1135-1142.
- Ewers, R.O. 2006. Karst aquifers and the role of assumptions and authority in science. Special Paper 404, Geological Society of America, Boulder, CO.
- Fernald, E.A. and E.D. Purdum. 1998. Water Resources Atlas of Florida. Florida State University. Library of Congress Catalog Number 98-072985 ISBN 0-9606708-2-3.
- Fisk, D.W. and I.S. Exley. 1976. Exploration and environmental investigations of the Peacock Springs Cave System. Hydrologic Problems in Karst Regions; Proceedings of Symposium held at Western Kentucky University, Bowling Green, KY.
- Florea, L.J. and H.L. Vacher. 2007. Eogenetic Karst Hydrology: Insights from the 2004 Hurricanes, Peninsular Florida. *Groundwater*. 45:439-446
- Foster, C.R. 2008. Valuing preferences for water quality improvement in the Ichetucknee Springs systems: a case study from Columbia County, FL. MS Thesis, University of Florida, Gainesville FL.
- Frydenbourg, R. 2006. Water Quality Study of the Ichetucknee River. Florida Department of Environmental Protection, Tallahassee, FL.
- Galloway, J. N., F.J. Dentener, D. G. Capone, E. W. Boyer, R. W. Howarth, S. P. Seitzinger, G. P. Asner, C. C. Cleveland, P. A. Green, E. A. Holland, D. M. Karl, A. F. Michaels, J. H. Porter, A. R. Townsend, and C. J. Vörösmarty. 2004. Nitrogen cycles: past, present, and future. *Biogeochemistry* 70: 153-226.
- Garman, K.M. and J.R. Garey. 2005. The transition of a freshwater karst aquifer to an anoxic marine system. *Estuaries and Coasts* 28:686-693
- German, E.R. 2003. Summary and Analysis of Measurements of Discharge from Blue Spring, near Orange City, Florida 1932-2002. St. Johns River Water Management District Special Publications #SJ2006-SP10, Palatka FL
- Graetz, D.A. and V. D. Nair. 1995. Fate of phosphorus in Florida spodosols contaminated with cattle manure. *Ecological Engineering* 5:163-181.
- Graves, G. A., Y. Wan, and D. L. Fike. 2004. Water quality characteristics of storm water from major land uses in south Florida. *Journal of the American Water Resources Association* 40(6):1405-1419.

- Ham, L. K., and H. H. Hatzell. 1996. Analysis of nutrients in the surface waters of the Georgia-Florida Coastal Plain study unit, 1970-91.: U. S. Geological Survey Water Resources Investigations Report 96-4037, 67 p. Reston, VA.
- Harper, H. H., Storm water chemistry and water quality. Obtained on 04-30-2008 from Web Link - <http://www.stormwaterauthority.org/assets/47chemistry.pdf>
- Hatzell, H.H. 1995. Effects of Waste-Disposal Practices on Ground-Water Quality at Five Poultry (Broiler) Farms in North-Central Florida, 1992-93. U.S. Geological Survey Water-Resources Investigations Report 95-4064, 28 p. Reston, VA.
- Hearne, J.W. and C. Howard-Williams. 1988. Modelling nitrate removal by riparian vegetation in a springfed stream: the influence of land use practices. *Ecological Modelling* 42:179-198.
- Hiers, J.K., R.K. Mitchell, L.R. Boring, J.J. Hendricks and R. Wyatt. 2003. Legumes native to longleaf pine savannas exhibit capacity for high N₂-fixation rates and negligible impacts due to timing of fire. *New Phytologist* 157:327-338.
- Hilton, J., M. O'Hare, M.J. Bowes and J.I. Jones. 2006. How green is my river? A new paradigm of eutrophication in rivers. *Science of the Total Environment* 365:66-83.
- Hornsby, H. D. 1994. The Use of $\delta^{15}\text{N}$ to Identify Non-point Sources of Nitrate-Nitrogen beneath Different Land Uses. M.S. Thesis, University of Florida, Gainesville, FL.
- Hornsby, D., and R. Mattson. 1997. Surface water quality and biological monitoring network annual report – 1996, 200p. Suwannee River Water Management District, Live Oak, FL.
- Hornsby, D., R. Mattson, and T. Mirti. 2002. Surface water quality and biological annual report 2001. Suwannee River Water Management District, WR-01-02-04. Live Oak, FL.
- Hornsby, D., R. Mattson, and T. Mirti. 2003. Surface water quality and biological annual report 2002. Suwannee River Water Management District, WR 02/03-03. Live Oak, FL.
- Hornsby, D., R. Mattson, and T. Mirti. 2004. Surface water quality and biological annual report 2003. Suwannee River Water Management District, WR 03/04-02. Live Oak, FL.
- Hornsby, D., R. Mattson, and T. Mirti. 2005. Surface water quality and biological annual report 2004. Suwannee River Water Management District, WR 04/05-02. Live Oak, FL.
- Hornsby, H.D. 2007. Influences on the Distribution and Occurrence of Nitrate-Nitrogen and Total Phosphorus in the Water Resources of the Suwannee River Water Management District. Ph.D. Dissertation, University of Florida, Gainesville FL.
- Hu, C.M., F.E. Muller-Karger and P.W. Swarzenski. 2006. Hurricanes, submarine groundwater discharge and Florida's red tides. *Geophysical Research Letters* 11:1-5.

- Hubbard, R.K. and J.M. Sheridan. 1989. Nitrate Movement to Groundwater in the Southeastern Coastal Plain. *Journal of Soil and Water Conservation* 44:20-27.
- Hubbell, D.H. and G. Kidder. 2003. Biological Nitrogen Fixation. University of Florida EDIS Publication #SL-16. Gainesville, FL.
- Hutchinson, G. E. 1957. A Treatise on Limnology. Geography, Physics and Chemistry, V. 1. John Wiley and Sons, Inc. New York, NY.
- Hynes, H.B.N. 1969. The Ecology of Running Waters. University of Toronto Press. Toronto.
- Jaber, F.H., S. Shukla, E.A. Hanlon, P.J. Stoffella, T.A. Obraz and H.H. Bryan. 2006. Groundwater phosphorus and trace element concentrations from organically amended sandy and calcareous soils of Florida. *Compost Science and Utilization* 14:6-15.
- Jokela, E.J and A.J. Long. 1999. Using soils to guide fertilizer recommendations for Southern Pines. University of Florida EDIS Publication #FR053. Gainesville, FL.
- Jones, G.W. and S.B. Upchurch. 1994 (revised 1998). Origin of nutrient in groundwater discharging from Kings Bay Springs. Southwest Florida Water Management District, Brooksville, FL.
- Jones, G.W., S.B. Upchurch and K.M. Champion. 1996. Origin of nitrate in groundwater discharging from Rainbow Springs, Marion County, FL. Southwest Florida Water Management District, Brooksville, FL.
- Karst Environmental Services. 1997. Ichetucknee Springs Water Quality Working Group Cooperative Dye Tracer; Rose Creek Swallet-Ichetucknee Springs Group. Florida Dept. of Environmental Protection, Tallahassee, FL.
- Katz, B. G. 1992. Hydrochemistry of the Upper Floridan aquifer in Florida. U. S. Geological Survey Water Resources Investigations Report 91-4196, 37p. Reston, VA.
- Katz, B.G., H.D. Hornsby, J.F. Bohlke and M.F. Mokrý. 1999. Sources and chronology of nitrate contamination in spring water, Suwannee River Basin, Florida. U. S. Geological Survey Water-Resources Investigations Report 99-4252. Reston, VA.
- Katz, B.G., R. Copeland, T. Greenhalgh, R. Ceryak and W. Zwanka. 2005. Using multiple chemical indicators to assess sources of nitrate and age of groundwater in a karstic spring basin. *Environmental and Engineering Geoscience* 11:333-346.
- Katz, B.G., A.R. Chelette and T.R. Pratt. 2004. Use of chemical and isotopic tracers to assess nitrate contamination and ground-water age, Woodville Karst Plain, USA. *Journal of Hydrology* 289:36-61.
- Katz, B.G. and J.F. Bohlke. 2000. Monthly variability and possible sources of nitrate in ground water beneath mixed agricultural land use, Suwannee and Lafayette Counties, Florida. U. S. Geological Survey Water Resources Investigations 2004-4219, Reston, VA.

- Katz, B.G., J.K. Bohlke and H.D. Hornsby. 2000. A multi-tracer approach for determining sources of nitrate contamination of ground water and springs, Lafayette County, Florida. U. S. Geological Survey Open File Report 200-0204, Reston, VA.
- Katz, B.G., J.K. Bohlke and H.D. Hornsby. 2001. Timescales for nitrate contamination of spring waters, northern Florida, USA. *Chemical Geology* 179:167-186.
- Kendall, C. 1998. Tracing Nitrogen Sources and Cycling in Catchments. *In* Isotope tracers in Catchment Hydrology, C. Kendall and J.J. McDonnell (Eds.) Elsevier Science B.V., Amsterdam pp. 519-576.
- Kincaid, T.R., G. Davies, R. DeHan and T.J. Hazlett. 2004. Characterizing rapid point-recharge to the Floridan Aquifer in the Woodville Karst Plain of North Florida – Implications for protecting Wakulla Springs. Paper No. 31-3. Abstract in 53rd Annual Geological Society of America Meeting (Southeastern Section), Washington DC, March 25-17, 2004.
- Knockenmus, L.A. and D.K. Yobbi. 2001. Hydrology of the Coastal Springs ground-water basin and adjacent parts of Pasco, Hernando and Citrus Counties, Florida. U. S. Geological Survey Water-Resources Investigations Report 01-4230. Reston, VA.
- Knowles, L., Jr., A.M. O'Reilly and J.C. Adamski. 2002. Hydrogeology and simulated effects of ground-water withdrawals from the Floridan aquifer system in Lake County and in the Ocala National Forest and vicinity, north-central Florida: U.S. Geological Survey Water-Resources Investigations Report 02-4207. Reston, VA
- Kroeger, K.D., P.W. Swarzenski, W.J. Greenwood and C. Reich. 2007. Submarine groundwater discharge to Tampa Bay: Nutrient fluxes and biogeochemistry of the coastal aquifer. *Marine Chemistry* 104:85-97.
- Lamb, S.T., W.D. Graham, C.B. Harrison and A.K. Alva. 1999. Impact of Alternative Citrus Management Practices on Groundwater Nitrate in the Central Florida Ridge. I: Field Investigation. *Transactions of the American Society of Agricultural Engineers* 42:1653-1668.
- Lambert, M.J. and W.C. Burnett. 2003. Submarine groundwater discharge estimates at a Florida coastal site based on continuous radon measurements. *Biogeochemistry* 66:55-73.
- Lamsal, S., S. Grunwald, G. L. Bruland, C. M. Bliss and N. B. Comerford. 2006. Regional hybrid geospatial modeling of soil nitrate-N in the Santa Fe River Watershed. *Geoderma* 135:233-247.
- Loper, D.E., W.M. Landing, C.D. Pollman, and A.B. Chan Hilton. 2005. Degradation of Water Quality at Wakulla Springs, FL: Assessment and Recommendations. Report of the Peer Review Committee on the Workshop Solving Water Pollution Problems in the Wakulla Springshed of North Florida. Florida Department of Environmental, Tallahassee, FL.

- Lopez-Zamora, I., C. Bliss, E.J. Jokela, N.B. Comerford, S. Grunwald, E. Barnard and G.M. Vasquez. 2007. Spatial relationships between nitrogen status and pitch canker disease in slash pine planted adjacent to a poultry operation. *Environmental Pollution* 147:101-111.
- MACTEC. 2007. Phase I Report: Wekiva River Basin nitrate sourcing study. St. Johns River Water Management District Special Report, Palatka, FL.
- Maddox, G.L., J.M. Lloyd, T.M. Scott, S.B. Upchurch and R. Copeland. 1992. Florida's Groundwater Quality Monitoring Program – Background Hydrochemistry. Florida Geological Survey Special Publication 34. Tallahassee, FL.
- Mansell, R.S., S.A. Bloom and P. Nkedi-Kizza. 1995. Phosphorus transport in Spodosols impacted by dairy waste. *Ecological Engineering* 5:281-299.
- Martin, J.B., and R.A. Dean. 2001. Exchange of water between conduits and matrix in the Floridan Aquifer. *Chemical Geology* 179:145-166.
- Mattson, R.A., E.F. Lowe, C.L. Lippincott, J.Di, and L. Battoe. 2006. Wekiva River and Rock Springs Run Pollutant Load Reduction Goals. St. Johns River Water Management District, Palatka, FL.
- McClain, M.E., E.W. Boyer, C.L.Dent, S.E. Gergel, N.B. Grimm, P.M. Groffman, S.C. Hart, J.W. Harvey, C.A. Johnston, E. Mayorga, W.H. McDowell and G. Pinay. 2002. Biogeochemical Hot Spots and Hot Moments at the Interface of Terrestrial and Aquatic Ecosystems. *Ecosystems* 6:301-312.
- McConnell, R. G., E. G. Araj and D. T. Jones. 1999. Developing nonpoint source water levels of service for Hillsborough County, Florida. Proceedings of the Sixth Biennial Stormwater Research and Watershed Management conference. Tampa, Florida, September 14-17, 1999. Southwest Florida Water Management District. Brooksville, Florida.
- McNeal, B.L., C.D. Stanley, W.D. Graham, P.R. Gireath, D. Downey and J.F. Creighton. 1995. Nutrient Loss Trends for Vegetable and Citrus Fields in West-Central Florida. *Journal of Environmental Quality*. 24:95-100.
- Meinzer, O.E. 1927. Large springs in the United States. United States Geological Survey Water Supply Paper 557. U. S. Geological Survey, Reston, VA.
- Miller, J.A. 1990. Groundwater Atlas of the United States: Alabama, Florida, Georgia and South Carolina. U. S. Geological Survey Publication HA 730-G. Reston, VA.
- Miller, D.N., Smith, R.L. and Böhlke, J.K., 1999, Nitrification in a shallow, nitrogen-contaminated aquifer, Cape Cod, Massachusetts, in Morganwalp, D.W., and Buxton, H.T. (Eds.), U.S. Geological Survey Toxic Substances Hydrology Program--Proceedings of the Technical Meeting, Charleston, S.C., March 8-12, 1999: U.S. Geological Survey Water-Resources Investigations Report 99-4018, p. 329-336. Reston, VA.

- Miller, G.L. and J.L. Cisar. 2005. Maintaining athletic fields. University of Florida EDIS Publication #262. Gainesville, FL.
- Mirti, T. and L. Mantini. 2006. Surface water quality and biological annual report 2005. Suwannee River Water Management District, WR 05/06-02, Live Oak, FL.
- Mitsch, W.J., J.W. Day Jr., J.W. Gillian, P.M. Groffman, D.L. Hey, G.W. Randall and N. Wang. 2001. Reducing Nitrogen Loading to the Gulf of Mexico from the Mississippi River Basin: Strategies to Counter a Persistent Ecological Problem. *BioScience* 51:373-388.
- Moore, P.J. and J.B. Martin. 2005. Exchange of water between conduit and matrix porosity in eogenetic karst? Evidence from a quantitative dye trace. Paper No. 193-4. Proceedings of Annual Meeting, Geological Society of America, Salt Lake City, UT, October 16-19, 2005. Boulder, CO.
- Morgan, K.T. and E.A. Hanlon. 2006. Improving citrus nitrogen uptake efficiency: Understanding Citrus N requirements. University of Florida EDIS Publication #SL240. Gainesville, FL.
- Morton, T.G., A.J. Gold, and W.M. Sullivan. 1988. Influence of overwatering and fertilization on nitrogen losses from home lawns. *Journal of Environmental Quality* 17:124-130.
- Munch, D.A., D.J. Toth, C. Huang, J.B. Davis, C.M. Fortich, W.L. Osburn, E.J. Phlips, E.L. Quinlan, M.S. Allen, M.J. Woods, P. Cooney, R.L. Knight, R.A. Clarke, S.L. Knight. 2006. Fifty-year retrospective study of the ecology of Silver Springs, Florida. Publication Number: SJ2007-SP4. St. Johns River Water Management District, Palatka, FL.
- Mylavarapu, R., G. Kidder and C.G. Chambliss. 2002. UF/IFAS Standardized Fertilization Recommendations for Agronomic Crops. University of Florida EDIS Publication #SL-129. Gainesville, FL.
- Mytyk, N.R. and J.J. Delfino. 2004. Evaluation of nitrate data in the Ocklawaha River Basin, Florida (1953-2002). *Journal of the American Water Resources Association*. 40:913-924.
- Nair, V.D., K.M. Portier, D.A. Graetz and M.L. Walker. 2004. An Environmental Threshold for Degree of Phosphorus Saturation in Sandy Soils. *Journal of Environmental Quality* 33:107-113.
- Obreza, T. 2002. Floridan Springs Land Use Information Tool. Soil and Water Science circular #CIR 1448. University of Florida EDIS Publication. Gainesville, FL. Obtained on 05/01/2008 from Web Link - <http://edis.ifas.ufl.edu/SS435>
- Odum, H. T. 1957. Primary Production Measurements in Eleven Florida Springs and a Marine Turtle-Grass Community. *Limnology and Oceanography* 2:85-97.
- Omernik, J. M. 1977. Nonpoint source-stream nutrient level relationships: a nationwide study. EPA-600/3-77-105. U.S. Environmental Protection Agency. Washington, DC.

- Panno, S.V., K.C. Hackley, H.H. Hwang and W.R. Kelly. 2001. Determination of the sources of nitrate contamination in karst springs using isotopic and chemical indicators. *Chemical Geology* 179:113-128.
- Park, D.M. 2006 Nitrogen leaching and St. Augustinegrass Turf Response to Lawn Maintenance Strategies. Ph.D. Dissertation, University of Florida, Gainesville, FL.
- Paytan, A., G.G. Shellenberger, J.H. Street, M.E. Gonneea, K. Davis, M.B. Young and W.S. Moore. 2006. Submarine groundwater discharge: an important source of new inorganic nitrogen to coral reef ecosystems. *Limnology and Oceanography* 51:343-348.
- Phelps, G.G., 2004. Chemistry of Ground Water in the Silver Spring Basin, Florida, with an emphasis on Nitrate. U. S. Geological Survey Scientific Investigations Report 2004-5144, Reston, VA.
- Phelps, G. G., S. J. Walsh, R. M. Gerwig and W. B. Tate. 2006. Characterization of the Hydrology, Water Chemistry, and Aquatic Communities of Selected Springs in the St. Johns River Water Management District, Florida, 2004. Open-File Report 2006-1107, U.S. Geological Survey. Reston, VA.
- Pittman, J. R., H. H. Hatzell and E. T. Oaksford. 1997. Spring contributions to water quality and nitrate loads in the Suwannee River during Baseflow in July 1995. U. S. Geological Survey Water Resources Investigation Report 97-4152. Reston, VA.
- Rabalais, N. 2002. Nitrogen in aquatic ecosystems. *Ambio* 31:102-112.
- Reay, W.G. 2004. Septic Tank Impacts on Ground Water Quality and Nearshore Sediment Nutrient Flux. *Ground Water* 42:1079-1089.
- Reckhow, K. H., Beaulac, M. N. and Simpson, J. T. 1980. Modeling phosphorus loading and lake response under uncertainty: A manual and compilation of export coefficients, U.S. EPA Report No. EPA-440/5-80-011, Office of Water Regulations, Criteria and Standards Division, U.S. Environmental Protection Agency, Washington, DC.
- Reed, S., D. Shinde, K. Konomi, K. Jayachandran, P. Nkedi-Kizza and M.R. Savabi. 2006. Phosphorus leaching potential from compost amendments in a carbonatic soil. *Soil Science* 171:865-873.
- Rosenau, J., G. Faulkner, C. Hendry and R. Hull. 1977. Springs of Florida: Florida Bureau of Geology Bulletin 31: revised. Florida Geological Survey, Tallahassee, FL.
- Scheffer, M., S. Carpenter, J. A. Foley, C. Folke and B. Walker. 2001. Catastrophic shifts in ecosystems. *Nature* 413:591-596.
- Schindler, D.W. 1977. Evolution of phosphorus limitation in lakes. *Science* 195:260-262.

- Scott, T.M., G.H. Means, R.P. Meegan, R.C. Means, S.B. Upchurch, R.E. Copeland, J. Jones, T. Roberts and A. Willet. 2004. Bulletin 66: Springs of Florida. Florida Geological Survey, Tallahassee, FL ISSN 0271-7832.
- Shoemaker, W.B., A.M. O'Reilly, N. Sepulveda, S.A. Williams, L.H. Motz and S. Quing. 2004. Comparison of Estimated Areas Contributing Recharge to Selected Springs in North-Central Florida by using Multiple Ground-water Flow Models. U.S. Geological Survey Open-File Report 03-448. Reston, VA.
- Sigua, G.C. and W.A. Tweedale. 2003. Watershed scale assessment of nitrogen and phosphorus loadings in the Indian River Lagoon basin, Florida. *Journal of Environmental Management* 67:363-372.
- Simon, K.S. 2000. Organic matter dynamics and trophic structure in Karst groundwater. Ph.D. Dissertation, Virginia Tech University, Blacksburg, VA.
- Slomp, C. and P. Van Capellen. 2004. Nutrient inputs to the coastal ocean through submarine groundwater discharge: controls and potential impact, *Journal of Hydrology* 295:64–86.
- Smith, R.L., J.K. Bohlke, S.P. Garabedian, K.M. Revesz and T. Yoshinari. 2004. Assessing denitrification in groundwater using natural gradient tracer tests with ^{15}N : In situ measurement of a sequential multi-step reaction. *Water Resources Research* v40, W07101.
- Smith, V.H., G.D. Tilman and J.C. Nekola. 1999. Eutrophication: impacts of excess nutrient inputs on freshwater, marine, and terrestrial ecosystems. *Environ. Pollut.* 100:179–196.
- Smith, V.H. 2006. Responses of estuarine and coastal marine phytoplankton to nitrogen and phosphorus enrichment. *Limnology and Oceanography* 51:377-384.
- Sollenberger, L.E.. 2006. General guidelines for managing pastures for dairy cows. University of Florida EDIS Publication #SS-AGR-94. Gainesville, FL.
- Suwannee River Water Management District (SRWMD). 2002. Ichetucknee Springs Basin Map. Obtained on 04-28-2008 from Web Link -<http://iche.pagelight.net/m/maps/Map-IcheBasin3-13-06.pdf>
- Staples, C.R., R.S. Tervola and E.C. French. 2003. Forage production practices by dairy producers in the Suwannee Valley. University of Florida EDIS Publication #CIR1049. Gainesville, FL.
- Stevenson, R., A. Pinowska, A. Albertin and J. O. Sickman. 2007. Ecological condition of algae and nutrients in Florida springs: The synthesis report. WM 858, Florida Department of Environmental Protection, Tallahassee, Florida.
- Stevenson, R., A. Pinowska and Y.-K. Wang. 2004. Ecological condition of algae and nutrients in Florida springs. Contract # WM858 Final Report. Florida Department of Environmental Protection. Tallahassee, FL.

- Strong, W. 2004. Temporal water chemistry trends within individual springs and within a population of Florida Springs. MS Thesis, University of Florida, Gainesville FL.
- Tank, J.L. and W.K. Dodds. 2003. Nutrient limitation of epilithic and epixylic biofilms in 10 North American streams. *Freshw. Biol.* 48: 1031–1049.
- Tarabe, J .L., J. S. Dinger, L. V. A. Sendlein and G. K. Felton, 1997. Land use impacts on water quality in small karst agricultural watersheds. In *Proceedings, Karst-Water Environment Symposium*, Virginia Polytechnic Institute and State University, October 30-31, Roanoke, Virginia, p. 99-109.
- Toth, D.J. 1999. Water quality and isotope concentrations from selected springs in the St. Johns River Water Management District. Special Publication SJ99-2, SJRWMD, Palatka, FL.
- Toth, D. J. and C. Fortich. 2002. Nitrate concentrations in the Wekiva groundwater basin with emphasis on Wekiwa Springs. Technical Publication SJ2002-2, St. Johns River Water Management District, Palatka, FL.
- Toth, D.J. and B.G. Katz. 2006. Mixing of shallow and deep groundwater as indicated by the chemistry and age of karstic springs. *Hydrogeology Journal* 14:1060-1080.
- Trenholm, L.E., E.F. Gilman, G.W. Knox and R.J. Black. 2002. Fertilizer and Irrigation Needs for Florida lawns and landscapes. University of Florida EDIS Publication #ENH860. Gainesville, FL
- Upchurch, S.B. and K.M. Champion. 2003. Geostatistical analysis of water level and water-quality data for the Ichetucknee Springshed. Suwannee River Water Management District Report # 004-00398. Live Oak, FL.
- Upchurch, S.B. and K.M. Champion. 2004. Delineation of springs protection areas at five first-magnitude springs in North Central Florida. Suwannee River Water Management District, Live Oak, FL.
- Upchurch, S.B., K.M. Champion, J.C. Schneider, D. Hornsby and R. Ceryak. 2004a. Identifying water-quality domains near Ichetucknee Springs, Columbia County Florida. U. S. Geological Survey Open File Report 2004-1332, Reston, VA.
- Upchurch, S.B., K.M.A. Champion, J.C. Schneider, D. Hornsby, R. Ceryak and W.D. Zwanka. 2004b. Defining springshed boundaries and water quality domains near first magnitude springs in North Florida. *Florida Scientist*. p.52
- Upchurch, S.B., J. Chen and C.R. Cain. 2007. Trends of nitrate concentrations in waters of the Suwannee River Water Management District, 2007. SDII Global Corporation Report #3017106. Suwannee River Water Management District. Live Oak, FL.
- Van Breemen, N., E. W. Boyer, C. L. Goodale, N. A. Jaworski, K. Paustian, S. Seitzinger, L. K. Lajtha, B. Mayer, D. Van Dam, R. W. Howarth, K. J. Nadelhoffer and G. Billen. 2002.

- Where did all the N go? Fate of N inputs to large watershed in the northeastern USA. *Biogeochemistry* 57/58: 267-293.
- Van Herpe, Y. and P. A. Troch. 2000. Spatial and temporal variations in surface water nitrate concentrations in a mixed land use catchment under humid temperate climatic conditions. *Hydrological Processes* 14: 2439-2455.
- Vitousek, P.M., J. Aber, R.W. Howarth, G.E. Likens, P.A. Matson, D.W. Schindler, W.H. Schlesinger and G.D. Tilman. 1997. Human alteration of the global nitrogen cycle: Causes and consequences. *Ecological Applications* 7:737-750.
- Vitousek, P.W., K. Cassman, C. Cleveland, T. Crews, C.B. Field, N.B. Grimm, R.W. Howarth, R. Marino, L. Martinelli, E.B. Rastetter, J.I. Sprent. 2002. Towards an Understanding of Biological Nitrogen Fixation. *Biogeochemistry* 57:1-45.
- Vollenweider, A. 1976. Advances in defining critical loading levels for phosphorus in lake eutrophication. *Mem. Ist. Ital. Idrobiol.* 33: 53-83.
- Wade, A.J., P.G. Whitehead G.M. Hornberger and D.L. Snook. 2002 On modeling the flow controls on macrophyte and epiphyte dynamics in a lowland permeable catchment: the River Kennet, southern England. *Sci. Total Environ.* 282:375-393.
- Walbridge, M.R. and B.G. Lockaby. 1994. Effects of forest management on biogeochemical functions in southern forests wetlands. *Wetlands* 14:10-17.
- Wang, H.D., W.G. Harris, K.R. Reddy and E.G. Falig. 1995. Stability of phosphorus in dairy-impacted soils under simulated leaching. *Ecological Engineering* 5:209-227.
- Weber, K.A. and R.G. Perry. 2004. Groundwater abstraction impacts on spring flow and base flow in the Hillsborough River Basin, Florida, USA. *Hydrogeology Journal* 14:1252-1264.
- Werner, C. 2000. Determination of groundwater flow patterns from cave exploration in the Woodville karst plain, Florida. *Florida Geological Survey Special Publication #46*, Tallahassee, FL.
- Wetzel, R. G. 1983. *Limnology*. Saunders College Publishing, Chicago, IL.
- Whitford, L. A. 1956. The Communities of Algae in the Springs and Spring Streams of Florida. *Ecology* 37:433-442.
- Wilson, W.L and W.C. Skiles. 1989. Partial reclassification of first magnitude springs of Florida. *Proceedings of the 3rd Multi-disciplinary conference on Sinkholes and Environmental Impacts of Karst Orlando FL* pp 65-72.
- Woodard, K.R., E.C. French, L.A. Sweat, D.A. Graetz, L.E. Sollenberger, B. Macoon, K.M. Portier, B.L. Wade, S.J. Rymph, G.M. Prine, and H.H. Van Horn. 2002. Nitrogen

Removal and Nitrate Leaching for Forage Systems Receiving Dairy Effluent. *Journal of Environmental Quality* 31:1980-1992.

Yobbi, D.K. 1992. Effects of tidal stage and groundwater levels on the discharge and water quality of springs in coastal Citrus and Hernando Counties, Florida. U. S. Geological Survey Water - Resources Investigations Report 92-4069. Reston, VA.

Zimmerman, A.R., P.J. Moore and J.B. Martin. 2006. Dissolved organic matter-mineral-microbe interaction in a karst aquifer: The Santa Fe Sink/Rise system, Floridan Aquifer, Florida. Abstract #B33A-1146 from American Geophysical Union Fall meeting, December 11-15, 2006, San Francisco, CA.

Biogeochemical Processes and Implications for Nutrient Cycling

Patrick W. Inglett, Kanika S. Inglett, and K. Ramesh Reddy
Department of Soil and Water Science
University of Florida

Summary

The availability and cycling of nutrients is determined by an interaction of physical, chemical, and biological processes in an ecosystem. This interaction of processes, collectively known as biogeochemistry, is important as it determines the forms, transformations, and ultimate fate of nutrients in a given system. This chapter focuses on biogeochemical processes in springs and spring runs with an examination of the role of springs as a potential ‘source’ or ‘sink’ for nutrients and pollutants.

The Literature: What is Known

- The effect of biogeochemical processes on spring water composition begins immediately upon emergence from the boil and continues throughout the entire length of a spring run. In this way, the biogeochemical character of a spring and its biota depend greatly on the chemical nature of the groundwater source.
- Key interfaces involved in elemental cycling in springs environments are biofilms, algal mats and hyporheic sediment zones. These are areas of high biological activity and as such, have the potential to display indicators of major processes and nutrient effects (e.g., through enzyme activities).
- A variety of processes are known to occur in springs including organic matter decomposition, nitrogen fixation, nitrification, denitrification, iron reduction, sulfate reduction, and associated processes involving phosphorus. The relative importance of each process depends greatly on the conditions of individual springs.
- Current data have increased our understanding of nutrient sources, and have provided indications of some nutrient transformations such as overall system productivity, potential biotic uptake and transformation of inorganic nutrients, and potential losses of nutrients from the system (e.g., gaseous losses or sediment storage).
- Elevated levels of nitrate in Florida springs are currently a major concern, especially due to the suggested correlation of nitrate with increased algal growth. There is clear evidence of elevated nitrate levels in many springs; however, there is a high likelihood that the effect of increased nitrate may be coupled to other nutrient levels (e.g., phosphorus or metals) or physico-chemical parameters (e.g., dissolved oxygen).

The Literature: What is Not Known

- Despite our understanding of biogeochemistry in other aquatic systems, there is little information regarding biogeochemical processes in spring systems where the focus has mainly centered on water column nutrients/water quality indicators. Consequently, our current biogeochemical models of Florida spring systems are more of a black-box with emphasis on water column nutrient levels and little understanding of individual processes or differences between systems of various types.
- There is little information to ascertain the involvement of processes/cycles controlling nitrate levels (e.g., plant uptake versus denitrification) or alternative pathways affecting nitrate conversion and loss (e.g., iron and sulfur involvement in lithotrophic denitrification).
- Among the studies which could advance our understanding of springs as sinks sources and transformers of nutrients are:
 - Expanding water quality data collection to include additional geochemical parameters (e.g., sulfide) could improve our ability to explain and predict individual spring responses to nutrients.
 - Increasing the frequency of water quality data collection (e.g., diel patterns) will offer additional insight into our ability to identify pathways involved in spring processing/cycling of nutrients.
 - Basing the collection of water quality data on stream segments will improve our ability to understand processes and spring run characteristics contributing to nutrient uptake and transformation.
 - Characterization of sediments (e.g., nutrient storages, organic matter distributions, mineral composition) would enable better assessments of benthic and hyporheic processes affecting both existing and future water quality (sediment memory).
 - Aquatic plant management efforts are likely to result in significant alteration of the spring environment through episodic deposition of organic matter, however, as yet there are no studies to document the potential for these activities to alter biogeochemical conditions (i.e., creating anoxic zones) and cycles (e.g., increasing denitrification loss of nitrate or increasing release of ammonium and phosphorus).
 - More studies are needed to document the involvement of mechanisms in observed declines in nitrate with distance in spring runs (i.e., dilution vs. biotic uptake vs. denitrification).
 - More exploratory work is necessary to determine the existence and importance of novel pathways of nitrate conversion (e.g., anammox and lithotrophic nitrate reduction).

INTRODUCTION

In combination with light, nutrient availability is a dominant factor controlling aquatic productivity. For this reason, nutrient levels, transformations, and fates are key factors in determining the health of aquatic resources such as spring ecosystems. Increased levels of nutrients in many spring systems are also a growing concern, particularly in Florida where a significant portion of the groundwater interacts with karst geology. This interaction gives a unique character to Florida springs as ecosystems, and has important implications for the ways in which these systems respond to, process and cycle nutrients.

The study of biogeochemistry deals with the interaction of biological systems with geochemical reactions which determines the overall cycling of elements within ecosystems. Both abiotic and biotically-controlled geochemical reactions can affect nutrient and mineral solubility, as well as reduction/oxidation (redox) chemistry, which can affect the composition and activity of the biotic system which in turn affects the water chemistry. Whether a spring system is a source or sink for nutrients and pollutants in the landscape is determined by the coupled biogeochemical processes occurring in its water column, sediments, biota, and adjacent floodplains.

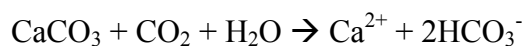
The potential biogeochemical reactions and pathways occurring in springs are numerous, and have been studied in varying levels of detail. Therefore the purpose of this review is 1) to describe the biogeochemical processes related to nutrient cycling in springs or similar systems, 2) summarize the available literature for Florida spring systems, and 3) highlight the needs and directions for future spring research. The major literature sources for this review were derived from published journal articles and government/agency reports. These documents included geochemical studies, biological/microbiological studies, and ecosystem/ecology studies focused on spring systems including those from Florida and other springs around the world. An overall lack of spring-specific data on many processes forced the use of literature pertaining to similar systems, such as chalk and other limestone-based streams. Finally, general stream literature was also used where appropriate to describe similar processes occurring in lotic (flowing) systems.

SPRING ENVIRONMENTS/ORGANISM GROUPS

Spring water chemistry

Water chemistry is one of the most important characteristics of a spring system which directly impacts its biological functioning. Because the primary source of spring water is groundwater, the characteristics of the different aquifers such as mineralogy and residence time will determine the overall chemical character of the spring receiving this outflow. Slack and Rosenau (1979) classified Florida springs into four types, in order of occurrence: 1) calcium-magnesium bicarbonate, 2) sodium chloride, 3) mixed (no dominant cation or anion) and, 4) calcium sulfate. This review will focus on the dominant spring water type in Florida - the hard water type, which has high calcium-magnesium-bicarbonate concentrations resulting from the interaction with limestone and dolostone host rock. However, other chemical constituents characterizing the other spring water types will also be addressed as they relate to specific processes.

Groundwater confined within the aquifer for extended periods of time undergoes significant changes as it emerges at the spring vent or boil and is directly introduced into conditions at the earth surface. Groundwater (at more or less equilibrium with subsurface temperature/ pressure/ mineral compositions) changes dramatically when introduced into the high oxygen/reduced pressure environment at the boil/vent/or seep (Figure 1). In general, soil/aquifer respiration processes increase the partial pressure of CO₂ in ground waters, which in limestone systems is responsible for the dissolution of the aquifer bedrock to form karst features. The equilibrium reaction for this process is given by the equation:



Dissolution of limestone and dolostone results in high levels of alkalinity (carbonate buffering) and dissolved constituents (e.g., calcium, magnesium, chloride, sulfate) which give rise to the chemical composition of most spring waters in Florida.

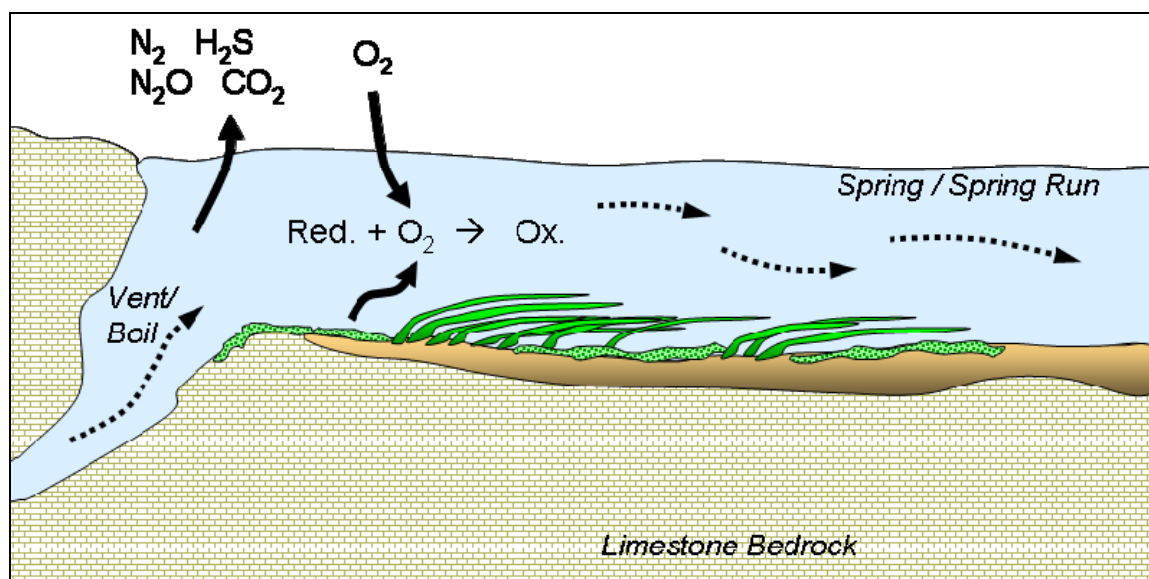


Figure 1 – Depiction of degassing and oxidative conversion of chemically reduced species (Red.) to oxidized (Ox.) forms following emergence of groundwater in a spring vent/boil.

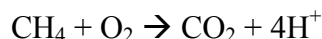
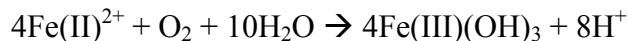
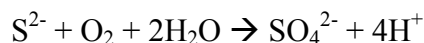
Emergence of groundwater at a boil or vent results in an immediate disequilibrium of the water with respect to CO₂, and as a result, degassing occurs. Loss of excess CO₂ shifts the dissolution equation toward precipitation of CaCO₃ which results in supersaturation of groundwater with respect to CaCO₃ (Dreybrodt *et al.* 1992). Other gaseous constituents of groundwater have the potential to degas upon emergence including N₂ (produced through aquifer (denitrification), the greenhouse gas N₂O from (from incomplete nitrification/denitrification processes), and caustic H₂S from sulfate reduction (evidenced by a rotten egg smell).

Supersaturation of CaCO₃ may further result in CaCO₃ precipitation and mineral formations near boil or seep areas (Drysdale *et al.* 2002; Liu *et al.* 2006). This phenomenon is not common in Florida, but the process of CaCO₃ precipitation can result in mineral encrustation in localized

areas of some springs, especially where processes such as photosynthesis further enhance supersaturation through uptake of CO₂. This process can result in mild calcifications on surfaces of submersed aquatic vegetation (SAV) or algae filaments (Berrie 1992).

If sufficient amounts of organic materials are present in the groundwater, respiration processes within confined aquifers result in a depletion of available oxygen potentially creating anaerobic conditions. Many springs report dissolved O₂ levels <1 mg L⁻¹ (Scott et al. 2004). Under anaerobic conditions, other oxidized species (e.g., NO₃⁻, Fe(III), and SO₄²⁻) can become chemically reduced (forming e.g., NH₄⁺, Fe(II), S²⁻). In extreme cases, the highly reduced gas, methane (CH₄) can even be formed. As a result, many groundwaters can contain a number of reduced species under low-oxidizing conditions. These reduced species are highly reactive, however, they can also persist in groundwaters (even under aerobic conditions) for significant periods of time (Darling and Goody 2006).

At the boil, chemically reduced spring waters encounter atmospheric levels of O₂ leading to a suite of chemical oxidation reactions:



Two important consequences of each of these oxidation reactions include: 1) consumption of O₂ and 2) the production of H⁺ ions. Depending on the redox status of the groundwater, consumption of oxygen may continue even after springwater emergence. As groundwater species are oxidized, the resulting acidification also increases the potential for dissolution of CaCO₃ (in systems supplied with highly reducing groundwater) while degassing and photosynthesis (reducing CO₂ levels) results in precipitation of CaCO₃ (Guasch *et al.* 1998). The balance between these two extremes determines the extent of calcification processes which is an important determinant of vegetative species composition (particularly algal assemblages) in spring systems (Freytet and Verrecchia 1998).

Reactive Zones

The high energy, lotic characteristics of springs create a variety of different zones where biogeochemical reactions can occur. The most important zones are the interfaces of the water column with sediments, epilithic/periphytic biofilms, and benthic mats of macroalgae (Figure 2). These interfaces are critical to nutrient cycling processes because of the sharp gradients they create in physical and chemical parameters (e.g., pH, O₂, redox). In addition, solutes are actively produced and consumed creating concentration gradients which further enhance solute movement and transport.

Biofilm

In aquatic systems, development of structural microbial assemblages, sometimes referred to as biofilms, is influenced by the habitats which may be present. In a stream or a spring run, the presence of rocks and stones, litter, detrital material, logs, plants and other submerged surfaces provide substrates for the microbial biofilms to establish. In well-developed stages, aquatic biofilms are known by names such as periphyton or aufwuchs.

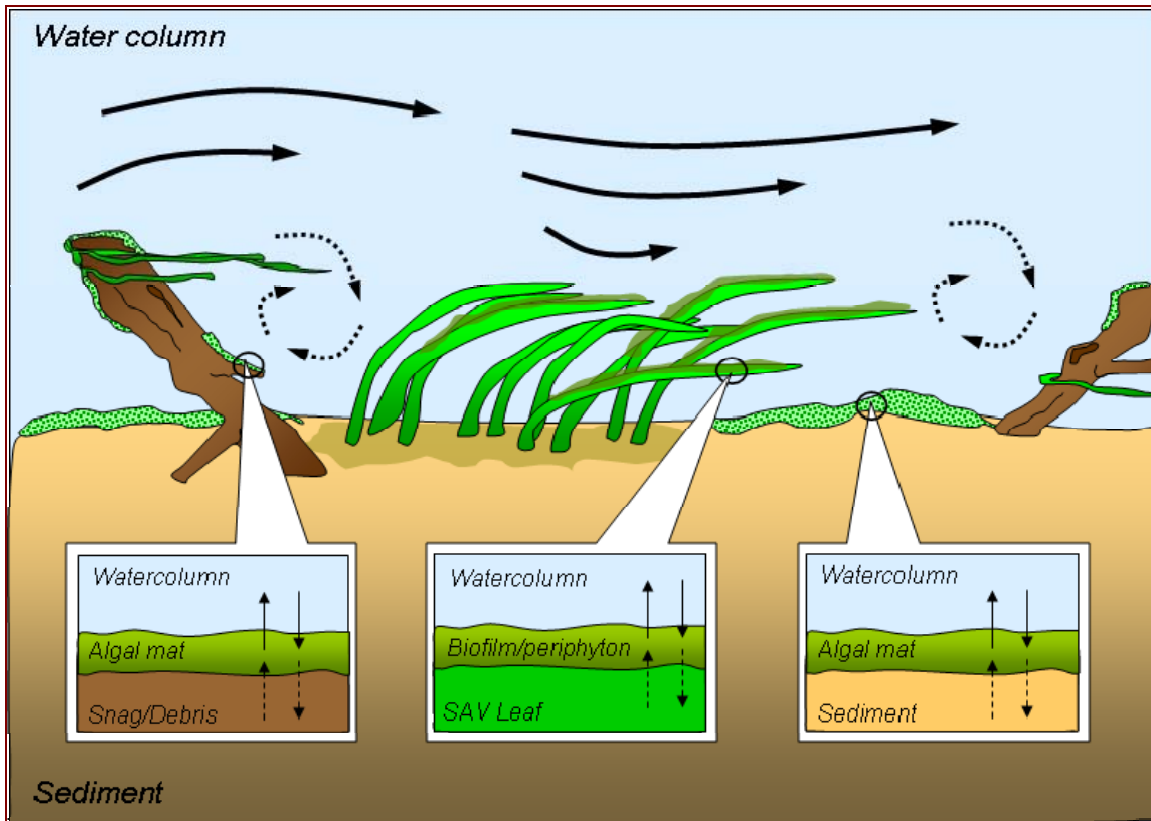


Figure 2 – Depiction of biogeochemical exchanges occurring at the biofilm, epiphyte, and benthic algal mat surfaces in a spring system.

Biofilm forming algae and bacteria actively exude substantial quantities of exopolymeric substances (EPS) into the environment that are primarily organic carbon (Hoagland *et al.* 1993; Costerton *et al.* 1995; Goto *et al.* 1999). This exudation of carbon can constitute a large proportion of carbon acquired by both bacteria and algae (Goto *et al.* 1999) and result in the accumulation of non-living organic carbon on surfaces in aquatic environments (Wetzel, Ward & Stock 1997; Frost & Elser 2002).

In aquatic systems like springs, biofilms are dominated by algae, diatoms, bacteria, and fungi. Exuded C provides the basis for other heterotrophic organisms to colonize, and as the biofilm develops, respiration can consume available oxygen to create anaerobic zones within the biofilm. The creation of anaerobic microsites and layers allow a myriad of other bacterial groups to become established. These groups represent important classes of biogeochemical processes

including denitrifiers, other anaerobic (iron reducers, sulfate reducers), and other aerobic organisms (nitrifiers, iron/sulfide oxidizers).

Benthic Algal Mats

Conspicuous mats of benthic algae are becoming a common feature of many spring systems (Stevenson *et al.* 2007). These macroscopic algal growths, similar to biofilms, are actually communities of microorganisms including: algae, bacteria, and fungi. The initial formation of mats is usually based on the structure provided by filamentous algae, which provide the framework for accretion of other organisms (e.g., diatoms, bacteria) and additional organic and inorganic materials (Stal 2000). The two most common algal taxa forming these mats in Florida systems are *Lyngbya* and *Vaucheria*, however a variety of other filamentous or colonial species can initiate mat formation (Stevenson *et al.* 2007).

As the algal filaments develop, accretion progresses, and secondary organisms begin to dominate and alter the mat's physical and chemical characteristics. Physical gradients (light, temperature) form as light penetration to deeper mat layers becomes limited (Jorgensen *et al.* 1983). In response to the physical gradients, photosynthetic mat organisms become structured (or in some species, migrate vertically) to maximize their location in the presence of light and temperature. (Stal 2000). With the localization of C fixation, nutrient gradients develop in response to increased autotrophic and subsequent heterotrophic growth. Gradients of reduced and oxidized compounds also form and drive mat structure and metabolism (Figure 3) (Pinckney and Paerl 1997; Stevenson *et al.* 2007). These gradients of nutrients and redox can occur vertically or in response to diel fluctuations of photosynthetically-induced oxygen, pH and C production. As a result, the character (i.e., species composition and physical characteristics) and associated functions of an algal mat can be drastically different both vertically and temporally within the mat.

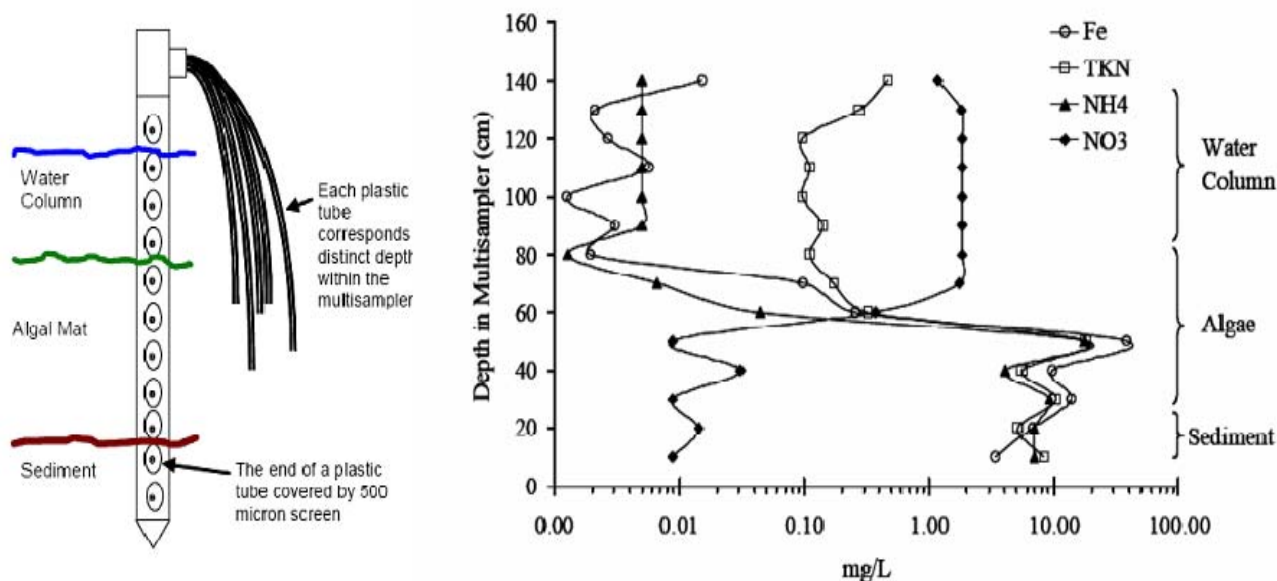


Figure 3 – Illustration of the sampling device and example of the measured profiles of nutrients from the study of benthic macroalgal mats by Stevenson, et al. (2007).

Sediments

In addition to a dissolved load, springs from carbonate aquifers have also been shown to be significant sources of sediments (Herman *et al.* 2006). In aquifers based in marine deposits (such as in Florida) these particles may be derived from the direct surface connections with underground conduits, or from particles release through erosion or dissolution of the aquifer material itself. As a result, sediments in spring flows can vary in composition from small organic materials, to clay particles, to sands and carbonate minerals (Herman *et al.* 2006; Mahler and Lynch 1999). The direct transport of surface derived materials also results in a strong dependence of sediment flux at the boil on the springshed characteristics and relationships between rainfall, runoff, recharge, and discharge. For example some springs, normally clear under low flow conditions, become turbid after storm events.

Not much is known about the composition and distribution of sediment types in Florida springs and spring runs, including information regarding particle size, mineralogy, or organic content. To our knowledge, only one study has attempted to characterize sediments/subaqueous soils from a spring system (Saunders 2007). In other stream environments, flow velocity is the most important determinant of sediment distribution patterns, therefore, it is likely the same would hold true for springs with flow velocities ranging from ca 1 to 100 cm s⁻¹. In general, particle sizes of sediment should decrease with passage downstream as channel widths widen, current velocity decrease, and progressively finer size classes are allowed to settle out. Saunders (2007) confirmed this pattern for the upper Chassahowitzka River where the areas near the boil were dominated by sands low in organic matter, and areas further downstream consisted of finer sands with higher organic content.

The main biogeochemical feature of spring run sediments is the presence or absence of redox gradients. In sediments, microbial respiration frequently consumes available O₂ leading to the formation of anaerobic zones at depth. Under these conditions O₂ contained in the water will diffuse downward to the anoxic sites, creating a gradient of O₂ and the presence of both aerobic and anaerobic sediment zones. In aerobic zones, microbes are involved in biogeochemical reactions and use oxygen as the primary electron acceptor, while in anaerobic layers, facultative and obligate anaerobes function using alternate electron acceptors (e.g., NO₃⁻, Fe(III), and SO₄²⁻) in their respiration.

One feature of sediments in high energy lotic systems is the high percentage of coarse particle size classes (e.g., sands) which greatly enhances advective processes (Figure 4). Sediments of high energy spring runs are also more likely to include varying stratigraphies with layers of different composition (e.g., organic matter) juxtaposed. In a manner analogous to that in biofilms or benthic mats, these types of sediment distributions serve to enhance the potential for varying reactions where reactants and products are more easily exchanged between reactive zones to greatly increase reaction rates (Harvey and Wagner 2000).

Characteristics of each of the sediment habitats in spring systems give rise to a variety of functional groups of organisms. Varying redox and nutrient conditions in sediments of springs likely result in the coexistence of both aerobic and anaerobic genera. This increased diversity of organisms and metabolisms should enhance the potential biogeochemical cycling of nutrients such as carbon, nitrogen, and phosphorus. Bacteria, in particular, are constantly responding and adjusting to carbon and nutrient availability, and thus, their activities can indicate conditions of availability. One of the ways microorganisms react to environmental conditions is through expression of enzymes which play a pivotal role in catalyzing the rate limiting steps of biogeochemical processes. For this reason, enzyme assays can serve as excellent indicators of microbial activities and environmental conditions (e.g., nutrient/contaminant impacts) of aquatic systems (Chrost 1991; Sinsabaugh *et al.* 1997).

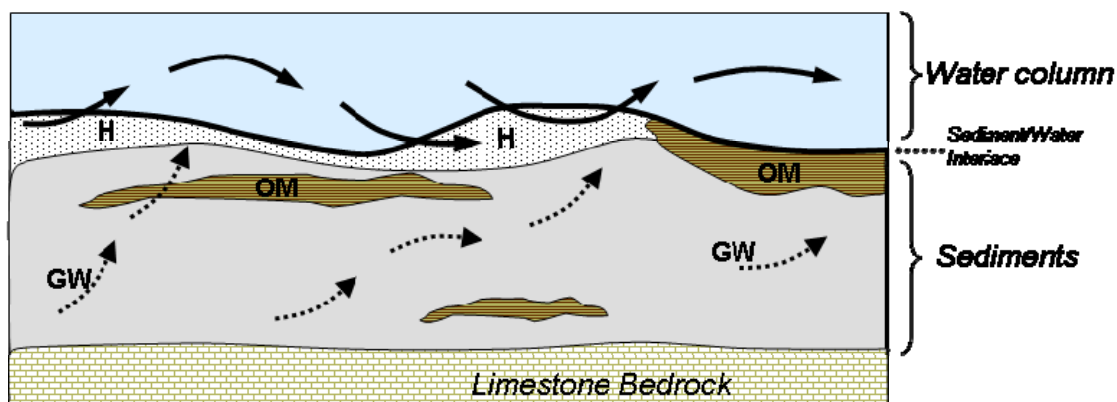


Figure 4 – Diagram of characteristics and hyporheic flow processes related to biogeochemical functions in a hypothetical spring run sediment profile. H, hyporheic zone; OM, organic matter concentration; GW, groundwater movement.

BIOGEOCHEMICAL PROCESSES

Carbon

As the major component of all life, carbon is arguably the most important of all biological elements in ecosystems. The cycling of C in spring systems has important implications for productivity, food-web dynamics, and metabolism of all spring biota. Consequently, the biogeochemical cycle of carbon involves complex interactions between and within organic and inorganic C reservoirs and involves numerous metabolic pathways and organism groups. These interactions have been widely studied by scientists in various disciplines.

Carbon Sources

The main sources of C to a spring system occur as 1) C sources in the groundwater; 2) C from direct or diffuse inputs of surface or groundwater along the spring run; 3) C inputs derived from riparian vegetation (litterfall); and 4) C fixed into biomass of spring autotrophs (primary producers). Of these, the C derived from autotrophic production within the spring run would be considered autochthonous (within-system) sources while the remainder are C sources external to (or allochthonous to) the spring run.

In aquatic systems, carbon is predominantly present as dissolved inorganic carbon (DIC), dissolved organic carbon (DOC), and as particulate organic (POC) and particulate inorganic (PIC) carbon forms. DIC is the primary form of C in hard water (limestone-based) springs, and is the primary form of C available for photosynthesis. For this reason, DIC is rarely limiting to autotrophic production in springs such as those in Florida. In contrast, ground waters in karst systems generally have low concentrations of DOC, and thus, much of the secondary production in springs is likely derived from autochthonous sources of C either directly, or following decomposition (Berrie 1992).

Perhaps one of the largest sources of C to spring systems is through the connections of many spring runs with extensive floodplains with forested, high-C soils (Whiting and Stamm 1995). This becomes significant during high flow periods which could result in significant exports of floodplain particulate C or leaching of C and subsequent increases in spring DOC concentrations. Hydrologic fluctuations (i.e., variations in rainfall and spring flow/discharge) can also lead to the introduction of variable amounts of high DOC surface water into groundwater systems (Pronk et al. 2006). Under high flow conditions there are also greater inputs of C from connected streams and discharges of surface or drainage waters.

As they are known to actively exude C compounds, both algae and SAV are likely important as autochthonous C sources in springs. These exuded compounds can range in size from low molecular weight (LMW) compounds such as sugars, proteins, amino acids, enzymes, phenolics, glycolate, and alkaloids (Sondergaard 1983) to high molecular weight (HMW) compounds (>10,000 Daltons, where a dalton $\approx$ the mass of one hydrogen atom) including primarily polysaccharides which can appear as slimes or algal sheathes (De Philippis and Vincenzini 1998; Stal 1994; Wetzel and Penhale 1979). The composition and production of extracellular C is

specific to both organism type and growth conditions including culture age, N source, temperature, salinity, P, and potassium (reviewed by De Philippis and Vincenzini 1998). Net release rates of 5-10% of total carbon fixation in macrophytes have been observed (Wetzel and Penhale 1979), while in some species of cyanobacteria, extracellular C production can represent up to 50-70% of dry weight (Bertocchi et al. 1990). Production of EPS has also been shown to increase with increasing irradiance in algal cultures (Otero and Vincenzini 2003; Renstrom and Bergman 1989). For this reason, light availability, and rates and patterns of algal photosynthesis/ photorespiration, can be a significant determinant of the quantity and quality of C compounds released within a spring system.

When present, EPS is considered a bioavailable C source that can stimulate bacterial respiration and productivity (Neely and Wetzel 1995; Espeland *et al.* 2001). Consequently, microbial associations have been shown to alter the composition of products excreted by the source plant (Sondergaard 1983). Overall, exuded C sources are viewed as highly available, particularly for the microbes associated with the algal cells or SAV leaves. In order to utilize exuded C substrates, bacteria must hydrolyze complex polymeric OM into simple utilizable forms by producing extracellular enzymes, in particular glucosidases (Chrost 1989; 1991; Eivazi and Tatabai 1988; Arsnotti 2003).

Decomposition

In the absence of direct exudation of C compounds, secondary production is based on C derived through decomposition. In most aquatic systems, this is the dominant pathway of C flow, and is the primary influence on the metabolic activity and diversity of microbes conducting many other biogeochemical processes. Springs are not known as accumulators of organic matter, perhaps due to their high flow velocity and (in most cases) continuous supply of well-oxygenated water. Temperature is seasonally controlled (20-24 °C), and so decomposition should occur at a moderate rate throughout the year. Also, the well-buffered hard waters of most spring systems should prevent low pH conditions from inhibiting microbial decomposition activity as in acid bogs.

As in other lotic systems, organic matter in springs tends to accumulate in dense vegetation stands, debris dams, and at the bottoms of large pools. In a slow moving spring run (upper Chassahowitzka River), Saunders (2007) observed large (>5 cm) organic material horizons with a patchy distribution. Similarly, in chalk streams, seasonal changes in beds of aquatic vegetation were shown to strongly affect flow velocities and rates of sediment and organic matter accumulation (Cotton *et al.*, 2006). For this reason, seasonality and management of SAV can have a direct impact on distribution of zones of organic matter accumulation and the biogeochemistry of a spring system. Aquatic vegetation management, including spraying of herbicides (e.g., Wakulla Springs State Park) can also contribute a significant amount of C (in large pulses) to spring runs.

Decomposition (or C mineralization) is a complex process beginning with the physical breakdown of macroscopic plant/algae tissues. The major constituents of this detrital plant matter are soluble substances (such as sugars, fatty acids, and amino acids), structural compounds (such as cellulose, hemi-cellulose, lignin and associated proteins), other water-

insoluble components (including fats, waxes and resins), and mineral matter (ash). The relative proportion of these constituents varies with type and source of detrital matter, degree of decomposition, and the age of the material. While SAV in springs contain more soluble and less structural C compounds than vegetation in the riparian zone, algae contain even fewer structural compounds. Approximate ranges in values for these constituents in plant material, peat, and soil organic matter are shown in Table 1 (Reddy and DeLaune 2008).

The initial step in the decomposition process is leaching of water soluble organic and inorganic compounds as a result of cell autolysis. Water soluble components include soluble carbohydrates, nucleotide bases, fatty acids, and amino acids. These components are readily bioavailable and serve as energy and nutrient sources to bacterial and fungal communities colonized on detrital plant tissue. Physical leaching of soluble components is generally complete within a few weeks of plant senescence, depending on structural components, temperature, and water flow. Leaching can be a significant factor in decomposition of non-lignocellulose materials such as algal mats and SAV (>50% mass loss). However, in detrital tissue containing lignocellulose materials (such as tree leaves and woody materials) only approximately 10-20% is lost within four weeks after immersion in the water column (Benner *et al.* 1985).

Table 1. Major carbon components of plant tissue, peat, and soil organic matter.

Component	Plants	Peat	SOM	Monomer	Linkage
	% composition				
Cellulose	15-60	15-30	2-10	Glucose	β -1,4 ether
Hemi-cellulose	10-30	10-40	0-2	5C & 6C sugars	β -1, 4 & β -1, 3 ether
Lignin	5-40	20-60	30-50	Phenyl propane	Aryl ether & C-C
Water soluble fatty acids, sugars, amino acids	10		<1	NA	NA
Ether extractable lipids, oils, waxes, etc.	1-8	2-10		fatty acids, sugars, phosphate	Esters & C-C
Proteins	2-20	4-20	2-20	amino acids	Peptide
Mineral matter	1-10	5-25			

After initial leaching and fragmentation, breakdown of plant detritus depends on the amount of major polymers, including lignin, cellulose, hemi-cellulose, lipids and waxes, and proteins. These structural components are mainly particulate in nature and must be broken down. In other aquatic systems, macroinvertebrate colonization is a key factor affecting observed litter decomposition rates; however, studies of their effect in springs are few and inconclusive. For example, in a study of four springs in Minnesota, Bortodziej and Perry (1990) found similar rates of decomposition of watercress (*Nasturtium officianale*) in different spring types despite significant differences in macroinvertebrate colonization. In the same study, they also found that macroinvertebrate colonization was correlated with decay rates of Boxelder (*Acer negundo*). Results such as these may indicate that macroinvertebrate shredder and grazer function may

depend on plant biomass type/quality (e.g., high versus low contents of structural compounds) in high energy spring environments.

Decomposition of particulate matter into smaller particles is an important process in determining C availability for secondary production and biogeochemical metabolism in spring systems. Plant detritus (either attached or detached from the plant) undergoes physical fragmentation through the action of waves and currents, UV exposure, and through grazing activities of macroinvertebrates (Dawson 1980). Fragmentation of plant detritus into fine particulate matter (FPOM) fraction (<1 mm) results in increased surface area, and accelerated microscale processes (such as enzymatic hydrolysis and catabolic activities). Coarse particulate matter (CPOM) being reduced into smaller fractions greatly enhances the surface area which fungi and bacteria can attack. In lotic environments, the action of macroinvertebrate shredders results in a transport of C particulates from the headwater reaches and a steady accumulation of fine particulate organic matter (FPOM) at lower stream zones (Webster *et al.* 1999). As it travels downstream, this FPOM material becomes increasingly more bioavailable through continued decomposition and the incorporation of added nutrients and algal derived particulates (Allan and Castillo 2003).

Even FPOM must first be converted into smaller metabolizable units before it can be assimilated by microbes as energy and nutrient sources. Extracellular enzymes secreted by microbes (bacteria and fungi) aid in hydrolysis of high molecular weight organic compounds associated with plant detritus and soil organic matter, which in their original form are too large for transport into the periplasmic space of the cell (Weiss *et al.* 1991). Microorganisms including bacteria and fungi are the dominant producers of extracellular enzymes. Selected examples of enzymes involved in degradation of cellulose, hemi-cellulose, and lignin are shown in Table 2. Breakdown of these structural polymers may require a multicomponent enzyme system including a wide range of microbial species. Rarely can a single microorganism produce all the enzymes required for breakdown of organic substrates.

Extracellular enzymes are generally considered as the rate limiting step in the overall degradation of organic matter. Kinetic limitations to enzymatic breakdown include slowing diffusion of enzymes and substrates, adsorption of enzymes on solid phases, and complexation of enzymes to humic substances (Sinsabaugh 1993; Wetzel 1991). Complexation of humic substances with enzymes may not be a significant issue in hard water springs as major cations (e.g., Ca^{2+}) react with humic acids and reduce the precipitation and inactivation enzymes. In soft water with low levels of base cations, the interference of humic substances on enzyme activities may be greater than hard water with Ca^{2+} and Mg^{2+} concentration in the range of 40-60 and 15-25 mg l^{-1} , respectively (Wetzel 1991).

Table 2. Enzymes involved in the degradation of polymeric C compounds (Sinsabaugh et al. 1991). EC number = Enzyme commission number.

Process	Enzymes	EC number	Substrates
Starch degradation	α,β,γ -amylase	3.2.1.1,2,3	Amylose
Cellulose degradation	Exocellulase	3.2.1.4	Cellulose
	Endocellulase	3.2.1.9.1	Cellulose
	β -glucosidase	3.2.1.2.1	Cellobiose
Hemi-cellulose degradation	Exoxylanase		Xylan
	Endoxylanase	3.2.1.8	Xylan
	β -xylosidase	3.2.1.37	Xylobiose
Lignin degradation	Phenol oxidase	1.10.3.12	Lignin
	Peroxidase	1.11.1.7	Lignin

Because enzyme activity is the rate limiting step in microbially mediated decomposition of plant detritus in wetlands and aquatic systems, many researchers have studied enzyme activities over scales ranging from the molecular to the ecosystem level (Sinsabaugh *et al.* 1993). Activities of β -Glucosidase, endocellulase and exocellulase have been measured as indicators of organic matter decomposition in wetlands and aquatic systems. Activity should be on a relative basis, when comparing the results from various ecosystems. Despite their use in other aquatic systems, there has not been any published report of carbon degrading enzyme expression in Florida springs.

As decomposition progresses, soluble or easily hydrolyzed compounds are selectively degraded yielding increased recalcitrance with age of detritus. Decomposer biomass is also incorporated as populations wax and wane. In this way, organic matter in waters and sediments can be viewed as a complex of plant, microbial, and animal products in various stages of decomposition. Continued chemical alteration of the C mixture ultimately results in the formation of highly recalcitrant C classes including humic and fulvic acids (Stevenson 1994). This process of stable organic matter formation results in aquatic systems serving as accumulators of C, and in springs, this process can be accentuated by increased deposition and burial of organic matter by sediments.

Nitrogen

Along with P, the high abundance of N in living biomass makes it one of the most highly demanded nutrients in aquatic systems. Nitrogen levels in many springs statewide have shown steady and dramatic increases over the past half century. In many cases, this excess N could result in significant changes in productivity; however, not all springs have exhibited changes with increasing N concentrations. The high level of N in some springs systems is also cause for significant concern (even if not related to within-spring impacts) from toxicological and landscape perspectives.

Numerous transformations and a suite of enzymes are involved in the transformation of N in aquatic systems (Table 3, Figure 5). Nitrogen is present in aquatic systems in organic forms and as inorganic forms such as dinitrogen gas (N_2), nitrate (NO_3^-), nitrite (NO_2^-), ammonium (NH_4^+), and trace gases such as N_2O . Organic N is derived primarily from amino-bonded C ($-NH_2$) such as amino acids and proteins, and nucleic acids, amino sugars. Generally, the sum of NO_3^-/NO_2^- , and NH_4^+ measured after filtration is taken to represent the dissolved inorganic N (DIN). The difference between the total dissolved N of a system and its DIN is then defined as the dissolved organic N (DON).

Table 3. Enzymes involved in various nitrogen cycle processes. From Reddy and DeLaune (2008).

Process	Enzymes	EC number	Substrates
N_2 fixation	Nitrogenase	1.18.6.1	N_2 gas
Amino acid degradation	Amidase/ deaminase	3.5.1.4	monocarboxylic acid amide
Amino acid degradation	L-Glutaminase	3.5.1.2	L-glutamine
Urea degradation	Urease	3.5.1.5	Urea
Nitrate reduction	Nitrate reductase	1.7.99	nitrogenous substrates
Protein degradation	Peptidase	3.4.21	Amides

Biological Nitrogen Fixation

Nitrogen is unavailable in the gaseous N_2 form and must be first converted (or fixed) to become bioavailable. One of the most studied enzymes (nitrogenase) is responsible for this conversion of N_2 gas to NH_4^+ , and is possessed by only select prokaryotic organisms including bacteria and cyanobacteria. Both of these groups are present in the biofilms, sediments and benthic algal mats of spring systems, however the potential for their expression of nitrogenase is uncertain.

A variety of factors can influence expression of nitrogenase enzymes including species composition, light availability, availability of P and metallic co-factors (Fe, Mo), oxygen levels, and NH_4^+ concentrations. In the case of the springs, NH_4^+ levels are generally not high, and should not be sufficient to suppress nitrogenase. Metal availability (in particular trace elements required for nitrogenase function) may be limiting in some springs; however, there are little data to support this conclusion. The presence of cyanobacteria in spring systems indicates that N-fixers may have a competitive advantage for N acquisition. It is true that many springs are N-limited, therefore, it is also likely that active N_2 fixation may be occurring. This has been documented in a number of stream systems; however, no data exist to ascertain the significance of this process for Florida springs. Furthermore, it is also uncertain what the fate of this fixed N would be in the spring environment.

Nitrogen uptake

In streams and springs with high biomass and productivity, nitrogen required for growth that is not provided by nitrogen fixation must be supplied by N uptake and assimilation from the water column. High production of algae and SAV in Florida spring runs should also contribute to high N assimilation rates especially in areas where growth is N limited (Notestein et al., 2003; Inglett et al., 2007). Of the two inorganic dissolved N forms, both NO_3^- and NH_4^+ are bioavailable and have been shown to be rapidly taken up by biota in headwater streams. Much of this headwater uptake is likely due to the high abundance of organic matter (leaf litter) in these systems. In one study of a low organic matter, brackish portion of the Chassahowitzka River, Saunders (2007) calculated rates of N loss (as NO_3^-) from the water column as high as $5 \text{ mg m}^{-2} \text{ d}^{-1}$, however; it was not determined what proportion of this N loss was due to biotic uptake, denitrification, or dilution.

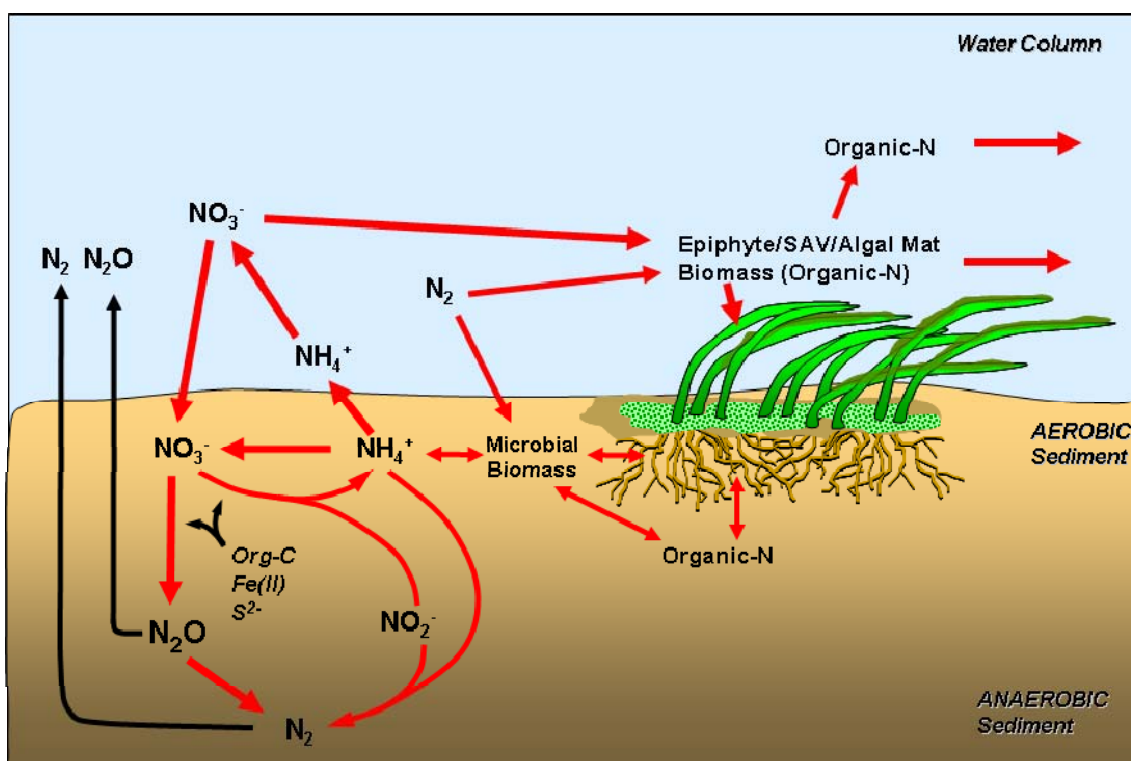


Figure 5 – Idealized diagram of the nitrogen cycle occurring in a typical spring run system.

In springs it is unclear whether the abundance of N in the water column is the main source of N to the plant/epiphyte communities, or if SAV derive the majority of their N through root uptake. Several studies have noted that both pathways may be equally important for productivity in SAV (compare Madsen and Cedergreen 2002 and Xie *et al.* 2005). Both NO_3^- and NH_4^+ are considered bioavailable; however, NO_3^- must first be reduced to NH_4^+ before it can be assimilated into biomass. The enzyme, nitrate reductase is functional during this process, and thus, can be used to show active incorporation of NO_3^- in vegetation (Melzer and Kaiser 1986). At least one study has used this enzyme activity to assess potential NO_3^- use by biota in springs

with the findings that 1) higher water column NO_3^- levels resulted in higher levels of NO_3^- reductase activity and 2) enzyme expression in biofilms differed depending on substrate type (Inglett *et al.* 2007) (Figure 6).

In addition to inorganic N forms, it has also been noted that organic forms of N, such as amino acids and other small molecular weight N compounds (e.g., urea) can be a significant source of N to both microbial/algal communities (e.g., Berman and Bronk 2003; Linares and Sundback, 2006) and wetland macrophytes. This is important not only because of its role in nutrition, but also because in many aquatic systems, the presence of organic forms of N (in particular, urea) has been shown to effect algal species composition (e.g., Heil *et al.* 2007). Thus, both quality as well as quantity of N may be important factors determining the impact or fate of N in springs.

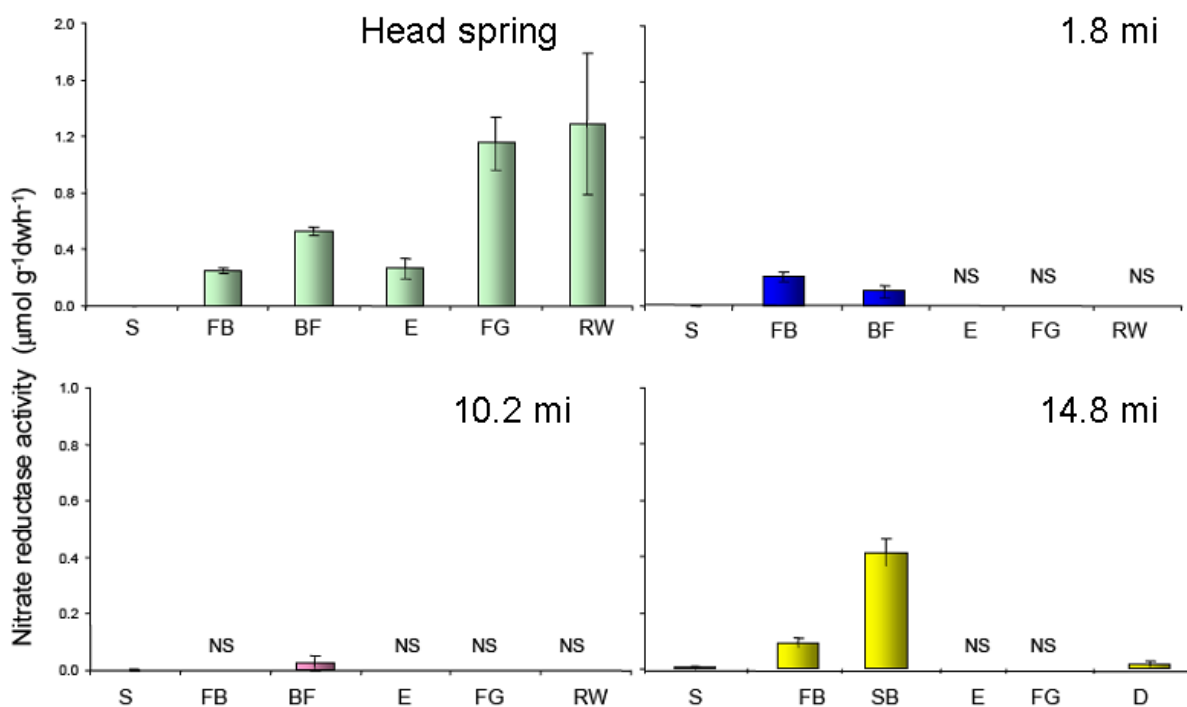


Figure 6 – Nitrate reductase activity ($\mu\text{mol NO}_2^-$ produced $\text{g}^{-1} \text{dw h}^{-1}$) in sediment and algal biofilms from various substrates (S, sediment; FB, filamentous benthic algae; BF, brown filamentous; E, epiphytic algae; FG, floating green algae; RW, rock wall biofilm; D, detrital material; SB, submerged bark biofilm) at four locations along the Wekiva River. (from Inglett *et al.* 2007).

Nitrogen mineralization

The biological transformation of organically combined nitrogen to ammonium nitrogen during the degradation of organic matter (ammonification) is one of the key mechanisms regulating the fate of nitrogen in aquatic systems. This process is strongly related to organic C decomposition, since a major portion of N in soil organic matter and plant detritus is bonded to C. As organic matter is decomposed, organic N is mineralized and released as ammonium. This process is achieved by a series of microbially-produced enzymatic processes (e.g. cellulose, cellulobioase,

glucosidase, aminopeptidase, protease etc.). Therefore, similar to C decomposition, the regulators of organic nitrogen mineralization include substrate quality, microbial biomass and enzyme activity, temperature, redox potential and hydrology. In a spring run, sites of ammonification would coexist with sites of organic matter/detrital matter accumulation or where organic matter has a rapid turnover as in the biofilms or the algal mats.

Depending on microbial N requirements, mineralized ammonium may be released, rapidly utilized by the microorganisms (immobilized), or taken up by plants. During decomposition, the C:N ratio reflects the mineralization-immobilization pattern of nitrogen, where a high C:N ratio promotes immobilization, while a lower ratio favors mineralization. During immobilization nitrogen is considered to be limiting to decomposer organisms. For this reason, initial N content of organic matter is a strong determinant of decomposition rates. Thus, organic matter with a low C:N ratio (such as algae or SAV) is considered labile, while those with high C:N ratios (such as wood, or senescent riparian vegetation) are considered more recalcitrant. Based on these factors, the production or consumption of NH_4^+ in the water column in a spring can be highly variable.

Ammonium in the water column is derived from (1) decomposition of organic matter in the water column; (2) mineralization of organic nitrogen in the aerobic soil/sediment layer; (3) mineralization of organic nitrogen in the biofilms; and (4) diffusion and mass flow of ammonium from anaerobic soil layer to aerobic soil/sediment layer and water column. Saunders (2007) found that sediments in the Chassahowitzka River were reducing at depth, while Stevenson et al. (2007) measured porewater NH_4^+ levels $>10 \text{ mg L}^{-1}$ under mats of *Vaucheria* sp. Both studies indicate that sediments in a spring run system can act as a significant source of ammonium to the overlying aerobic soil layer and water column. Flux of ammonium is accomplished by diffusion, advection, bioturbation, and mixing at and near the soil-floodwater interface.

Once NH_4^+ enters the water column, a variety of processes can affect its fate in a spring run/system. Ammonium is bioavailable, and therefore can be rapidly assimilated by phytoplankton, biofilm organisms, or SAV. Alternatively, if pH is high (>8) a significant proportion of NH_4^+ will be in the form of gaseous NH_3 which can volatilize (flux out of the water column). Volatilization of NH_3 can be significant in highly productive systems; however, in flowing waters with a high buffering capacity, it is unlikely that losses via this pathway are significant.

By far, the most likely fate of NH_4^+ in the well-oxygenated water column of a spring run will be nitrification where microorganisms oxidize NH_4^+ to NO_3^- . Autotrophic bacteria are dominantly responsible for the process of nitrification, and therefore these organisms do not require organic matter to function. Nitrifying populations of bacteria are likely to be found in all components of spring systems, and should be particularly concentrated at the aerobic/anaerobic interfaces where NH_4^+ and O_2 will both be available.

Denitrification

Nitrate has a high oxidation potential (similar to oxygen) and can be used by a variety of organism groups as an electron acceptor (becoming chemically reduced). One of the most

significant and highly studied processes reducing nitrate is the process of denitrification where organisms couple organic C oxidation to nitrate reduction. This process is almost exclusively anaerobic (a few aerobic examples have been found). Many of the organisms capable of denitrification are facultative and are capable of surviving in transitional (moderately anaerobic) or fluctuating aerobic/anaerobic conditions. In fact, in many aquatic systems denitrification zones occur in close proximity to the aerobic zones of NO_3^- production (nitrification).

Denitrifying organisms are predominantly heterotrophic. Therefore high organic matter C deposits (sediments, debris dams, biofilms, and algal mats) are the likely zones for occurrence of denitrification in spring systems. Alternatively, turbulent flow in many springs would likely be sufficient to advect significant quantities of water column NO_3^- into anaerobic sediments in the hyporheic zone (Triska *et al.* 1993; Duff *et al.* 1998). Hyporheic zones include regions beneath the stream channel and regions adjacent to the channel where stream water is exchanging with interstitial waters at rates and scales larger than those limited by diffusion. The majority of springs are too well oxygenated for denitrification to proceed at any great rate in the water column; however, dense SAV or heavy biofilm growths possess enough C and can sufficiently reduce water flow to induce anaerobic conditions either spatially (e.g., in microsites) and/or temporally (short-term transient events or diel cycles). This would be particularly important at night in the absence of photosynthesis.

To date, the only reported measurements of denitrification potential in Florida springs have been conducted in Wekiwa Springs/Wekiva River by Inglett *et al.* (2007). In that study, potential denitrification rates were measured in sediments and algal biofilms at four sites ranging from the headspring to 14.8 miles downstream (Figure 7). Observed rates ranged from 10 $\text{nmol N}_2\text{O produced gdw}^{-1} \text{ h}^{-1}$ in surface sediments (0-10 cm) to 170 $\text{nmol N}_2\text{O produced g}^{-1}\text{dw h}^{-1}$ in biofilms collected from bark samples from the headspring. The rates measured in the Wekiwa/Wekiva system are similar to DEA rates reported in wetlands (0.5 to 20 $\text{mg N}_2\text{O kg}^{-1} \text{ soil h}^{-1}$; White and Reddy 2003), estuarine sediments (15-130 $\text{nmol N cm}^{-3} \text{ d}^{-1}$; Joye *et al.* 1996), and in periphyton mats (1.9 $\mu\text{mol N}_2\text{O m}^{-2} \text{ h}^{-1}$; Triska and Oremland, 1981). Based on their results, Inglett *et al.* (2007) concluded that despite a conclusive trend in DEA downstream (along a depletion gradient of surface water NO_3^-) denitrification appeared to be a significant pathway for N removal from the system.

Alternative N pathways

Conversion of NO_3^- can occur by additional pathways. Some of these have been identified for a number of years while others have emerged more recently (reviewed by Burgin and Hamilton 2007) (Figure 8). Many of these pathways have yet to be identified in springs or streams; however, the potential exists for these processes to account for significant reduction of NO_3^- in aquatic systems. For this reason, we will discuss them briefly here.

The high energetic potential of using NO_3^- as an electron acceptor is not solely possessed by heterotrophic bacteria. Several pathways have also been identified that can reduce NO_3^- through the oxidation of other reduced compounds. Identification of these new mechanisms has challenged the classical view of denitrification in aquatic systems. Among these, NO_3^- reduction can be coupled to the oxidation of either reduced iron (Fe(II)) or sulfur (S^0 , S^{2-}). The importance

of these lithotrophic pathways to overall rates of denitrification has not yet been determined. Likewise, in springs and lotic systems, Fe(II) and S^{2-} -based denitrification has received little attention. It is not unlikely that these pathways could be significant given the presence of iron and sulfur in many spring systems and the myriad of reactions occurring at the oxic/anoxic interfaces of microbial mats, biofilms, or sediments.

Another pathway for NO_3^- reduction can convert NO_3^- into NH_4^+ . This process, called dissimilatory nitrate reduction to ammonium (DNRA), is different from the assimilatory process in that NH_4^+ produced is not directly incorporated into biomass. Fermentative DNRA couples organic matter oxidation to NO_3^- reduction by fermentation reactions (Tiedje 1988).

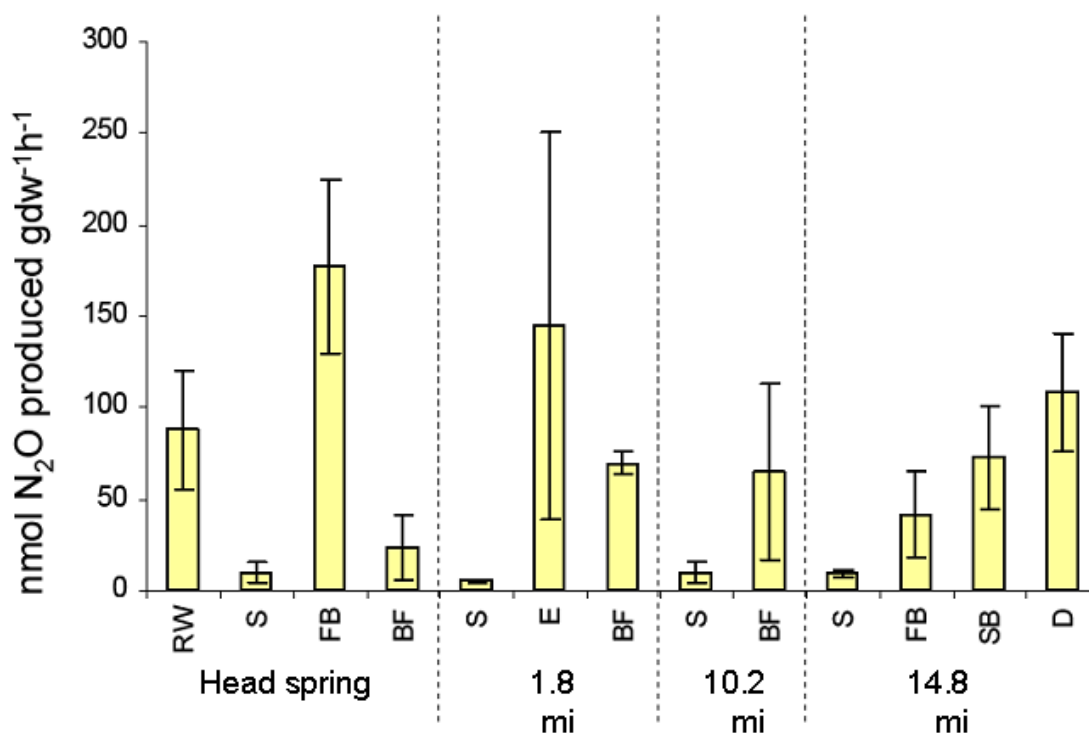


Figure 7 – Denitrifying potential in sediments, and algal biofilms collected from various substrata. S, sediment; FB, filamentous benthic algae; BF, Brown filamentous algae; E, epiphytic biofilms; RW, Biofilms attached to rock wall; D, detrital material; SB, algal biofilm on submerged bark. (From Inglett et al. 2007)

Another form of DNRA is chemolithautotrophic and couples NO_3^- reduction to oxidation of reduced S (e.g., S^{2-}). Strongly reducing conditions with high contents of organic matter or high concentrations of reduced Fe and S are required for DNRA. As stated for chemotrophic denitrification, conditions may exist for DNRA activity in springs; however, these areas would be highly localized to accumulations of organic matter and/or slow or no flow conditions.

Most recently, a novel pathway for N conversion to N_2 has been identified which adds even more uncertainty to the aquatic N cycle. The process known as anaerobic ammonium oxidation (Anammox) has now been identified in a number of freshwater systems including lakes and

wetlands. This process occurs in strictly anaerobic conditions, and couples the reduction of NO_2^- with the oxidation of NH_4^+ to produce N_2 gas. Anammox bacteria appear to be autotrophic, and the presence of organic matter slows the anammox process. Another important requirement for the anammox process is the presence of NO_2^- which is rarely observed in most systems.

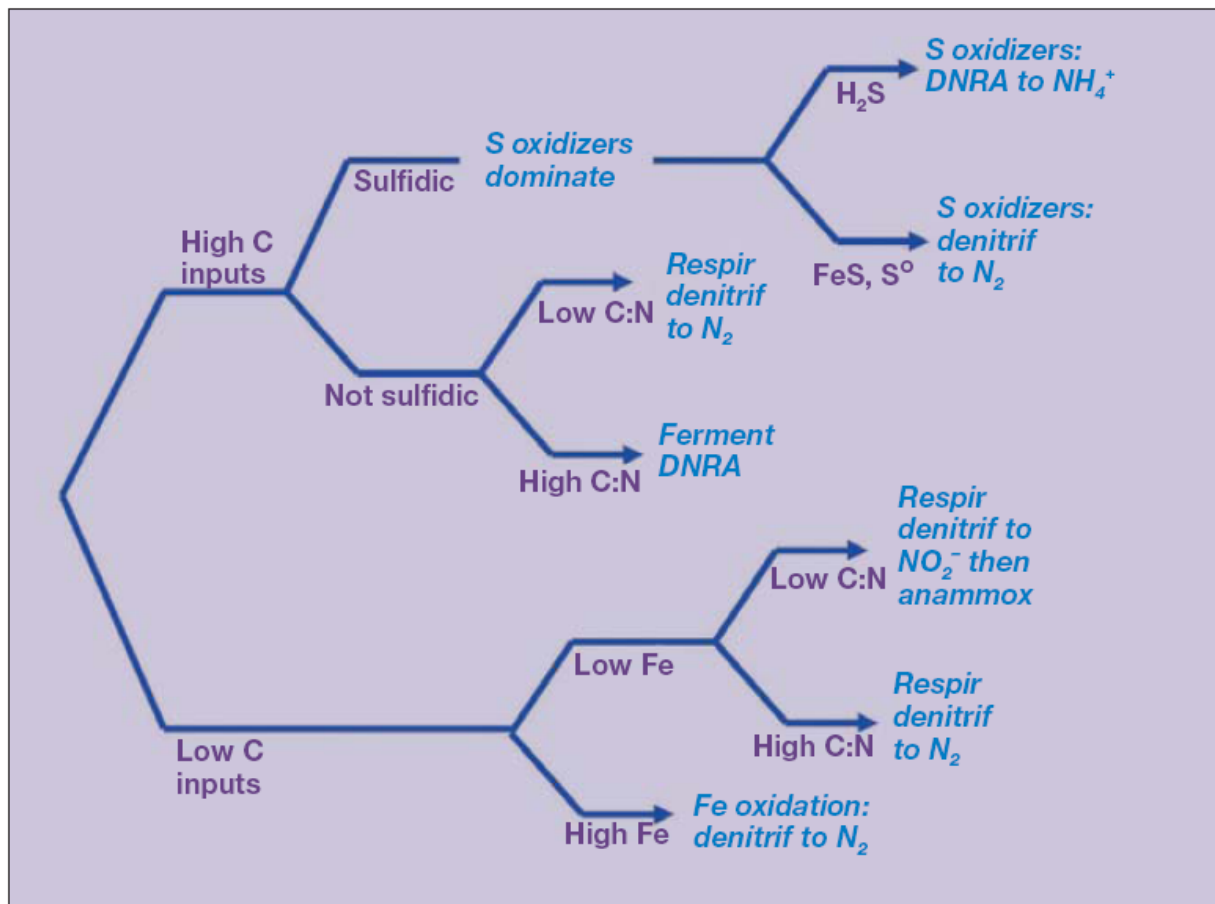


Figure 8 – Hypothesized controls on predominant dissimilatory pathways of NO_3^- removal. C inputs refer to labile organic carbon available to microbes. Sulfidic refers to the presence of either free sulfide (S^{2-}), elemental S (S^0). Of these S forms, only free sulfide inhibits denitrification and thus promotes DNRA. C:N ratios refer to the ratio of labile organic carbon to nitrate. Respir = respiratory; denitrif = denitrification; DNRA = dissimilatory nitrate reduction to ammonium; ferment = fermentative. (From Burgin and Hamilton 2007).

Nitrite accumulation is possible however, and several conditions of spring systems may be adequate for NO_2^- accumulation to occur. The formation of NO_2^- is largely a byproduct of incomplete denitrification or partial ammonium oxidation. For NO_2^- accumulation to occur in the denitrification and DNRA processes, NO_3^- reduction must occur at a greater rate than that of NO_2^- reduction. One way in which incomplete denitrification can occur is the lack of suitable organic substrates, or high concentrations of NO_3^- . Similarly, in the nitrification pathway, elevation of NO_2^- concentrations can occur only if the oxidation of NH_4^+ is greater than that of NO_2^- . Both of these scenarios have been reported to occur in the aquatic environment (Herbert 1982; Smith *et al.* 1997). *Nitrobacter* spp., which are responsible for the oxidation of NO_2^- in

the nitrification process, may be partially inhibited by free ammonia (NH_3) (Anthonsieu *et al.* 1976; Smith *et al.* 1997), leading to NO_2^- accumulation. Likewise, NO_2^- accumulation is a common trait of DNRA (Cole 1988) resulting from either inhibitory effects of NO_3^- on NO_2^- reductase (Smith, 1982) or repression of this enzyme (Paul and Beauchamp 1989).

Higher than expected NO_2^- levels ($100\text{--}200\ \mu\text{g N l}^{-1}$) have been reported in some European rivers, particularly in watersheds receiving large inputs of nitrogenous pollution (Smith *et al.* 1995; Kelso *et al.* 1997). In one study, Kelso *et al.* (1997) found that NO_2^- accumulation in six Irish rivers corresponded with NO_3^- declines via DNRA activity. This process was occurring in areas with high organic matter contents (Kelso *et al.* 1999), leading these authors to conclude that high NO_3^- concentrations, free ammonia, or high flow velocity created conditions suitable for NO_2^- accumulation to occur. All of these studies suggest NO_2^- may be much more abundant than previously thought. Therefore, it is likely that NO_2^- levels may be sufficient to support alternative N cycling pathways (such as anammox) in more aquatic ecosystems than previously thought.

Overall N Cycle

It is uncertain what role spring systems play as sinks, sources, or transformers of N. Several studies have reported declining inorganic N concentrations (primarily NO_3^-) with distance down spring run/river (e.g., DeBrabandere *et al.* 2007; Inglett *et al.* 2007; Mytyk and Delfino 2004) (Figure 7). In general lotic systems should result in a transformation of N, including conversion of DIN to DON through biotic uptake and senescence. Increases of DON with distance through a run have also been observed (Inglett *et al.*, 2007; Wetland Solutions, Inc., 2006). The study by Wetland Solutions, Inc. (2006) also indicates that DON production in spring runs is likely the result of excess N, where Wekiva and Rock Springs Run (both NO_3^- -impacted) show much higher production of DON in specific river segments, while Alexander and Juniper spring runs (reference conditions) show smaller production (or even net reduction) of DON.

It is also quite likely that springs are active zones of denitrification. Evidence of denitrification in springs comes from at least one study (Inglett *et al.* 2007), and the conditions exist for other unexplored areas where denitrification could occur (Saunders 2007). Areas with direct inputs of reduced groundwater into sediments with low organic matter content, or water column NO_3^- being advected into anaerobic sediments, are also key conditions for alternative denitrification pathways to occur in springs (Grimaldi and Chaplot 2000). In systems with significant quantities of iron or sulfur, additional lithotrophic N loss mechanisms may also be operating. Nitrogen cycle studies and budgets of springs are not available at this time. For this reason it is difficult to attribute the several examples of declining NO_3^- to either the process of biotic uptake or denitrification; however, this question is of critical importance for management of springs as nutrient sources.

Phosphorus

Phosphorus (P) is one of the major nutrients limiting productivity in freshwater ecosystems. During the last five decades, many studies have been conducted to determine the fate of P in freshwater systems, including springs, streams and other aquatic ecosystems. At the landscape

level, streams and wetlands form a critical interface between uplands and adjacent water bodies, as all of these ecosystems are hydrologically linked. Water and associated nutrients (such as P) are transported from uplands either by subsurface or surface flow. An idealized P cycle for spring systems is shown in Figure 9.

Both biotic and abiotic mechanisms regulate relative pool sizes and transformations of P compounds within the water column and sediment. Alterations in these fractions can occur during flow in streams and wetlands that depend on the physical, chemical, and biological characteristics of the systems (Meyer and Likens 1979). Thus, when evaluating P fate and transport in springs/spring runs, both biotic and abiotic processes must be considered. Biotic processes include assimilation by vegetation, biofilm/periphyton and sediment microorganisms. Abiotic processes include sedimentation, adsorption by sediments and organic/inorganic substrates, precipitation, and exchange processes between sediment and the overlying water column.

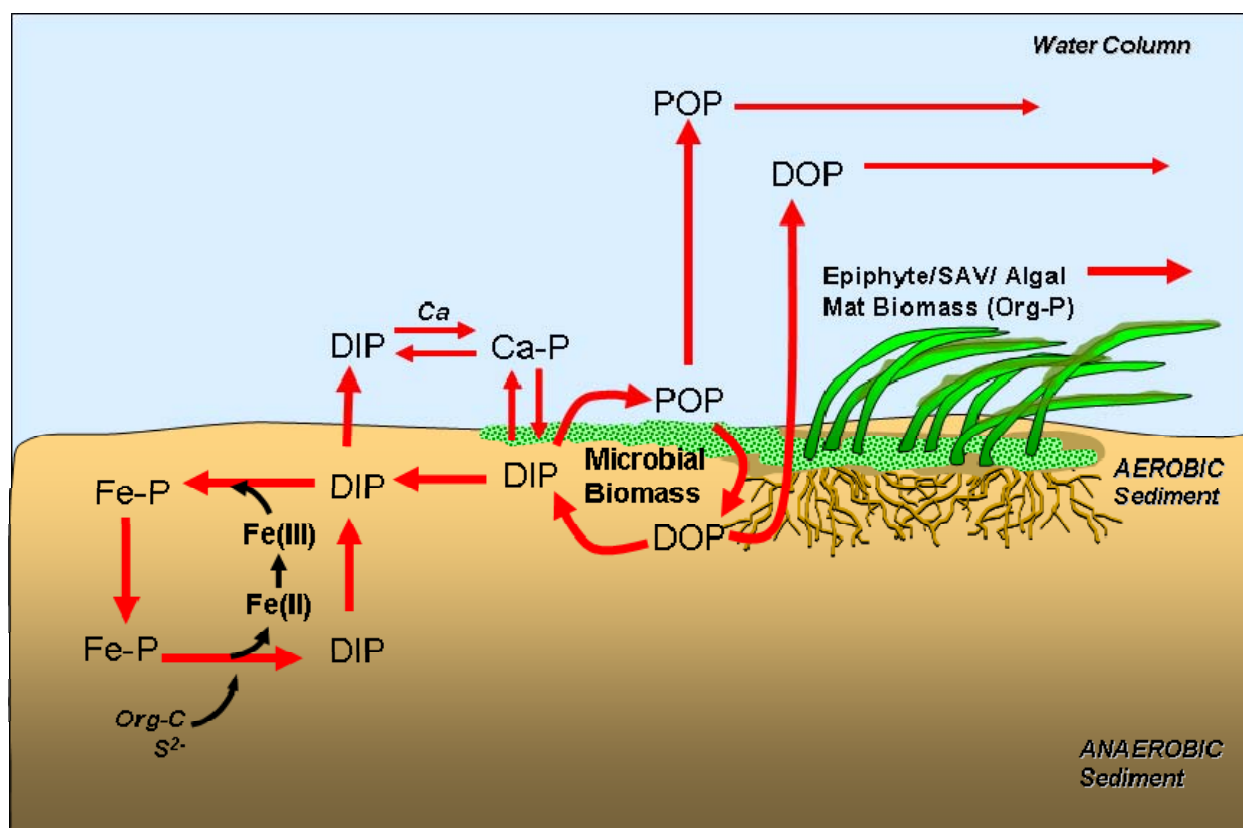


Figure 9 – Idealized diagram of the phosphorus cycle occurring in a typical spring run system. PIP=particulate inorganic P, POP=particulate organic P, DIP=dissolved inorganic P, DOP=dissolved organic P, Fe-P=iron bound P, Ca-P=calcium bound P.

Forms of phosphorus in water column and sediments

Phosphorus entering a spring system is typically present in both organic and inorganic forms. The relative proportion of each form depends upon the geology, soil, vegetation and land use

characteristics of the aquifer, or springshed. To trace the transport and transformations of P, it is convenient to classify forms of P entering these systems as (1) dissolved inorganic P (DIP); (2) dissolved organic P (DOP); (3) particulate inorganic P (PIP), and (4) particulate organic P (POP) (Figure. 9). The particulate and soluble organic fractions may be further separated into labile and refractory components. Dissolved inorganic P is considered bioavailable, whereas organic and particulate P forms generally must undergo transformations to inorganic forms before being considered bioavailable.

Inorganic P forms in sediments are characterized based on their differential solubilities in various chemical extractants. The fractionation schemes include the following pools: (1) exchangeable P; (2) Fe and Al-P or non-apatite P; (3) Ca- and Mg-bound P or apatite P; and (4) residual P or nonreactive P (Hieltjes and Lijklema 1980; van Eck 1982; Psenner *et al.* 1988; Cooke *et al.* 1992; Olila *et al.* 1995; Ruttenberg 1992; Reddy *et al.* 1998). The example in Figure 10 shows labile and non-labile pools of P in selected stream sediments of south Florida (Reddy *et al.* 1995a). In this example, the inorganic P extracted with neutral salt such as KCl represents loosely absorbed P, which usually accounts for less than 2% of the total P. This pool of P is considered bioavailable as it is sufficiently labile to enter porewater for uptake of plants or potential flux into the overlying water column.

The NaOH-P_i represents inorganic P associated with Fe and Al, and represents P not readily available. The HCl-P_i represents P associated with Ca/Mg, is also relatively stable and not readily available. Alkali extractable organic P includes both readily available organic P (microbial biomass P) and slowly available organic P (P associated with fulvic and humic acids). Residual P represents highly resistant organic P or unavailable mineral bound P not extracted either with alkali or acid. The Ca-bound P such as apatite has been found to be unavailable (Pettersson 1986; Gunatilaka 1988), while the redox-sensitive Fe-bound P may become available under anaerobic conditions (Figure 9) (Wildung *et al.* 1977; Furumai and Ohgaki 1982; Hosomi *et al.* 1981).

Although these categories allow some evaluation of properties, mobility, and quantitation, the extent of bioavailability among each of the organic P fractions can be obscure and variable. Bioassays with microbes (bacteria, algae) can yield insights on instantaneous bioavailability, but clearly sorption and desorption reactions can shift the solubilities and availabilities rapidly. These exchange reactions are markedly influenced by microbially-induced redox shifts and hence can change rapidly in water and especially in sediments.

Organic P forms may dominate the water column, with the majority of P occurring as particulates in biomass of algae and macrophytes. Some of the organic P may be associated with dissolved organic phases. The relative proportion of organic P in sediments of springs, spring runs and streams may be smaller as compared to riparian zones. In many streams accumulation of organic matter may be lower compared with riparian zones, thus resulting in lower accumulation of organic P. In organic matter, P is a major constituent, as nucleic acids (DNA and RNA), in phospholipids of membranes, and as monoesters of a variety of compounds, particularly those involved in biochemical pathways. In microorganisms and algae, more than half of the organic P is in nucleic acids, whereas phospholipids and monoesters constitute the remainder in varying proportions (Magid *et al.* 1996). Many organisms can store orthophosphate

or polyphosphates (Cembella *et al.* 1983, 1984). In plants, inositol hexaphosphate (IHP) can form a major storage compound for P, particularly in seeds.

The epiphytic community living on submerged surfaces acquires P from both the water column and from the supporting 'host' substrate. Dissolution of inorganic substrates such as minerals can potentially provide some essential nutrients to algae and microbes colonizing on them. Although relatively little of the total P pool within actively growing macrophytes is released, this released P can be important to certain epiphytic species that grow adnate to the macrophyte tissue (Moeller *et al.* 1988). Even when P concentration in the overlying water is high, some nutrients are obtained from the macrophyte simply because diffusion within the complex epiphytic community is too slow to meet demands (Wetzel 1993a). The periphyton, rather than the macrophytes, functions as the primary scavenger for limiting nutrients such as P from the water column.

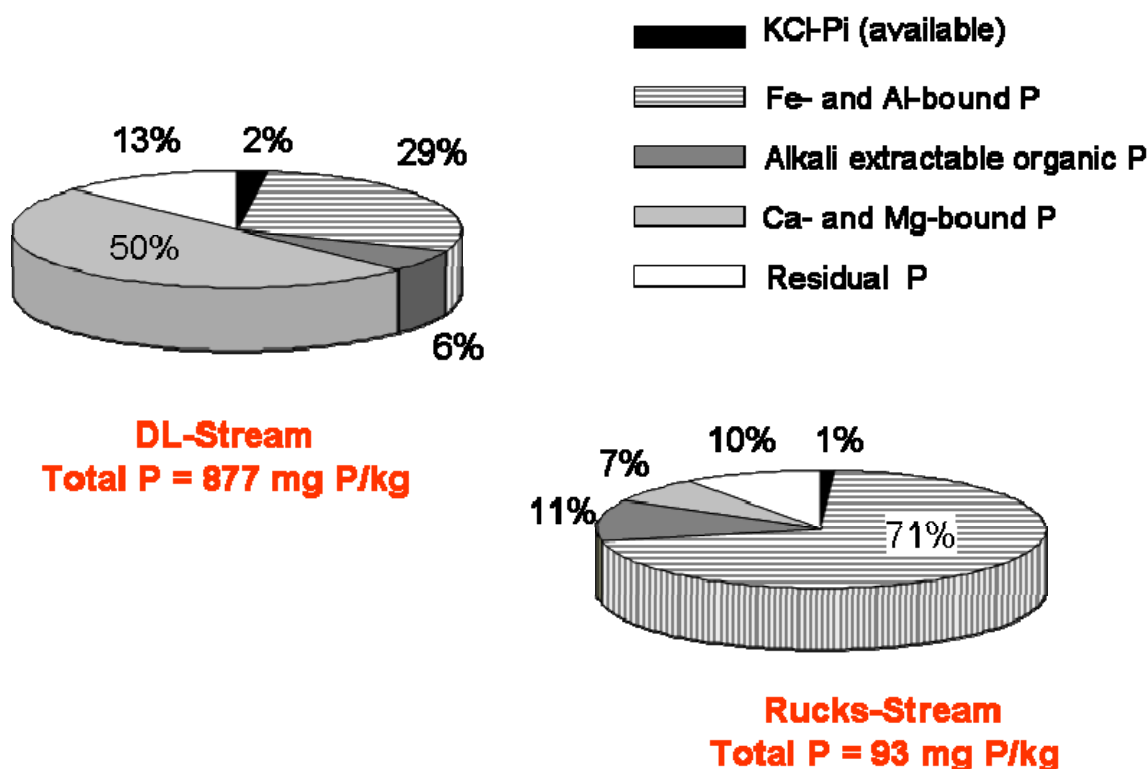


Figure 10 – Fractionation of sediment phosphorus in South Florida streams dominated by calcium (DL Stream) and iron (Rucks Stream). (From Reddy and DeLaune 2008).

Mineralization of organic phosphorus

Active cycling of organic P in sediments and water column is largely mediated by microbial metabolism. In order to understand cycling of organic P it is essential to evaluate the organically-bound P within compounds of the microbial biomass and the organismal dynamics, particularly the bacteria, as they influence organic P dynamics. Microbial metabolism influences rates of mineralization of organic P in two primary ways: (1) by direct biochemical mobilization using extracellular or periplasmic hydrolases, particularly from inositol phosphates, and (2)

through alteration of ionic composition, redox, pH, and other conditions that in turn can alter the efficacy of P binding to particulate organic matter, clays, and other soil particles, as well as solubility of organic P and its potential enzymatic hydrolysis (Reddy *et al.* 2005).

The availability of phosphate monoesters requires enzymatic cleavage of the ester linkage joining the inorganic P group to the organic moiety. Such hydrolysis is achieved by phosphomonoesterases (phosphatases) bound to or within the cell membrane or by dissolved enzymes released extracellularly within the interstitial solution adjacent to the cells. There is a general lack of specificity for the organic moiety that include, beyond phosphate monoesters, substrates such as diesters and phosphoanhydrides such as pyrophosphates, ADP, and ATP. The phosphatases of bacteria, algae, fungi, and higher plants are constitutive inorganic P-irrepressible enzymes, which tend to be intracellular and function in intermediary metabolism, or are phosphate ester-induced inorganic P-repressible enzymes, which are usually membrane-bound and function in extracellular P cleavage (Cembella *et al.* 1983).

Bacteria and microalgae growing on soil particles and within interstitial water of sediments of aquatic ecosystems are able to utilize exogenous organic P compounds through enzymatic hydrolysis of terminal phosphate groups. A broad spectrum of dissolved organic P compounds can sustain growth of these organisms, including glycerophosphate, D-glucose 6-phosphate (G-6-P), adenosine 5'-monophosphate (AMP), cytidine 5'-monophosphate (CMP), guanosine 5'-monophosphate (GP), adenylic acids, and phosphonate compounds (Cembella *et al.* 1983, 1984). Because of the high reactivity of solubilized P, the distance between sites of enzymatic hydrolysis of organic P and sites of uptake must be short, often in immediate juxtaposition (Tarafdar and Jungk 1987). Inactivation by reaction with the soil matrix increases with time after release and with greater available surface areas associated with decreasing size of soil aggregates (Linquist *et al.* 1997a).

Expectedly, a positive correlation has been found between bacterial biomass and phosphatase activity in surficial lake sediments (Reichardt 1978). Correlations between enzyme activities and bacterial biomass were less robust several centimeters below the sediment-water interface. A higher affinity of phosphatases was found in sediments where a low mobility of sediment P occurred (Pettersson unpublished; cited in Boström *et al.* 1982). The lowest substrate affinity (highest half-saturation constants) was found in organic sediments with low chemical adsorption capacities that release P under anaerobic conditions. Low availability of P in sediments often induces production of phosphatase activity with high affinity for substrates.

Biotic and Abiotic Ca Interactions

In calcium dominated streams, the presence of high Ca^{2+} can result in formation of complex calcium phosphate compounds of varying solubilities such as calcium phosphate, dicalcium phosphate, beta-tricalcium phosphate, octacalcium phosphate, and hydroxyapatite. Under these conditions, the phosphorus concentration in the pore water of calcareous sediments is a function of Ca^{2+} activity. Solubility of these compounds decreases with an increase in Ca content. Insoluble beta-tricalcium phosphate is more likely to be found at a high pH. Thermodynamically, apatite is the most stable compound, while at relatively high phosphate concentrations, dicalcium phosphate or octacalcium phosphate may form and slowly transform to the more stable phase,

hydroxyapatite. These precipitation reactions can occur on surfaces of calcite. The amount of exposed surface will determine the amount of phosphorus precipitated. In Ca-saturated clay, calcium phosphate will precipitate as a separate phase above pH 6.5; however, this depends on the concentration of phosphate ions in sediment pore water.

Algal communities can play a major role in regulating P concentrations of the water column. Algae can assimilate both organic and inorganic forms of P (Bentzen *et al.* 1992), and can induce marked changes in pH and dissolved oxygen concentration of water column and soil-floodwater interface (Carlton and Wetzel 1988). On a diurnal basis these processes can increase pH to as high as 10, depending upon the buffering capacity of the water column. These changes can potentially influence the solubility of P, especially in streams. Some studies (e.g., Hartley *et al.* 1997) have demonstrated that this process can result in significant co-precipitation of phosphorus with calcite in the presence of photosynthesizing algae, like *Chlorococcum* sp.

Retention of inorganic phosphorus by precipitation will be significant in spring waters with high Ca^{2+} and alkalinity. In calcium-dominated streams (e.g., chalk streams) a significant portion of water column phosphorus can co-precipitate with CaCO_3 where dissolved Ca^{2+} is available. House (1990) attributed only 6% of the overall phosphorus removal to co-precipitation, while the remainder was due to biological uptake. However, Salinger *et al.* (1993) found metastable calcium phosphate species to be a predominant form of phosphorus transported in the River Jordan. Several studies showed inhibition of calcite growth in the presence of high phosphorus concentrations (Avnimelech 1980; Dove and Hochella 1993) while at low phosphorus concentrations, coprecipitation of phosphorus with calcite has been observed (House and Donaldson 1986; Giannimaras and Koutsoukos 1987; Kleiner 1988). Approximately 75-90% of the phosphorus precipitated was solubilized when pH levels decreased to below 8 as a result of an increase in carbon dioxide levels (Diaz *et al.* 1994).

Biotic and Abiotic Fe Interactions

In spring and stream sediments dominated by iron minerals, reduction of ferric (Fe(III)) hydroxides and complexes results in ferrous Fe (Fe(II)), and adsorbed phosphate to be mobilized into soil pore water (Figure 9). Such conditions are of particular importance in areas where organic matter (and reducing conditions) can be transient, or when ground water varies temporally between aerobic and anaerobic states. Under strongly reducing conditions where sulfate is reduced to hydrogen sulfide, some S^{2-} can react with iron compounds (both Fe(III) and Fe(II)) resulting in the precipitation of Fe-S compounds. In this manner, sulfide formation coupled to sulfate reduction can displace iron-bound P to enhance the release of P into the interstitial waters (Wetzel 2001). The relative P release from sediments can be significantly higher as sulfate concentrations increase from natural or anthropogenic sources, particularly in oligotrophic, softwater lakes and rivers. In highly reduced soils with low sulfate content, microbial reduction generates mostly Fe(II) compounds from microbial reduction of Fe(III) oxide. PO_4^{3-} can be retained with Fe(II) compounds, but Fe-associated PO_4^{3-} is released when amorphous Fe(III) oxide is converted to iron sulfides (Roden and Edmonds 1997). Thus, the conversion of reactive soil Fe compounds to iron sulfides by sulfate-reducing bacteria can lead to a more efficient release of Fe-associated PO_4^{3-} than does direct microbial Fe(III) oxide reduction.

Overall P Cycle

Springs with high N availability should respond with higher rates of P uptake and subsequent release of DOP following senescence of biomass. Many springs do show such an increase of DOP with distance from the boil (e.g., Wekiva; Inglett *et al.* 2007). In these cases, springs should act as transformers of P or act as a small to moderate sink. In other cases, springs may actually serve as sources of P. This could occur through accumulation and mineralization of riparian vegetation deposited in the spring run, or solubilization of P contained in sediments emerging at the boil.

The process of P exchanges across the sediment-water interface is regulated by mechanisms associated with mineral-water equilibria, sorption processes (particularly ion exchange), oxygen and other electron acceptor-dependent redox interactions, and the physiological and behavioral activities of many biota from bacteria, algae to other living communities. Exchange rates between various deposits of P and the interstitial water of the sediments depend on local adsorption and diffusion coefficients and their alteration by enzyme-mediated reactions of the microbiota. The sink/source function of springs could be transient, where there are periods of storage/transformation followed by periods of flux/release. For this reason, whether individual springs act as sinks, sources, or transformers of P is highly dependent on the spring, and its physical, chemical, and biological characteristics.

Sulfur

The idealized sulfur cycle for spring systems is shown in Figure 11. The predominant forms of sulfur are organic-S (existing mostly as protein/AA-S), sulfide (S^{2-}), and sulfate (SO_4^{2-}).

Sulfide Oxidation

Emerging groundwater potentially contains quantities of S^{2-} that become oxidized when contacting atmospheric and photosynthetically-produced O_2 near the boil/vent. This reaction is thermodynamically favorable, and several groups of bacteria (e.g., *Thiobacillus* spp.) can utilize this energy yield to fix atmospheric C (lithoautotrophy), or respire organic C (heterotrophy). Data from several springs indicate this process may be occurring. Sulfide is rarely determined in routine monitoring, but some springs show post-boil increases in SO_4^{2-} (Wekiva, e.g.; Wetlands Solutions, Inc. (2005)) indicating that S^{2-} oxidation could be occurring.

Springs with high SO_4^{2-} content may also host this process, but it likely occurs pre-boil (e.g., Juniper Springs). Other evidence for sulfur oxidizing pathways in spring systems comes from a study by Caldwell *et al.* (1975) who found large numbers of S-oxidizing bacteria including the genera *Thiothrix* and *Thiocystis* in a sulfur spring in the Florida Keys (Flowing Well) and several springs associated with lakes in Michigan. These bacteria were found attached as filaments or mucilage-encased microcolonies on aerobic surfaces of plants, interspersed with other filamentous algae, or on decomposing organic matter. Gradient culture techniques revealed that these S-oxidizing genera were culturable even at the lowest S levels tested ($55 \mu\text{mol S l}^{-1}$).

Sulfate Reduction

Sulfate present in the water column of spring runs can be utilized as an electron acceptor by select bacteria decomposing simple organic substrates (dissimilatory sulfate reduction). This process where SO_4^{2-} becomes reduced to S^{2-} only occurs under highly reducing conditions with redox potentials less than 200 mV. For this reason, measurable sulfate reduction is likely only possible in slow-moving spring runs or areas with high organic matter sediments (algal mats, SAV beds, litter accumulations).

Sulfate reducers are obligate anaerobes that couple oxidation of organic substrates to carbon dioxide with the reduction of the terminal electron acceptor sulfate to sulfides (Widdel 1998). Sulfate reducing bacteria cannot synthesize hydrolytic enzymes, thus they cannot hydrolyze polymers such as polysaccharides, and many groups cannot use monomers such as monosaccharides (e.g., glucose) as substrates for energy. As a result, sulfate reducers are dependent on fermenting bacteria to oxidize monomers to simple readily utilizable organic compounds.

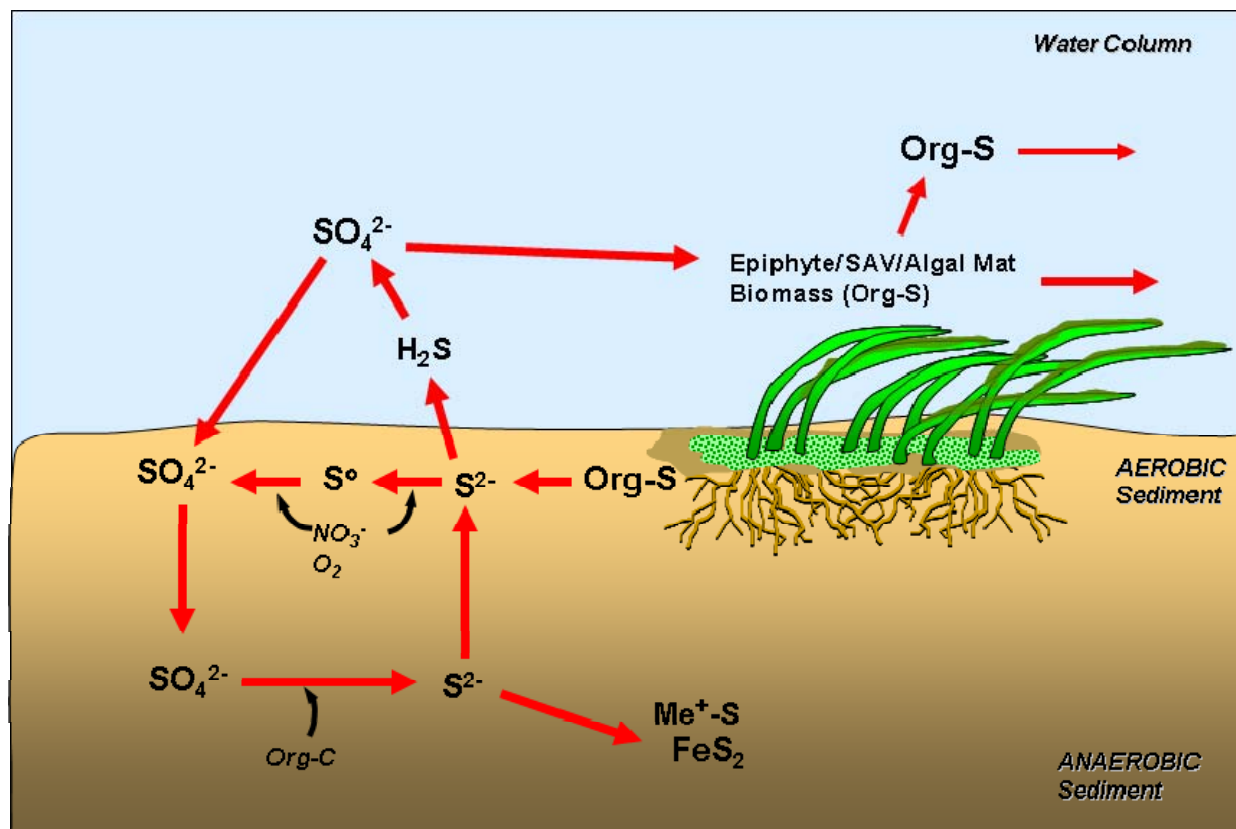


Figure 11 – Idealized diagram of the sulfur cycle occurring in a typical spring run system.

Overall S Cycle

Because of the prevalence of oxidizing conditions in the water column, most spring runs should result in a net export of oxidized S species (S^{2-} oxidized post boil). With the exception of the initial degassing at the boil of some high S springs, most Florida springs should not emit significant amounts of S as H_2S . The only other significant quantity of S compounds should be through the transport (loss) of organic-S in organic matter carried downstream.

EFFECTS OF INCREASED NUTRIENTS

Carbon/Organic Matter Impacts

Common ecological theory would predict that addition of nutrients to a nutrient-limited system will enhance productivity and lead to greater overall cycling of C through the organic pool. However, a study of four spring runs by Wetland Solutions, Inc. (2005) found that spring runs with higher nutrient levels (Wekiva and Rock Springs) had lower ecosystem productivity estimated through total system metabolism (DO gain/loss) than the reference spring runs (Alexander and Juniper). Increased nutrients leading to algal dominance and growth (even if not resulting in an overall increased productivity) would still reflect a change in the quality of organic matter in the system and could have cascading effects through other heterotrophic communities both locally and further downstream.

Other aspects of the C cycle in springs could be altered through the addition of C. Increased C inputs could occur through increased sewage/pollutant discharges which would act to raise the concentration of solids C or DOC. Management of exotics/invasives could also have profound impacts on nutrient dynamics through increased and episodic deposition of C following herbicide application. The effects of large discharges of C into streams are well known and most likely the same effects apply to springs, spring runs and springsheds. In particular, the introduction of large C quantities increase respiration losses of oxygen and other electron acceptors and increase production of significant quantities of reduced compounds potentially affecting many of the nutrient cycles, including N (increased denitrification), or P (increased release of iron-bound P).

Nitrogen Impacts

In the natural state, most Florida springs contain high levels of inorganic P, and based on N:P ratios, are N-limited. In the N-limited state, springs would be considered highly susceptible to N pollution. One of the key responses to N in these cases would be increased biomass or shifts in dominant species of all groups, including algae, macrophytes, fungi and bacteria. One example of this would be that under N-limiting conditions there should be a dominance of particular N-fixing microbiota. With the shifts in species composition, changes in C abundance and quality can also be expected. For example, increased algal production would result in lower amounts of structural plant C compounds (cellulose, lignin) and an overall, more available C supply for aquatic heterotrophs.

Nitrate is by far the most commonly reported N pollutant, and has increased dramatically, in Florida's major springs during the last 30 years (Scott *et al*, 2004). With this trend, many springs

are increasingly becoming P limited (Figure 12) (Inglett *et al.* 2007; Frazer *et al.* 2001). Aside from effects of incomplete denitrification (producing NO_2^- and potentially N_2O), it is currently uncertain if high levels of NO_3^- can have any other adverse impacts to biogeochemical processes.

Phosphorus Impacts

In general, many springs already have high amounts of bioavailable P with SRP levels >80 ppb. High levels of bioavailable P lead to the general observation of low water column N:P ratios in most springs (i.e., those unaffected by NO_3^- pollution) (Figure 12). As in other aquatic systems, elevated P levels should result in higher overall productivity, or if limited by some other nutrient (or light) a higher potential productivity level. For this reason, P availability may determine the overall threshold response of a given spring system to another nutrient, such as N. This response may be visible only through increased productivity of certain spring species; however, in this manner, high-P springs may demonstrate a greater response (either through greater overall production or that of individual species) or be more susceptible to increased N.

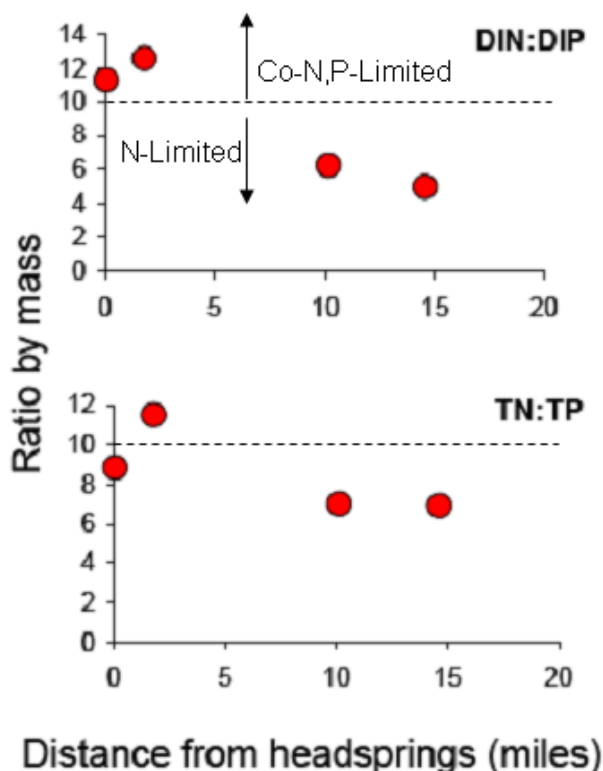


Figure 12 – Ratios of dissolved inorganic N:P and total N:P (mass basis) in the Wekiva river in relation to theoretical boundary between conditions of N limitation and conditions co-limited by N and P. (From Inglett *et al.* 2007)

Sediments in spring systems have the capability to store P as Ca-P or Fe-P complexes, and thus could be a reservoir of P that becomes mobilized upon increased levels of N. Fluctuations in water column P levels will determine if the sediments act as a sink or source, as low water

column P levels will favor flux of sedimentary P. The response of some systems to additions of P has been observed as a decrease in macrophytes chlorophyll levels. This may reflect changes in the microbial composition or the stoichiometric balance of N:P and C:P which could shift the dominance of autotrophs to more heterotrophic communities. Increased heterotrophy would have cascading type effects on the balance of aerobic/anaerobic conditions, and thus, would also effect the cycling of redox-sensitive elements such as N, P, Fe, and S.

Sulfur Impacts

It is uncertain what role S may be playing in the biogeochemistry of Florida springs. Sulfur can be significant as an electron acceptor (as SO_4^{2-}) with a toxic byproduct of S^{2-} . Also, S^{2-} can become a powerful electron donor for particular organism groups and can diversify the pathways for NO_3^- removal through denitrification. Furthermore, the impacts of sulfur may not be immediately visible from data collected at the boil/vent. The oxidation pathways and processes may develop slowly following groundwater emergence and may be temporally variable. These effects may also be spatially localized to zones of significant S input or transformation such as the mixing of spring water with contrasting water high in S (e.g., that observed when tributaries meet).

SUMMARY AND CONCLUSIONS

Based on the above discussion, springs are clearly dynamic systems with a myriad of potential biogeochemical processes/reactions and interactions among elemental cycles. Although the majority of these basic biogeochemical processes have been identified in other aquatic systems, many may not be universally applied to spring systems because of their unique features including karst-derived water chemistry, and relatively constant temperature and flow conditions. A diversity of conditions within spring systems also gives rise to numerous microbially active zones where conditions may exist for as yet unexplored processes and pathways.

Nutrient cycles in spring systems are dominated by the conversion of inorganic to organic forms. Organic matter (dissolved and particulate forms) is therefore an important component of the spring system as it is both an internal supply of nutrients and a form of nutrient export. Carbon is also the basis of many other anaerobic biogeochemical reactions, and is thus an important determinant in the cycling of other nutrients including nitrogen, phosphorus, and metals. Despite this importance, organic matter distributions, concentrations, and quality types within spring systems are relatively unstudied, but may have an importance for how individual springs process and store nutrients. Also, aquatic plant management practices can be a contribution of organic matter deposition in spring runs (affecting internal nutrient cycling); however, the importance of the process is undetermined.

Nitrogen has been a nutrient of great interest in the Florida springs due to its trend of increasing concentrations in the springs which are associated to changes in spring appearance, especially increases in algae. In addition to external loads of N through NO_3^- , nitrogen fixation is an important processes contributing to N, but is also currently unstudied in Florida springs. There are several pathways which can act to convert NO_3^- (reducing its concentration), with the dominant most likely being heterotrophic denitrification or plant assimilation. The importance

of these two pathways will largely determine if a spring is a sink or source of N; however, current studies have not attempted to partition N flow through each pathway. High flow rates and patchy distributions of organic matter also indicate that conditions in many springs could support several alternative (novel) pathways of NO_3^- reduction, but again, these have received no attention.

Phosphorus may also play a key role in regulating species composition or productivity in a spring system. A variety of biotic and abiotic processes act to determine the biogeochemical cycling of phosphorus in spring systems. The generally high calcium content of many spring waters leads to the potential for accumulation of Ca-P compounds associated with biotic growth and mineral forms in sediments. Organic matter and associated enzymatic hydrolysis of organic P compounds is also another key mechanism regulating both accumulation and bioavailability of phosphorus in springs. Despite the significance of these processes; however, the general lack of studies focusing on sediment properties currently limits our understanding of P cycling, or its importance as an internal nutrient supply mechanism.

Several other elements could have importance for nutrient cycling in spring systems including sulfur and iron. Iron participates in redox reactions that determine both its form and solubility/mobility and its particular interaction with PO_4^{3-} (affecting P availability). Iron is also significant as a potential limit to algal growth in certain highly alkaline systems. Like iron, sulfur can undergo dynamic transformations through redox processes in alternating aerobic/anaerobic systems like springs. Presence of sulfide is likely only a problem (toxicity) in certain sulfur spring systems; however, there is a possibility that sulfide-driven denitrification may be a significant process reducing NO_3^- levels in some aquifers and in some spring runs.

Management and Policy Implications

Nutrient enrichment of Florida springs is major concern. The steady increase in nutrient concentrations observed in many Florida springs during the past four decades threatens the economic and ecological value of these springs. Nonpoint sources of nutrients dominate eutrophication processes of many Florida springs. Thus, most recommendations involve the use of alternative land management practices in the watershed in an effort to reduce the overall load to these springs. The key management questions often asked are: (1) Will springs respond to external nutrient load reduction?, and (2) If so, how long will it take for these systems to recover and reach their background condition?

The question of system impact is important for management of spring systems. Nutrient limitation and biogeochemical processes are a very interactive to determine the biotic response of a given spring to external nutrient loads. The chemistry of spring source water is crucial to determine the types of metabolic pathways and diversity of organisms that will populate/dominate a spring ecosystem. In particular, microbial communities will likely demonstrate responses to changes in nutrient conditions immediately through changes in species or functional groups and through activities of enzymes which are produced in response to their external chemical environment. In this way, monitoring of biogeochemical processes may serve as an early warning indicator of spring health.

Much of the nutrients added to springs can be retained within the system through the accumulation of large reserves in detrital tissue and/or reactive forms in sediments. These nutrient stores can serve as a nutrient source for long period of time, even after external loads are reduced. As discussed in this paper, various biogeochemical processes in sediment and water column regulate the mobility and reactivity of stored nutrients. The cycling of nutrients can extend the time required for springs to reach their original condition, with a lag time from a few years to several decades, depending on the extent of internal nutrient supply. This lag time for recovery should be considered in developing management strategies and monitoring efforts, where environmental managers must recognize that the recovery process is not immediate, even despite successful reductions in external loads.

To determine the role of internal nutrient supply from sediments, it is important to document storages and fluxes of nutrients between sediment, vegetation, and water column. At this time little or no information is available on internal cycling of nutrients and its overall role in regulating eutrophication process. When considering internal cycling of nutrients in springs, several issues need be addressed. These issues are: (1) what is the relative bioavailability of various nutrient forms stored in sediments and water column? (2) how stable are the stored nutrients and under what conditions could they be released back into the water column? and (3) how long could the stored nutrients serve as a source to the water column to maintain eutrophic conditions, once external loads are reduced? Thus, monitoring internal nutrient storages on a regular basis is equally as important as monitoring external nutrient loads. Such information will be useful to the state's Department of Environmental Protection as it attempts to establish nutrient criteria and Total Maximum Daily Loads (TMDLs) for springs.

RESEARCH NEEDS

Biogeochemistry is one of the least studied aspects of spring systems. The complexity of biogeochemical pathways, the complexity of the high energy/lotic spring environment, and the diversity of spring water types makes it difficult to form any wide-ranging generalizations. For this reason, biogeochemistry is also one of the aspects of spring systems requiring additional effort to increase our understanding of spring nutrient impacts. Based on the review of literature presented, the following are our recommendations for research related to the effects and consequences of nutrients in calcareous spring systems.

Specific Research Recommendations

Biogeochemical Characterization

There is general lack of data on characterization of spring systems for biogeochemical purposes. Characterization data and long term measurements of water chemistry are available; however, the addition of some parameters to this monitoring are warranted, including sulfide (S^2) and reduced iron (Fe(II)). Also, there is a large uncertainty in the function of sediments for storage and cycling of nutrients. Identification of biogeochemically active zones will depend on knowledge of sediment mineralogy, organic matter contents and qualities, and stratigraphic morphology. For this reason, data should also be collected to characterize the biogeochemical properties of spring run sediments including basic nutrient chemistry, mineralogy, and potential

storages of nutrients in the sediments of most springs/runs. Better mapping of spring run sediment characteristics can also help improve modeling of nutrient dynamics within a given spring run (including sediment function as sink or source of nutrients).

Source and Fate of N

Research is needed to understand the fate of N within the spring system. This would include understanding of biotic uptake processes (algal/macrophyte uptake), importance of different N sources (NH_4^+ , NO_3^- , DON), and the occurrence, rates and importance of biological N_2 -fixation. Whole spring run N budgets should be performed to better isolate the processes responsible for N decline, and these data put in the context of nutrient limitation of systems of differing geology, channel morphology, water chemistry, and biotic productivity. Given the potential for structuring aquatic microbial communities, the presence and effects of potential DON sources (including urea) should be investigated in relation to algal composition, microbial activity, and community nutrient limitation. Potential pathways of NO_3^- loss should also be investigated, including identification of hotspots of denitrification as well as the potential occurrence and conditions regulating any novel N loss pathways (e.g., lithotrophic Fe(II)/S^{2-} oxidation coupled to denitrification, or anammox).

A variety of techniques can be employed to help answer some of these questions regarding N cycling and fate in spring systems. Determination of system N uptake can be done in small batch or whole stream segments (Saunders 2007; Wetland Solutions, Inc. 2005). Relative estimates of enzyme activities are simple to conduct and provide information regarding spatial or temporal distribution of processes (Inglett *et al.* 2007). Other enzyme assays can be used to provide quantitative estimates of N processes such as the determination of denitrification using the traditional acetylene inhibition assay (DEA technique; Inglett *et al.* 2007) or N_2 fixation assays (Inglett *et al.* 2004). It is well known that natural abundance level stable N isotopic methods can be used to assess sources of N in spring systems; however, the analysis of $\delta^{15}\text{N}$ can also provide information on rates of N uptake or denitrification (De Brabandere *et al.* 2007). Experiments utilizing tracer levels of ^{15}N can also provide useful identification of N pathways (e.g., novel NO_3^- reduction pathways) as well as quantitative information of pathways and flows (e.g., N_2 fixation, N uptake, and denitrification).

Carbon Dynamics

Carbon sources and distribution play a key role in structuring the biogeochemistry of the spring system, therefore better understanding is needed regarding the sources and processing of C in spring systems. This would include identification and quantification of autochthonous and allochthonous C sources (quantities and qualities), availability and cycling of different C types, and investigation of the importance of different C sources for respiration processes and denitrification. The role of aquatic plant management in the distribution and fate of C within particular systems is also of significant concern as it constitutes a significant source of C and nutrients within the system.

Sulfur Distribution and Function

Little attention is given to sulfur contents of ground waters, except where smell or taste issues are concerned; however, S may be a key element regulating several biogeochemical cycles including N and P. For this reason, more emphasis should be given to S as it relates to biogeochemical processes including its distribution and redox state in spring environments (i.e., locations of oxidized and reduced S accumulations). One of the more important aspects of the uncertain role of sulfur is its potential involvement in regulating N and P biogeochemistry, therefore, studies linking redox processes with denitrification or P flux from sediments are potentially useful for elucidating the functioning of S in some nutrient-impacted spring systems.

Coupled Biogeochemical Cycles

Identifying and understanding biogeochemical pathways is of critical importance; however, as should be evident from this review, biogeochemical processes do not act independently in natural systems. From the basic concept of organic matter and biotic productivity, it can be seen that elements (and thus elemental cycles) are tied together (or coupled) so that the pathways of one cycle inherently affect the pathways of another element.

Currently, there have been no attempts to understand the coupled nature of cycles (N and P; S, N, and P; S and trace metals) in spring systems. Not only could this have important implications for understanding both the localized effects of nutrients on the biota (e.g., questions of N versus P limitation), but it could also have application to modeling the function of these systems as sinks, sources or transformers of nutrients and C at the landscape scale. For this reason, there should be increased focus on assessing the potential for linkages between biogeochemical cycles (C, N, P, and S) as they relate to landscape patterns of geomorphology, species composition/productivity, land use, and nutrient impact. In addition, data sets (both current and future) should incorporate the concepts of coupled biogeochemical cycles when collecting data to assess spatial and temporal scales.

REFERENCES

- Alfaro C., and M. Wallace. 1994. Origin and classification of springs and historical review with current applications. *Environmental Geology* 24:112-124.
- Allan, J.D. and M.M. Castillo. 2007. *Stream Ecology: Structure and Function of Running Waters*. 2nd Edition. Springer Netherlands.
- Anthonisen, A.C., R.C. Loehr, T.B.S. Prakasam and E.G. Srinath. 1976. Inhibition of nitrification by ammonia and nitrous acid, *Journal of Water Pollution Control Federation* 48: 835–852.
- Bartodziej W. and J.A. Perry. 1990. Litter processing in diffuse and conduit springs. *Hydrobiologia* 206:87-97.
- Benner, R., M.A. Moran and R.E. Hodson. 1985. Effects of pH and plant source on lignocellulose biodegradation rates in two wetland ecosystems, the Okefenokee Swamp and a Georgia salt marsh. *Limnology and Oceanography*. 30: 489 - 499.
- Bentzen, E., W. D. Taylor and, E. S. Millard. 1992 The importance of dissolved organic phosphorus to phosphorus uptake by limnetic plankton. *Limnology and Oceanography* 37, 217–231.
- Berrie, A. D. 1992. The chalk-stream environment. *Hydrobiologia* 248:3-9.
- Berman, T. and D. A. Bronk. 2003. Dissolved organic nitrogen: a dynamic participant in aquatic ecosystems. *Aquatic Microbial Ecology* 31:279-305.
- Bertocchi, C., L. Navarini, and A.Cesàro. 1990. Polysaccharides from cyanobacteria. *Carbohydrate Polymers* 12: 127–153.
- Boström, B., M. Jansson and C. Forsberg. 1982. Phosphorus release from lake sediments. *Arch. Hydrobiol. Beih.* 18: 5–59.
- Burgin, A.J., and S.K. Hamilton. 2007. Have we overemphasized the role of denitrification in aquatic ecosystems? A review of nitrate removal pathways. *Frontiers in Ecology and the Environment* 5: 89-96.
- Caldwell D.E., S.J. Caldwell and J.M. Tiedje. 1975. An ecological study of the sulfur oxidizing bacteria from the littoral zone of a Michigan lake and a sulfur spring in Florida. *Plant and Soil* 43:101-114.
- Carlton, R.G. and R.G. Wetzel. 1988. Phosphorus flux from lake sediments: effects of epipellic algal oxygen production, *Limnology and Oceanography* 33:562–570.

- Cembella, A.D., N.J. Antia, and P.J. Harrison. 1984a. The utilization of inorganic and organic phosphorus compounds as nutrients by eukaryotic microalgae: a multidisciplinary perspective: part 1. *CRC Critical Reviews in Microbiology*, 10: 317-391.
- Cembella, A.D., N.J. Antia and P.J. Harrison. 1984b. The utilization of inorganic and organic phosphorus compounds as nutrients by eukaryotic microalgae: a multidisciplinary perspective: part 2. *CRC Critical Reviews in Microbiology*, 11, 13-81.
- Chróst, R.J. 1991. *Microbial Enzymes in Aquatic Environments*. - Springer-Verlag, New York, str. 385.
- Cole, J. A. 1988. Assimilatory and dissimilatory reduction of nitrate to ammonia, p. 281-329. In J. A. Cole, and S. J. Ferguson (Eds.), *The nitrogen and sulphur cycles*. Cambridge University Press, Cambridge, United Kingdom.
- Cooke, J.G. 1992. Phosphorus removal processes in a wetland after a decade of receiving a sewage effluent. *Journal of Environmental Quality*. 21:733-739.
- Costerton, J.W., Z. Lewandowski, D.E. Caldwell, D.R. Korber and H.M. Lappin-Scott. 1995. Microbial biofilms. *Annual Reviews of Microbiology* 49: 711-747.
- Cotton, J.A., G. Wharton, J.A.B. Bass, C.M. Heppell, and R.S. Wotton. 2006. The effects of seasonal changes to in-stream vegetation cover on patterns of flow and accumulation of sediment. *Geomorphology* 77:320-334
- Darling, W.G. and D.C. Gooddy. 2006. The hydrogeochemistry of methane: Evidence from English groundwaters. *Chemical Geology* 229:293-312.
- Dawson, F.H. 1980. The origin, composition and downstream transport of plant material in a small chalk stream. *Freshwater Biology* 10:419-435.
- De Brabandere L., T.K. Frazer and J.P. Montoya. 2007. Stable nitrogen isotope ratios of macrophytes and associated periphyton along a nitrate gradient in two subtropical, spring-fed streams. *Freshwater Biology* 52:1564-1575.
- DePhilippis R. and M. Vincenzini. 1998. Exocellular polysaccharides from cyanobacteria and their possible applications. *Federation of European Microbiological Scientists, Microbiology Reviews*. 22:151-175.
- Diaz, O.A., K.R. Reddy and P.A. Moore, Jr. 1994. Solubility of inorganic phosphorus in stream water as influenced by pH and calcium concentration. *Water. Research*. 28:1755-1763.
- Dove P.M. and M.F. Hochella, Jr. 1993. Calcite precipitation mechanisms and inhibition by orthophosphate: In situ observation by scanning force microscopy. *Geochimica et Cosmochimica Acta* 57 :705-714.

- Dreybrodt, W., D. Buhmann, J. Michaelis and E. Usdowski. 1992. Geochemically controlled calcite precipitation by CO₂ outgassing - field-measurements of precipitation rates in comparison to theoretical predictions. *Chemical Geology* 97:285-294.
- Drysdale, R.N., M.P. Taylor and C. Ihlenfeld. 2002. Factors controlling the chemical evolution of travertine-depositing rivers of the Barkly karst, northern Australia. *Hydrological Processes* 16:2941-2962.
- Duff, J.H., F. Murphy, C.C. Fuller, F.J. Triska, J.W. Harvey and A.P. Jackman. 1998. A mini drivepoint sampler for measuring pore water solute concentrations in the hyporheic zone of sand-bottom streams. *Limnology and Oceanography* 43:1378-1383.
- Eivazi, F. and M.A. Tabatabai. 1988. Glucosidases and galactosidases in soils. *Soil Biology and Biochemistry* 20:601-606.
- Espeland, E. M., S.N. Francoeur and R.G. Wetzel. 2001. Influence of algal photosynthesis on biofilm bacterial production and associated glucosidase and xylosidase activities. *Microbial Ecology* 42:524-530.
- Florida Springs Task Force. 2006. Florida's Springs: Strategies for Protection and Restoration. Report by the Florida Springs Task Force. Florida Department of Environmental Protection. Tallahassee, Florida.
- Frazer, T.K., M.V. Hoyer, S.K. Notestein, J.A. Hale and D.E. Canfield Jr. 2001. Physical, Chemical, and Vegetative Characteristics of Five Gulf Coast Rivers. Report prepared for South Water Florida Water Management District. West Palm Beach, Florida.
- Frost, P.C. and J.J. Elser. 2002. Effects of light and nutrients on the accumulation and elemental composition of epilithon in boreal lakes. *Freshwater Biology* 47: 173-184.
- Freytet, P. and E. P. Verrecchia. 1998. Freshwater organisms that build stromatolites: a synopsis of biocrystallization by prokaryotic and eukaryotic algae. *Sedimentology* 45:535-563.
- Furumai, H. and S. Ohgaki, 1988. Radiochemical analysis of phosphorus exchange kinetics between sediments and water under aerobic conditions. *Journal of environmental Quality* 17: 205-212.
- Goto, N., T. Kamawura, O. Mitamura and H. Terai. 1999. Importance of extracellular organic carbon production in the total primary production by tidal flat diatoms in comparison to phytoplankton. *Marine Ecology Progress Series* 190:289-295.
- Grimaldi, C. and V. Chaplot. 2000. Nitrate depletion during within-stream transport: Effects of exchange processes between streamwater, the hyporheic and riparian zones. *Water Air and Soil Pollution* 124:95-112.

- Guasch, H., J. Armengol, E. Marti and S. Sabater. 1998. Diurnal variation in dissolved oxygen and carbon dioxide in two low-order streams. *Water Research* 32:1067-1074.
- Hartley, A.M., W.A. House, B.S.C. Leadbeater and M.E. Callow. 1997. Co-precipitation of phosphate with calcite in the presence of photosynthesising green algae. *Water Research* 31: 2261–2268.
- Harvey, J.W. and B.J. Wagner. 2000. Quantifying hydrologic interactions between streams and their subsurface hyporheic zones. pp 3-44. In: J.B. Jones and P.J. Mulholland (Eds.): *Streams and Groundwaters*. Academic Press.
- Heil, C.A., M. Revilla, P.M. Glibert and S. Murasko. 2007. Nutrient quality drives differential phytoplankton community composition on the West Florida Shelf. *Limnology and Oceanography* 52:1067–1078.
- Hoagland K.D., J.R. Rosowski, M.R. Gretz, S.C. Roemer. 1993. Diatom extracellular polymeric substances: function, fine structure, chemistry, and physiology. *Journal of Phycology* 29:537–566.
- House, W.A. 1990. The prediction of phosphate coprecipitation with calcite in freshwaters. *Water Research*. 24 : 1017–1023.
- Inglett K.S., P.W. Inglett and K.R. Reddy. Microbial Enzyme Activity in Wekiwa Springs. Palatka, FL: St. John's River Water Management District; 2007.
- Inglett, P.W., K.R. Reddy and P.V. McCormick. 2004. Periphyton chemistry and nitrogenase activity in a nutrient-impacted Everglades ecosystem. *Biogeochemistry* 67: 213-233.
- Joye, S.B., S.V. Smith, J.T. Hollibaugh and H. W. Paerl. 1996. Estimating denitrification rates in estuarine sediments: a comparison of stoichiometric and acetylene based methods. *Biogeochemistry* 33: 197-215.
- Kelso, B.H. L., R.V. Smith and R.J. Laughlin. 1999. Effects of carbon substrates on nitrite accumulation in freshwater sediments. *Applied and Environmental Microbiology* 65:61-66.
- Kelso, B.H.L., R.V. Smith, R.J. Laughlin and S.D. Lennox. 1997. Dissimilatory nitrate reduction in anaerobic sediments leading to river nitrite accumulation. *Applied and Environmental Microbiology* 63:4679-4685.
- Linares, F. and K. Sundback. 2006. Uptake of dissolved free amino acids (DFAA) by microphytobenthic communities. *Aquatic Microbial Ecology* 42:175-186.
- Liu, Z.H., Q. Li, H.L. Sun, C.J. Liao, H.J. Li, J.L. Wang, and K.Y. Wu. 2006. Diurnal variations of hydrochemistry in a travertine-depositing stream at Baishuitai, Yunnan, SW China. *Aquatic Geochemistry* 12:103-121.

- Madsen, T.V. and N. Cedergreen. 2002. Sources of nutrients to rooted submerged macrophytes growing in a nutrient-rich stream. *Freshwater Biology* 47:283-291.
- Magid, J., H. Tiessen and L.M. Condron. 1996. Dynamics of organic phosphorus in soils under natural and agricultural ecosystems. p. 429–466. In A. Piccolo (ed.) *Humic substances in terrestrial ecosystems*. Elsevier, Oxford.
- Mahler B.J. and F.L. Lynch. 1999. Muddy waters: temporal variation in sediment discharging from a karst spring. *Journal of Hydrology* 214:165-178.
- Melzer, A. and R. Kaiser. 1986. Seasonal-variations in nitrate content, total nitrogen, and nitrate reductase activities of macrophytes from a chalk stream in upper bavaria. *Oecologia* 69:606-611.
- Meyer, J.L. and G.E. Likens. 1979. Transport and transformation of phosphorus in a forest stream ecosystem, *Ecology*, 60: 1255–1269.
- Moeller, R.E., J.M. Burkholder and R.G. Wetzel, 1988 Significance of sedimentary phosphorus to a rooted submersed macrophyte (*Najas flexilis* (Willd.) Rostk. and Schmidt) and its algal epiphytes. *Aquatic Botany* 32 : 261–281.
- Neely, R.K. and R.G. Wetzel. 1995. Simultaneous use of ¹⁴C and ³H to determine autotrophic production and bacterial protein production in periphyton. *Microbial Ecology* 30:227-237.
- Notestein S.K., T.K. Frazer, M.V. Hoyer and D.E. Canfield. 2003. Nutrient limitation of periphyton in a spring-fed, coastal stream in Florida, USA. *Journal of Aquatic Plant Management* 41:57-60.
- Olila, O.G., K.R. Reddy and W.G. Harris. 1995. Forms and distribution of inorganic phosphorus in sediments of two shallow eutrophic lakes in Florida. *Hydrobiology* 302:147–161.
- Otero, A. and M. Vincenzini. 2003. Extracellular polysaccharide synthesis by Nostoc strains as affected by N source and light intensity, *Journal of Biotechnology*. 102, 143–152.
- Paul, J.W. and E.G. Beauchamp. 1989 Denitrification and fermentation in plant-residue-amended soil. *Biology and Fertility of Soils* 7 :303–309.
- Pettersson, K. 1986. The fractional composition of phosphorus in lake sediments of different characteristics. In P.G. Sly (Ed.) *Sediments and Water Interactions*. pp. 149 - 55. Springer, New York.
- Pinckney, J.L. and H.W. Paerl. 1997. Anoxygenic photosynthesis and nitrogen fixation by a microbial mat community in a Bahamian hypersaline lagoon. *Applied and Environmental Microbiology* 63: 420 426.

- Pronk, M., N. Goldscheider and J. Zopfi. 2006. Dynamics and interaction of organic carbon, turbidity and bacteria in a karst aquifer system. *Hydrogeology Journal* 14:473-484.
- Reddy, K.R., O.A. Diaz, L.J. Scinto and M. Agami. 1995 Phosphorus dynamics in selected wetlands and streams of the Lake Okeechobee Basin. *Ecological Engineering* 5:183–207.
- Reddy, K. R., Y. Wang, W.F. DeBusk, M.M. Fisher and S. Newman. 1998. Forms of soil phosphorus in selected hydrologic units of the Florida Everglades. *Journal of Soil Science Society America* 62:1134-1147.
- Reichardt W. 1978. Responses of phosphorus remobilizing Cytophaga species to nutritional and thermal stress. *Verhandlungen der Internationalen Vereinigung für Theoretische und Angewandte Limnologie* 20:2227-2232.
- Renstrom E. and B. Bergman. 1989 Glycolate metabolism in cyanobacteria. 1. Glycolate excretion and phosphoglycolate phosphatase activity. *Plant Physiology* 75:137–143.
- Roden, E.E. and J.W. Edmonds. 1997. Phosphate mobilization in iron-rich anaerobic sediments: microbial Fe(III) oxide reduction vs. iron-sulfide formation. *Arch. Hydrobiol.* 139:347-378.
- Saunders, T. 2007. Multi-Scale Analysis Of Benthic Biogeochemical Properties And Processing In A Spring-Fed River And Estuary. PhD Dissertation. University of Florida. Gainesville, FL.
- Scott, T.M., G.H. Means, R.P. Meegan, R.C. Means, S.B. Upchurch and R.E. Copeland. 2004. Springs of Florida (CD version). Florida Geological Survey Bulletin No. 66. Florida Department of Environmental Protection. Tallahassee, FL.
- Sinsabaugh, R. L., R. K. Antibus, A. E. Linkins, C. A. McClaugherty, L. Rayburn, D. Repert and T. Weiland. 1993. Wood Decomposition: Nitrogen and Phosphorus Dynamics in Relation to Extracellular Enzyme Activity. *Ecology* 74: 1586-1593.
- Sinsabaugh, R. L. 1994. Enzymic analysis of microbial pattern and process. *Biology and Fertility of Soils* 17:69-74.
- Sinsabaugh, R.L., S. Findlay, P. Franchini and D. Fisher. 1997. Enzymatic analysis of riverine bacterioplankton production. *Limnology and Oceanography* 42:29–38.
- Slack, L.J., J.C. Rosenau. 1979. Water Quality of Florida Springs. Map Series 96. Tallahassee, Florida.: U.S. Geological Survey and Florida Department of Environmental Regulation; 1979.
- Smith, C.J., R.D. DeLaune and W.H. Patrick, Jr. 1982. Nitrate reduction in *Spartina alterniflora* marsh soil. *Journal of Soil Science Society America* 46:748-750.

- Smith, R.V., R.H. Foy, S.D. Lennox, C. Jordan, L.C. Burns, J.E. Cooper and R.J. Stevens. 1995. Occurrence of Nitrite in the Lough Neagh River System Published in Journal of Environmental Quality 24:952-959.
- Smith, R.V. L.C. Burns, R.M. Doyle, S.D. Lennox, B.H.L. Kelso, R.H. Foy and R.J. Stevens. 1997. Free ammonia inhibition of nitrification in river sediments leading to nitrite accumulation. Journal of Environmental Quality 26: 1049–1055.
- Sondergaard, M. 1983. Heterotrophic utilization and decomposition of extracellular carbon released by the aquatic angiosperm *Littorella uniflora* (L.) Aschers, Aquatic Botany 16: 59–73.
- Stal, L.J. 2000. Microbial mats and Stromatolites. In The Ecology of Cyanobacteria. Their Diversity in Time and Space. Whitton, B.A., and Potts, M. (Eds). Dordrecht, The Netherlands : Kluwer Academic Publishers, pp. 61–120.
- Stal, L.J. 2000. The ecology of cyanobacteria. Kluwer Academic Publishers, Dordrecht.
- Stevenson, R.J., A. Pinowska, A. Albertin and J.O. Sickman. 2007. Ecological condition of algae and nutrients in Florida springs: The Synthesis Report. For Contract Number WM 858 Florida Department of Environmental Protection. Tallahassee, FL. 8 pp.
- Stevenson, F. J. 1994. Humus chemistry, 2nd ed. Wiley & Sons.
- Tiedje, J.M. 1988. Ecology of denitrification and dissimilatory nitrate reduction to ammonium. In: A.J.B. Zehnder, Editor, Biology of Anaerobic Microorganisms, Wiley, New York. pp. 179–244.
- Triska, F. J., J. H. Duff, and R. J. Avanzino. 1993. The role of water exchange between a stream channel and its hyporheic zone in nitrogen cycling at the terrestrial-aquatic interface. Hydrobiologia 251:167-184.
- Triska, F. J., and R.S. Oremland. 1981. Denitrification associated with periphyton communities. Applied and Environmental Microbiology 42: 745-748.
- Webster, J.R., P.J. Mulholland, J.L. Tank, H.M. Valett, W.K. Dodds, B.J. Peterson, W.B. Bowden, C.N. Dahm, S. Findlay, S.V. Gregory, N. B. Grimm, S.K. Hamilton, S.L. Johnson, E. Marti, W.H. McDowell, J.L. Meyer, D.D. Morrall, S.A. Thomas, and W.M. Wollheim. 2003. Factors affecting ammonium uptake in streams - an inter-biome perspective. Freshwater Biology 48:1329-1352.
- Weiss, M.S., J. Abele, W. Weckesser, W. Welte, E. Schultz and G.E. Schulz, 1991. Molecular architecture and electrostatic properties of a bacterial porin, Science 254:1627–1630.

- Wetland Solutions, Inc. 2005. Pollutant Load Reduction Goal (PLRG) Analysis for the Wekiva River and Rock Springs Run, Florida. Report prepared for St Johns River Water Management District. Palatka, FL.
- Wetzel R.G. 2001. Limnology, Lake and River Ecosystems. Academic Press, San Diego, CA.
- Wetzel, R.G., 1991. Extracellular enzymatic interactions: storage, redistribution, and interspecific communication. In: Chróst RJ (ed) Microbial enzymes in aquatic environments. Springer-Verlag, New York, pp 6–28.
- Wetzel, R.G., and P.A. Penhale. 1979. Transport of carbon and excretion of dissolved organic carbon by leaves and roots and rhizomes in seagrasses and their epiphytes. *Aquatic Botany*. 6: 149-158.
- Wetzel, R.G., A.K. Ward and M. Stock. 1997. Effects of natural dissolved organic matter on mucilaginous matrices of biofilm communities. *Arch. Hydrobiologie* 139:289-299.
- Whiting P.J., and J. Stamm. 1995. The hydrology and form of spring-dominated channels. *Geomorphology* 12:233-240.
- Wildung, R.E., R.L. Schmidt and R.C. Rouston, 1977. The phosphorus status of eutrophic lake sediments as related to changes in limnological conditions—phosphorus mineral components. *J. Envir. Qual.* 6: 100–104.
- Xie, Y.H., S.Q. An, and B.F. Wu. 2005. Resource allocation in the submerged plant *Vallisneria spiralis* related to sediment type, rather than water-column nutrients. *Freshwater Biology* 50:391-402.

Nutrient Effects on Spring Flora and Fauna

*Charles A. Jacoby, Thomas K. Frazer and Edward J. Phlips
Department of Fisheries and Aquatic Sciences
University of Florida*

Summary

Many of Florida's springs and spring runs are enriched in nitrate due to broad-scale contamination of groundwater supplies. This observation fosters two primary and interrelated concerns regarding the effects of nutrients on flora and fauna in spring systems. High nitrate concentrations can affect fauna directly through toxicity. In addition, high nitrate concentrations can promote eutrophication or an increase in organic matter, which drives a diverse array of responses and feedbacks in aquatic systems that comprise a eutrophication progression scheme.

The Literature: What is Known

Florida's springs and spring runs are enriched in nitrate due to broad-scale contamination of groundwater supplies. As a result, the potential for eutrophication becomes a major concern. A eutrophication progression scheme suggests that increased nutrient delivery to aquatic systems favors production of fast-growing algae that ultimately outcompete and displace native vascular plants (Duarte 1995). In some of Florida's spring systems, both the apparent proliferation of nuisance algae and the apparent decline of native vascular plants are consistent with such a progression and a cue that management actions are needed.

In general, nutrients can affect the faunal assemblages in aquatic systems in three primary ways: 1) toxicity, 2) changes to trophic webs and 3) changes in habitats. Elevated concentrations of ammonia and nitrate can lead to increased mortality and sublethal effects. At this time, lethal effects are not an overwhelming concern in most spring systems. However, the potential for sublethal effects should be considered during discussions of management actions, especially given the uncertainty factors suggested for most criteria. The potential for changes in trophic webs and habitats, along with flow-on effects on faunal assemblages does exist. The form and magnitude of any changes are determined by complex interactions among bottom-up and top-down processes, such as grazing pressure, habitat use and predation pressure. The outcomes of such interactions clearly relate to sustainable management of spring systems.

The Literature: What is Not Known

There are few quantitative data that definitively link changes comprising the eutrophication progression scheme to increased nitrate loads in spring systems. In fact, the eutrophication progression scheme predicts that nonlinear responses may have "decoupled" these systems from

contemporary concentrations of nutrients in the water column. Currently, patterns in the distribution and abundance of plants and algae do correlate with other physical and chemical parameters, such as light availability. However, little is known about the individual or combined effects of the various forcing factors or the form and strength of potential feedback mechanisms, including those linked to nutrient concentrations.

At this time, there are no data to support rigorous evaluation of bottom-up and top-down influences on faunal communities. For example, changes in faunal assemblages have not been linked to changes in vegetated communities and changes in grazer abundance have not been linked to changes in floral assemblages. In addition, sublethal effects of nitrate may not translate to effects on populations, assemblages or ecosystems.

Recommendations for Future Research

Management of nutrients in spring ecosystems would benefit from compilation of inventories, collection of baseline data, and completion of diagnostic studies focused on bottom-up and top-down interactions. Ultimately, unforeseeable, emergent properties that arise when management is implemented at real-world, spatiotemporal scales will create a need to manage adaptively.

Efficient and effective research to improve management of Florida's springs and spring-fed systems requires input from multiple stakeholders. Initial suggestions for discussion include:

- inventories and baselines designed to:
 - measure nutrients, oxygen, carbon, light, flow, substrates, grazing, algae, plants, invertebrates, fish, and other key drivers and valued components of spring systems chosen with the best available information and, eventually, with guidance from the results of diagnostic studies
 - target systems where effectiveness of management can be assessed (e.g., systems with total maximum daily loads, minimum flows and levels, pollution load reduction goals, surface water improvement plans or basin management action plans)
 - sample synoptically or at spatial and temporal scales that support rigorous analyses of interactions (note that these inventories and baselines form the platform for adaptive management)
 - balance breadth with depth (e.g., optimize taxonomic detail and replication)
- diagnostic studies that determine assimilation of nutrients by flora as key elements in nutrient budgets for spring systems, including contributions by epiphytes, macroalgae, vascular plants and microphytobenthos or microalgae found in sediments
- diagnostic studies that determine how nutrients and other drivers affect overgrowth, shading and other relationships among periphyton, macroalgae and vascular plants in an effort to determine the need for management actions, including aquatic plant management and restoration of native species
- diagnostic studies designed to:
 - focus on species of algae and plants that are hypothesized or known to play major roles in nutrient assimilation

- extend beyond nitrogen and phosphorus to include other potentially limiting factors and interactions among limiting factors that can significantly influence the outcomes of management (e.g., micronutrients, iron, oxygen, carbon, light, flow and substrate type)
- explore relationships and consequences across multiple levels of biological and ecological complexity, including uptake and other physiological responses, growth and reproduction of individual organisms, and ecological changes in populations or assemblages to promote the success of management actions at the system level (note that some of the key, large-scale relationships form the core of an adaptive management approach)
- elucidate the direction, magnitude and form of limitations (e.g., nonlinear and nonreversible) to identify suitable targets and goals for management actions
- diagnostic studies to identify and elucidate changes in composition and function of faunal assemblages related to changes in habitats in an effort to identify habitats to be protected or restored by management actions
- diagnostic studies to determine palatability of flora to grazers, rates of grazing, and the form and magnitude of predation by primary consumers in an effort to identify flora, grazers and trophic links to be protected or restored by management actions
- diagnostic studies to identify and elucidate the toxic effects of ammonia and nitrate beyond physiological and individual levels of organization (e.g., population and assemblage effects) in an effort to determine threshold levels, safety factors and the need for management actions

INTRODUCTION

Anthropogenic activities have increased the delivery of nutrients in aquatic systems of all types resulting in concerns about the biotic integrity of these systems. In fact, excessive growth of primary producers in water bodies due to high inputs of nutrients, especially phosphorus and nitrogen, has been cited as the most important form of pollution in lentic and lotic systems (Mainstone and Parr 2002; Hilton *et al.* 2006). For example, high levels of nutrients, especially nitrogen and phosphorus, are reported to threaten wadeable streams, the shallow, freshwater systems that represent about 90% of the length of flowing waters in the United States (Figure 1; USEPA 2006). Florida's spring-fed systems share key features with these and other lotic systems because they are often relatively shallow and they rely on primary production that arises from periphyton, algae and vascular plants rather than phytoplankton. Thus, an understanding of the effects of nutrients on shallow, freshwater ecosystems represents a key concern in Florida and beyond.

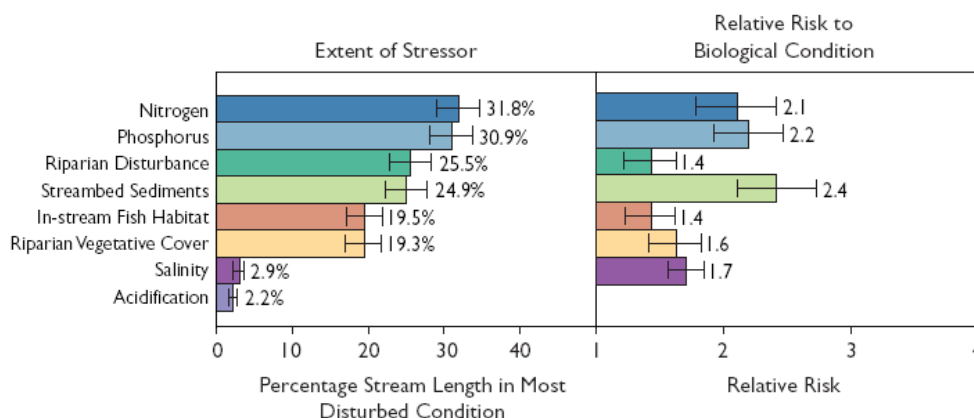


Figure 1 – *Spatial extent of stressors and associated relative risks or relative likelihood of degradation from biological reference conditions in wadeable streams of the United States (USEPA 2006).*

Signs of stress from increased nutrients in aquatic systems have led to development of narrative standards or numeric criteria as important management responses. Nutrient standards and criteria have been set in response to: 1) adverse effects on humans and domestic animals, 2) aesthetic impairment, 3) interference with human use, 4) negative impacts on aquatic ecology, and 5) excessive nutrient transport to downstream systems (Dodds and Welch 2000). These five concerns interact. For example, systems exhibiting negative ecological impacts probably fail to be aesthetically pleasing or support a full range of human uses. In fact, aesthetics and direct human use typically relate to the health of aquatic flora and fauna, e.g., a balance between macrophytes and filamentous algae, the absence of algal blooms, and the presence of healthy fisheries. Flora and fauna also influence the transport of nutrients to downstream systems through processes such as uptake and cycling. Thus, an understanding of nutrient effects on flora and subsequent effects on fauna become important in managing nutrients for almost any purpose.

In Florida, past and present land uses have resulted in broad-scale nutrient contamination of groundwater (Cohen *et al.* Chapter 2). This nutrient-laden groundwater exists within a very

permeable, karst setting, with myriad pathways between aquifers and surface waters (Knight and Notestein Chapter 1; Cohen *et al.* Chapter 2). In fact, freshwater springs function as conduits that discharge contaminated groundwater into surface waters. Once nutrients, such as nitrogen and phosphorus, are mixed into spring-fed, surface waters, they attain the greatest potential to negatively alter the ecology of aquatic ecosystems. The effects of increased nitrogen in the form of nitrate raise particular concerns for flora and fauna associated with Florida's springs and their downstream receiving waters.

Nitrate as a Compound of Concern

Why the focus on nitrate? Nitrate is a nitrogen compound that occurs naturally in aquatic systems, including Florida's springs. Aquatic plants and algae assimilate nitrate as a way to gain nitrogen, which is one of the elements that contributes to their growth and production. Concerns arise when nitrate concentrations become toxic or an increase in the supply of nitrate or another limiting factor stimulates excess plant and algal growth creating undesirable aesthetic and ecological consequences. Such an increase in plant or algal growth is commonly referred to as eutrophication (c.f. Nixon 1995). The potential eutrophication of Florida's spring systems is a major concern for many resource managers in the state (Knight and Notestein Chapter 1). In fact, the current view among many (if not all) scientists and resource managers is that plant and algal populations in Florida's spring-dominated ecosystems are undergoing major structural and functional changes, due, in large part, to increases in anthropogenic enrichment of nutrient levels in groundwater and the consequent nitrification of spring discharges.

This widely held view is not without merit. There is, in fact, a growing body of literature on the chemistry of spring discharges that supports the conclusion that nutrient concentrations in springs, and nitrate concentrations in particular, are increasing (Cohen *et al.* Chapter 2). The perception that increased algal biomass has led to the displacement of native macrophytes, on the other hand, appears to be based largely on anecdotal accounts and qualitative observations (see Frazer *et al.* 2006b). Nevertheless, the prevalence of such reports is a compelling reason for concern. It is fair to say, however, that there is little direct evidence that either definitively links the observed increases in algae to increased nitrate delivery to spring systems or demonstrates that the purported changes have compromised the ecological health and integrity of these systems. Our goal is to articulate what we know about the factors that affect submersed plants and algae in Florida's spring systems, the relationships among nutrients and spring flora, the habitat associations of spring fauna, and the potential toxic effects of some nitrogen compounds. From this synthesis, we aim to draw guidance or recommendations for policy and management. Where sufficient information is lacking, our goal is to suggest potential remedies.

PRIMARY PRODUCERS IN SPRING ECOSYSTEMS AND FACTORS AFFECTING THEIR ABUNDANCE AND DISTRIBUTION

Florida's springs often are perceived as stable-state ecosystems in which major chemical constituents, temperature and discharge characteristics of individual springs are essentially constant (Odum 1957b). In fact, there is substantial variability in chemical and physical attributes among the state's 700+ springs (Odum 1957a; Jones *et al.* 1997; Scott *et al.* 2002; Strong 2004), and, in some cases, variability within spring systems (Odum 1957b). Patterns in

the abundance and distribution of spring-associated flora and fauna should be expected to vary accordingly. We would argue that spring-dominated ecosystems, like all other ecosystems, are, in fact, dynamic in nature and exist (on some scale) as heterogeneous environments in which various chemical, physical and biological processes interact to determine ecological structure and function. Thus, the inherent complexities in spring-dominated ecosystems must be recognized, and any broad generalizations related to observed patterns and presumed processes should be evaluated objectively.

For example, it is important to recognize that nitrate availability is only one of many factors with the potential to directly influence the abundance and distribution of plants and algae in Florida's spring systems. Other essential nutrients, particularly phosphorus, also are likely to be important determinants of plant and algal abundance (Frazer *et al.* 2001a; Notestein *et al.* 2003; Kurz *et al.* 2004; Frazer *et al.* 2006b; Stevenson *et al.* 2007). In addition, we would be remiss if we failed to acknowledge that other, naturally variable, chemical properties of groundwaters and surface waters influence the vegetative characteristics of Florida's springs and their downstream receiving waters. For example, concentrations of dissolved gases, such as oxygen and carbon dioxide, exert a profound influence on production of submersed aquatic plants and algae (Sand-Jensen 1989, Sand-Jensen and Borum 1991). In addition, vegetative assemblages in several of Florida's spring systems have been shown to vary with specific conductance and salinity (Whitford 1956; Frazer *et al.* 2001b; Hoyer *et al.* 2004; Frazer *et al.* 2006a). One also must consider physical attributes of various spring systems in any attempt to ascertain the relative importance of factors affecting broad-scale or fine-scale patterns in plant and algal abundance. For example, water depth, light availability, stream velocity, flow regimes, and characteristics of substrates all represent important considerations (Butcher 1933, Hynes 1972).

Beyond chemical and physical influences, biological interactions and ecological processes may influence patterns of plant and algal abundance. Grazing on aquatic plants and algae can be significant, and it may serve to moderate the potential negative influences of nutrient over-enrichment (Duarte 1995; Hauxwell *et al.* 1998). In addition, competition for space, light and/or nutrients can alter the species composition of algal and plant assemblages. Changes in these patterns may, in turn, affect higher-order organisms present in the systems, particularly those that use submersed aquatic vegetation when foraging or taking refuge. Thus, the indirect effects of nutrients represent a focus of this chapter and a logical complement to the discussion of direct impacts on spring-associated flora.

Light

Light availability is arguably among the most important factors directly affecting the abundance and distribution of aquatic plants and algae. Without sufficient light, plants and algae cannot utilize nutrients effectively. Light transmittance in aquatic systems is affected primarily by suspended solids and dissolved organic substances (Kirk 1994). Suspended solids include algal cells (Canfield and Hodgson 1983), nonvolatile suspended solids (Canfield and Bachmann 1981; Hoyer and Jones 1983) and detrital material (Buiteveld 1995).

All of the "in-water" constituents that reduce light availability are generally in low concentrations in groundwater serving as the origin of flow for Florida's springs and spring runs. For example, Florida springs with discharges of $5 \text{ m}^3 \text{ s}^{-1}$ or higher (1st magnitude springs) had the

lowest concentrations of dissolved organic matter yet reported ($13 \pm 1.6 \mu\text{M C L}^{-1}$), and springs with lower discharges exhibited only somewhat higher values (Duarte *et al.* 2007). Thus, Florida's springs are not surprisingly among the clearest waters in the world (Odum 1957b; Rosenau *et al.* 1977; Duarte and Canfield 1990a).

Nevertheless, light availability is likely to limit the distribution and production of submersed aquatic vegetation in Florida's spring systems in many instances. For example, Duarte and Canfield (1990b) investigated 31 springs and spring runs in interior central and northern Florida and concluded that shading by riparian vegetation was a primary determinant of primary productivity and macrophyte standing crops in these systems. It is interesting to note that these investigators reported negative rates for daily maximum production in several spring runs devoid of "vegetation," and it was assumed that biochemical oxygen demand exceeded any production by benthic and/or pseudoplanktonic algae in these systems. It was further suggested that oxygen concentrations in groundwater emanating as spring discharge may, in some cases, be too low to support the respiratory demands of aquatic macrophytes (see additional discussion below).

In a separate study of five spring-fed rivers along the Gulf coast, Frazer *et al.* (2001a) suggested that light availability was generally sufficient to support net photosynthesis of submersed aquatic vegetation, but they also noted that terrestrial canopy coverage along some shoreline areas may reduce incident light to a level that restricts the abundance and distribution of aquatic plants and algae. Correlations with the percentage of shoreline canopy cover in the Weeki Wachee River, for example, accounted for 26% of the variation in total vegetative biomass, 21% of the variation in filamentous macroalgal biomass, and 8% of the variation in macrophyte biomass. As the percent canopy cover increased, the total vegetative biomass decreased, which led these authors to suggest that canopy cover in the Weeki Wachee River does influence the distribution and abundance of aquatic plants.

There are few other quantitative studies of the relationship between light and submersed aquatic vegetation in Florida's spring systems, and we did not find experimental investigations that might indicate the magnitude of light limitation in those springs subject to shading by riparian vegetation. This is somewhat surprising as Odum suggested in his seminal work (Odum 1957b) that primary production in Silver Springs (and other spring systems in Florida; Odum 1957a) is linearly related to light intensity.

In addition to shading by riparian vegetation, there is a widely held perception that the accumulation of algae on macrophytes reduces the photosynthetic efficiency of the host plant due to shading. This scenario is, in fact, a crucial element of the argument that eutrophication of Florida's spring systems has led to a proliferation of nuisance algae and concomitant decline of native macrophytes. A key to effective management of Florida's springs will be to understand the factors and processes that interact to either accelerate or decelerate this eutrophication progression scheme (see Duarte 1995 and also Valiela *et al.* 1997). At this time, there is no direct evidence that accumulations of periphyton on macrophytes have reduced their growth rates in Florida's spring systems. The potential for such an effect has been inferred from laboratory studies with portions of plants (Sand-Jensen 1977; Chen *et al.* 2007) and relatively few, empirical field studies in estuarine and coastal marine systems (Deegan *et al.* 2002; see also Heck *et al.* 2000). It is likely, however, that the diffusion of carbon dioxide (CO_2) or active uptake of bicarbonate (HCO_3^-) is hindered by increased boundary layer effects created by a layer

of algae. Thus, the effects of changes in light climate will be mediated by stream velocity and the supply of carbon, especially dissolved inorganic carbon (DIC). There is a need to quantify the relationships among light climate, DIC availability, stream velocity, algal abundance and macrophyte production because such relationships have profound implications for management of spring systems.

Carbon and Oxygen Balance in Macrophytes

At saturating light levels, the maximum rate of photosynthetic carbon fixation by submersed vascular plants exceeds the respiratory carbon demand of leaves and belowground tissues (Hemminga and Duarte 2000). This outcome holds only if DIC is in ample supply. Because concentrations of DIC in Florida's springs are naturally high due to microbially mediated remineralization of organic matter in the groundwater system, this situation typically applies (Inglett *et al.* Chapter 3).

Many springs (particularly 1st magnitude springs) are supersaturated with DIC and there is, in fact, a net flux of gaseous CO₂ from the springs to the atmosphere at the point of discharge and for some distance downstream during the equilibration process (Duarte *et al.* 2007). Thus, the supply of inorganic carbon is not likely to limit primary production in spring systems, at least in those areas in close proximity to a groundwater source. Mediation by biological (algal mat formation) or physical (water velocity) processes, however, may result in localized depletions of DIC. At such fine scales, the potential exists for DIC limitation, but we have insufficient data to evaluate the existence or ultimate effect of such limitation.

Oxygen is a byproduct of photosynthesis and a key chemical constituent of all systems that support biological communities. Any factor or combination of factors that reduces primary production in spring systems will necessarily reduce the availability of dissolved oxygen. The potential consequences of reduced oxygen availability on faunal assemblages may be intuitively obvious, but the consequences of low oxygen concentrations on flora are less clear.

Rooted aquatic plants require dissolved oxygen to support aerobic respiration, especially in belowground tissues. Reduced photosynthetic capacity compromises the supply of oxygen, and such a change may negatively affect plants by disrupting their carbon balance (see Hemminga and Duarte 2000). Oxygen deficits might be expected to occur where macrophytes are highly epiphytized or covered by extensive macroalgal growth because of increased respiration and/or boundary layer effects on diffusion. We reiterate, however, that there are no experimental studies clearly demonstrating a negative effect of epiphytes or macroalgae on vascular plants in Florida's spring systems, although there are a number of empirical investigations that are suggestive of such a cause and effect relationship (e.g., Frazer *et al.* 2006b; Jacoby *et al.* 2007). In those spring systems that exhibit chronic hypoxia, one might expect rooted macrophytes to be more susceptible to the potential effects of algal overgrowth. It is interesting to note that Stevenson *et al.* (2004) reported a significant negative relationship between dissolved oxygen concentrations and algal cover based on a broad survey of springs in Florida. The nature of this relationship merits further investigation, especially in light of recent information that suggests a broad-scale decline in dissolved oxygen concentrations in Florida's springs (Heffernan *et al.* unpublished data).

Stream Velocity and Substrate

Water movement can affect the gas exchange, physiology and growth form of plants and algae, particularly periphyton. In addition, stream velocity can determine the characteristics of the substrate, which, in turn, influence the viability of plants and algae.

For example, a stream/river bed consisting of bare rock or large stones that are continually being rolled or scoured will have little submersed aquatic vegetation, while a river bed that is comprised largely of mud, silt and sand has the potential to support abundant aquatic vegetation (Butcher 1933; Allan 1995). Systems with flow rates greater than 0.60 m sec^{-1} tend to have heavy rock substrates, and systems with progressively slower flow have light gravel, sand, silt and mud substrates that are more favorable for aquatic plant growth.

All of Florida's spring runs are considered low gradient streams, and they seldom exhibit flow rates in excess of 0.60 m sec^{-1} . Therefore, substrates within these systems generally are conducive to the colonization and subsequent production of many types of submersed aquatic vegetation (see Frazer *et al.* 2001a) if nutrients, light and other conditions are suitable. However, sections of spring systems may not support all types of submersed aquatic vegetation. For example, exposed limestone is prevalent in the immediate vicinity of spring vents, and outcrops of limestone are distributed patchily throughout many spring runs. Rooted macrophytes will not colonize these areas, although algae does grow successfully near spring vents and limestone outcrops are colonized by algae and bryophytes (Whitford 1956; Frazer *et al.* 2001a; Kurz *et al.* 2003 and 2004; Hoyer *et al.* 2004; Stevenson *et al.* 2004 and 2007).

In the context of this review, stream velocity will be a concern primarily because of its effects on the periphyton assemblages associated with macrophytes. Although submersed vascular plants and large macroalgae in springs draw considerable attention, epiphytic microalgae also are an important component of spring systems. In fact, epiphytic algae and benthic mats can be major, or even dominant, elements of the primary producer community, in terms of both productivity and biomass (Quinlan *et al.* 2008). The composition of algal communities, however, varies considerably between different spring ecosystems (Whitford 1956), and it might be expected to vary temporally due to seasonal differences in light availability (see above) or more stochastic variations in flow regimes that occur as a consequence of climate variability or anthropogenic demands on source water (Odum 1957b).

In systems with relatively high flow rates, periphyton associated with macrophytes or other substrates are comprised mostly of low-lying mucilaginous diatoms that are resistant to sloughing even at high velocities (Biggs *et al.* 1998). Long, filamentous algal species are much less resistant to high velocity environments. Indeed, for such a species, Biggs *et al.* (1998) reported a linear decrease in ash-free dry mass of periphyton as a function of near-bed velocity. To our knowledge, there are no rigorous experimental studies in Florida spring systems that quantify the effects of flow on periphyton biomass or species composition. There are, however, several empirical investigations in which both flow and periphyton abundance on macrophytes have been measured. For example, Frazer *et al.* (2001a) found no significant relationship between flow rates and periphyton associated with macrophytes in any of the five spring-fed, coastal rivers they investigated. In a subsequent study of these same systems, however, statistically significant decreases in periphyton associated with macrophytes in the Weeki

Wachee River coincided with an increase in flow (Frazer *et al.* 2006b). Kurz *et al.* (2004) found no significant relationship between periphyton abundance on macrophytes and flow in the main stem of the Ichetucknee River. It should be noted, however, that periphyton abundance on macrophytes was significantly higher in several feeder springs where flow rates were significantly less (Kurz *et al.* 2004; see also Dormsjo 2007; Politano unpublished data).

These findings are counter-intuitive because reduced flows are expected to increase boundary layer thickness. Boundary layers determine, in part, the availability of nutrients (or other chemicals such as dissolved oxygen and free dissolved inorganic carbon) to the periphyton. When boundary layers are thick, as in areas with slow-moving water, nutrients and other chemicals must diffuse or be actively transported across large distances. Thinner boundary layers facilitate contact between cells and nutrients or other chemicals. The steepness of the concentration gradient across the boundary layer determines transport rate, per Fick's law:

$$J = -D \frac{\partial \phi}{\partial \chi}$$

where J is the diffusion flux in, for example, moles $\text{m}^{-2} \text{s}^{-1}$, D is the diffusion coefficient or diffusivity in $\text{m}^2 \text{s}^{-1}$ (determined by temperature and the properties of both materials – here, water and cell cytoplasm), ϕ is the concentration gradient per unit length in moles m^{-3} , and χ is the length in m of the boundary layer. Depletion of nutrients in a slow-moving system decreases the concentration gradient, $\partial \phi / \partial \chi$, so periphyton come to have limited access to nutrients. Even minute increases in stream velocity ($< 0.1 \text{ cm/s}$) have been shown to increase photosynthesis of aquatic macrophytes (Westlake 1967), presumably by maintaining a steep concentration gradient of nutrients near the plants' surfaces or by reducing the concentration of metabolic by-products that might impair photosynthesis. In general, periphyton biomass increases as velocity increases until shear reaches a level that initiates sloughing (Biggs and Hickey 1994; Biggs *et al.* 1998). Clearly, the relationship between water velocity and periphyton dynamics in Florida's spring systems merits further investigation.

Nutrients

Although modified and influenced by other factors, the availability of nutrients plays a major role in governing productivity in natural systems. In freshwaters, phosphorus generally is considered the nutrient that most frequently limits the production of plants and algae (Wiebe 1931; Schindler 1971). Nitrogen, however, can and does limit primary production in many instances (see Vitousek and Howarth 1991). Other macronutrients and micronutrients (e.g., potassium, calcium, magnesium, sulfur, iron, manganese, copper, zinc, molybdenum, sodium, cobalt, chlorine, bromine, silicon, boron, and iodine) also can limit plant and algal production depending on their relative abundances and the particular physiologies of the taxa present in the system. In some situations, plants and algae may be limited by the availability of dissolved inorganic carbon, although there is little indication that this might be the case in any of Florida's springs, except perhaps in algal mats. Due to their import, our focus here is on nitrogen and phosphorus and their potential to limit the production of submersed aquatic vegetation in Florida's springs and spring runs.

Rooted vascular plants, e.g., *Vallisneria americana* and *Sagittaria kurziana*, are generally assumed to acquire nitrogen and phosphorus largely from sediment porewaters (Chambers *et al.* 1989), although some research suggests that many plants (some of which are present in Florida's spring systems) are capable of nutrient uptake through their aboveground tissues (see DeBrabandere *et al.* 2007 and references therein). There has been no experimental work to demonstrate unequivocally that any submersed vascular plant in a Florida, spring-fed system is limited by either nitrogen or phosphorus. Moreover, empirical data generated in a large number of spring systems suggests that there is no significant linkage between surface water nutrients and production of macrophytes.

For example, Canfield and Hoyer (1988a and b) carried out an intensive investigation of 17 inland streams (many of which were spring-fed) to determine if the abundance of aquatic macrophytes (composite category including both rooted vegetation and macroalgae) was related to nutrient enrichment. Standing crops of macrophytes in these systems were not correlated with in-stream concentrations of total phosphorus or total nitrogen. Furthermore, in a subsequent investigation, Duarte and Canfield (1990b) sampled 31 spring runs and similarly found that standing crops of submerged vegetation were not significantly correlated with either total nitrogen or total phosphorus.

Frazer *et al.* (2001a) investigated the relationship between nutrient concentrations in surface waters and characteristics of submersed aquatic vegetation in five spring-fed coastal rivers subjected to increasing nitrate delivery. They found that statistically significant, positive relationships between nitrate and standing crops of either macrophytes or filamentous macroalgae were evident only in the Chassahowitzka and Homosassa Rivers (Table 1). Mean nitrate concentrations declined markedly at downstream sites in both rivers, which is indicative of rapid nitrate removal. Subsequent research in the Chassahowitzka River suggests, however, that the vast majority of the nitrate removal occurs as a consequence of denitrification (Saunders 2007; see also DeBrandere *et al.* 2007) rather than uptake and assimilation of nitrate by submersed aquatic vegetation. Denitrification also may be operating in the Homosassa River where nitrate concentrations decline markedly along the river's length even though little vegetation remains in the system (Frazer *et al.* 2006b). It is noteworthy that Frazer *et al.* (2001a) reported that soluble reactive phosphorus was correlated with macrophyte and macroalgal biomass in the Chassahowitzka and Homosassa rivers, and they suggested that phosphorus might be a more important determinant of vegetative biomass than nitrate in these two rivers. Notestein *et al.* (2003) subsequently determined that phosphorus does in fact limit algal growth in the Chassahowitzka River. The addition of soluble reactive phosphorus resulted in significantly higher periphyton accumulation on artificial substrates relative to nitrate amended treatments or controls (no nutrient addition). Frazer *et al.* (2001a) reported that soluble reactive phosphorus was correlated with macroalgal biomass in the Weeki Wachee River as well, so phosphorus also may limit the growth of algae in this river.

Table 1. Pairwise Pearson Product-Moment correlations between log₁₀–transformed annual mean nutrient concentrations and log₁₀–transformed summer mean biomass for macroalgae, all vegetation, macrophytes and periphyton from ten transects in four coastal rivers during 1998, 1999 and 2000 (n = 30). Data for the Withlacoochee River were not shown because plants were largely absent from the system below the dam at Inglis where the substrate (largely rock) was unfavorable (from Frazer *et al.* 2001a).

Nutrient	Biomass	Correlation coefficient	Probability
CHASSAHOWITZKA			
Ammonium	Macroalgae	-0.31	0.09
Nitrate	Macroalgae	0.63	< 0.05
Soluble reactive phosphorus	Macroalgae	0.55	< 0.05
Total nitrogen	Macroalgae	0.21	0.27
Total phosphorus	Macroalgae	-0.19	0.31
Ammonium	All vegetation	-0.46	< 0.05
Nitrate	All vegetation	0.79	< 0.05
Soluble reactive phosphorus	All vegetation	0.68	< 0.05
Total nitrogen	All vegetation	0.29	0.12
Total phosphorus	All vegetation	-0.31	0.10
Ammonium	Macrophytes	-0.38	< 0.05
Nitrate	Macrophytes	0.70	< 0.05
Soluble reactive phosphorus	Macrophytes	0.61	< 0.05
Total nitrogen	Macrophytes	0.33	< 0.05
Total phosphorus	Macrophytes	-0.20	0.29
Ammonium	Periphyton	-0.34	0.07
Nitrate	Periphyton	0.28	0.14
Soluble reactive phosphorus	Periphyton	0.23	0.23
Total nitrogen	Periphyton	0.36	0.06
Total phosphorus	Periphyton	-0.42	0.83
CRYSTAL			
Ammonium	Macroalgae	-0.22	0.24
Nitrate	Macroalgae	0.38	< 0.05
Soluble reactive phosphorus	Macroalgae	-0.46	< 0.05
Total nitrogen	Macroalgae	-0.48	< 0.05
Total phosphorus	Macroalgae	-0.43	< 0.05
Ammonium	All vegetation	-0.13	0.48
Nitrate	All vegetation	0.23	0.22
Soluble reactive phosphorus	All vegetation	-0.33	0.07
Total nitrogen	All vegetation	-0.70	< 0.05
CRYSTAL (continued)			
Total phosphorus	All vegetation	-0.28	0.14
Ammonium	Macrophytes	-0.12	0.52
Nitrate	Macrophytes	0.21	0.26
Soluble reactive phosphorus	Macrophytes	-0.32	0.09
Total nitrogen	Macrophytes	-0.69	< 0.05
Total phosphorus	Macrophytes	-0.26	0.16
Ammonium	Periphyton	-0.44	< 0.05
Nitrate	Periphyton	0.18	0.40
Soluble reactive phosphorus	Periphyton	0.10	0.63
Total nitrogen	Periphyton	-0.34	0.11

Nutrient	Biomass	Correlation coefficient	Probability
Total phosphorus	Periphyton	0.01	0.97
HOMOSASSA			
Ammonium	Macroalgae	-0.34	0.07
Nitrate	Macroalgae	0.60	< 0.05
Soluble reactive phosphorus	Macroalgae	0.44	< 0.05
Total nitrogen	Macroalgae	0.34	0.07
Total phosphorus	Macroalgae	-0.55	< 0.05
Ammonium	All vegetation	-0.37	< 0.05
Nitrate	All vegetation	0.64	< 0.05
Soluble reactive phosphorus	All vegetation	0.49	< 0.05
Total nitrogen	All vegetation	0.25	0.19
Total phosphorus	All vegetation	-0.66	< 0.05
Ammonium	Macrophytes	-0.31	0.09
Nitrate	Macrophytes	0.43	< 0.05
Soluble reactive phosphorus	Macrophytes	0.32	0.09
Total nitrogen	Macrophytes	0.02	0.92
Total phosphorus	Macrophytes	-0.62	< 0.05
Ammonium	Periphyton	0.44	< 0.05
Nitrate	Periphyton	0.12	0.53
Soluble reactive phosphorus	Periphyton	-0.25	0.20
Total nitrogen	Periphyton	0.57	< 0.05
Total phosphorus	Periphyton	-0.37	< 0.05
WEEKI WACHEE			
Ammonium	Macroalgae	-0.47	< 0.05
Nitrate	Macroalgae	0.20	0.30
Soluble reactive phosphorus	Macroalgae	0.54	< 0.05
Total nitrogen	Macroalgae	-0.12	0.53
Total phosphorus	Macroalgae	-0.36	< 0.05
Ammonium	All vegetation	-0.48	< 0.05
Nitrate	All vegetation	-0.02	0.90
Soluble reactive phosphorus	All vegetation	0.29	0.12
Total nitrogen	All vegetation	-0.23	0.21
Total phosphorus	All vegetation	-0.24	0.20
Ammonium	Macrophytes	-0.33	< 0.05
Nitrate	Macrophytes	-0.22	0.25
Soluble reactive phosphorus	Macrophytes	0.04	0.82
Total nitrogen	Macrophytes	-0.30	0.10
Total phosphorus	Macrophytes	-0.13	0.51
Ammonium	Periphyton	0.43	< 0.05
Nitrate	Periphyton	-0.46	< 0.05
Soluble reactive phosphorus	Periphyton	-0.32	0.12
Total nitrogen	Periphyton	-0.32	0.13
Total phosphorus	Periphyton	-0.04	0.85

Kurz *et al.* (2004) reported no statistically significant, positive relationships between nutrients and coverage or biomass of submersed aquatic vegetation in the main stem of the Ichetucknee River. There was a weak, but statistically significant, negative correlation between terrestrial canopy cover and submersed aquatic vegetation cover suggesting that, in some cases, light may limit the distribution of macrophytes. In a complementary analysis, these investigators related a suite of chemical and physical parameters to periphyton abundance on macrophytes in several small spring runs adjoining the main river. Periphyton abundance was not correlated with either nitrate or total nitrogen concentrations, but it was significantly correlated with soluble reactive

phosphorus concentrations suggesting phosphorus limitation.

The issue of nutrient limitation of algal production can be viewed at several levels of organization, from individual algal cells or filaments to complex mat communities. For example, the nitrate half saturation constants for the growth of the common filamentous green alga *Cladophora* range from 100–200 $\mu\text{g l}^{-1}$ (Lohman and Priscu 1992), and recent research on growth saturating concentrations of nitrate for *Lyngbya wollei* suggests values between 100–200 $\mu\text{g l}^{-1}$ (Stevenson *et al.* 2007). Saturation levels for the growth of natural populations of benthic algae in Sycamore Creek, Arizona (Grimm and Fisher 1986) and Saline Creek, Missouri (Lohman *et al.* 1991) were 55 and 100 $\mu\text{g l}^{-1}$, respectively. Thus, the limited literature listing levels of nitrate that saturate the growth rates of natural, benthic, algal mats suggests that nitrate concentrations currently observed in the water column of many springs are not limiting. However, this does not preclude the possibility of nitrogen limitation in large, well-developed algal mat communities, where growth may be impacted by diffusion rates and nutrient gradients within the mat. In fact, Stevenson *et al.* (2007) showed that water column concentrations limiting growth may be considerably higher for mats than for exposed, individual algal cells or filaments. Half saturation constants for phosphorus exhibit similar variability. Constants have been reported to vary from 9 to 45 $\mu\text{g l}^{-1}$ for the green alga *Spirogyra* (Borchardt *et al.* 1994) and from 15 to 240 $\mu\text{g l}^{-1}$ for *Cladophora* (Lohman and Priscu 1992). Lower values of 0.6 to 6 $\mu\text{g l}^{-1}$ were reported for mixed periphytic diatoms (Bothwell 1985). Half saturation constants for natural, benthic, algal mats ranged from 7 to 50 $\mu\text{g l}^{-1}$ (Wuhrmann and Eichenberger 1975; Welch *et al.* 1988; Horner *et al.* 1990).

In contrast to the widespread and dramatic increase in nitrogen levels in many Florida springs, phosphorus concentrations are reported to have remained similar to historic levels (Stevenson *et al.* 2007; Munch *et al.* 2006). Current phosphorus concentrations vary considerably among springs, from low levels in systems like the Weeki Wachee River (Frazer *et al.* 2001a and 2006b) to high concentrations in systems like Silver Springs and the Ichetucknee River and springs (Munch *et al.* 2006; Kurz *et al.* 2003 and 2004). Some springs exhibit concentrations that fall below the reported saturation levels for growth of benthic algae. The possibility that phosphorus may be a limiting factor for algal growth in some springs has been further highlighted by recent observations of high N/P ratios in plant and algal samples from several Florida springs (Stevenson *et al.* 2007). However, some springs with very low phosphorus concentrations in the water column have extensive benthic algal mats (Frazer *et al.* 2001a and 2006b). We hypothesize that the mobilization of phosphorus from sediments may provide sufficient nutrients to sustain this biomass. This hypothesis is supported by observations of increasing phosphorus levels in the pore water of some benthic algal mats (Stevenson *et al.* 2007). The absence of sufficient information on nutrient dynamics within algal mat communities in spring ecosystems hampers our ability to predict the outcomes of changes in nutrient loads.

Community Responses to Increased Nutrients

Plant and algal communities appear to exhibit qualitatively similar responses to increased nutrient loads. The primary responses and the mechanisms by which algae replace submersed vascular plants have been reviewed in depth by Duarte (1995), and we reiterate the key points from his significant contribution.

Interactions between supplies of nutrients and light availability, two resources that most often limit the production of plants and algae, are at the root of observed changes in floral assemblages (Duarte 1995). Because both plants and algae require the same basic resources (nutrients and light), they are likely to compete (intra-specifically and inter-specifically) for the resource that is in the shortest supply (Liebig's Law of the Minimum). At low nutrient concentrations in the water column and under favorable light conditions, slow-growing, rooted vascular plants are superior competitors owing to their relatively low nutrient requirements, their capacity to efficiently recycle nutrients internally and their ability to access sedimentary nutrient stores. In contrast, algae become more abundant when nutrient limitation is released, in large part, by capturing light more efficiently.

In the eutrophication progression scheme laid out by Duarte (1995), faster growing macroalgae and microflora, i.e., periphyton, can ultimately overgrow long-lived and relatively slow-growing plants and algae, e.g., rooted vascular plants and macroalgae with thick fronds. This change exacerbates light limitation and reduces scope for growth for the vascular plants and "thick" algae. Ultimately, these long-lived forms are outcompeted and extirpated from the system. In extreme cases of nutrient over-enrichment, the fast-growing, benthic algae will be replaced by planktonic microalgae via the same mechanism. The short residence times for water in Florida's springs and most spring runs make this final stage in the progression unlikely.

A critical point in Duarte's (1995) review, however, is that a change in the structure of the vegetative community is not a continuous, gradual process that runs parallel to the rate of increased nutrient delivery. Rather, changes occur abruptly. Sudden shifts in the community, in many cases, are not tightly coupled to increased nutrient loading, and once a shift has occurred, the system can become decoupled from existing concentrations of nutrients in the water column. Thus, indirect effects of nutrient inputs and complex feedback mechanisms must be involved. For example, fast-growing algae tend to put less energy into creating structural tissues so they tend to be subject to higher grazing rates. Increased algal respiration during blooms may create hypoxic or anoxic conditions that kill grazers, which decreases grazing pressure on the fast-growing algae and creates a positive feedback in the eutrophication progression. Thus, there are likely to be nonlinear responses and thresholds that need to be fully understood in order to predict the longer-term consequences of nutrient over-enrichment for vegetative communities in Florida's various spring systems.

One potentially key shift in the floral communities in Florida's springs is from palatable species to unpalatable species, especially *Lyngbya wollei*. Recent evidence indicates that this cyanobacterium may have the capacity to produce neurotoxins that affect ecosystem structure and function, as well as human health (Carmichael *et al.* 1997; Onodera *et al.* 1997; Teneva *et al.* 2003; Berry *et al.* 2004). For example, it has been hypothesized that heavy infestations of *Lyngbya* on the skin of manatees in springs may be related to recent observations of health problems (Bledsoe *et al.* 2006). From a human health perspective, it is unclear whether *Lyngbya* toxins are associated with recent reports of contact dermatitis by recreational users of springs.

A final point relates to the recovery of submerged aquatic vegetation communities following nutrient remediation and reduction. Recovery is likely to be a very slow process, in large part, because it involves the replacement of fast-growing species with relatively slow-growing species. Duarte (1995) employed a simulation model that predicted recovery times of centuries

for systems originally occupied by slow-growing seagrasses. It is worth noting here that many of the historically dominant vascular plants in Florida's spring systems (e.g., *Vallisneria americana* and *Sagittaria kurziana*) share morphologies and life histories with these seagrasses. Expectations regarding responses to nutrient reduction should be tempered by these considerations.

EFFECTS OF NUTRIENTS ON FAUNA

Florida's 700+ springs represent important aquatic habitats for fauna that are subject to stress by increased nutrients. Key elements of spring systems resemble key elements of many lotic or flowing water systems (Figure 2; Vannote *et al.* 1980; USEPA 2006). Therefore, effects of nutrients can be elucidated from science conducted in these springs and by extracting key principles drawn from beyond Florida and from other aquatic systems.

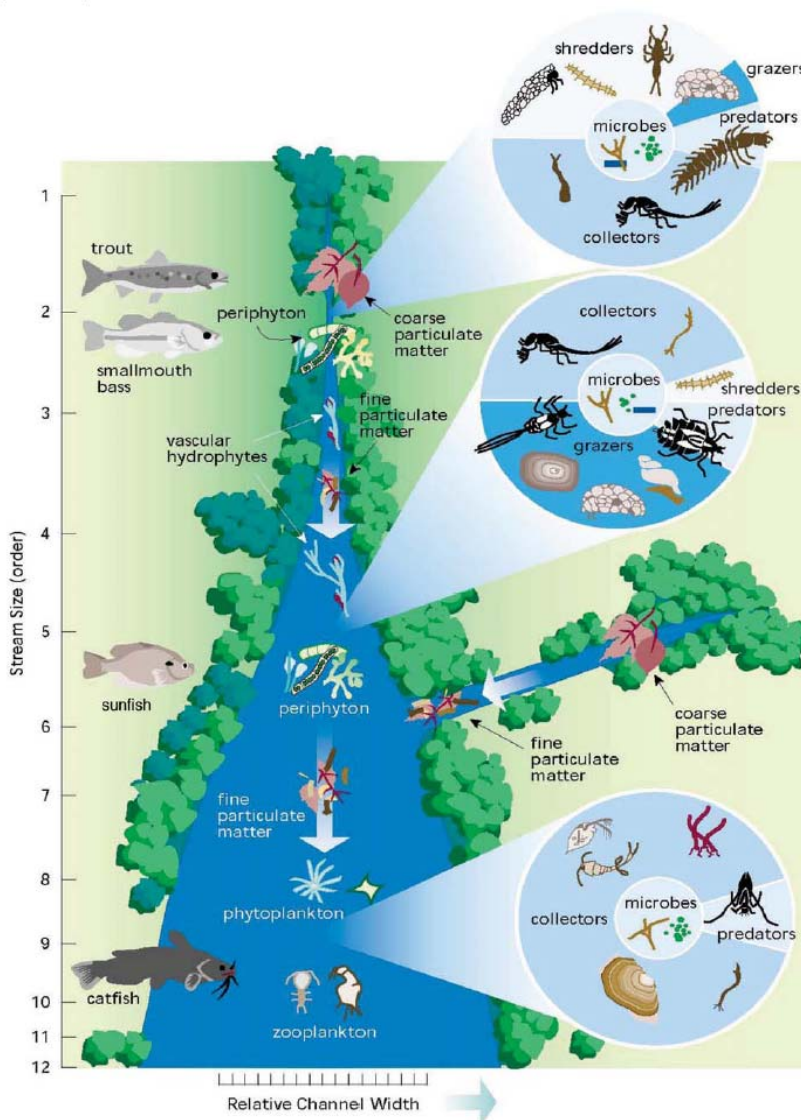


Figure 2 – Key components of lotic ecosystems (USEPA 2006).

Components of Spring Ecosystems

In general, phytoplankton and zooplankton represent minor components of lotic systems until they are relatively large, deep and slow flowing; therefore, the focus falls on benthic organisms and trophic links. The base of trophic webs in flowing systems includes allocthonous material, or external inputs such as leaves from terrestrial vegetation, and autocthonous material that is produced in the system. Autocthonous material becomes more important as shading by riparian vegetation decreases and in-stream primary producers photosynthesize more effectively. Key primary producers in flowing systems include macroalgae, vascular macrophytes and periphyton, with these algal species growing on almost all biotic and abiotic surfaces. Primary producers supply food to primary consumers dominated numerically by a variety of invertebrates, especially snails and larvae of aquatic insects. Primary and secondary consumers include invertebrates and fish, with piscivorous fish representing the major tertiary consumers.

Past and recent surveys of faunal assemblages in Florida's springs documented species that fill the expected ecological niches. For example, invertebrates from five functional feeding groups were found in the Wekiva and Ichetucknee Rivers (Warren *et al.* 2000; Steigerwalt 2005). These groups comprise grazers on attached algae or microbiota, shredders that consume coarse particles of living or dead plant material, gatherers that collect fine particles of organic detritus, filterers of suspended particulate organic matter, and predators feeding on live animal prey. Similarly, fish in the Wekiva River spanned the expected trophic roles, including detritivores, herbivores that often feed on algae, planktivores, invertivores and piscivores of various sizes (Warren *et al.* 2000).

Karst habitats in Florida support cave fauna or stygobiota and obligate fauna in springs that are not found in other types of aquatic systems (Walsh 2001; Shelton 2005). Nearly one third of stygobites have recorded distributions limited to single cave systems, and 67% of these taxa have been found in 10 systems or less. Therefore, a high percentage of these species are listed as of special concern, rare, threatened or endangered. Obligate fauna of springs include hydrobiid and pleurocerid snails with highly restricted ranges leading to about eight species being considered endangered, threatened or of special concern (Walsh 2001). For example, the upper St Johns River basin holds ten species of rare and endemic snails, with *Aphaostracon monas*, *Floridobia alexander*, *Floridobia petrifons* and *Floridobia wekiwae* found only at a single spring and *Aphaostracon pycnum* found at two springs (Shelton 2005).

In aquatic systems, nutrients exert effects on animals primarily through changes in primary producers or direct toxicity. Changes in primary producers flow through ecosystems to affect animals primarily by altering habitats or trophic interactions. This section focuses on these indirect effects and direct toxicity.

Relationships Between Nutrients and Invertebrates in Florida Springs

Nutrients can affect the type and amount of flora found in spring systems. In turn, changes in vascular plants, attached macroalgae and mats of filamentous algae can alter the food and refuge available to invertebrates in Florida springs. However, few studies have assessed invertebrate assemblages in different types of vegetation to obtain a synoptic view.

A survey of the Homossassa and Weeki Wachee Rivers found differences in the number of species and relative densities of certain insects along the length of the waterways (Sloan 1956). Habitats were classified according to the areal coverage of dominant macrophytes. Our reanalysis of the data showed that numbers of species did not correlate with variations in coverage from 10% to 70%, and the relative density of mayflies was positively correlated with increasing cover of macrophytes in the Homosassa River but not in the Weeki Wachee River. In general, the insect assemblages appeared to vary primarily according to concentrations of dissolved oxygen near spring boils and salinity near the estuarine endpoints of the rivers.

In Sulphur Springs Run, quantitative samples taken in bare sediment and algal mats with a petite Ponar dredge showed no significant differences in numbers of individuals and no obvious differences in assemblage composition (Allen *et al.* 2001). An introduced snail, *Tarebia granifera*, dominated all samples, and evenness and diversity indices indicated assemblages dominated by few species.

A more in-depth survey of four key habitats in the Wekiva River yielded similar and statistically equal numbers of invertebrates, i.e., 20,000–34,000 individuals m⁻² (Warren *et al.* 2000). Sampling methods were designed specifically for each habitat; however, the comparative efficiencies of the different methods were not assessed. Therefore, the data support general comparisons of faunal assemblages among habitats, but detailed quantitative comparisons may prove unreliable.

The relative abundance of different functional types varied among habitats (Figure 3; Warren *et al.* 2000). Gatherers were found in all habitats, and they dominated bare sediments. The relative importance of grazers increased in floating mats composed primarily of *Hydrocotyle umbellata* (water pennywort) and beds of *Vallisneria americana* (tape grass). Predators were found in all habitats in similar relative abundances. Filterers were most common in beds of *Vallisneria americana* and essentially absent from floating mats, which was attributed to the increased flow measured at sites with *Vallisneria americana*. Shredders, which are considered key components of most shallow freshwater systems, represented less than 1% of the organisms sampled. Overall, this survey indicated that altering the areal coverage and species compositions of habitats might lead to changes in invertebrate assemblages.

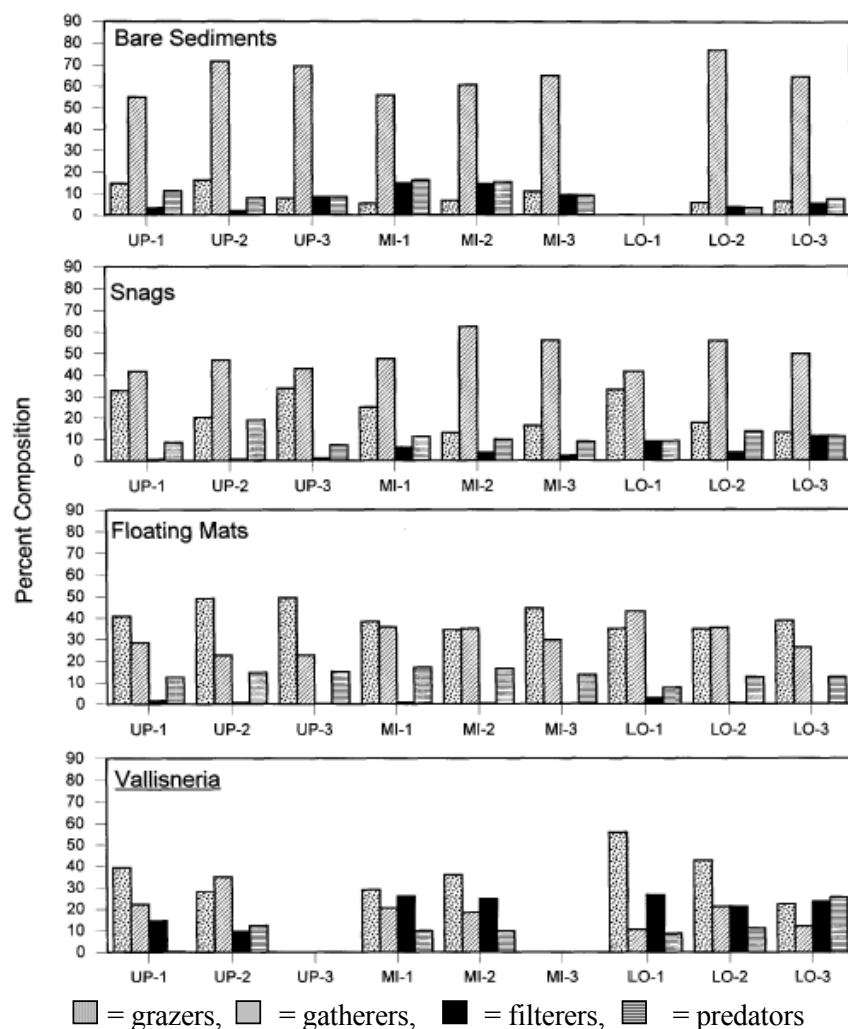


Figure 3 – Relative abundance of functional groups of aquatic invertebrates in May/June and October samples taken at multiple sites in the Wekiva River (Warren *et al.* 2000).

Invertebrate assemblages in lotic systems are used as indicators of ecological health (e.g., USEPA 2006). For example, Florida has two biotic indices, the Stream Condition Index (SCI) that relies on laboratory processing of samples and the more rapid Biological Reconnaissance (BioRecon) that uses sorting in the field (Fore *et al.* 2006).

Indices combine various metrics derived from standardized sampling of invertebrate assemblages, e.g., number of taxa, abundances of specific taxa, and relative abundances or percentage dominance of selected taxa. The concept that invertebrate taxa exhibit some consistency in their response to disturbances underpins biotic indices. In Florida and elsewhere, biotic indices were developed empirically using samples of invertebrates collected from locales chosen to represent different levels of disturbance. The levels of disturbance used to classify locales combined multiple factors, such as habitat quality, one or more water quality parameters, and evaluation of land use. Overall, these indices provide indications of differences or changes in assemblages; however, the causes of such differences or changes typically are derived from correlations with auxiliary data on water quality, habitat quality, or other putative forcing factors.

Interpreting correlations between biotic indices and forcing factors may be less than straightforward. For example, over a 14-year period, invertebrate abundance was positively correlated with nitrate concentrations in the waters of the Suwannee River basin (Hornsby *et al.* 2004). In contrast, number of taxa, diversity, and evenness were negatively correlated with nitrate concentrations (Hornsby *et al.* 2004). These results were interpreted as indicating that higher nitrate concentrations led to an increase in the absolute number of invertebrates and a decrease in the biodiversity of the invertebrate assemblage. However, 17 of the 40 taxa that were common in these samples have been classified as indicative of clean water in the Florida Department of Environmental Protection's Florida Index, a metric for surface water quality based on invertebrate assemblages.

In Florida, assessments have been conducted in various streams. Analysis of assessments conducted after recalibration of the Stream Condition Index (SCI) showed that SCI values were not significantly correlated with nitrate–nitrite concentrations or habitat assessment scores (Table 2; Figure 4). In nine springs with very poor to poor SCI values, nitrate–nitrite concentrations ranged from 0.02 to 1.90 mg L⁻¹. Concentrations in four springs with fair SCI values ranged from 0.06 to 1.60 mg L⁻¹, which is a nearly identical range. Correlations with nitrate–nitrite concentrations and habitat assessment scores accounted for less than 1% and 16% of the variation in the data, respectively. In contrast, SCI values were significantly correlated with dissolved oxygen concentrations, with a positive correlation that accounted for 36% of the variation in the data (Table 2; Figure 4). Such results illustrate the complexities associated with interpreting biotic indices, and they provide little insight into the form and magnitude of ecological responses to nutrient concentrations.

Table 2. Results from sampling in springs after recalibration of the Stream Condition Index (Agharahami 2006a and b; Deck 2005a and b; Deck 2006a, b and c; Patronis 2006a, b, c, d, e and f). VP = very poor; P = poor; F = fair; < DL = below detection limit; < PQL = below practical quantitation limit; O = optimal; SO = sub-optimal; LO = low optimal; I–F = impaired–fair; I = impaired; F = fair.

Spring	Sampling date (DD-MM-YY)	Stream Condition Index		NO _x	NH ₃ (mg L ⁻¹)	TP	DO	Habitat Assessment		Overall rank
		Score	Rank					Score	Rank	
Rock (upper)	25-05-06	11	VP	1.40	< DL	0.11	4.2	134	O	I–F
Alexander	07-06-06	17	VP	0.04	< DL	< PQL	3.7	119	SO	I
Volusia Blue	26-04-05	17	VP	0.57	< DL	0.08	2.5	105	SO	I
Wakulla	11-04-06	20	P	0.37	< DL	< PQL	6.6	129	O	I
Manatee	21-06-06	21	P	1.90	< DL	< PQL	2.6	98	SO	I–F
Ponce de Leon	22-06-06	32	P	0.25	< DL	< PQL	7.0	114	SO	I
Silver Glen	08-06-06	32	P	0.02	< DL	< PQL	6.8	118	SO	I
Wekiwa	26-04-05	35	P	1.10	< DL	0.13	3.6	117	SO	I–F
Blue Hole	22-06-06	36	P	0.42	0.02	< PQL	6.9	111	LO	I–F
Ichetucknee	18-04-06	40	P	0.57	< DL	< PQL	4.5	145	O	F
Silver River	07-06-06	46	F	1.30	< DL	< PQL	6.3	129	O	F
Rainbow	25-05-05	47	F	1.60	< DL	< PQL	—	140	O	F
Rock (lower)	25-08-06	47	F	1.40	< DL	0.10	5.4	126	O	I–F
Juniper	08-06-06	51	F	0.06	< DL	< PQL	8.7	129	O	F

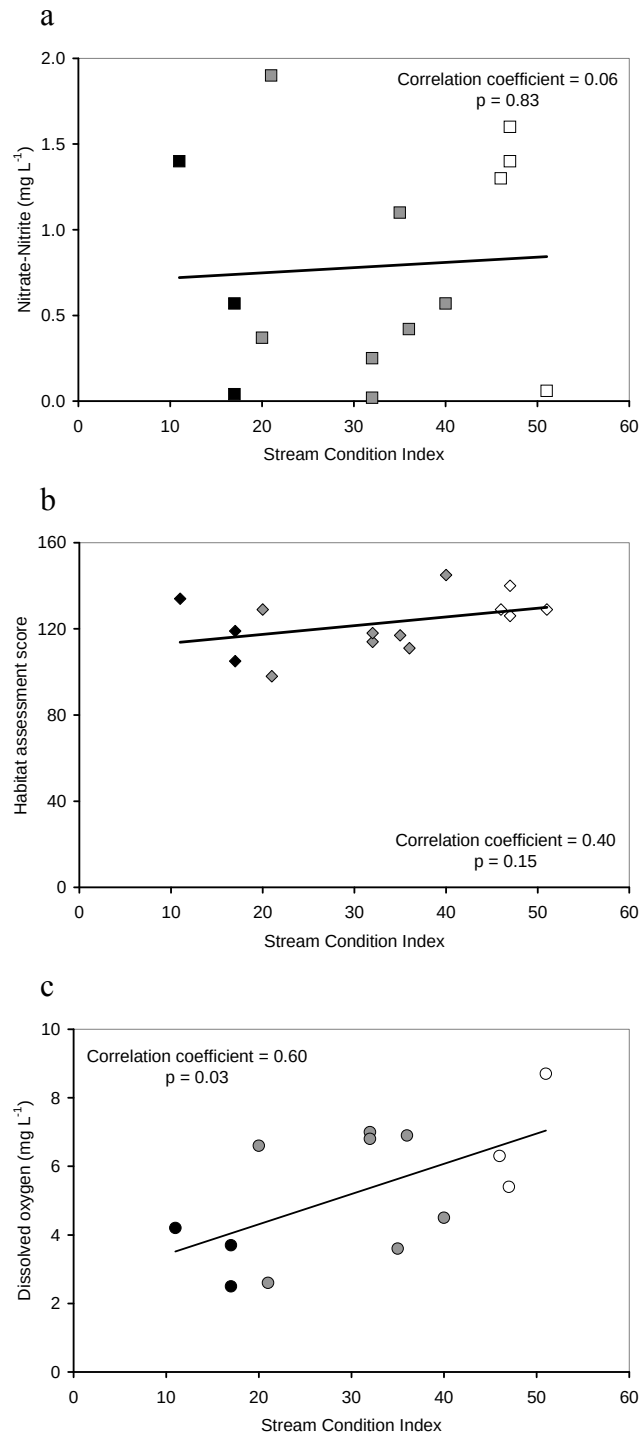


Figure 4 – Correlations between Stream Condition Indices (SCI) and (a) nitrate–nitrite concentrations, (b) habitat assessment scores and (c) concentrations of dissolved oxygen (Agharahimi 2006a and b; Deck 2005a and b; Deck 2006a, b and c; Patronis 2006a, b, c, d, e and f). black squares, triangles and circles = very poor SCI values; gray squares, triangles and circles = poor SCI values; white squares, triangles and circles = fair SCI values; lines provided to illustrate the correlations

Relationships Between Nutrients and Fish in Florida Springs

By affecting the flora of springs and other aquatic systems, nutrients also can affect fish that rely on this flora for food and shelter, including fish species that provide considerable economic value. Florida's lotic systems contain 289 species, with 113 species native to North America and 16 species endemic to Florida and adjacent portions of Alabama and Georgia (Bass 1991). Unfortunately, most studies, such as a broad survey of fish in streams throughout Florida, lack detailed information about assemblages in specific habitats (Bass and Cox 1985).

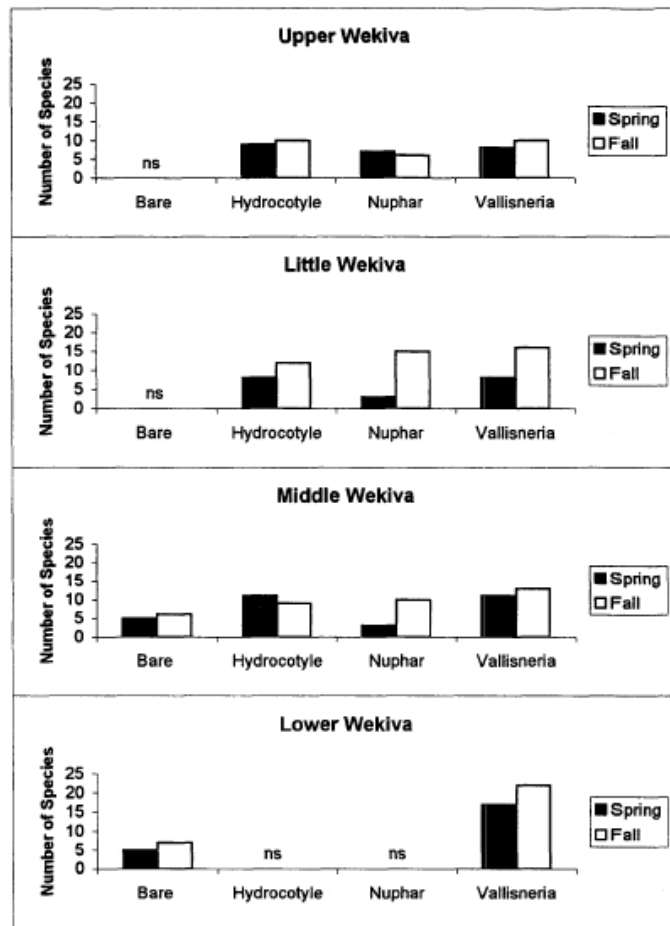
For example, the fish community in Silver Springs has been examined in two studies separated by approximately 50 years (Odum 1957b; Munch *et al.* 2006). The assemblages were reported to be similar, with the primary difference being reduced numbers of mullet and catfish ascribed to disrupted migratory patterns following construction of a dam. However, neither study focused on differences in fish assemblages among habitats.

In contrast, two habitat classes were included in a survey of 16 Florida streams (Canfield and Hoyer 1988a and b). These streams were sampled with blocknets and electrofishing gear as part of a study assessing the effects of nutrients from treated sewage effluent on the Wekiva River. Habitat classes were limited to open and closed forest canopy, and sampling was biased towards fish with total lengths of over 100 mm. Regardless, higher standing stocks and biomasses were found in reaches with an open forest canopy, which coincided with reaches where macrophytes were more abundant.

Detailed data on fish assemblages in specific habitats comes from a second study of the Wekiva River (Warren *et al.* 2000). Throw traps and a combination of blocknets and electrofishing were used to sample fish in four specific habitats: bare sediment, *Hydrocotyle umbellata*, *Nuphar advena* subspecies *lutea* (spatterdock) and *Vallisneria americana*.

Throw traps and blocknets collected forty species of fish from various reaches, with more species collected from vegetated habitats (Figure 5). *Hydrocotyle umbellata* yielded the highest mean density of fish, followed by *Vallisneria americana*, *Nuphar advena* and bare sediment (Figure 6). In contrast, samples from *Vallisneria americana* tended to yield the greatest biomass because these samples contained more sunfish in the family Centrarchidae (Figures 7–11). Samples from *Hydrocotyle umbellata* were dominated by small, livebearing Poeciliidae, and samples from *Nuphar advena* and bare sediment contained large numbers of small minnows in the family Cyprinidae and killifishes in the family Fundulidae (Figures 8–11). Mullet also were found in samples taken from within blocknets set over bare sediment in the Lower Wekiva River (Figures 10 and 11). These differences in fish assemblages were attributed predominantly to interactions among characteristics of the habitats and the biology and ecology of fish species. Similar to comparisons for Silver Springs, broad comparisons between the two studies of the Wekiva River indicated that the fish assemblage had changed little between 1985–1987 and 1997 (Canfield and Hoyer 1988a; Warren *et al.* 2000). Thus, we do not have data linking changes in fish assemblages to changes in nutrient concentrations in springs at this time.

a



b

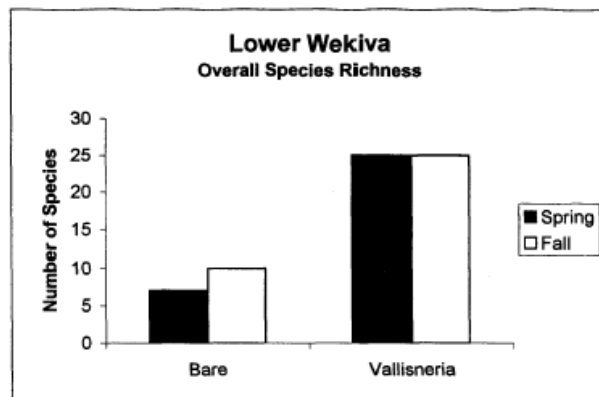
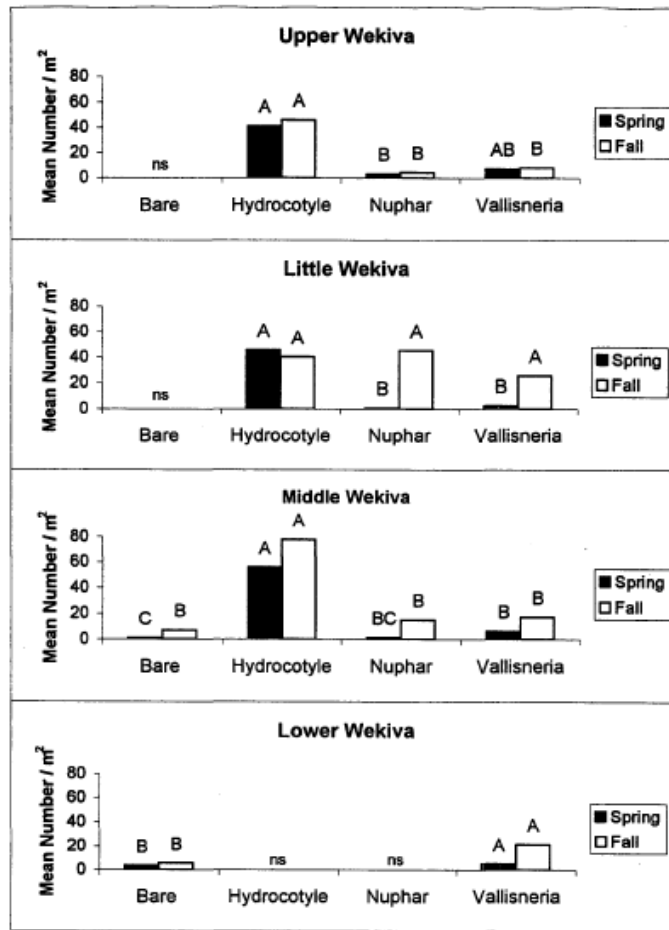


Figure 5 – Species richness in (a) throw trap and (b) blocknet samples (Warren et al. 2000).

a



b

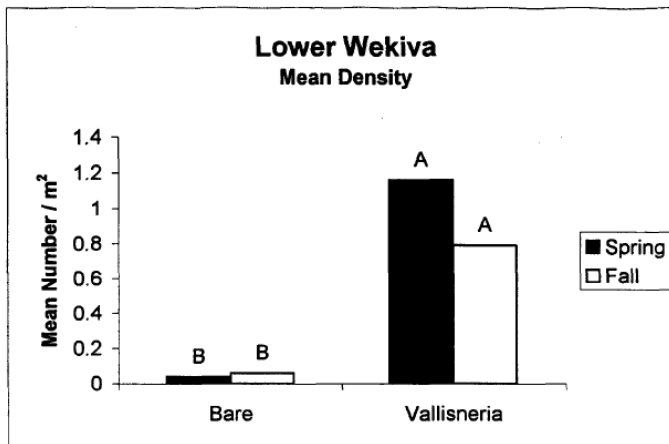
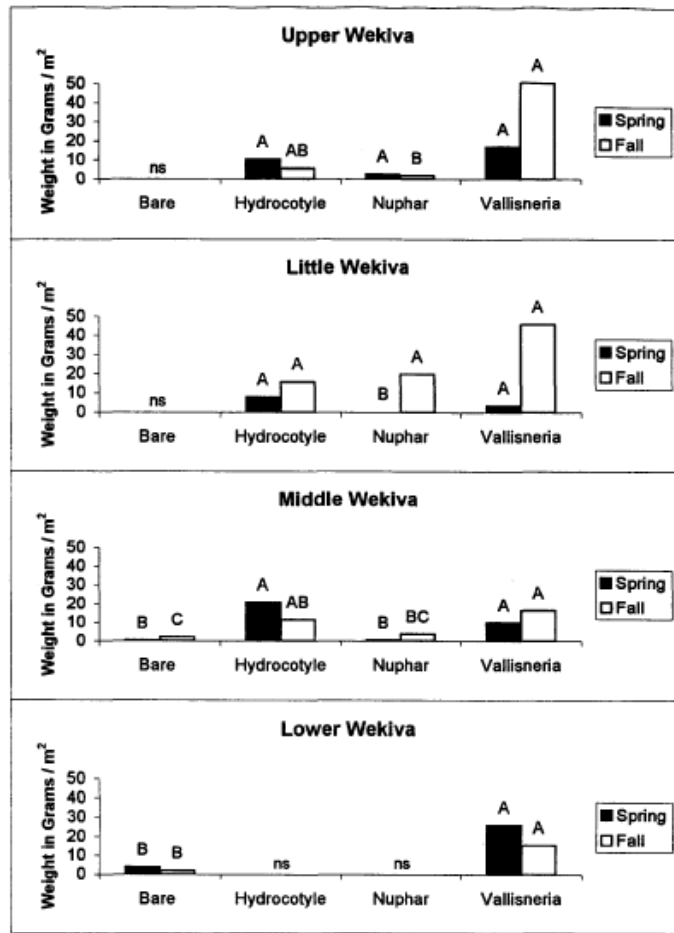


Figure 6 – Densities of fish in (a) throw trap and (b) blocknet samples (Warren et al. 2000).

a



b

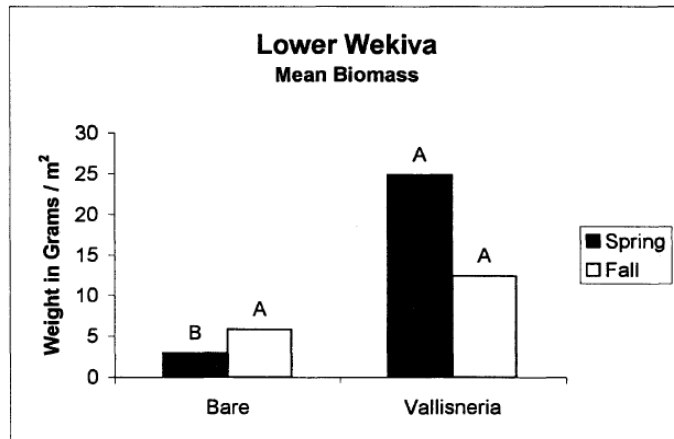
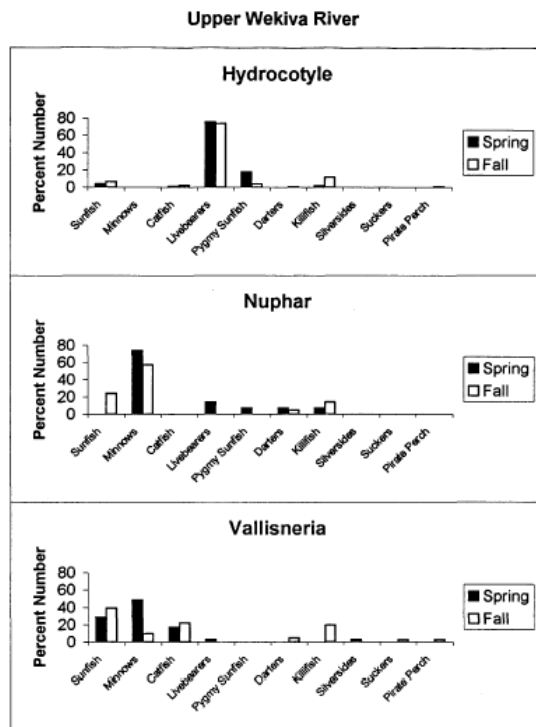
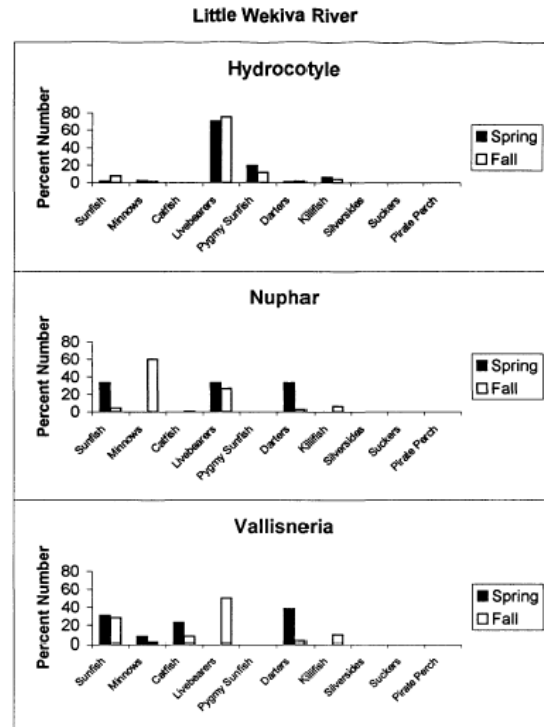


Figure 7 – Biomass of fish in (a) throw trap and (b) blocknet samples (Warren et al. 2000).

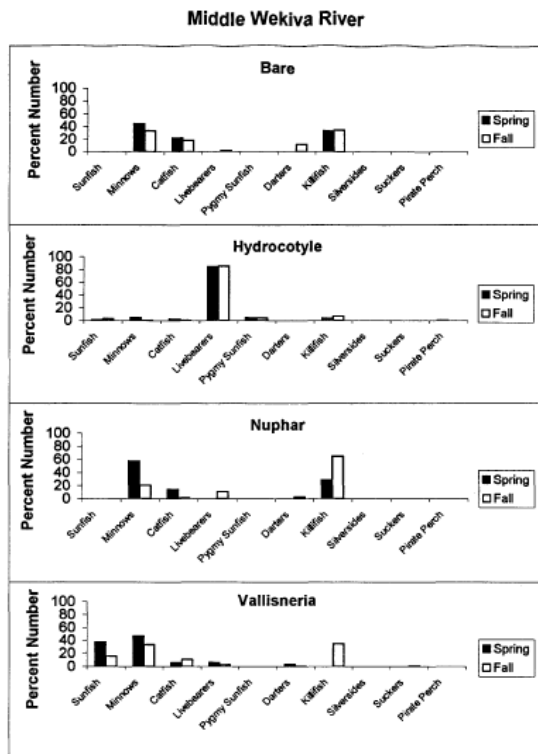
a



b



c



d

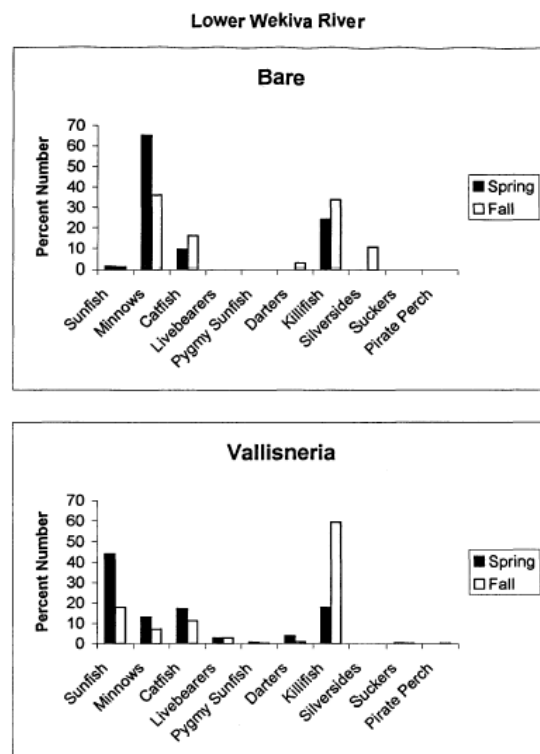
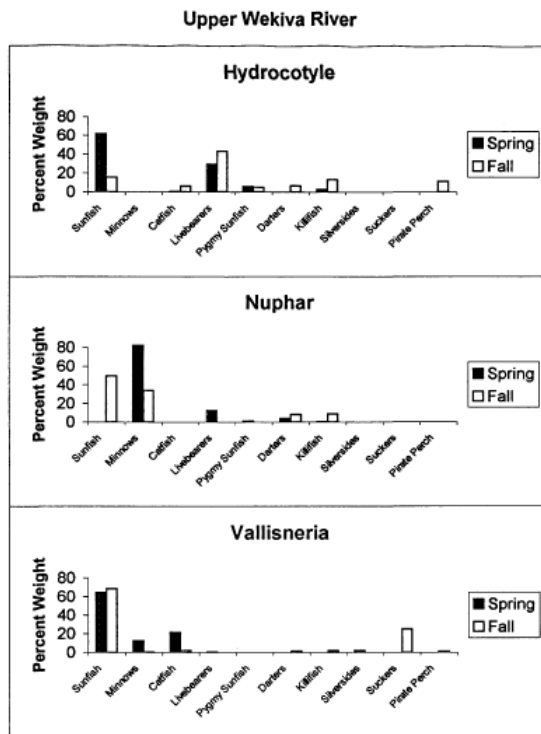
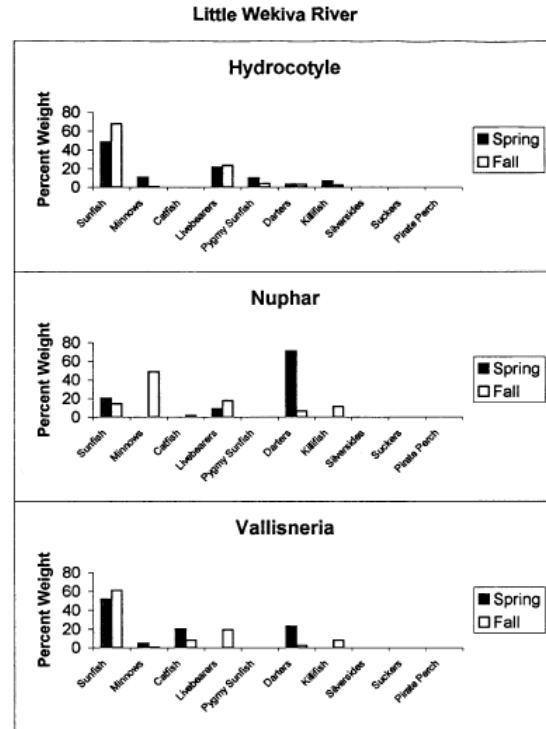


Figure 8 – Assemblage composition by abundance in throw trap samples (Warren et al. 2000).

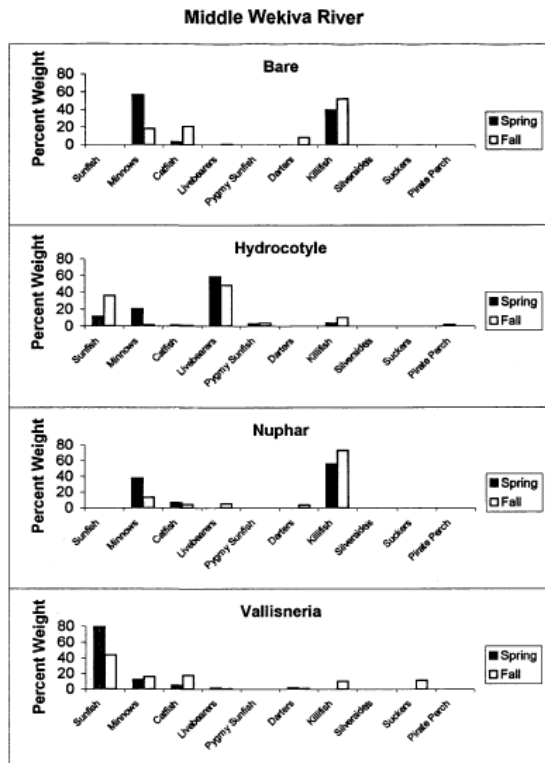
a



b



c



d

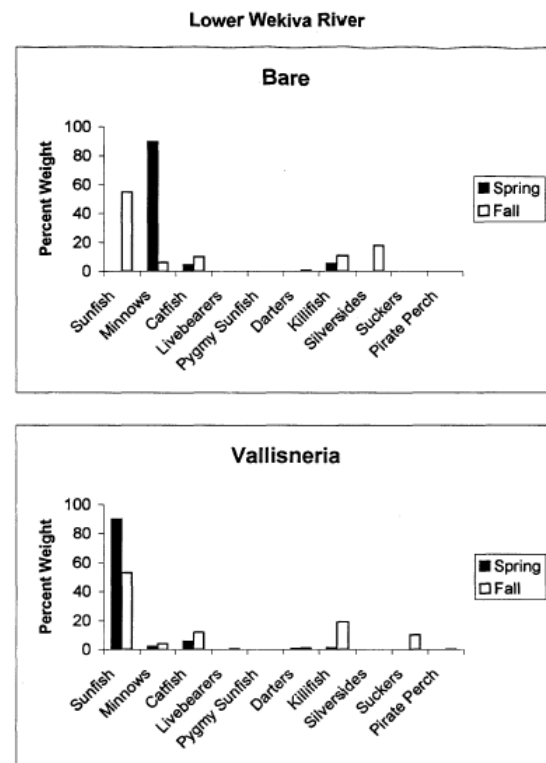


Figure 9 – Assemblage composition by biomass in throw trap samples (Warren et al. 2000).

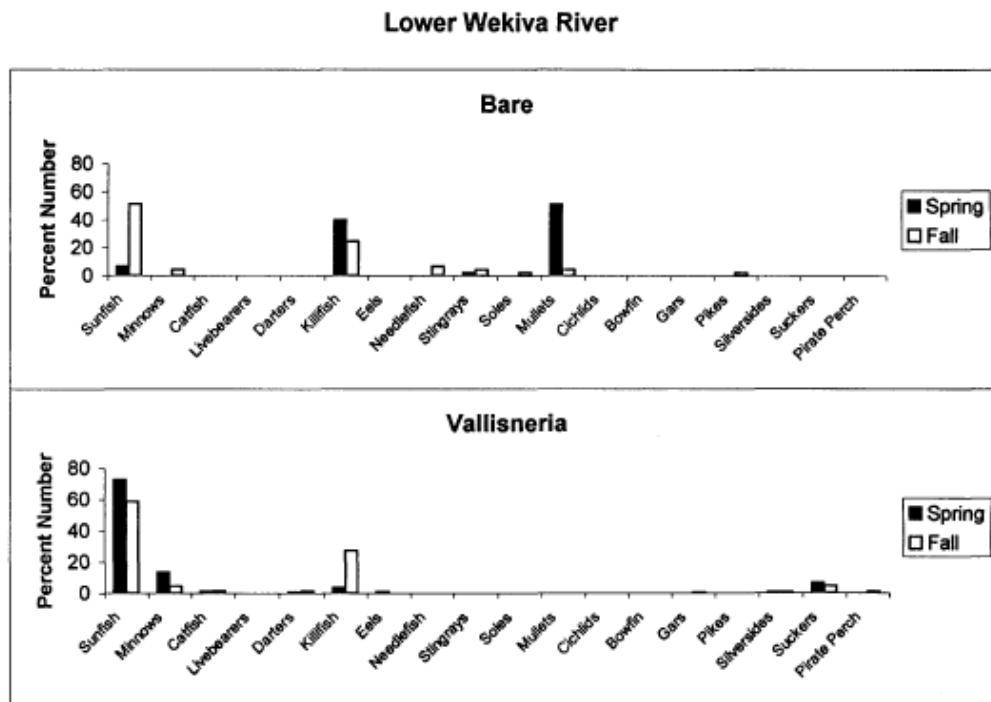


Figure 10 – Assemblage composition by numbers for blocknet samples (Warren et al. 2000).

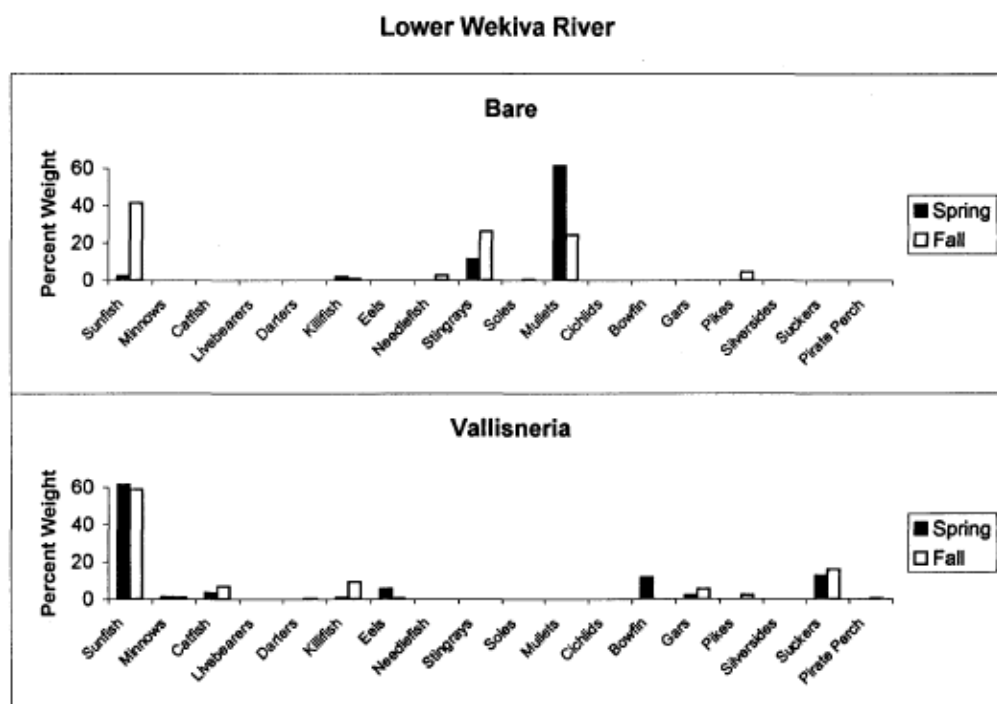


Figure 11 – Assemblage composition by biomass for blocknet samples (Warren et al. 2000).

Summary of Relationships Between Nutrients and Fauna in Florida Springs

In summary, surveys of faunal assemblages in Florida springs have suggested the possibility of indirect influences from nutrients mediated through differences or changes in habitats. However, results of repeated surveys indicate faunal assemblages have not changed even if nitrate levels have risen. Unfortunately, these studies were not designed to identify the form and magnitude of interactions among nutrient inputs, primary producers and fauna.

Studies conducted in streams outside Florida and in lakes can provide additional insights into how nutrients affect habitat use and trophic relationships. Such insights can guide future work in Florida's spring ecosystems.

Nutrient Effects Operating Through Ecosystem Processes

Interactions among animals and habitats vary not only among species but also among life history stages or ages within species. Such interactions may result in nonlinear effects on key parameters such as growth rates (Mittelbach and Osenberg 1993; Diehl and Kornijów 1998). For example, fish may rely heavily on macrophytes for refuge from predation in the early portion of their life histories even if it reduces their growth rate (Figure 12). A nonlinear change in growth rate may be associated with changing habitat use after achieving a size refuge (S) from piscivores, which emphasizes the importance of having detailed information on the form and magnitude of responses to changes in habitats (Figure 11). Such information is not available for most species of fish, including most species found in Florida springs.

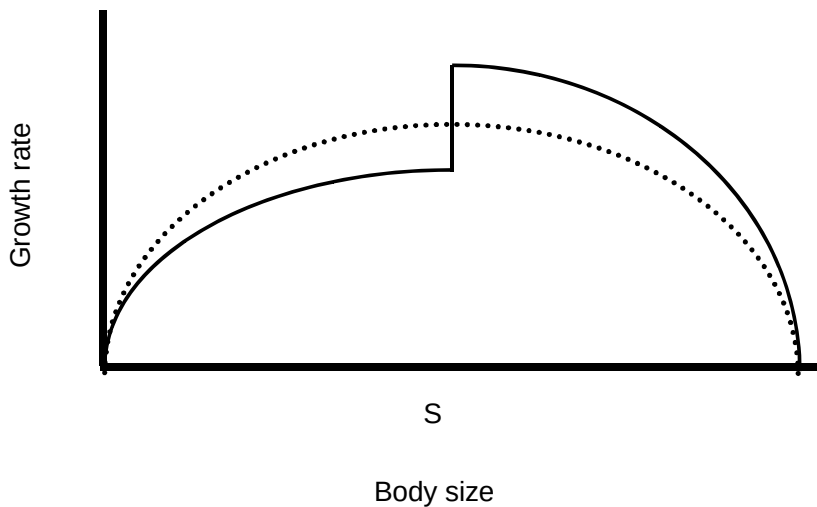


Figure 12 – Diagram depicting a change in growth rate experienced by a fish when it switches from a suboptimal habitat used as a refuge from predators to a more optimal habitat once it has achieved a size refuge (adapted from Diehl and Kornijów 1998). Solid line represents growth rate exhibited by a fish that switches from one habitat to another once it achieves a size refuge from piscivores at body size S. Dotted line represents the growth rate of a fish able to use all available habitats and food resources due to the absence of piscivores. The difference between the lines represents the cost or benefit associated with the use of each habitat.

Up to some level, increased nutrient inputs can increase the productivity of macrophytes, which provides more food for herbivores and may lead to increases in secondary and tertiary consumers. The role of aquatic macrophytes as a food source for the most numerous grazers remains a controversial issue (Sheldon 1987; Brönmark 1990; Sheldon 1990; Newman 1991). Living macrophytes (mosses, flowering plants and macroalgae) have been regarded as a little used food source due to high C:N ratios (e.g., 20–1,340), large quantities of cellulose and lignin, decreased digestibility of their proteins and presence of secondary chemicals that retard grazing (Brönmark 1990). Larger grazers, such as manatees, turtles and *Pomacea paludosa*, the Florida apple snail, do graze macrophytes. The effect of this grazing can be significant (Hauxwell *et al.* 2004; Jacoby *et al.* 2007). In addition, some insects, crayfish, birds and mammals have been reported to reduce macrophyte biomass through consumption or damage during grazing on periphyton (Cummins and Klug 1979; Mann 1988; Lodge 1991; Lodge *et al.* 1998; Newman 1991).

Regardless of their contribution as a source of food, macrophytes do provide a significant substratum for periphyton, which is grazed heavily by the most abundant animals. As discussed above, periphyton can outcompete macrophytes for resources, such as light and nutrients. Excessive growth of periphyton has the potential to lead to loss of macrophytes, with subsequent effects on refuge and trophic interactions.

Grazers can mediate the growth and effects of periphyton. Experiments using elevated tiles as a mean of excluding the herbivorous larvae of the caddisfly, *Helicopsyche borealis*, demonstrated effects of grazing on biomass and turnover of microalgae (Lamberti and Resh 1983). In grazed treatments, biomass, measured as chlorophyll *a* cm⁻², was 5–500 times lower and turnover, measured as oxygen production per unit chlorophyll *a*, was approximately 5 times higher (Lamberti and Resh 1983). Meta-analyses of experiments comparing grazers at ambient densities to treatments without grazers indicated that grazers significantly reduced periphyton biomass in 70% of experiments and measurably altered the taxonomy or physiognomic structure of assemblages in 81% of experiments (Feminella and Hawkins 1995). Typically, less than 70% of experiments showed effects on productivity, and the effects varied with the parameter measured (Feminella and Hawkins 1995). Significant effects were equally likely in laboratory and field experiments and across durations of less than and greater than 4 weeks, although factors such as the total amount of periphyton accrued, the type of grazer manipulated, and the total biomass of grazers influenced the magnitude of the effects recorded.

Grazers represent multiple levels of organismal complexity, and they interact with periphyton and each other in complex ways. For example, the extracellular polysaccharide sheath produced by *Lyngbya wollei* deterred grazing by the amphipod *Hyallela azteca* (Camacho and Thacker 2006). In streamside experimental troughs, herbivorous protozoa were shown to graze on benthic diatoms, with estimated consumption rates varying from 4,000 diatoms cm⁻² h⁻¹ in systems with few or no macrograzers to 150 diatoms cm⁻² h⁻¹ in systems with large numbers of macrograzers, supposedly due to competition or predation (McCormick 1991).

Overall, the effects of nutrients in aquatic systems appear to be mediated by a combination of bottom-up and top-down effects. For example, larvae of the chironomid *Orthocladius rivulorum* build tubes and harvest the diatoms growing on them. Addition of phosphorus and phosphorus plus nitrogen to a stream led to a greater biomass of periphyton and larger larvae (Hershey

et al. 1988). Nitrogen and phosphorus appeared to be co-limiting factors as indicated by greater accumulation of periphyton downstream of combined additions (Hershey *et al.* 1988). The system involved a positive feedback loop, with larvae in fertilized reaches growing larger, building larger tubes that supported more periphyton, and, in turn, having more food to harvest (Hershey *et al.* 1988). In addition to interactions among nutrients, periphyton may respond to other limiting factors and grazing. Periphyton in streamside, flow-through channels exhibited statistically significant increases above controls only when nitrogen and phosphorus were added, light was increased, and grazing was eliminated (Rosemond 1993). In addition, manipulating single factors led to different responses. For example, increased light elicited both a physiological response resulting in decreased chlorophyll *a* concentrations in cells and a change in the periphyton assemblage when algae adapted to low light conditions were lost (Rosemond 1993).

All the bottom-up influences of nutrients and light and top-down influences of grazing can be mediated through actual or potential trophic interactions. Manipulations of pools in a stream demonstrated that grazing minnows controlled periphyton growth unless predatory fish were present, in which case predation and avoidance of predation led to increased standing crops of periphyton in deeper sections of the stream (Power *et al.* 1985).

In some cases, spring systems may exhibit very complex trophic cascades, which involve reciprocal interactions among predators and prey that result in ecological changes across trophic links. Manipulations of lakes demonstrated that such effects remain stable across a range of conditions (Carpenter *et al.* 1987; Carpenter *et al.* 2001). For example, a reference lake was characterized by variable productivity of phytoplankton related to the effects of climatic factors and the natural dynamics of food webs. Manipulating numbers of zooplanktivores and piscivores in other lakes yielded consistent changes in zooplankton assemblages and their grazing, which led to altered phytoplankton assemblages and productivity. For example, gelatinous, colonial green algae became more abundant in a lake with reduced feeding on zooplankton. Additions of significant quantities of nitrogen and phosphorus did not disrupt the trophic cascade. Piscivorous fishes reduced numbers of zooplanktivorous fishes to an extent that allowed zooplankton numbers to increase. The resulting increased grazing by zooplankton controlled the phytoplankton assemblage.

Over time, the interactions among bottom-up and top-down effects can change. For example, nutrient additions to a river led to increased primary production in years 1 and 2, with increased production of insects and fish lagging until years 3 and 4 (Peterson *et al.* 1993). Competition among insects moderated the flow of increased primary production through the trophic web (Peterson *et al.* 1993).

Given the complexity of potential interactions, it is not surprising that an attempt to correlate standing crop of fish with phosphorus levels in streams led to the conclusion that increases in fish biomass with increased phosphorus were greater at lower initial phosphorus concentrations (Hoyer and Canfield 1991). Other responses of lotic systems to increased nutrients also are likely to be nonlinear, with the potential for thresholds and feedback loops.

In fact, nonlinear responses, such as thresholds and feedback loops, characterize one of the most cogent descriptions of eutrophication (Duarte 1995). In the eutrophication progression, interactions among nutrients, plants and algae, and grazers combine to produce changes that are not linearly correlated with nutrient concentrations. With large and chronic increases in nutrients, an aquatic system is highly likely to follow a qualitative progression from long-lived, rooted, vascular plants that provide a key structural habitat to systems dominated by fast-growing macroalgae and microalgae and potentially to systems dominated by phytoplankton if residence times are long enough. Nonlinearities make the quantitative responses of any given system difficult to predict, without detailed information.

In addition to effects on trophic interactions among primary producers, grazers and consumers, nutrient enrichment also may alter interactions between parasites and hosts. Additions of nutrients to mesocosms led to increased algal production, higher densities of snails, greater production of trematode cercariae, and ultimately, increased infection of frogs yielding deformities that decreased their survival (Johnson *et al.* 2007). The prevalence of such interactions and their consequences in aquatic systems remains unknown.

Nutrient Effects Operating Through Toxicity

Ammonia, nitrate and other chemicals can have toxic effects at a variety of levels from sublethal effects on the physiology, development, reproduction, behavior or morphology of individual organisms through to lethal effects that operate at the level of populations, assemblages and ecosystems (Mattson *et al.* 2006; Mattson *et al.* 2007). In general, toxicological experiments address endpoints related to individuals. For example, acute toxicity often is addressed by determining a concentration that kills 50% of the test organisms over a defined time interval, or an LC₅₀. Florida law contains a definition of a 96-hour LC₅₀, which is a concentration that kills 50% of the test organisms over a 4-day period (Florida Administrative Code Chapter 62–302.200). Sublethal endpoints can also be used to yield concentrations that cause a defined effect in a defined time interval. Terms for such endpoints include least observable effect level (LOEL), which is the lowest concentration at which a change of interest is observed, or no observable effect level (NOEL), which is the concentration at which a change of interest ceases to be observed. In addition, experiments can examine chronic toxicity or the effect of longer exposures to lower concentrations of toxicant; however, the time needed to conduct such experiments has led to various approaches to extrapolate results of acute tests. The results of laboratory experiments documenting effects on individuals typically are extrapolated to predict ecotoxicological effects, or effects at the population, assemblage or ecosystem levels. Effects at higher levels of organization may arise from density-mediated changes resulting from the death of organisms or trait-mediated changes resulting from sublethal influences, with extrapolations from laboratory results often relying on untested effects on reproductive success or trophic links. Trait-mediated effects represent a primary focus because they typically occur at lower levels of contamination.

Predictions of ecotoxicological effects may employ uncertainty factors to account for limitations imposed by testing relatively few individuals of relatively few species for relatively short periods at concentrations that cause an observable effect (Mattson *et al.* 2006). For example, an intraspecies uncertainty factor can be used to account for variation in sensitivity among individuals within a species. The USEPA recommended an intraspecies uncertainty factor

of 10 applied to any NOEL especially for endangered species (Mattson *et al.* 2006). An interspecies uncertainty factor ranging from 1 to 1,000 may be applied to account for uncertainties associated with extrapolating toxicokinetics (processes determining uptake rates, distribution among tissues, detoxification and elimination) and toxicodynamics (processes determining effects such as enzyme inhibition, enzyme facilitation and binding to DNA) from one species to another (Mattson *et al.* 2006). The magnitude of the uncertainty factor can be derived from allometric scaling of body sizes, known variation in acute and chronic sensitivity, and best professional judgment. Another uncertainty factor is used to translate the results of short-term studies to protection during long-term exposures. This adjustment accounts for the facts that contaminants often reach equilibrium levels only after long-term exposure; physiological compensations to toxins may fail after longer periods of exposure; latent, adverse effects may appear after exposure ceases; and longer exposures may affect life history stages that are more sensitive than those tested. Larger adjustments are needed when available data come from studies much shorter than the life expectancy of the target organism or much shorter than the time needed to achieve equilibrium concentrations in the tissues of the target organism. An uncertainty factor also can be used to predict NOELs from observed LOELs, with severe effects calling for a larger factor and unbounded LOELs from steep dose-response curves requiring smaller uncertainty factors than unbounded LOELs from curves with shallow slopes. Whenever they are applied, uncertainty factors lower the concentration considered acceptable in the environment.

The toxicity of aqueous solutions of ammonia, nitrite and nitrate has received attention primarily due to harmful effects in closed circulating systems, such as aquaria or fish hatcheries, and through drinking water for livestock that has been contaminated by urine, manure or fertilizer (Armstrong 1979; Shimura *et al.* 2002; Mattson *et al.* 2006). Ammonia tends to be more toxic than nitrite, which is typically more toxic than nitrate (Armstrong 1979).

Toxicity of Ammonia

The USEPA has invested significant effort in identifying water quality criteria for ammonia (e.g., USEPA 1999). Their results provide important guidance for establishing criteria related to concentrations of ammonia considered safe in aquatic environments. Some key findings from their analysis of data related to ammonia toxicity are:

- toxicity of ammonia can depend on the ionic composition, pH and temperature of water due to poorly understood mechanisms, with pH dependence strongly suggesting joint toxicity of unionized ammonia and ammonium ions
- ionic composition generates small effects on ammonia speciation in freshwater, and its other effects on toxicity are poorly established; therefore, the ionic composition of water was not considered in the derivations of criteria
- temperature can strongly affect the relative amounts of unionized ammonia and ammonium ion, but its effect on the toxicity of ammonia is not strongly indicative of joint toxicity so it was addressed strictly by an empirical approach

- pH effects were described by equations that include basic features of joint toxicity due to unionized ammonia and ammonium ion, along with an empirical component that addressed the incomplete knowledge of these effects

Detailed and updated analysis of acute toxicity data yielded criteria expected to protect aquatic life, except for unusually sensitive species. Criterion maximum concentrations (CMCs) drawn from acute toxicity tests address short-term exposure, and analysis of chronic toxicity data yields criterion continuous concentrations (CCCs) that address long-term exposure. The ultimate efficacy of the proposed criteria will be known only after monitoring. For example, chronic exposures to ammonia showed that a mayfly species in New Zealand would be protected minimally by the proposed criteria (Hickey *et al.* 1999). In Florida springs, the effects on obligate residents in springs and stygobiota represent special concerns. For example, a survey of stygobitic crayfish linked their presence or absence to ammonia concentrations in source water (Spanjer and Cipollini 2006). Regardless of the associated uncertainties, the proposed criteria are based on detailed interpretation of the best available information. Given temperature (T) and pH of a waterbody, the proposed criteria are:

1. The one-hour average concentration of total ammonia nitrogen (in mg-N L⁻¹) does not exceed, more than once every three years on the average, the CMC (acute criterion) calculated as:

$$\text{CMC} = \frac{0.275}{1 + 10^{7.204 - \text{pH}}} + \frac{39.0}{1 + 10^{\text{pH} - 7.204}} \text{ where salmonid fish are present}$$

$$\text{CMC} = \frac{0.411}{1 + 10^{7.204 - \text{pH}}} + \frac{58.4}{1 + 10^{\text{pH} - 7.204}} \text{ where salmonid fish are not present}$$

- 2A. The thirty-day average concentration of total ammonia nitrogen (in mg-N L⁻¹) does not exceed, more than once every three years on the average, the CCC (chronic criterion) calculated as:

$$\text{CCC} = \left(\frac{0.577}{1 + 10^{7.688 - \text{pH}}} + \frac{2.487}{1 + 10^{\text{pH} - 7.688}} \right) \cdot \text{Minimum of } (2.85, 1.45 \cdot 10^{0.028 \cdot (25 - T)})$$

where early life history stages of fish are present

$$\text{CCC} = \left(\frac{0.577}{1 + 10^{7.688 - \text{pH}}} + \frac{2.487}{1 + 10^{\text{pH} - 7.688}} \right) \cdot 1.45 \cdot 10^{0.028 \cdot (25 - \text{Maximum of } (T, 7))}$$

where early life history stages of fish are not present

- 2B. In addition, the highest, four-day average concentration of total ammonia nitrogen (in mg-N L⁻¹) within the 30-day period should not exceed 2.5 times the CCC.

Toxicity of Nitrate

Nitrate (NO_3^-) and nitrite (NO_2^-) coexist as the two major forms of oxidized nitrogen in aquatic systems. Nitrifying bacteria produce nitrite from organic forms of nitrogen and from ammonia as part of the nitrogen cycle (Lewis and Morris 1986). In aerobic environments, nitrite concentrations tend to be low because nitrite is converted rapidly to nitrate, a more stable form (Guillette and Edwards 2005). Analyses of nitrate in aquatic systems typically measure both nitrate and nitrite (Edwards *et al.* 2004). The solubility of nitrate means that any nitrate not taken up by plants or converted to nitrogen gas by denitrification is transported in surface water and groundwater.

Like all chemicals, the toxicity of nitrate and nitrite is mediated by its uptake and metabolism. Nitrate and nitrite enter animals either through permeable membranes, such as the gills of fish or tadpoles and the skin of adult amphibians, or through the gut wall after ingestion, which is the primary means for birds and mammals. It appears that the chloride transport mechanism of gill membranes actively transports nitrate (Jensen 2003; Lewis and Morris 1986). Nitrate in body fluids can be converted to nitrite or it can accumulate because of hepatic detoxification of nitrite (Edwards *et al.* 2004).

Several detrimental effects have been ascribed to nitrate. Concerns related to drinking water, including groundwater, have centered on nitrate interference with hemoglobin in the bloodstream resulting in a reduced ability to carry oxygen that leads to tissue hypoxia and cyanosis. In vertebrate animals, nitrate oxidizes the iron in hemoglobin molecules disrupting the reversible binding of oxygen and causing methemoglobinemia (Lewis and Morris 1986). In human infants, the resulting cyanosis is one cause of blue baby syndrome. Nitrate also can act as an endocrine disruptor, interfere with steroid hormone synthesis, affect sperm motility and viability, affect fecundity, or be toxic to embryos (Edwards *et al.* 2004; Edwards 2005; Guillette and Edwards 2005; Edwards *et al.* 2006a; Edwards and Guillette 2007). In fact, nitrate levels in some freshwater systems may reach and be sustained at levels that lead to declines in amphibians (Rouse *et al.* 1999).

Nitrate toxicity represents a concern in Florida springs because nitrate levels have risen during the past decades (Mattson *et al.* 2006; Mattson *et al.* 2007). Estimates of nitrate toxicity are available for a variety of organisms (Table 3; Camargo *et al.* 2005; Corrao *et al.* 2006; Mattson *et al.* 2007 and references therein). The bulk of the tests have been conducted on fishes, amphibians and aquatic invertebrates, including crustaceans, insects, and mollusks.

Table 3. Nitrate concentrations yielding 50% mortality in 96-hour tests (96-hour LC₅₀) or other changes deemed relevant, e.g., altered growth, time to metamorphosis or reproductive characteristics (Camargo *et al.* 2005; Corrao *et al.* 2006; Mattson *et al.* 2007).

Taxonomy	Life stage	96-hour LC ₅₀ (mg L ⁻¹ NO ₃ -N)	Other threshold (mg L ⁻¹ NO ₃ -N)
Order: Ephemeroptera			
<i>Baetis vernus</i>	Nymph		0.73
<i>Potamanthus luteus</i>	Nymph		0.70
<i>Baetis fuscatus</i>	Nymph		0.74
<i>Cloeon bifidum</i>	Nymph		0.72
<i>Ephemerella lenoki</i>	Nymph		0.74
<i>Heptagenia sulphurea</i>	Nymph		0.70
Order: Trichoptera			
<i>Cheumatopsyche pettiti</i>	Early instar larvae	113.5	2.4
	Last instar larvae	165.5	3.5
<i>Hydropsyche exocellata</i>	Last instar larvae	269.5	11.9
<i>Hydropsyche occidentalis</i>	Early instar larvae	97.3	1.4
	Last instar larvae	109	2.2
Order: Cladocera			
<i>Ceriodaphnia dubia</i>	Neonates		7.1–56.5
<i>Daphnia magna</i>	Neonates		358
<i>Daphnia</i> sp.	Adults		34.8–87.1
Order: Amphipoda			
<i>Eulimnogammarus toletanus</i>	Adults	85.0	4.4
<i>Eulimnogammarus echinosetosus</i>	Adults	62.5	2.8
Order: Decapoda			
<i>Cherax quadricarinatus</i>	Juveniles		1,000
<i>Astacus astacus</i>	Juveniles		14
<i>Penaeus monodon</i> (marine)	Protozoa		0.23
<i>Macrobrachium rosenbergii</i>	Juveniles		160
	Juveniles		175
Class: Gastropoda			
<i>Pomacea paludosa</i>	Adults & juveniles	> 500	> 500
<i>Potamopyrgus antipodarum</i>	Adults	1,042	195
Family: Salmonidae			
<i>Oncorhynchus mykiss</i>	Eggs		1.1
	Fry		1.1 - 4.5
	Fry		2.3
	Fingerlings	1,355	14
<i>Oncorhynchus kisutch</i>	Eggs		4.5
	Fry		4.5
<i>Oncorhynchus tshawytscha</i>	Eggs		4.5
	Fry		2.3 & 4.5
	Fingerlings	1,310	
<i>Oncorhynchus clarki</i>	Eggs		2.3 & 4.5
	Fry		4.5 & 7.6
<i>Salvelinus namaycush</i>	Swim-up fry	1,121.4	
	Embryo		100
	Alevin	2,342.5	400
	Embryo to swim-up fry		1.6
<i>Coregonus clupeaformis</i>	Swim-up fry	1,902.7	
	Embryo		25
	Alevin	2,185.7	25
	Embryo to swim-up fry		6.25

Taxonomy	Life stage	96-hour LC ₅₀ (mg L ⁻¹ NO ₃ -N)	Other threshold (mg L ⁻¹ NO ₃ -N)
Family: Moronidae			
<i>Morone</i> sp. hybrid	Unknown (juveniles?)		200
Family: Centrarchidae			
<i>Lepomis macrochirus</i>	Fingerlings	1,975	761
<i>Micropterus salmoides</i>	Fingerlings?	140	
<i>Micropterus treculi</i>	Fingerlings	1,261	
Family: Ictaluridae			
<i>Ictalurus punctatus</i>		1,355–1,423	90
Family: Cyprinidae			
<i>Pimephales promelas</i>	Larvae	1,010–1,607	358
<i>Catla catla</i>	Fry		1,484
Family: Poeciliidae			
<i>Gambusia affinis</i>	Embryos		4
	Adults		4
<i>Poecilia reticulatus</i>	Fry	191	
Family: Adrianichthyidae			
<i>Oryzias latipes</i>	Spawning		30
	Juveniles		50
Family: Bufonidae			
<i>Bufo bufo</i>	Tadpoles	384.8	22.6
<i>Bufo americanus</i>	Tadpoles	13.6–39.3	
	Fertilized eggs		9.0
<i>Bufo terrestris</i>	Tadpoles		30.0
	Tadpoles		4.9
<i>Xenopus laevis</i>	Embryos		24.8
	Tadpoles	1,655.8	65.6
Family: Hylidae			
<i>Hyla versicolor</i>			20
<i>Litoria caerulea</i>	Tadpoles		22.7
<i>Pseudacris triseriata</i>	Tadpoles	17	10.0
<i>Pseudacris regilla</i>	Embryos	643	56.7
	Tadpoles	1,749.8	30.1
Family: Ranidae			
<i>Rana pipiens</i>	Tadpoles	22.96	10.0 & 30.0
<i>Rana clamitans</i>	Tadpoles	32.4	
<i>Rana sylvatica</i>	Fertilized eggs		9.0
<i>Rana pretiosa</i>	Newly-hatched larvae		16.5
<i>Rana temporaria</i>	Larvae		5
<i>Rana aurora</i>	Embryos		29.0
Family: Ambystomatidae			
<i>Ambystoma maculatum</i>	Fertilized eggs		9.0
<i>Ambystoma jeffersonianum</i>	Fertilized eggs		9.0
<i>Ambystoma gracile</i>	Newly-hatched larvae		23.4
Family: Salamandridae			
<i>Triturus vulgaris</i>	Larvae		17.4
Order: Crocodilia			
<i>Alligator mississippiensis</i>	Juveniles		0.01–0.04

Nitrate concentrations from 0.23 mg L⁻¹ NO₃-N to over 1,000 mg L⁻¹ NO₃-N produced effects on invertebrates. Lethal concentrations in 96-hour tests ranged from 62.5 mg L⁻¹ for an adult amphipod to over 1,000 mg L⁻¹ for an adult snail. The lowest concentration causing an effect was 0.23 mg L⁻¹, which was reported for a larval stage of a marine shrimp. The lowest levels recorded or calculated to be of import for freshwater species were 0.70 mg L⁻¹ NO₃-N for nymphs of mayfly species when they were subjected to a mixture of nitrate, nitrite and ammonia. A value of 2.2 mg L⁻¹ was calculated as a safe concentration for long-term exposure of caddisfly larvae to nitrate alone. In general, early life history stages appear to be most sensitive, and freshwater invertebrates appear to be more sensitive than marine invertebrates. Thus, nitrate toxicity may have its most severe ecotoxicological effect on invertebrate growth and development rates, due to greater effects on larval phases.

Toxicity values for the effects of nitrate on fishes range from 1.1 mg L⁻¹ NO₃-N for least observable and no observable effects on eggs to over 1,000 mg L⁻¹ NO₃-N for effects on early life history stages. Channel catfish (*Ictalurus punctatus*), largemouth bass (*Micropterus salmoides*), bluegill (*Lepomis macrochirus*), and mosquitofish (*Gambusia holbrooki*) all exhibited responses to nitrate in laboratory experiments or abnormalities correlated with nitrate concentrations in freshwater habitats. Impacts on eggs, embryos or fry may represent special concerns. Responses may vary with environmental conditions and exposure. For example, increased salinity may buffer the toxic effects of nitrate and nitrite, and longer-term exposures may produce increased tolerance (Knepp and Arkin 1973; Russo *et al.* 1981).

Amphibians have been promoted as sentinel species or species that will provide an early warning of the ecological effects of toxicants. They suit this role because their skin increases uptake rates for contaminants as a byproduct of being adapted for respiration and hydration and because they have complex life histories spanning aquatic and terrestrial habitats. Negative effects of nitrate on amphibians include decreased activity, reduced feeding, disequilibrium, deformities, mortality, and altered timing of metamorphosis. Evidence points to nitrate acting as an endocrine disruptor. Overall, sensitivity to nitrate varies among amphibian species, with 13.6 mg L⁻¹ to over 1,000 mg L⁻¹ being reported to cause mortality in embryos over 96 hours and 4.9 mg L⁻¹ to 65 mg L⁻¹ reported to cause other effects in tadpoles. Factors such as water chemistry and the type of nitrogen compound introducing the nitrate may influence toxicity. For example, tadpoles of *Bufo terrestris*, the southern toad, raised at nitrate levels of 30 mg L⁻¹ took less time than controls to reach metamorphosis in water prepared by reverse osmosis and about 6 days longer than controls in unfiltered spring water (Edwards *et al.* 2006b). Furthermore, tests using ammonium nitrate may yield results that confound ammonia and nitrate toxicities. In addition, chronic, sublethal effects may not appear within the 96-hour time limit used in many assays. The role of nitrate toxicity in the decline of amphibian populations is confounded by habitat destruction and the impacts of introduced species; however, nitrate toxicity should factor into amphibian conservation.

Toxicity tests using birds and most mammals are lacking, and one study addressed nitrate effects on the reptile, *Alligator mississippiensis*. Preliminary findings indicate that nitrate concentrations between 0.01–0.04 mg L⁻¹ NO₃-N appear to affect alligators (Guillette and Edwards 2005). Plasma testosterone levels in both male and female juvenile alligators were negatively correlated with nitrate levels, and estradiol levels in juvenile females were positively correlated with nitrate levels. Toxicity to birds and mammals probably occurs through ingestion of contaminated water.

Herds of cattle were unaffected by exposure to water contaminated with 0–44 mg L⁻¹ NO₃-N; were at risk if continually exposed to 133–220 mg L⁻¹; and exhibited losses at 221–660 mg L⁻¹, more losses at 661–880 mg L⁻¹, and heavy losses above 880 mg L⁻¹ (http://www.vetmed.ucdavis.edu/vetext/INF-BE_cca/INF-BE_cca01/INF-BE_cca01111.html). In addition, the human health standard for nitrate in drinking water is 10 mg L⁻¹ (<http://www.dep.state.fl.us/water/drinkingwater/standard.htm>).

Average nitrate levels in 92% of 130 Florida springs were reported to be below 2 mg L⁻¹; therefore, they were typically lower than concentrations reported to cause effects on animals (Munch *et al.* 2006). However, nitrate concentrations exceed levels of concern in some springs, and they may reach levels of concern for short periods in other springs, especially after the application of safety factors. Given the uncertainty surrounding estimates of toxicity, nitrate concentrations in Florida's springs do represent a cause for concern.

Summary of Nutrient Effects on Fauna in Springs

In summary, a synthesis of information indicates that nutrients can affect faunal assemblages in aquatic systems. Effects are generated in three primary ways: 1) toxicity, 2) changes to trophic webs, and 3) changes in habitats.

Toxicity from elevated ammonia concentrations and changes to respiratory functioning from elevated nitrate concentrations are well-established facts. In addition, evidence of other detrimental effects from elevated nitrate concentrations is accumulating. Increases in concentrations of nitrate may initially lead to changes in traits of individual organisms. These sublethal effects on individuals could translate to detrimental effects on populations, assemblages or ecosystems, although we lack definitive data on these outcomes. Concentrations of ammonia and nitrate in most Florida springs have not reached toxic levels, but concentrations are of concern in some springs. The ecotoxicological effects of nutrients should factor into management of nutrients in Florida's springs.

Increases in concentrations of nutrients also can change trophic webs and habitats, with outcomes determined by complex interactions among bottom-up and top-down processes. At this time, we lack the data needed to rigorously evaluate the role of nutrients in creating perceived and observed changes in the habitats or trophic webs of Florida springs.

Overall, management of nutrients in spring ecosystems would benefit from diagnostic studies of bottom-up and top-down interactions. These interactions, with their associated complexity and nonlinearity, ultimately determine the level of management needed to protect springs ecosystems. Furthermore, the complex and nonlinear nature of key interactions make it highly likely that management applied at real world, spatiotemporal scales will generate unforeseen and unforeseeable responses or emergent properties, which create a need to manage adaptively.

RESEARCH TO IMPROVE MANAGEMENT OF NUTRIENTS IN SPRINGS

Florida's springs and spring runs are enriched in nitrate due to broad-scale contamination of groundwater supplies. As a result, the potential for eutrophication becomes a major concern. The eutrophication progression scheme suggests that increased nutrient delivery to aquatic systems favors production of fast-growing algae that ultimately outcompete and displace native vascular plants (Duarte 1995).

In some of Florida's spring systems, both the apparent proliferation of nuisance algae and the apparent decline of native macrophytes are consistent with such a progression. However, we have few quantitative data that definitively link these changes to an increase in nitrate delivery, and the eutrophication progression scheme predicts that nonlinear responses in systems may have "decoupled" them from contemporary concentrations of nutrients in the water column. Currently, patterns in the distribution and abundance of plants and algae do correlate with other physical and chemical parameters. However, we know little about their individual or combined effects or the form and strength of potential feedback mechanisms, including those linked to nutrient concentrations. Overall, numerous processes and their interactions probably dictate the structure and function of submersed aquatic vegetation, and changes in these vegetated communities generate effects on faunal assemblages.

In general, nutrients can affect the faunal assemblages in aquatic systems in three primary ways: 1) toxicity, 2) changes to trophic webs, and 3) changes in habitats. Toxicity from elevated concentrations of ammonia and nitrate is not a major concern in most Florida springs at this time. In addition, sublethal effects of nitrate on individuals may not impact populations, assemblages or ecosystems. Regardless, the ecotoxicological effects of nutrients should factor into management of nutrients. Changes in trophic webs and habitats, along with flow-on effects on faunal assemblages, are determined by complex interactions among bottom-up and top-down processes. At this time, we lack data to support rigorous evaluation of the role of nutrients in such changes.

Overall, management of nutrients in spring ecosystems would benefit from compilation of inventories, collection of baseline data, and completion of diagnostic studies focused on bottom-up and top-down interactions. The interactions, complexities and nonlinearities uncovered by these studies should influence the management of spring systems. Furthermore, the likelihood that unpredictable, emergent properties will arise when management is implemented at real world, spatiotemporal scales creates a need to manage adaptively.

Designing, implementing, evaluating and applying research that improves management of Florida's springs and spring-fed systems requires input from multiple stakeholders, including policy makers, managers, the public, and scientists from many disciplines. Initial targets for discussion include:

- inventories and baselines designed to:
 - measure nutrients, oxygen, carbon, light, flow, substrates, grazing, algae, plants, invertebrates, fish, and other key drivers and valued components of spring systems chosen with the best available information and, eventually, with guidance from the results of diagnostic studies

- target systems where effectiveness of management can be assessed (e.g., systems with total maximum daily loads, minimum flows and levels, pollution load reduction goals, surface water improvement plans or basin management action plans)
- sample synoptically or at spatial and temporal scales that support rigorous analyses of interactions (note that these inventories and baselines form the platform for adaptive management)
- balance breadth with depth (e.g., optimize taxonomic detail and replication)
- diagnostic studies that determine assimilation of nutrients by flora as key elements in nutrient budgets for spring systems, including contributions by epiphytes, macroalgae, vascular plants and microphytobenthos or microalgae found in sediments
- diagnostic studies that determine how nutrients and other drivers affect overgrowth, shading and other relationships among periphyton, macroalgae and vascular plants in an effort to determine the need for management actions, including aquatic plant management and restoration of native species
- diagnostic studies designed to:
 - focus on species of algae and plants that are hypothesized or known to play major roles in nutrient assimilation
 - extend beyond nitrogen and phosphorus to include other potentially limiting factors and interactions among limiting factors that can significantly influence the outcomes of management (e.g., micronutrients, iron, oxygen, carbon, light, flow and substrate type)
 - explore relationships and consequences across multiple levels of biological and ecological complexity, including uptake and other physiological responses, growth and reproduction of individual organisms, and ecological changes in populations or assemblages to promote the success of management actions at the system level (note that some of the key, large-scale relationships form the core of an adaptive management approach)
 - elucidate the direction, magnitude and form of limitations (e.g., nonlinear and nonreversible) to identify suitable targets and goals for management actions
- diagnostic studies to identify and elucidate changes in composition and function of faunal assemblages related to changes in habitats in an effort to identify habitats to be protected or restored by management actions
- diagnostic studies to determine palatability of flora to grazers, rates of grazing, and the form and magnitude of predation by primary consumers in an effort to identify flora, grazers and trophic links to be protected or restored by management actions
- diagnostic studies to identify and elucidate the toxic effects of ammonia and nitrate beyond physiological and individual levels of organization (e.g., population and assemblage effects) in an effort to determine threshold levels, safety factors and the need for management actions

REFERENCES

- Agharahimi, H. 2006a. EcoSummary: Ichetucknee Springs 4/18/2006. Florida Department of Environmental Protection, Tallahassee, Florida. 1 p.
- Agharahimi, H. 2006b. EcoSummary: Wakulla Springs 4/11/2006. Florida Department of Environmental Protection, Tallahassee, Florida. 1 p.
- Allan, J.D. 1995. Stream ecology: structure and function of running waters. 1st Edition. Chapman and Hall, London. 400 pp.
- Allen, M., D. Murie and G. Warren. 2001. An evaluation of fish and invertebrate communities in Sulphur Springs, Florida during a period of water diversion. Final Report. Southwest Florida Water Management District, Brooksville, Florida. 72 pp.
- Armstrong, D.A. 1979. Nitrogen toxicity to crustacea and aspects of its dynamics in culture systems. pp. 329–360. In: Lewis, D.H. and J.K. Leong (eds.). Proceedings of the Second Biennial Crustacean Health Workshop. Texas A & M University Sea Grant Report TAMU–SC–79–114.
- Bass, D.G., Jr. 1991. Riverine fishes of Florida. pp. 65–83. In: Livingston, R.J. (ed.). The rivers of Florida. Springer–Verlag, New York, New York. 289 pp.
- Bass, D.G., Jr. and D.T. Cox. 1985. River habitat and fishery resources of Florida. pp. 121–187. In: Seaman, W., Jr. (ed.). Florida aquatic habitat and fishery resources. American Fisheries Society, Kissimmee, Florida. 543 pp.
- Berry, J.P., M. Miroslav, R.E. Gawley, M. Wang and K.S. Rain. 2004. Pharmacology and toxicology of pahayokolide A, a bioactive metabolite from a freshwater species of *Lyngbya* isolated from the Florida Everglades. Comparative Biochemistry and Physiology Part C 139: 231–238.
- Biggs, B.J.F. and C.W. Hickey. 1994. Periphyton responses to a hydraulic gradient in a regulated river in New Zealand. Freshwater Biology 32: 49–59.
- Biggs, B.J.F., D.G. Goring and V.I. Nikora. 1998. Subsidy and stress responses of stream periphyton to gradients in water velocity as a function of community growth form. Journal of Phycology 34: 598–607.
- Bledsoe, E.L., K.E. Harr, M.F. Cichra, E.J. Philips R.K. Bonde and M. Lowe. 2006. A comparison of algal mat communities associated with free-ranging and captive Florida manatees (*Trichechus manatus latirostris*). Marine Mammal Science 22: 997–1003.
- Borchardt, M.A., J.P. Hoffmann and P.W. Cook. 1994. Phosphorus uptake kinetics of *Spirogyra fluviatilis* in flowing water. Journal of Phycology 30: 403–417.
- Bothwell, M.L. 1985. Phosphorus limitation of lotic periphyton growth rates: An intersite comparison using continuous flow troughs. Limnology and Oceanography 30: 527–542.

- Brönmark, C. 1990. How do herbivorous freshwater snails affect macrophytes? –A comment. *Ecology* 71: 1212–1215.
- Buiteveld, H. 1995. A model for calculation of diffuse light attenuation (PAR) and Secchi depth. *Netherlands Journal of Aquatic Ecology* 29: 55–65.
- Butcher, R.W. 1933. Studies on the ecology of rivers. I. On the distribution of macrophytic vegetation in the rivers of Britain. *Journal of Ecology* 21: 58–91.
- Camacho, F.A. and R.W. Thacker. 2006. Amphipod herbivory on the freshwater cyanobacterium *Lyngbya wollei*: chemical stimulants and morphological defenses. *Limnology and Oceanography* 51: 1870–1875.
- Camargo, J.A., A. Alonso and A. Salamanca. 2005. Nitrate toxicity to aquatic animals: a review with new data for freshwater invertebrates. *Chemosphere* 58: 1255–1267.
- Canfield, D.E., Jr. and R.W. Bachmann. 1981. Prediction of total phosphorus concentrations, chlorophyll *a*, and Secchi depths in natural and artificial lakes. *Canadian Journal of Fisheries and Aquatic Sciences* 38: 414–423.
- Canfield, D.E., Jr. and L.M. Hodgson. 1983. Prediction of Secchi disk depths in Florida lakes: impact of algal biomass and organic color. *Hydrobiologia* 99: 51–60.
- Canfield, D.E., Jr. and M.V. Hoyer. 1988a. The nutrient assimilation capacity of the little Wekiva River. Report to Department of Public Works, Altamonte Springs, Florida. 288 pp.
- Canfield, D.E., Jr. and M.V. Hoyer. 1988b. Influence of nutrient enrichment and light availability on the abundance of aquatic macrophytes in Florida streams. *Canadian Journal of Fisheries and Aquatic Sciences* 45: 1467–1472.
- Carmichael, W.W., W.R. Evans, Q.Q. Yin, P. Bell and E. Moczydlowski. 1997. Evidence for paralytic shellfish poisons in the freshwater cyanobacterium *Lyngbya wollei*. *Applied and Environmental Microbiology* 63: 3104–3110.
- Carpenter, S.R., J.J. Cole, J.R. Hodgson, J.F. Kitchell, M.L. Pace, S. Bade, K.L. Cottingham, T.E. Essington, J.N. Houser and D.E. Schindler. 2001. Trophic cascades, nutrients and lake productivity: whole-lake experiments. *Ecological Monographs* 71: 163–186.
- Carpenter, S.R., J.F. Kitchell, J.R. Hodgson, P.A. Cochran, J.J. Elser, D.M. Lodge, D. Kretchmer, X. He and C.N. von Ende. 1987. Regulation of lake primary productivity by food web structure. *Ecology* 68: 1863–1876.
- Chambers, P.A., E.E. Prepas, M.L. Bothwell and H.R. Hamilton. 1989. Roots versus shoots in nutrient uptake by aquatic macrophytes in flowing waters. *Canadian Journal of Fisheries and Aquatic Sciences* 46: 435–439.

- Chen, C., D. Yin, B. Yu and H. Zhu. 2007. Effect of epiphytic algae on photosynthetic function of *Potamogeton crispus*. *Journal of Freshwater Ecology* 22: 411–420.
- Corrao, N.M., P.C. Darby and C.M. Pomory. 2006. Nitrate impacts on the Florida apple snail, *Pomacea paludosa*. *Hydrobiologia* 568: 135–143.
- Cummins, K.W. and M.J. Klug. 1979. Feeding ecology of stream invertebrates. *Annual Review of Ecology and Systematics* 10: 147–172.
- DeBrabandere, L., T.K. Frazer and J.P. Montoya. 2007. Stable nitrogen isotope ratios of macrophytes and associated periphyton in two subtropical, spring-fed streams. *Freshwater Biology* 52: 1564–1574.
- Deck, T. 2005a. EcoSummary: Rainbow Springs 5/25/2005. Florida Department of Environmental Protection, Tallahassee, Florida. 1 p.
- Deck, T. 2005b. EcoSummary: Volusia Blue Springs 4/26/2005. Florida Department of Environmental Protection, Tallahassee, Florida. 2 pp.
- Deck, T. 2006a. EcoSummary: Manatee Springs 6/21/2006. Florida Department of Environmental Protection, Tallahassee, Florida. 1 p.
- Deck, T. 2006b. EcoSummary: Rock Springs 5/25/2006. Florida Department of Environmental Protection, Tallahassee, Florida. 1 p.
- Deck, T. 2006c. EcoSummary: Wekiwa Springs 4/26/2005. Florida Department of Environmental Protection, Tallahassee, Florida. 1 p.
- Deegan, L.A., A. Wright, S.G. Ayvazian, J.T. Finn, H. Golden, R.R. Merson and J. Harrison. 2002. Nitrogen loading alters seagrass ecosystem structure and support of higher trophic levels. *Aquatic Conservation: Marine and Freshwater Ecosystems* 12: 193–212.
- Diehl, S. and R. Kornijów. 1998. Influence of submerged macrophytes on trophic interactions among fish and macroinvertebrates. pp. 24–46. In: Jeppesen, E., M. Søndergaard, M. Søndergaard and K. Christoffersen (eds.). *Ecological studies 131: the structuring role of macrophytes in lakes*. Springer, New York. 425 pp.
- Dodds, W.K. and E.B. Welch. 2000. Establishing nutrient criteria in streams. *Journal of the North American Benthological Society* 19: 186–196.
- Dormsjo, K. 2007. Oxygen mediated grazing impacts in Florida springs. University of Florida, MS Thesis. 48 pp.
- Duarte, C.M. 1995. Submerged aquatic vegetation in relation to different nutrient regimes. *Ophelia* 41: 87–112.
- Duarte, C.M. and D.E. Canfield, Jr. 1990a. Light absorption in Florida springs. *Florida Scientist* 2: 118–122.

- Duarte, C.M. and D.E. Canfield, Jr. 1990b. Macrophyte standing crop and primary productivity in some Florida spring-runs. *Water Resources Bulletin* 26: 927–934.
- Duarte, C., Y. Prairie, T. Frazer, M. Hoyer, S. Notestein, D. Canfield and R. Martinez. 2007. High CO₂ flux from Florida springs. 30th Congress of the International Association of Theoretical and Applied Limnology, Montreal, Canada, 2007. [Abstract]
- Edwards, T.M. 2005. Environmental influences on mosquitofish reproduction. Ph.D Dissertation. University of Florida, Gainesville, Florida. 187 pp.
- Edwards, T.M. and L.J. Guillette Jr. 2007. Reproductive characteristics of male mosquitofish (*Gambusia holbrooki*) from nitrate-contaminated springs in Florida. *Aquatic Toxicology* 85: 40–47.
- Edwards, T.M., L.J. Guillette Jr., K. McCoy and T. Barbeau. 2004. Effects of nitrate/nitrite on two sentinel species associated with Florida's springs. Technical Report to the Florida Department of Environmental Protection, Tallahassee, Florida. 102 pp.
- Edwards, T.M., K.A. McCoy, T. Barbeau, M.W. McCoy, J.M. Thro and L.J. Guillette Jr. 2006a. Environmental context determines nitrate toxicity in Southern toad (*Bufo terrestris*) tadpoles. *Aquatic Toxicology* 78: 50–58.
- Edwards, T.M., H.D. Miller and L.J. Guillette Jr. 2006b. Water quality influences reproduction in female mosquitofish (*Gambusia holbrooki*) from eight Florida springs. *Environmental Health Perspectives* 114: 69–75.
- Feminella, J.W. and C.P. Hawkins. 1995. Interactions between stream herbivores and periphyton: a quantitative analysis of past experiments. *Journal of the North American Benthological Society* 14: 465–509.
- Fore, L.S., R. Frydenborg, D. Miller, T. Frick, D. Whiting, J. Espy and L. Wolfe. 2006. Development and testing of biomonitoring tools for macroinvertebrates in Florida streams (Stream Condition Index and BioRecon). Report to the Florida Department of Environmental Protection, Tallahassee, Florida. 122 pp.
- Frazer, T.K., M.V. Hoyer, S.K. Notestein, J.A. Hale and D.E. Canfield, Jr. 2001a. Physical, chemical and vegetative characteristics of five Gulf coast rivers. Final Report (Volume I). Southwest Florida Water Management District, Brooksville, Florida. 359 pp.
- Frazer, T.K., S.K. Notestein, M.V. Hoyer, J.A. Hale and D.E. Canfield, Jr. 2001b. Frequency and duration of pulsed salinity events in Kings Bay. Final Report. Southwest Florida Water Management District, Brooksville, Florida.
- Frazer, T.K., S.K. Notestein, C.A. Jacoby, C.J. Littles, S.R. Keller and R.A. Swett. 2006a. Effects of storm-induced salinity changes on submersed aquatic vegetation in Kings Bay, Florida. *Estuaries and Coasts* 29(6A): 943–953.

- Frazer, T.K., S.K. Notestein and W.E. Pine Jr. 2006b. Changes in the chemical and vegetative characteristics of the Homosassa, Chassahowitzka and Weeki Wachee Rivers. Final Report. Southwest Florida Water Management District, Brooksville, Florida. 163 pp.
- Grimm, N.B. and S.G. Fisher. 1986. Nitrogen limitation in a Sonoran desert stream. *Journal of the North American Benthological Society* 5: 2–15.
- Guillette, L.J., and T.M. Edwards. 2005. Is nitrate an ecologically relevant endocrine disruptor in vertebrates? *Integrative and Comparative Biology* 45: 19–27.
- Hauxwell, J., J. McClelland, P.J. Behr and I. Valiela. 1998. Relative importance of grazing and nutrient controls of macroalgal biomass in three temperate shallow estuaries. *Estuaries* 21: 347–360.
- Hauxwell, J.A., C.W. Osenberg and T.K. Frazer. 2004. Conflicting management goals: manatees and invasive competitors inhibit restoration of a native macrophyte. *Ecological Applications* 14(2): 571–586.
- Heck, K.L., Jr., J.R. Pennock, J.F. Valentine, L.D. Coen and S.A. Sklenar. 2000. Effects of nutrient enrichment and small predator density on seagrass ecosystems: an experimental assessment. *Limnology and Oceanography* 45: 1041–1057.
- Hemminga, M.A. and C.M. Duarte. 2000. *Seagrass ecology*. Cambridge University Press, Cambridge. 298 pp.
- Hershey, A.E., A.L. Hiltner, M.A.J. Hullar, M.C. Miller, J.R. Vestal, M.A. Lock, S. Rundle and B.J. Peterson. 1988. Nutrient influence on a stream grazer: *Orthocladus* microcommunities respond to nutrient input. *Ecology* 69: 1383–1392.
- Hickey, C.W., L.A. Golding, M.L. Martin and G.F. Croker. 1999. Chronic toxicity of ammonia to New Zealand freshwater invertebrates: a mesocosm study. *Archives of Environmental Contamination and Toxicology* 37: 338–351.
- Hilton, J., M. O'Hare, M.J. Bowes and J.I. Jones. 2006. How green is my river? A new paradigm of eutrophication in rivers. *Science of the Total Environment* 365: 66–83.
- Horner, R.R., E.B. Welch, M.R. Seeley and J.M. Jacoby. 1990. Responses of periphyton to changes in current velocity, suspended sediment and phosphorus concentration. *Freshwater Biology* 24: 215–232.
- Hornsby, D., R. Mattson and T. Mirti. 2004. Surfacewater quality and biological annual report. Report to the Suwannee River Water Management District, Live Oak, Florida. 234 pp.
- Hoyer, M.V. and D.E. Canfield Jr. 1991. A phosphorus-fish standing crop relationship for streams? *Lake and Reservoir Management* 7: 25–32.

- Hoyer, M.V., T.K. Frazer, S.K. Notestein and D.E. Canfield. 2004. Vegetative characteristics of three low-lying Florida coastal rivers in relation to flow, light, salinity and nutrients. *Hydrobiologia* 528: 31–43.
- Hoyer, M.V. and J.R. Jones. 1983. Factors affecting the relation between phosphorus and chlorophyll a in midwestern reservoirs. *Canadian Journal of Fisheries and Aquatic Sciences* 40: 192–199.
- Hynes, H.B.N. 1972. *The ecology of running waters*. University of Toronto Press, Toronto. 556 pp.
- Jacoby, C.A., T.K. Frazer, R.A. Swett, S.R. Keller and S.K. Notestein. 2007. Kings Bay vegetation evaluation. Final Report. Southwest Florida Water Management District, Brooksville, Florida. 172 pp.
- Jensen, F.B. 2003. Nitrite disrupts multiple physiological functions in aquatic animals. *Comparative Biochemistry and Physiology Part A* 135: 9–24.
- Johnson, P.T.J., J.M. Chase, K.L. Dosch, R.B. Harston, J.A. Gross, D.J. Larson, D.R. Sutherland and S.R. Carpenter. 2007. Aquatic eutrophication promotes pathogenic infection in amphibians. *Proceedings of the National Academy of Science USA* 104: 15781–15786.
- Jones, G.W., S.B. Upchurch, K.M. Champion and D.J. Dewitt. 1997. Water-quality and hydrology of the Homosassa, Chassahowitzka, Weeki Wachee, and Aripeka Spring complexes, Citrus and Hernando Counties, Florida (origin of increasing nitrate concentrations). Ambient Ground-Water Quality Monitoring Program. Southwest Florida Water Management District, Brooksville, Florida. 167 pp.
- Kirk, J.T.O. 1994. *Light and photosynthesis in aquatic ecosystems*. 2nd Edition. Cambridge University Press, Cambridge. 507 pp.
- Knepp, G.L. and G.F. Arkin. 1973. Ammonia toxicity levels and nitrate tolerance of channel catfish. *The Progressive Fish-Culturist* 35: 221–224.
- Kurz, R.C., P. Sinphay, W.E. Hershfeld, A.B. Krebs, A.T. Peery, D.C. Woithe, S.K. Notestein, T.K. Frazer, J.A. Hale and S.R. Keller. 2003. Mapping and monitoring submerged aquatic vegetation in Ichetucknee and Manatee Springs. Final Report. Suwannee River Water Management District, Live Oak, Florida. 190 pp.
- Kurz, R.C., D.C. Woithe, S.K. Notestein, T.K. Frazer, J.A. Hale and S.R. Keller. 2004. Mapping and monitoring submerged aquatic vegetation in Ichetucknee Springs – 2004. Final Report. Suwannee River Water Management District, Live Oak, Florida. 163 pp.
- Lamberti, G.A. and V.H. Resh. 1983. Stream periphyton and insect herbivores: an experimental study of grazing by a caddisfly population. *Ecology* 64: 1124–1135.
- Lewis, W.M. and D.P. Morris. 1986. Toxicity of nitrite to fish: a review. *Transactions of the American Fisheries Society* 115: 183–195.

- Lodge, D.M. 1991. Herbivory on freshwater macrophytes. *Aquatic Botany* 41: 195–224.
- Lodge, D.M., G. Cronin, E. van Donk and A. Froelich. 1998. Impact of herbivory on plant standing crop: comparisons among biomes, between vascular and nonvascular plants, and among freshwater herbivore taxa. pp. 149–175. In: Jeppesen, E., M. Søndergaard, M. Søndergaard and K. Christoffersen (eds.). *Ecological studies 131: the structuring role of macrophytes in lakes*. Springer, New York. 425 pp.
- Lohman, K., J.R. Jones and C. Baysinger-Daniel. 1991. Experimental evidence for nitrogen limitation in a north Ozark stream. *Journal of the North American Benthological Society* 10: 14–23.
- Lohman, K. and J.C. Priscu. 1992. Physiological indicators of nutrient deficiency in *Cladophora* in the Clark Fork of the Columbia River, Montana. *Journal of Phycology* 28: 443–448.
- Mainstone, C.P. and W. Parr. 2002. Phosphorus in rivers – ecology and management. *The Science of the Total Environment* 282–283: 25–47.
- Mann, K.H. 1988. Production and use of detritus in various freshwater, estuarine, and coastal marine ecosystems. *Limnology and Oceanography* 33: 910–930.
- Mattson, R.A., M. Lehmensiek and E.F. Lowe. 2007. Nitrate toxicity in Florida springs and spring-run streams: a review of the literature and its implications. Professional paper, SJ2007–PP1, St. Johns River Water Management District, Palatka, Florida. 31 pp.
- Mattson, R.A., E.F. Lowe and C.L. Lippincott. 2006. Potential nitrate toxicity to aquatic animals in the Wekiva River and Rock Springs run and associated nitrate concentration targets. Appendix E. pp. 984–1001. In Mattson, R.A., E.F. Lowe, C.L. Lippincott, J. Di and L. Battoe. 2006. *Wekiva River and Rock Springs Run pollutant load reduction goals*. Report to the Florida Department of Environmental Protection, Tallahassee, Florida. 1054 pp.
- McCormick, P.V. 1991. Lotic protistan herbivore selectivity and its potential impact on benthic algal assemblages. *Journal of the North American Benthological Society* 10: 238–250.
- Mittelbach, G.G. and C.W. Osenberg. 1993. Stage-structured interactions in bluegill: consequences of adult resource variation. *Ecology* 74: 2381–2394.
- Munch, D.A., D.J. Toth, C. Huang, J.B. Davis, C.M. Fortich, W.L. Osburn, E.J. Phlips, E.L. Quinlan, M.S. Allen, M.J. Woods, P. Cooney, R.L. Knight, R.A. Clarke, S.L. Knight. 2006. Fifty-year retrospective study of the ecology of Silver Springs, Florida. Publication Number: SJ2007-SP4. St. Johns River Water Management District, Palatka, FL.
- Newman, R.M. 1991. Herbivory and detritivory on freshwater macrophytes by invertebrates: a review. *Journal of the North American Benthological Society* 10: 89–114.

- Nixon, S.W. 1995. Coastal, marine eutrophication – definition, social causes, and future concerns. *Ophelia* 41: 199–219.
- Notestein, S.K., T.K. Frazer, M.V. Hoyer and D.E. Canfield, Jr. 2003. Nutrient limitation of periphyton in a spring-fed stream coastal stream in Florida, USA. *Journal of Aquatic Plant Management* 41: 57–60.
- Odum, H.T. 1957a. Primary production measurements in eleven Florida springs and a marine turtle-grass community. *Limnology and Oceanography* 2: 85–97.
- Odum, H.T. 1957b. Trophic structure and productivity of Silver Springs, Florida. *Ecological Monographs* 27: 55–112.
- Onodera, H., M. Satake, Y. Oshima, T. Yasumoto and W.W. Carmichael. 1997. New saxitoxin analogues from the freshwater filamentous cyanobacterium *Lyngbya wollei*. *Natural Toxins* 5: 146–151.
- Patronis, J. 2006a. EcoSummary: Alexander Springs 6/7/2006. Florida Department of Environmental Protection, Tallahassee, Florida. 1 p.
- Patronis, J. 2006b. EcoSummary: Blue Hole Springs 6/22/2006. Florida Department of Environmental Protection, Tallahassee, Florida. 1 p.
- Patronis, J. 2006c. EcoSummary: Juniper Springs 6/8/2006. Florida Department of Environmental Protection, Tallahassee, Florida. 1 p.
- Patronis, J. 2006d. EcoSummary: Ponce de Leon Springs 6/22/2006. Florida Department of Environmental Protection, Tallahassee, Florida. 1 p.
- Patronis, J. 2006e. EcoSummary: Silver River Springs 6/7/2006. Florida Department of Environmental Protection, Tallahassee, Florida. 1 p.
- Patronis, J. 2006f. EcoSummary: Silver Glen Springs 6/8/2006. Florida Department of Environmental Protection, Tallahassee, Florida. 1 p.
- Peterson, B.J., L. Deegan, J. Helfrich, J.E. Hobbie, M. Hullar, B. Moller, T.E. Ford, A. Hershey, A. Hiltner, G. Kipphut, M.A. Lock, D.M. Fiebig, V.L. McKinley, M.C. Miller, J.R. Vestal and R. Ventullo and G. Volk. 1993. Biological responses of a tundra river to fertilization. *Ecology* 74: 653–672.
- Power, M.E., W.J. Matthews and A.J. Stewart. 1985. Grazing minnows, piscivorous bass, and stream algae: dynamics of a strong interaction. *Ecology* 66: 1448–1456.
- Quinlan, E.L., E.J. Phlips, K.A. Donnelly, C.H. Jett, P. Sleszynski and S. Keller. 2008. Primary producer biomass and nutrient load in Silver Springs, Florida, USA. *Aquatic Botany* 88: 247–255.

- Rosemond, A.D. 1993. Interactions among irradiance, nutrients, and herbivores constrain a stream algal community. *Oecologia* 94: 585–594.
- Rosenau, J.C., G.L. Faulkner, C.W. Hendry Jr. and R.W. Hull. 1977. Springs of Florida. Florida Department of Natural Resources. Bureau of Geology Bulletin No. 31 (revised). 461 pp.
- Rouse, J.D., C.A. Bishop and J. Struger. 1999. Nitrogen pollution: an assessment of its threat to amphibian survival. *Environmental Health Perspectives* 107: 799–803.
- Russo, R.C., R.V. Thurston and K. Emerson. 1981. Acute toxicity of nitrite to rainbow trout (*Salmo gairdneri*): effects of pH, nitrite species, and anion species. *Canadian Journal of Fisheries and Aquatic Sciences* 38: 387–393.
- Sand-Jensen, K. 1977. Effect of epiphytes on eelgrass photosynthesis. *Aquatic Botany* 3: 55–64.
- Sand-Jensen, K. 1989. Environmental variables and their effect on photosynthesis of aquatic plant communities. *Aquatic Botany* 34: 5–25.
- Sand-Jensen, K. and J. Borum. 1991. Interactions among phytoplankton, periphyton, and macrophytes in temperate freshwaters and estuaries. *Aquatic Botany* 41: 137–175.
- Saunders, T.J. 2007. Multi-scale analysis of benthic biogeochemical properties and processing in a spring-fed river and estuary. University of Florida, PhD Dissertation. 163 pp.
- Schindler, D.W. 1971. Carbon, nitrogen and phosphorus and the eutrophication of freshwater lakes. *Journal of Phycology* 7: 321–329.
- Scott, T.M., G.H. Means, R.C. Means and R.P. Meegan. 2002. First magnitude Springs of Florida. Open File Report 85. Florida Geological Survey, Tallahassee, USA. 151 pp.
- Sheldon, S.P. 1987. The effects of herbivorous snails on submerged macrophyte communities in Minnesota lakes. *Ecology* 68: 1920–1931.
- Sheldon, S.P. 1990. More on freshwater snail herbivory: a reply to Brönmark. *Ecology* 71: 1215–1216.
- Shelton, D.N. 2005. The rare and endemic snails of selected springs within the St Johns River Water Management District. St Johns Water Management District Special Publication SJ2006–SP17, Palatka, Florida. 32 pp.
- Shimura, R., K. Ijiri, R. Mizuno and S. Nagaoka. 2002. Aquatic animal research in space station and its issues – focus on support technology on nitrate toxicity. *Advances in Space Research* 30: 803–808.
- Sloan, W.C. 1956. The distribution of aquatic insects in two Florida springs. *Ecology* 37: 81–98.
- Spanjer, G.R. and M.L. Cipollini. 2006. Relationship between physiochemical factors and distribution of stygobitic crayfish in southeastern caves. *Southeastern Naturalist* 5: 17–26.

- Steigerwalt, N.M. 2005. Environmental factors affecting aquatic invertebrate community structure on snags in the Ichetucknee River, Florida. MSc Thesis, University of Florida, Gainesville, Florida. 96 pp.
- Stevenson, R.J., A. Pinowska and Y. Wang. 2004. Ecological condition of algae and nutrients in Florida Springs. Final Report WM 858. Florida Department of Environmental Protection, Tallahassee, Florida. 101 pp.
- Stevenson, R.J., A. Pinowska, A. Albertin and J.O. Sickman. 2007. Ecological condition of algae and nutrients in Florida Springs. The Synthesis Report WM 858 Florida Department of Environmental Protection, Tallahassee, Florida. 58 pp.
- Strong, W.A. 2004. Temporal water chemistry trends within individual springs and within a population of Florida springs. University of Florida, MS Thesis. 54 pp.
- Teneva, I., D. Asparuhova, B. Dzhambov, R. Mladenov and K. Schirmer. 2003. The freshwater cyanobacterium *Lyngbya aeruginosa-coerulea* produces compounds toxic to mice and to mammalian and fish cells. *Environmental Toxicology* 18: 9–20.
- USEPA. 1999. 1999 update of ambient water quality criteria for ammonia. EPA-822-R-99-014. USEPA, Washington, D.C. 153 pp.
- USEPA. 2006. Wadeable streams assessment: a collaborative survey of the nation's streams. EPA 841-B-06-002. Washington, D.C. 98 pp.
- Valiela, I., J. McClelland, J. Hauxwell, P.J. Behr, D. Hersh and K. Foreman. 1997. Macroalgal blooms in shallow estuaries: controls and ecophysiological and ecosystem consequences. *Limnology and Oceanography* 42: 1105–1118.
- Vannote, R.L., G.W. Minshall, K.W. Cummins, J.R. Sedell and C.E. Cushing. 1980. The river continuum concept. *Canadian Journal of Fisheries and Aquatic Sciences* 37: 130–137.
- Vitousek, P.M. and R.W. Howarth. 1991. Nitrogen limitation on land and in the sea: how can it occur? *Biogeochemistry* 13: 87–115.
- Walsh, S.J. 2001. Freshwater macrofauna of Florida karst habitats. pp. 78–88. In: Kuniansky, E.L. (ed) U.S. Geological Survey Karst Interest Group Proceedings, Water-Resources Investigations Report 01–4011.
- Warren, G.L., D.A. Hohlt, C.E. Cichra and D. VanGenechten. 2000. Fish and aquatic invertebrate communities of the Wekiva and Little Wekiva Rivers: a baseline evaluation in the context of Florida's minimum flows and levels statutes. Special Publication SJ2000–SP4 of the St. Johns River Water Management District, Palatka, Florida. 559 pp.
- Welch, E.B., J.M. Jacoby, R.R. Horner and M.R. Seeley. 1988. Nuisance levels of periphytic algae in streams. *Hydrobiologia* 157: 161–168.

- Westlake, D.F. 1967. Some effects of low-velocity currents on the metabolism of aquatic macrophytes. *Journal of Experimental Botany* 18: 187–205.
- Whitford, L.A. 1956. The communities of algae in the springs and spring streams of Florida. *Ecology* 37: 433–442.
- Wiebe, A.H. 1931. Dissolved phosphorus and inorganic nitrogen in the water of the Mississippi River. *Science* 73: 652.
- Wuhrmann, K. and E. Eichenberger. 1975. Experiments on the effects of inorganic enrichment of rivers on periphyton primary production. *Verhandlungen Internationale Vereinigung Limnologie* 19: 2028–2034, 1975.

Ecosystem Implications of Invasive Aquatic Plants and Aquatic Plant Control in Florida Springs

*Jason M. Evans
School of Forest Resources and Conservation
University of Florida*

Summary

Nonnative and nuisance plants such as water hyacinth, water lettuce, and hydrilla are a primary management concern in many Florida springs. In fiscal year 2005 – 2006, the Department of Environmental Protection's Bureau of Invasive Plant Management spent approximately \$173,000 to control these plants in springs, primarily through the use of chemical herbicides. This chapter reviews a broad range of literature to outline what is known and unknown about 1) the history of these plants and their control in Florida; 2) the growth potential of the nonnative plants in springs as a function of elevated nitrate-nitrogen concentrations; 3) the social and ecological consequences of aquatic plant overgrowth; 4) the ecological risks associated with current aquatic plant control methods; and 5) the potential benefits of alternative aquatic plant management approaches in some springs systems.

The Literature: What is Known

- Major problems with nonnative plants in Florida began with the introduction of water hyacinth, a floating aquatic plant, into the St. Johns River in the late 19th century. Water hyacinth was documented in several springs ecosystem along the St. Johns River by the mid 1890s. Chemical control programs have maintained water hyacinth populations at low levels throughout Florida since the mid-1970s.
- Historical sightings by William Bartram indicate that water lettuce, a floating aquatic plant, has been present in a number of Florida springs since at least 1765. Scientists disagree as to whether water lettuce was present in Florida before European colonization, or was introduced by early Spanish settlers. Chemical control programs have maintained water lettuce at low levels throughout Florida since the mid-1970s.
- Hydrilla, a submersed aquatic plant, became established in several areas of Florida, including the Kings Bay/Crystal River springs complex, by 1960. Sustained control of hydrilla has proven more difficult than the floating plants in Florida. Most aquatic plant management costs in Florida springs ecosystems over 2005 – 2006 were associated with chemical control of hydrilla.
- There are clear relationships between nitrogen enrichment and increased growth of water hyacinth, water lettuce, and hydrilla in non-flowing aquatic systems. Such overgrowth

can have severe adverse effects on native plant communities, navigation, fisheries, and recreational desirability.

- Water hyacinth and water lettuce emit allelopathic compounds capable of suppressing a number of algal taxa. Water hyacinth, water lettuce, and hydrilla all can be effective competitors with nuisance algae due to nutrient uptake, shading, faunal habitat, direct filtration, and allelopathic mechanisms.
- Ecosystem surveys indicate that water hyacinth, water lettuce, and hydrilla provide attractive habitat for crayfish, apple snails, amphipods, fish, manatees, and other springs fauna at moderate levels of coverage.
- Copper and diquat herbicides may have significant toxicological effects on algal and faunal community dynamics at levels used for aquatic plant control.
- *Lyngbya wollei*, a filamentous cyanobacterium of great concern in many Florida springs, is notable for its relative resistance to herbicidal compounds as compared to other common algal and cyanobacteria taxa.
- Depression of dissolved oxygen due to decaying biomass is a primary concern to animals following aquatic plant control.
- Biotypes of hydrilla that are resistant to fluridone, a systemic herbicide commonly used for hydrilla control in Florida lakes, have been documented in recent years. There is also increased concern about the potential evolution of hydrilla strains that are resistant to Aquathol, the contact herbicide most commonly used to control hydrilla in springs.
- Established biological control organisms are known to adversely affect water hyacinth, water lettuce, and hydrilla in some springs systems, although biocontrol organisms generally do not maintain aquatic plant populations at low levels achieved by chemical control. A promising biological control for hydrilla, *Cricotopus lebetis*, has been documented in Kings Bay/Crystal River.

The Literature: What is Not Known, and Recommendations for Future Research

- The few studies available for springs and other flowing waters have not definitively determined a concentration of nitrate-nitrogen in springs that would be limiting to any of the nonnative plants. Nutrient assays in flowing water mesocosms and/or *in situ* field studies are needed to develop nitrate-nitrogen limitation values for nonnative plants in springs conditions.
- Observations from several springs suggest a “boom-bust” successional sequence in which nonnative plants first out-compete native plant communities, and then suffer catastrophic population crashes associated with aquatic plant control or natural disturbances. It is hypothesized, but not known, that succession of springs into algal-dominated ecosystem states may be promoted by the nutrient pulses and ecological openings associated with the rapid loss of aquatic plant populations.

- The effects of allelopathic compounds emitted by nonnative plants on algal dynamics in springs ecosystem are not presently known.
- Ecosystem effects of long-term aquatic plant control have not been well-studied in the specific context of Florida springs. Variables such as dissolved nutrients, dissolved oxygen, biomass deposition, and floral and faunal community structure should be monitored before and after major aquatic plant control operations in Florida springs.
- Water hyacinth and water lettuce are currently being managed for algal-suppression, nutrient recovery, and biomass utilization in a number of tropical countries, including places in which they are considered nonnative. While it is not known if such methods would be helpful in springs ecosystems, careful experimentation with floating plant treatment methods may be worthwhile in highly degraded springs ecosystems where these plants are established.
- Long-term effects of biocontrol organisms, including the possibility of improved efficacy over time, are not well-studied in nonnative plant populations in springs ecosystems. Increased research into biocontrol organisms and experimental release in springs ecosystems, particularly those affected by hydrilla, should be a priority for adaptive ecosystem management.

INTRODUCTION

One of the primary management concerns in many of Florida's freshwater spring systems is the growth of nonnative invasive plants. Although there are more than a dozen nonnative aquatic plants established in Florida's springs ecosystems, the vast majority of historic and ongoing management expense is associated with three species: water hyacinth (*Eichhornia crassipes*), hydrilla (*Hydrilla verticillata*), and water lettuce (*Pistia stratiotes*) (Bureau of Invasive Plant Management 2007). Many researchers and managers fear that rising nitrate-nitrogen levels in Florida springs may further promote growth of these, and perhaps other, nonnative plants to the overall detriment of native plants and animals (e.g., Florida Springs Task Force 2000; Loper *et al.* 2005).

Aquatic plant control programs that primarily target hydrilla, water hyacinth, and/or water lettuce are actively employed in several major springs systems, including Rainbow River, Silver River, Wekiva River, Weeki Wachee River, Wakulla River, and Kings Bay/Crystal River (Bureau of Invasive Plant Management 2007). Selective application of chemical herbicides is the primary operational method for aquatic plant control, although manual and mechanical harvest methods are also used in some springs systems. Approximately \$173,000 was spent by the Florida Department of Environmental Protection (DEP) for aquatic plant control in springs ecosystems in 2005 – 2006. Over 80% of this amount was allocated for herbicidal suppression of hydrilla in Rainbow River, Weeki Wachee River, Wakulla River, and Silver River (Bureau of Invasive Plant Management 2007).

This review chapter begins by generally describing the introduction, ecological effects, and historical control of the major invasive aquatic plant species in Florida. Available scientific literature is then used to explore four sets of questions raised by the presence of invasive plants and their ongoing management in Florida springs:

1. To what extent is increased nitrate-nitrogen a factor in the spread of invasive plants, and at what level is invasive plant growth limited by nitrate-nitrogen in springs?
2. What are the potential implications of invasive plant proliferation on ecosystem structure and function in springs?
3. What are the potential implications of aquatic plant control on ecosystem structure and function, particularly in terms of shifting springs toward more algal-dominated ecosystem?
4. For springs in which increased algal dominance is the primary conservation concern, are there opportunities for experimenting with alternative aquatic plant management strategies that attempt to utilize the known functions of extant invasive plants in support of long-term ecosystem recovery goals?

Major Invasive Aquatic Plants: History and Control in Florida

Water Hyacinth

Water hyacinth is a floating aquatic plant native to South America's Amazon River drainage. Introduced into many countries throughout the subtropics and tropics in the late 19th and early 20th centuries, water hyacinth is now commonly regarded as one of the world's most problematic invasive plant species (Holm *et al.* 1977). A number of researchers have found that, under ideal conditions, water hyacinth is more productive than any other known vascular plant (Gopal 1987). This extremely high productive potential permits water hyacinth to quickly overgrow and out-compete other plant species (Schmitz *et al.* 1993), particularly in ecosystems affected by elevated nutrient levels and other forms of anthropogenic disturbance (Gopal 1987).

The ecological and economic effects of water hyacinth overgrowth are often quite dramatic and severe. Along with the competitive displacement of native plant communities, one of the most common ecological consequences of water hyacinth overgrowth is severe depression of dissolved oxygen in underlying waters due to the synergistic effects of rapid deposition of organic matter from senescing leaves, restriction of phytoplankton production due to shading, and interference with atmospheric oxygen exchange (Penfound and Earle 1948; Joyce 1985). Development of anoxic conditions under water hyacinth can directly lead to exclusion of fish and other oxygen-dependent species, thereby radically changing the structural composition of faunal communities (Schmitz *et al.* 1993). In addition, human economies are often adversely affected by restricted navigation, loss of fisheries access, and siltation of drainage systems that can be associated with the formation of substantial water hyacinth cover in a water body (Gopal 1987).

It is generally accepted that water hyacinth was first introduced into Florida in 1885 by a Palatka-area farmer who obtained a specimen from an exhibit at the 1884-1885 World's Industrial and Cotton Centennial Exposition held in New Orleans (Buker 1982). The plant was apparently propagated in a small garden pond, with excess plants periodically thrown into the nearby St. Johns River (Buker 1982). The subsequent effects of this introduction are legendary. By the early 1890s, the discarded plants had multiplied to such an extent that extremely large floating mats of water hyacinth became established at many locations along the St. Johns River and its tributaries (see Figure 1). Boat navigation and logging operations along the river flood plain were both severely curtailed, and massive accumulations of the plant were even reported to structurally undermine the columns of several railroad bridges (Webber 1897).

Aided in large part by farmers who valued the prolific plant for cattle forage (Buker 1982) and an organic mulch source for citrus trees planted in sandy soils (Maltby 1963), water hyacinth continued to spread rapidly into many of the state's other drainage basins throughout the first half of the 20th century. Water hyacinth was reported in several springs of the St. Johns River basin, including Volusia Blue Spring, Green Cove Springs, Silver River, and the Wekiva River, as early as the 1890s (Webber 1897), and introductions into new springs systems continued throughout the 20th century. Reports from the Panhandle's spring-fed St. Marks River suggest that water hyacinth was first introduced into that system as late as the 1970s (Bartodziej and Leslie 1998).

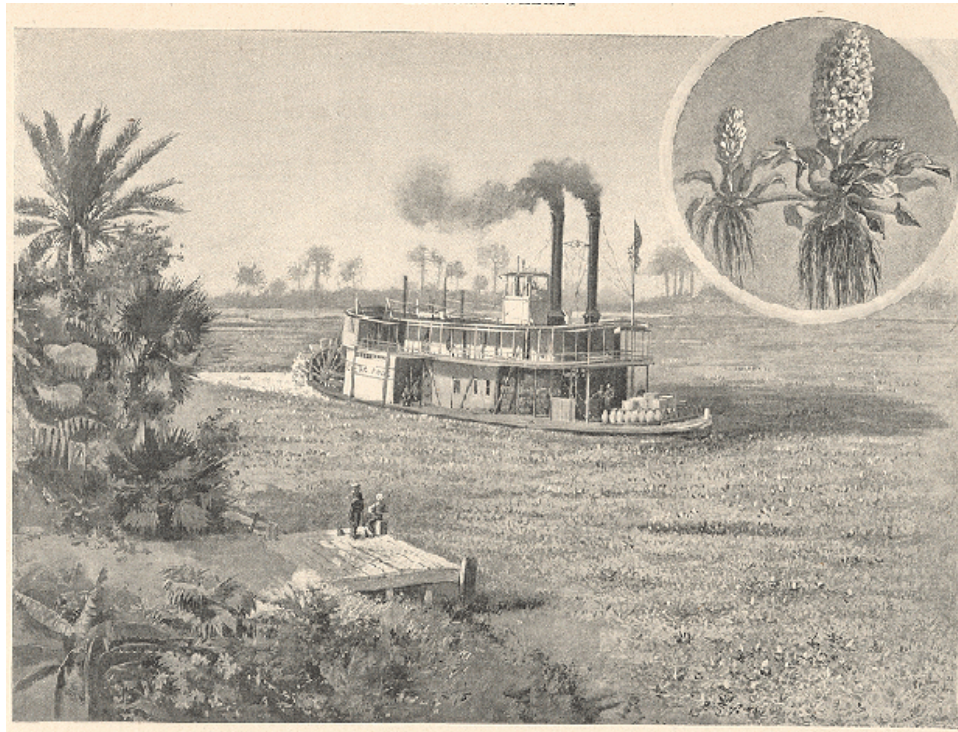


Figure 1 – *Water hyacinth overgrowth in St. Johns River. Illustration from March 19, 1898 edition of Harper's Weekly, as adapted by University of Florida Center for Aquatic and Invasive Plants.* <http://aquat1.ifas.ufl.edu/guide/stboatbg2.gif>

The history and evolution of efforts to bring water hyacinth under control in Florida are almost as legendary as the plant's rapid spread. The United States Rivers and Harbors Act of 1899 contained specific provisions authorizing the United States Army Corps of Engineers to destroy water hyacinth in navigable waters, and the Florida Legislature at nearly the same time enacted a law that prohibited the intentional transfer of water hyacinth into new waterways (Buker 1982). Sodium arsenite and other inorganic herbicide sprays were briefly used by the Corps of Engineers for hyacinth control around the turn of the century, but reports of severe cattle mortality associated with these sprays led both the Florida Legislature and U.S. Congress to prohibit use of these compounds in Florida by 1905 (Buckman and Company 1930).

As a result of this prohibition, most hyacinth control efforts from the turn of the century through the 1940s involved three techniques: 1) construction of physical barriers to prevent movement of plants into new areas; 2) manual labor to dislodge plants and facilitate downstream discharge into the Atlantic Ocean; and 3) mechanical shredding and/or harvest of plants using large machines (Buckman and Company 1930; Buker 1982 see Figure 2). While such methods were successful in terms of removing major plant blockages, they apparently were insufficient for abating the proliferation of water hyacinth. Thus, the spread and areal extent of water hyacinth coverage continued to increase in Florida throughout the first half of the 20th century, peaking at approximately 51,000 acres in the early 1960s (Schardt 1997; see Figure 3).



Figure 2 – Water hyacinth shredder in the Withlacoochee River, circa 1940. Photo by United States Army Corps of Engineers, as adapted by the University of Florida Center for Aquatic and Invasive Plants. <http://plants.ifas.ufl.edu/guide/mechconold7js.jpg>

By all accounts, the invention of the organic phenoxy herbicide 2,4-D in 1942 marked an important turning point in water hyacinth control. Unlike the inorganic herbicidal sprays used previously, 2,4-D effectively controlled water hyacinth at dosages that posed little direct toxic risk to cows, fish, and other animals (Joyce 1982), likely because its mode of herbicidal action specifically targets plant hormonal production. A number of 2,4-D-based spraying programs that targeted heavily concentrated populations of water hyacinth in Florida commenced in the late 1940s and continued to expand throughout the 1950s and 1960s (Schardt 1997).

While these early 2,4-D programs were successful in rapidly suppressing water hyacinths, many observers expressed concerns about mass nutrient releases, heavy organic detritus loads, and severe algal blooms that tended to follow large-scale aquatic plant control operations (e.g., Clugston 1963; Tilghman 1963). Over the late 1960s and early 1970s, aquatic plant control researchers and practitioners addressed these concerns by developing a management philosophy that came to be known as maintenance control (Schardt 1997). Adopted into state law in 1974 as the official guiding principle for aquatic plant management, maintenance control is defined by the operational goal of maintaining water hyacinths (and other invasive nonnative aquatic plants)

at the “lowest feasible level” (Florida Statute 369.22). Inherent in this objective is a pragmatic acknowledgment that eradication of the invasive aquatic plants is impractical, but that control at population numbers that do not interfere with beneficial uses of water bodies can be maintained. Aside from the obvious objective of effectively suppressing nonnative plants, some research suggests that maintenance of plants at small populations may reduce overall detrital loading and herbicide use as compared to less frequent treatment of large plant populations (Joyce 1985; Schardt 1997). Since the 1970s the maintenance control program has greatly reduced the overall population of water hyacinth throughout the state (see Figure 3), generally through sustained use of 2,4-D, diquat dibromide (a contact herbicide), and glyphosate (a systemic herbicide) (Bureau of Invasive Plant Management 2007). Potential implications of herbicidal control methods used for water hyacinths and other invasive plants in springs ecosystems are discussed in more detail in later sections of this chapter.

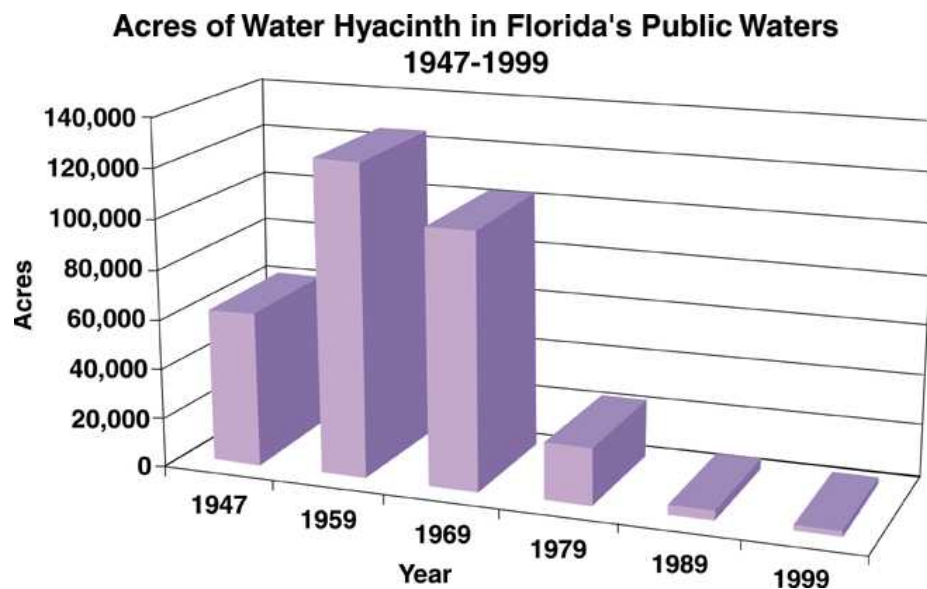


Figure 3 – *Effects of maintenance control operations on water hyacinth populations in Florida.* Graph adapted from Florida Department of Environmental Protection, Bureau of Invasive Plant Management. <http://www.dep.state.fl.us/lands/invaspec/images/Graph%20wh%20acres.jpg>

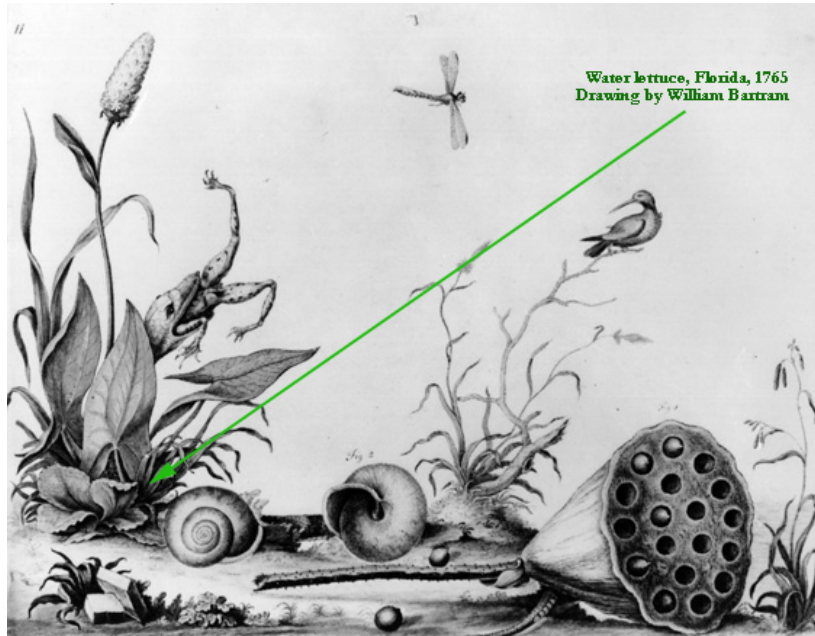


Figure 4 – *Water lettuce in Florida, 1765. Drawing by William Bartram, as adapted by Swarthmore College.* <http://www.swarthmore.edu/Humanities/kjohnsol/pictures/stratiotes.jpg>

Water Lettuce

Like water hyacinth, water lettuce is a floating aquatic plant that can commonly reach nuisance levels in Florida and other areas of the tropics and subtropics (Holm *et al.* 1977). The basic economic and ecological concerns about water lettuce are quite similar to those of water hyacinth, namely that its prolific floating growth habit can serve as an impediment to navigation, block drainage canals, out-compete native plants, and radically change aquatic communities through increased siltation and depression of dissolved oxygen concentrations (Schmitz *et al.* 1993).

Unlike water hyacinth, there is significant uncertainty as to the origins of water lettuce and its introduction to Florida. Most of this uncertainty derives from William Bartram's frequent reports of water lettuce along the Suwannee River and St. Johns River during his Florida travels in the 18th century (Stuckey and Les 1984). Some researchers speculate that water lettuce observed by Bartram possibly stemmed from an introduction of the plant during the Spanish colonial period (e.g., Stuckey and Les 1984), while others argue that water lettuce's Florida population may have preceded European contact by millennia (e.g., Stoddard 1989). Bartram's writings make specific note of large water lettuce populations in or near the Suwannee River's Manatee Springs and several springs along the St. Johns River, indicating that these springs have had water lettuce populations for well over two centuries. Other historical accounts in springs include Webber's (1897) sighting of large water lettuce populations in the Wekiva River during the late 19th century, and Carr's (1994) reports of water lettuce as a common component of springs ecosystems throughout north Florida during the 1940s. Field observations by Odum (1957) suggest that water lettuce growth in Silver Springs during the mid 20th century followed distinct

seasonal patterns and that large population accumulations were often suppressed by insect herbivory.

It is commonly suggested that water hyacinth's similar habitat requirements and superior competitive abilities led to a large-scale displacement of water lettuce in Florida during the late 19th and early 20th centuries (Schmitz *et al.* 1993; Carr 1994). However, large populations of water lettuce quickly emerged in Florida and other states after the commencement of water hyacinth control in the 1950s, likely due to water lettuce's relative resistance to 2,4-D (Eggler 1953; United States Army Corps of Engineers 1973). Researchers during the mid 1960s discovered that water lettuce was controlled effectively by diquat dibromide (Weldon and Blackburn 1967), and since that time water lettuce and mixed stands of water lettuce and water hyacinth in Florida have been almost exclusively treated with this herbicide as part of maintenance control programs (Mossler and Langeland 2006). One exception is the spring-fed Ichetucknee River, where a control program based solely on hand removal of plants has drastically reduced water lettuce populations in much of the river over the past several years.

Hydrilla

Hydrilla is a submersed aquatic plant native to Southeast Asia and Africa. Commonly imported into Florida by the aquarium trade during the mid 20th century, naturalized populations of hydrilla were identified in several Florida waterways by the early 1960s (Schmitz *et al.* 1993). Over subsequent decades the plant has rapidly spread into many aquatic systems throughout Florida and the southeast United States. Of the \$29 million requested by Florida's Bureau of Invasive Plant Management (2007) for aquatic plant control in public waters for 2007 – 2008, well over half (\$16 million) is marked for ongoing hydrilla suppression. The Bureau of Invasive Plant Management (2007) also reported that approximately \$142,000 was spent for hydrilla control in spring systems such as Wakulla River, Weeki Wachee River, Silver River, and Rainbow River in fiscal year 2005 – 2006.

Several features make hydrilla an extremely effective and problematic invasive species. Perhaps most critical to its spread is the viability of even very small plant fragments, which are often inadvertently brought into new water bodies by boat trailers and propellers (Schmitz *et al.* 1993). Once established in a water body, hydrilla has the ability to grow from sediments up to the water surface (often referred to as "topping out") and form a canopy that can effectively shade out native submersed species, severely restrict navigation, and interfere with flood control structures (Schmitz *et al.* 1997; Jones and Beardall 2005). In addition, hydrilla's root system is characterized by many large tubers that often resprout after leafy growth is suppressed through herbicides or other disturbance (Schardt 1997). Some research suggests that hydrilla may also have lower light requirements for photosynthesis relative to native submersed plants, thereby allowing it to colonize deeper areas of water bodies that previously would have been free of vascular plant growth (Van *et al.* 1976). Like the floating species discussed above, large-scale hydrilla coverage can result in the depression of dissolved oxygen levels due to reduced atmospheric diffusion and suppression of phytoplankton production in underlying waters (Schmitz *et al.* 1993). Dense hydrilla also has been known to adversely affect sports fisheries by providing increased habitat cover that restricts prey availability for species such as large mouth bass (Bureau of Invasive Plant Management 2007).



Figure 5 – *Hydrilla* in Wakulla Springs, 1998. Photo by Vic Ramey, University of Florida Center for Aquatic and Invasive Plants <http://aquat1.ifas.ufl.edu/wakhyd.jpg>

Although the deleterious effects of hydrilla overgrowth are quite dramatic, some research indicates that hydrilla can benefit certain fish and wildlife populations. For example, it is commonly reported that moderate hydrilla coverage provides superior game fish habitat (Schmitz *et al.* 1993), which leads many fishermen to advocate for management strategies that maintain significant hydrilla coverage in popular fishing lakes (Jones and Beardall 2005). Hydrilla is also known to provide highly attractive habitat for manatees (Campbell and Irvine 1977), certain macroinvertebrates (Schramm and Jirka 1989), and diverse assemblages of native water fowl (e.g., Johnson and Montalbano 1984; Esler 1990). Thus, one of the most complex challenges currently facing Florida's aquatic plant managers is development of techniques that better maintain the positive habitat values of hydrilla in areas where it is permanently established, while still preventing severe overgrowth and spread of the plant into new areas (Jones and Beardall 2005).

Modern hydrilla control methods in Florida rely heavily upon fluridone, a slow-acting systemic herbicide, and endothall, a fast-acting contact herbicide (Jones and Beardall 2005). Because effective treatment by fluridone requires long contact times that are prohibitively difficult and expensive to obtain in flowing systems, a dipotassium salt formulation of endothall (trade name Aquathol) is typically used for hydrilla control in springs (DEP 2005). However, serious concerns about the long-term sustainability of current chemical control methods are raised by recent findings of independently evolved fluridone-resistant hydrilla biotypes in Florida lakes frequently treated with fluridone (Michel *et al.* 2004). Although no endothall-resistant strains have been identified, many researchers argue that future development of resistance among hydrilla populations repeatedly treated with endothall, such as those in springs, is possible or perhaps even inevitable (Jones and Beardall 2005).

Diquat and copper (including chelated copper and copper sulfate formulations) are the major herbicides aside from fluridone and endothall that are currently listed for hydrilla control (Langeland 1996; Bureau of Invasive Plant Management 2007). Copper and diquat were commonly used for hydrilla control in the spring-fed Kings Bay/Crystal River complex during the 1970s and early 1980s (Haller *et al.* 1983), but apparently with uneven operational success (Dick 1989). Recent research indicates that copper and diquat may be most effective against hydrilla when applied together and/or in combination with endothall (e.g., Pennington *et al.* 2001), and such a strategy may be increasingly employed in Florida due to resistance concerns (Jones and Beardall 2005). However, increased use of copper for hydrilla control in some Florida springs is problematized by regulatory language that places restrictions on copper herbicide usage in areas frequented by manatees (State of Florida Division of Administrative Hearings 1993). These restrictions on copper herbicides were adopted by the Florida DEP in response to the documentation of elevated copper levels in the tissues of Kings Bay/Crystal River manatees (O'Shea 1984) and in the sediments of water bodies, including Kings Bay/Crystal River, in which copper was commonly used as an herbicide/algacide throughout the 1970 and 1980s (Leslie 1992). Toxicological concerns associated with chemical control of hydrilla are discussed at greater length in subsequent sections of this chapter.

NITRATE-NITROGEN AND NONNATIVE PLANTS IN SPRINGS

The increased nitrate-nitrogen contamination observed in springs throughout Florida is of great concern to ecosystem managers and the general public. Most direct research into the ecosystem effects of nitrate-nitrogen in springs has focused on filamentous algae such as *Lyngbya wollei* and *Vaucheria* sp. (Cowell and Dawes 2004; Stevenson *et al.* 2004). However, significant concerns have also been expressed about the potential for nitrate-nitrogen to favor the proliferation of water hyacinth, water lettuce, hydrilla, and other invasive nonnative plants (Florida Springs Task Force 2000; Loper *et al.* 2005).

Although there is a fairly large body of literature that describes nutrient uptake of these aquatic plants for the purposes of wastewater treatment and other forms of environmental remediation (see Ho and Tsang 1998; Gu 2006), much less direct productivity research has been conducted at nutrient concentrations or conditions relevant to those in Florida springs. As discussed in more detail below, the available literature strongly suggests that nitrogen limitation of these plants in most Florida springs would only occur, if at all, at the upper bounds of background aquifer nitrate-nitrogen concentrations.

Water Hyacinth and Nitrogen Limitation

A topic explored throughout the vast literature about water hyacinth ecology and control is the growth and uptake responses of water hyacinth to increased loading of nutrients. A common observation is that water hyacinth problems tend to be most serious in waters that suffer from nutrient enrichment, and, thus, nutrient mitigation is often recommended as a strategy for reducing plant growth (Gopal 1987). Limitation by either phosphorus or nitrogen is most common, although low levels of calcium, potassium, and iron have also been found to limit water hyacinth growth (Gopal 1987). While nitrogen limitation to water hyacinths is frequently indicated when N/P ratios are less than 7 (Wilson *et al.* 2005), experimental trials indicate that, at

very high nutrient levels, dissolved nitrogen typically will be depleted by water hyacinth stands at higher rates than phosphorus due to both luxury uptake by plants and denitrification (Reddy and Tucker 1983).

The natural concentrations of phosphorus, calcium, phosphorus and iron in typical Floridan aquifer water (Scott *et al.* 2004) are of sufficient quantity to make it unlikely that water hyacinth historically would have been limited by these nutrients in most Florida spring ecosystems. While long-term enrichment trends observed in springs provide a compelling rationale for considering nitrate-nitrogen the parameter of most concern for water hyacinth growth in Florida springs, the few direct studies of water hyacinths in springs have not definitively determined a concentration of nitrate-nitrogen that might limit biomass production. For example, Bartodziej and Leslie (1998), in a long-term study on the spring fed St. Marks River, report a water hyacinth biomass doubling time of 10 days at nutrient levels of 0.28 mg/l TN¹ and 0.06 mg/l TP. Because this biomass doubling time is essentially the same as those recorded in Japanese experiments (Sato and Kondo 1981, cited in Bartodziej and Leslie 1998) where water hyacinth was grown under conditions of extremely high nutrient enrichment (28 mg/l TN and 7.7 mg/l TP), Bartodziej and Leslie (1998) conclude that the observed nutrient levels in the St. Marks River were not a limiting factor for water hyacinth growth. Similarly, Odum's (1957) measures of water hyacinth productivity in Silver River, which at the time of study in the mid 1950s had a nitrate-nitrogen level of 0.4 mg/l, indicate that nutrients were not a major limiting factor.

Two recently developed water hyacinth models present nitrogen concentration values that could be expected to limit water hyacinth growth in some aquatic systems. Wilson *et al.* (2005) develop a synthetic model indicating that water hyacinth growth responds to nitrogen concentrations according to a logarithmic function, with the most dramatic increases in specific growth rate occurring between 0.1 and 1 mg/L of TN. While these nitrogen concentrations clearly fall within a range of direct relevance to Florida springs, direct inference of these results into springs conditions is confounded by the model's stated omission of flow velocity effects on nutrient availability and growth response. A water hyacinth growth model developed by Mahujchariyawong and Ikeda (2001) for Thailand's Tha-Chin River suggests that maximum growth rate of the water hyacinth requires 0.16 mg/l TN and 0.02 mg/l TP. Although this model does have the notable advantage of accounting for nutrient availability and replacement as affected by flow velocity, inferential caution is warranted due to important morphological, chemical, and climatic differences between the Tha-Chin River and typical Florida springs systems.

Perhaps the most intriguing clue about potential nitrate-nitrogen thresholds for water hyacinth in Florida springs comes from Webber's (1897) observation of water hyacinth plants showing a stunted growth form in the Silver River during the late 19th century. A data record reported by the USGS from 1907 indicates a nitrate-nitrogen concentration of 0.03 mg/l in Silver Springs (Munch *et al.* 2006). Taken together with the scientific literature discussed above, it is reasonable to hypothesize that Webber's (1897) observations may be indicative of nitrate-nitrogen serving as a physiological constraint to water hyacinth growth in the Silver River at the

¹ All nitrogen concentrations reported by Bartodziej and Leslie (1998) are in terms of TN. Relative contribution of nitrate-nitrogen to the TN measurement is not given.

background water quality levels of the late 19th and early 20th century. Confirmation of this suggested relationship, however, would require detailed assays of water hyacinth growth response to variable nitrate-nitrogen concentrations in flowing mesocosms, and/or comparative field studies of water hyacinth growth characteristics in springs systems, including those with background levels of nitrate-nitrogen.

Water Lettuce and Nitrogen Limitation

The similarity of growth and uptake responses observed for water hyacinth and water lettuce under experimental nutrient treatments (e.g., Aoi and Hayashi 1996) may make it reasonable to assume that the potential nutrient limitation thresholds for water lettuce growth in Florida springs are similar to those of water hyacinth. For example, it is well-established that water lettuce, like water hyacinth, will remove much higher levels of dissolved nitrogen than are necessary to sustain its maximum growth (Aoi and Hayashi 1996). Schmitz *et al.* (1993) hypothesize, while also noting the lack of specific studies testing this hypothesis, that increased levels of nitrogen may favor water lettuce to out-compete native submersed plants in freshwater systems throughout Florida.

Unfortunately, there is still very little research suggestive of the nitrate-nitrogen concentrations that might limit water lettuce production in Florida springs. Productivity measurements given by Odum (1957) indicate that growth of water lettuce in Silver Springs, much like water hyacinth, was not limited by nitrate-nitrogen levels of 0.4 mg/l. Instead, Odum's (1957) work suggests that extreme accumulation of water lettuce in Silver Springs was largely prevented by downstream export, seasonal senescence, and insect attack. More anecdotally, Webber's (1897, 13) reports of "large quantities of the water lettuce" in the Wekiva River during the late 19th century could suggest that background nutrient levels in that particular spring fed river were not a serious limiting factor for water lettuce growth. As suggested above for water hyacinth, detailed growth assays and/or comparative field studies would be needed to make more definitive determinations about the effects of nitrate-nitrogen enrichment on water lettuce population dynamics in Florida springs.

Hydrilla and Nitrogen Limitation

As a rooted submersed plant, determination of dissolved nutrient limitation for hydrilla is inherently more difficult than for the floating plants due to the confounding influences of sediment nutrient availability and uptake. With that said, a variety of evidence is suggestive of important relationships between hydrilla growth and increased nitrogen enrichment in Florida's aquatic systems. For example, tank experiments clearly indicate that hydrilla's growth and ability to out-compete native tape grass (*Vallisneria americana*) under high light conditions increases as a function of increased sediment nitrogen (Smart *et al.* 1994; Van *et al.* 1999). Similarly, Barko and Smart (1986) identified positive correlations between hydrilla shoot density and sediment nitrogen levels in field studies of North American lakes. More recent field surveys presented by Gu (2006) indicate a marginally significant relationship between dissolved total nitrogen and the extent of hydrilla occurrence in Florida lakes, although stronger correlative relationships were identified with other water quality parameters such as alkalinity, pH, and total dissolved phosphorus.

It must be cautioned, however, that straightforward inference from these studies into Florida springs conditions is confounded by at least two factors: 1) whether or not there is a significant positive relationship between dissolved nitrate-nitrogen and sediment nitrogen in springs ecosystems; and 2) what effects stream flow may have on dissolved nutrient availability for hydrilla and other submersed plants (Canfield and Hoyer 1988). Following this second point, Terrell and Canfield (1996) found that dissolved nitrogen availability for aquatic plants in Kings Bay/Crystal River, which had a mean TN concentration of approximately 0.26 mg/l at the time of study (neither nitrate-nitrogen contribution to TN nor sediment nitrogen were reported), greatly exceeded the biological demands necessary for maximum growth and accumulation of hydrilla. Based on this finding, Terrell and Canfield (1996) concluded that nutrient reduction likely was not an effective strategy for reducing growth of hydrilla in Kings Bay/Crystal River. Detailed studies that take into account dissolved nutrient availability, sediment nutrient stores, flow rates, native plant competition, and hydrilla productivity would be needed to determine if nitrate-nitrogen reduction is a feasible strategy for hydrilla suppression in the context of other Florida springs.

NONNATIVE PLANTS AND ALGAL COMMUNITY DYNAMICS

While overgrowth of nonnative invasive plants is a serious management issue, most conservation and management concern in Florida springs over recent years has been associated with increased cover of filamentous algae and cyanobacteria such as *Vaucheria* sp. and *Lyngbya wollei* (Stevenson *et al.* 2004). Given the strong trophic and structural associations between native aquatic plants, epiphytic algae, and animal communities historically found in springs ecosystems (Odum 1957), it stands to reason that the obvious structural changes in plant community caused by invasive plant growth potentially could trigger structural changes in the algal and animal communities.

This section utilizes scientific literature about major invasive plants to explore two mechanisms by which these plants might contribute to a successional trajectory in which undesirable algae become dominant in springs ecosystems. The first proposed mechanism, referred to as “boom bust,” focuses on the implications of the increased productivity, biomass accumulation, and vulnerability to catastrophic losses and rapid community reorganization that are associated with invasive plant communities. The second proposed mechanism focuses on the allelopathic properties of the invasive plants, with particular attention to the potential implications of algicidal allelopathy.

Boom-Bust Hypothesis

Perhaps the most basic functional trait shared by water hyacinth, water lettuce, hydrilla and other invasive aquatic plant species is higher productivity relative to competing native plants (Schardt 1997). Thus, the introduction of a successful invasive aquatic plant is almost axiomatically associated with a boom cycle in which more biomass is produced and accumulated in the ecosystem. Another feature of water hyacinth, water lettuce, and hydrilla in Florida is that these initial booms are often followed by rapid population crashes, or busts. These busts can be caused by aquatic plant control or a variety of stochastic natural events such as saltwater storm surges

(Terrell and Canfield 1996), high water/floods (Bartodziej and Leslie 1998; Bureau of Invasive Plant Management 2007), and killing frosts (Joyce 1985; Schardt 1997).

Figure 6 gives a simplified diagram of mechanisms by which a boom bust cycle associated with invasive plants potentially could lead to increased nuisance algae in springs systems. The diagram shows that one major ecosystem effect often associated with invasive plants is competitive displacement of native plant species (e.g., Schmitz *et al.* 1993; Bartodziej and Leslie 1998), some of which may have previously suppressed the growth of problematic algae such as *Lyngbya wollei* (see Doyle and Smart 1998). While there is significant evidence to suggest that hydrilla, water hyacinth, and water lettuce are likely to suppress algal production through shade, nutrient uptake, and other feedbacks (e.g., Cohen 1993; Cowell and Botts 1994; Kim *et al.* 2001), it is plausible that the sequence of competitive displacement of native plants followed by a bust cycle characterized by destruction of dominant invasive plant populations may favor succession by opportunistic filamentous algae. Filamentous algae have been observed to fill in such ecological voids after aquatic plant control of hydrilla in Kings Bay/Crystal River (Cowell and Botts 1994) and Wakulla River (Loper *et al.* 2005). Similarly, Evans (2007) observed an apparent increase of filamentous algal biomass in the Ichetucknee River following manual removal of water lettuce. Large algal blooms following control of water hyacinths, while not specifically documented in Florida springs systems, have been documented in other ecosystem contexts (see Clugston 1963; Bicudo *et al.* 2007).

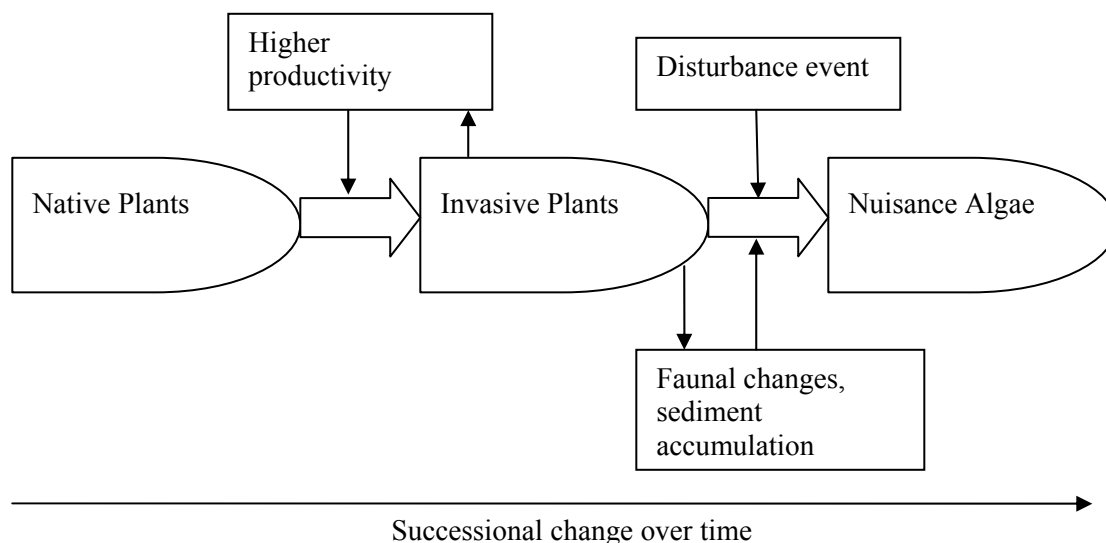


Figure 6 – Conceptual diagram of boom-bust hypothesis in Florida springs

A mechanistic feedback that may further favor proliferation of nuisance algae after a boom bust invasive plant cycle is implied by the work of Stevenson *et al.* (2007), who found that nutrient enrichment of sediments was significantly associated with presence of nuisance algae in springs. While there has to date been no detailed study of nutrient accumulation in springs sediments as a function of aquatic plant control or nonnative plants, aquatic plant control activities were suggested as a possible source of enriched sediments documented by Wetland Solutions, Inc. (2006) in the Wekiva River and Rock Springs Run system. More detailed study of such

relationships appears warranted in springs, particularly because invasive plant growth and control has been linked with nutrient enrichment of sediments in other ecosystem contexts. For example, Brenner *et al.* (1999) suggested that the introduction and subsequent chemical treatment of water hyacinth and hydrilla likely was a major contributor to nutrient enrichment and bulk density increases documented in the sediments of Lake Hell ‘n’ Blazes from approximately 1900 to 1995. Similarly, Grimshaw (2002) identified chemical treatment of water hyacinth and water lettuce as a significant source of nutrient-rich organic sediments in the Kissimmee River and Lake Okeechobee. In a highly detailed study of water hyacinth control (based on a “trituration” technique of shredding the aquatic plants and loading the biomass into the water column) in Mexico’s Valsequillo reservoir, Mangas-Ramirez and Elias-Gutierrez (2004) recorded increases of ammonia from 3 mg/l to 60 mg/l in sediment interfaces, a 320% increase in dissolved nitrate-nitrogen, declines in dissolved oxygen to below 0.4 mg/l, increased rates of organic sedimentation, disappearance of most fish, and large blooms of cyanophytes in the reservoir following weed trituration.

Although these studies are suggestive of the impacts that invasive aquatic plants and subsequent control efforts may have in terms of sediment enrichment in springs, it is important to note that a variety of factors such as flow velocity, external inputs of organic matter, upwelling of nutrient rich groundwater through karst streambeds, and the densities and accumulation of plant biomass in specific springs would all be expected to exert significant influence over sediment nutrient levels. Detailed measurements of sediment nutrients, dissolved nutrients, and plant/algae community characteristics in discrete samples taken directly before, directly after, and in sequential intervals following aquatic plant control would provide invaluable information about the overall ecosystem effects of current management techniques on springs ecosystems.

Allelopathy Hypothesis

Algal community composition in springs and other streams are clearly shaped by ecological factors such as nutrient availability, flow velocity, light intensity, grazer abundance, and substrate quality (e.g., Stevenson *et al.* 2007). In addition to these more general ecosystem variables, algal communities are also shaped by complex competitive and/or synergistic interactions between algae and vascular plants at the species level. Emission of allelopathic compounds, or compounds that directly suppress the growth of other primary producers, is increasingly regarded as one of the most important, if not well understood, competitive factors in aquatic systems (Gross 2003).

Several scientific studies indicate that water hyacinth, water lettuce, and hydrilla all emit allelopathic compounds that restrict growth of algal and/or plant competitors. In the case of water hyacinth, Jin *et al.* (2003) conducted lab experiments indicating that various compounds extracted from water hyacinth roots had algicidal properties on *Chlorella* sp., *Scenedesmus obliquus*, and undifferentiated phytoplankton that were comparable in activity to copper sulfate – a commonly used commercial algicide. Similarly, Aliotta *et al.* (1991) isolated several allelopathic chemicals from water lettuce that showed inhibitory effects on seventeen of nineteen algal cultures, with *Lyngbya kuetzingii* and *Chlorella saccharophila* showing no inhibition. While specific algicidal compounds have not been identified in hydrilla to date, Kulshresthna and Gopal (1983) did find that hydrilla negatively affected the growth of vascular aquatic plant

Ceratophyllum sp. through allelopathic mechanisms. However, Glomski *et al.* (2002) later argued that allelopathy is only a very minor factor in hydrilla's overall competitive success against other aquatic plants.

The potential implications of algicidal allelopathy in the floating plants are interesting to consider in the context of Florida springs systems. On the one hand, allelopathic emissions from floating plants may be a mechanism by which fringe mats of floating plants in spring runs serve as a constraint for algal growth and accumulation in habitat areas beyond those covered by the plants, including beds of native submersed plants located in the main stream flow. If this is the case, then the algicidal properties of floating plants may potentially serve as a buffer against algal overgrowth in nutrient-enriched springs. On the other hand, it is plausible that persistent presence of allelopathic compounds with algicidal properties might select for relatively resistant algal taxa, potentially including *Lyngbya* sp. (e.g., Aliotta *et al.* 1991).

Better understanding of the algicidal activity of floating plant allelopathic emissions on springs-specific algae species would require isolation of algicidal compounds and detailed bioassays similar to those conducted by Aliotta *et al.* (1991) and Jin *et al.* (2003). In addition, measurements of the concentration ranges for such compounds in the water of springs would be required to understand the extent to which allelopathic mechanisms may be an important driver of algal community selection in springs communities.

AQUATIC PLANT CONTROL AND ALGAL SUCCESSION

Control of nonnative invasive plants is one of the most common management actions performed in Florida's aquatic ecosystems, including many of the state's springs. As discussed above, chemical control using herbicides registered by the EPA for use in aquatic systems is the primary tool used by aquatic plant managers. The most obvious ecological concern associated with use of aquatic herbicides is non-target damage to native plants, algae, and animal communities, either through direct toxicology of herbicides or the ecological consequences of rapid plant senescence. Although aquatic plant managers and herbicide applicators take great precautions to avoid major non-target impacts, the complexities of ecosystems make some non-target damage unavoidable.

This section reviews literature associated with two of the most plausible and commonly suggested mechanisms by which chemical control of nonnative invasive plants can disrupt aquatic ecosystems: 1) preferential selection of herbicide resistant algae species; and 2) suppression of key algal-grazing fauna through direct toxicology and/or habitat destruction. Potential implications of these mechanisms for Florida springs, particularly in terms of succession towards filamentous algae/cyanobacteria communities, are also discussed.

Herbicide Selection Hypothesis

Development of herbicide resistance among algae has been repeatedly demonstrated at both the cellular level of individual species (i.e., a specific algal species evolves resistance to an herbicide) and the ecological level of community assemblages (i.e., more herbicide-resistant species become dominant) (e.g., Solberg and Higgins 1993; Boswell *et al.* 2002; Garcia-Villada *et al.* 2004; Cooke *et al.* 2005; Lopez-Rodas 2007). Thus, a major concern associated with

repeated use of herbicides in aquatic systems is the potential selection for herbicide-resistant algal biotypes. In particular, recent research suggests that some herbicide-resistant algal species often may be less palatable and/or nutritious to algal-grazing fauna, thus causing a cascade effect on faunal community structure and overall ecosystem organization (e.g., Weiner *et al.* 2007). This section discusses potential algal-selection concerns associated with the major herbicides used in Florida springs: copper, diquat, endothall, glyphosate, and 2,4-D. When relevant information is available, attention is particularly given to potential selection concerns associated with *Lyngbya wollei*.

Copper

Copper compounds are most often used in aquatic systems as algaecides, but are listed an approved method for control of hydrilla and other submersed plants species in Florida (Bureau of Invasive Plant Management 2007). Largely due to concerns about sediment contamination and bioaccumulation risks in manatees (O'Shea 1984; Facemire 1991; Leslie 1992), copper herbicides have not been widely used in Florida since the early 1990s. However, copper herbicides were used extensively for hydrilla control in the Kings Bay/Crystal River ecosystem during the 1970s and 1980s (Haller *et al.* 1983), and currently are being researched as a potential option for filamentous algae control in Kings Bay/Crystal River.

Development of copper resistant algal communities is a well-documented risk associated with long-term usage of copper herbicides. Recent research, for example, indicates that repeat exposure to copper sulphate can facilitate evolution of copper-resistant strains in both the cyanobacterium *Microcystis aeruginosa* (Garcia-Villada *et al.* 2004) and the green algae *Chlamydomonas reinhardtii* (Boswell *et al.* 2002). Cooke *et al.* (2005) report that repeated treatment with copper sulfate resulted in increasingly copper resistant algal communities in a number of lakes and reservoirs throughout the northeastern United States. With such selection dynamics in mind, it is notable that *Lyngbya* sp. and *Oscillatoria* sp., which are problematic taxa in some Florida springs (Stevenson *et al.* 2004), are known for their ability to develop copper resistant biotypes (Spencer and Lembi 2005). Evans *et al.* (2007) argue that such selection dynamics may provide a key clue for better understanding of algal community dynamics in Florida spring systems, such as Kings Bay/Crystal River, where copper herbicides have been used historically.

Diquat

Scientific literature indicates that concerns associated with selection of herbicide-resistant algae communities may also be associated with large-scale use of diquat dibromide in Florida springs. Diquat is most commonly used for treatment of mixed stands of water lettuce and water hyacinth, but has also been used for control of hydrilla and other submersed species in some springs systems (Haller *et al.* 1983). Although residues of diquat do accumulate in aquatic sediments, most recent research suggests that diquat forms complex bonds with sediments that render it biologically unavailable (Emmett 2002).

Bioassay research indicates that there is a wide range of tolerances among algal taxa to diquat exposure. Peterson *et al.* (1997) found that 50% inhibition of biomass production occurred

among two green algae taxa (*Scenedesmus quadricauda* and *Selenastrum capricornutum*) at concentrations of approximately 0.6 mg/l of diquat, while 50% growth inhibition for diatoms (*Nitzschia* sp. and *Cyclotella meneghiniana*) and cyanobacteria (*Oscillatoria* sp. and *Pseudoanabaena* sp.; *Microcystis* sp.) occurred at concentrations approximately one order of magnitude lower (0.074 mg/l and 0.079 mg/l of diquat, respectively). Philips *et al.* (1992), however, found a wider range of diquat sensitivity among the taxonomic groups, with *Euglena gracilis*, *Chlorella vulgaris*, and *Skeletonema costatum* showing high levels of tolerance to diquat (50% inhibition predicted at over 2.94 mg/l). *Lyngbya wollei* showed a higher level of tolerance to diquat (50% inhibition predicted at a range of 0.081 mg/l to 0.205 mg/l of diquat) in the Philips *et al.* (1992) bioassays as compared to the cyanobacteria tested by Peterson *et al.* (1997). Aquatic plant control observations indicate that diquat often proves ineffective for long-term control of *Lyngbya wollei* (Bayne 2005), which may be suggestive of an evolutionary resistance capability with regards to diquat in this cyanobacterium.

A potential implication of the differential tolerances exhibited by algal-taxa is that repeat treatment with diquat may exert a chronic selective pressure that favors community-level dominance by diquat-resistant species and/or biotypes over time. Much like with the copper herbicides, diquat treatment history and sediment residues may be an important variable to consider in studies of algal community dynamics in Florida springs where this herbicide has been commonly used for aquatic plant control.

Endothall

The dipotassium salt formulation of endothall, which is generally referred to by the trade name Aquathol, is the primary herbicide used for control of hydrilla in flowing water systems. While Aquathol is not typically recommended for algae control purposes, an amine endothall salt (trade name Hydrothol) is registered for control of filamentous algae and submersed plants in Florida. However, Hydrothol is not commonly used in Florida's public waters due to its relatively high toxicity to fish and other aquatic fauna. Field observations suggest that Hydrothol applications often prove ineffective for *Lyngbya wollei* control (DuBose *et al.* 1997), and, as noted above for diquat, such observations may be indicative of an evolutionary resistance to endothall-based compounds among *Lyngbya* sp. Specific bioassays testing the algaecidal action of Aquathol would be needed to determine if repeated use of this compound has significant implications for algal community structure in Florida springs.

Glyphosate

An aquatic-registered form of glyphosate (trade name "Rodeo") is sometimes used for control of water hyacinths in Florida (Bureau of Invasive Plant Management 2007). While generally not used as an algaecide in aquatic environments, bioassays indicate that glyphosate does have algaecidal action. Wong (2000) reported significant growth inhibition of *Scenedesmus quadricauda* at 2 mg/l of glyphosate and complete inhibition at 20 mg/l. In very recent bioassay work with *Microcystis auroginosa*, Lopez-Rodas *et al.* (2007) reported considerable inhibition in the cyanobacterium from 10 mg/l to 60 mg/l of glyphosate solution, and observed the evolution of glyphosate resistant *M. auroginosa* biotypes at concentrations of 120 mg/l. While the glyphosate concentrations of concern to Lopez-Rodas *et al.* (2007) are at least an order of

magnitude over realistic field concentrations associated with aquatic plant control (Langeland 2006), it is plausible that the lower end of concentrations showing growth inhibition in the Wong (2000) experiment may be reached during aquatic plant control operations. Bioassays testing glyphosate response curves of algal species in Florida springs would be needed to better determine algal-selection risks associated with this herbicide.

2,4-D

Algal toxicity bioassays with 2,4-D have found that this herbicide is generally non-toxic and even stimulatory to most algae and cyanobacteria at concentrations used for aquatic plant control (Okay and Gaines 1996; Wong 2000). The likely reason for the stimulatory effect is that 2,4-D's mode of herbicidal action is mimicry of the plant hormone auxin, rather than direct targeting of photosynthesis mechanisms. Toxic effects on algae are reported at over 200 mg/l of 2,4-D by both Okay and Gaines (1996) and Wong (2000), but such concentrations are well outside of those associated with aquatic plant control. Interestingly, Okay and Gaines (1996) report that the amine form of 2,4-D is preferentially consumed as a nitrogen source over nitrate-nitrogen by the phytoplankton *Phaedactylum tricornutum* and *Dunaliella tertiolecta* when 2,4-D is found at concentrations up to 100 mg/l, meaning that changes in algal community could be promoted by 2,4-D through an enrichment mechanism, rather than a toxicity mechanism. Like with the other herbicides, specific bioassays testing growth response to 2,4-D among algal species found in Florida springs would be needed to better understand the community level effects of this herbicide.

Attractor – Catastrophe Hypothesis

A final mechanism by which invasive plants and their subsequent management may profoundly affect ecosystem structure in springs is through a sequential cycle that can be deemed “attractor-catastrophe,” which is somewhat similar to the boom-bust cycle discussed above. The basic thrust of this hypothesis is that nonnative invasive plants can become preferred habitat, or serve as an “attractor,” for key faunal species, but that this habitat ultimately becomes a persistent sink for faunal populations due to the bust cycle “catastrophes” that affect nonnative plant communities. Although any habitat disturbance that destroys non-native plant communities is potentially a catastrophic sink for associated faunal communities, primary focus is given here to the non-target toxic effects and/or general habitat disturbance that may be associated with aquatic plant control activities. The major rationale for this focus is that aquatic plant control activities are unique in the sense that they are directly controlled by management agencies, and thus may be adjusted for the purposes of adaptive learning.

Habitat Values of Water Hyacinth

Bartodziej and Leslie's (1998) long-term study of ecological communities associated with water hyacinth in the St. Marks River clearly demonstrates the high habitat values that can be provided by this nonnative plant in Florida springs. Contrary to other ecosystem contexts in which large mats of water hyacinth have been clearly shown to depress dissolved oxygen, coverage by water hyacinth in the flowing waters of the St. Marks River did not show significant oxygen profile differences as compared to strap-leaf sag (*Sagittaria kurziana*) or other native plant

communities. While native strap-leaf sag in the St. Marks River was reduced by water hyacinth expansion, it was not displaced entirely as the water hyacinth community was rarely observed by Bartodziej and Leslie (1998) to reach more than 25% coverage along the river width (see Figure 7) due to consistent flushing of the floating plants by river current.



Figure 7 – Water hyacinth fringe in River Rise Spring #3, St. Marks River. Photo by Northwest Florida Water Management District (2006).

http://www.nwfwmd.state.fl.us/rmd/springs/Wakulla_StMarks/photos/rise3_1.jpg

Long-term faunal surveys indicated that the community associated with water hyacinths was generally more diverse in terms of invertebrate taxa and included significantly higher abundances of spring run crayfish (*Procambarus paludosus*), amphipods (*Hyalella azteca*), grass shrimp (*Palaemonetes paludosus*), and several fish species as compared to strap leaf sag communities (see Figure 8). Apple snails (*Pomacea paludosa*) were also found to have much higher population densities in water hyacinth compared to strap leaf sag. Conversely, rasp elimia snail (*Elimia floridensis*) populations in strap leaf sag were much higher than those found in water hyacinth communities (see Figure 8). Surveys of bird populations among water hyacinth in the St. Marks River indicated that water hyacinth was commonly used for forage habitat by little blue herons (*Egretta caerulea*) and tri-colored herons (*Egretta tricolor*), and was also observed to increase available nesting habitat for the common moorhen (*Gallinula chloropus*) (Bartodziej and Weymouth 1995).

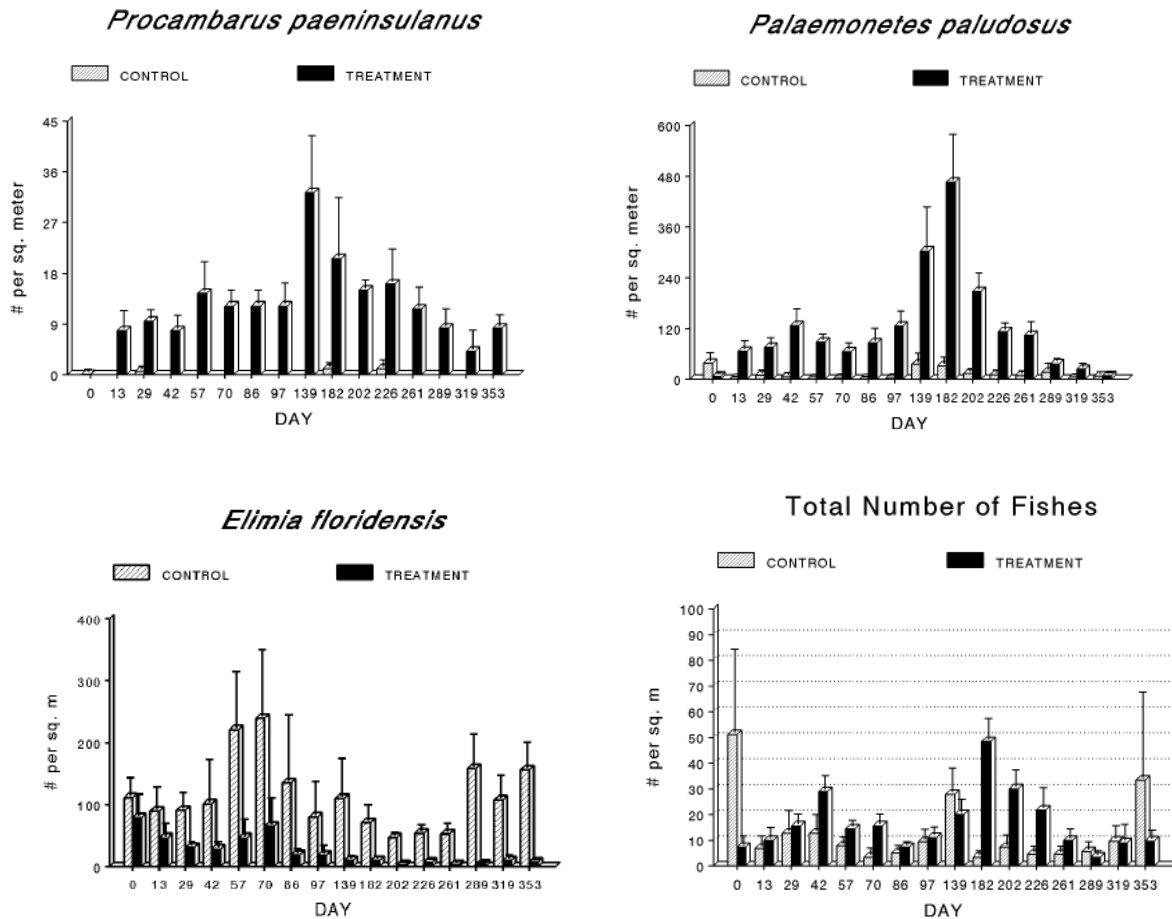


Figure 8 – Ecosystem survey results from St. Marks River (Bartodziej and Leslie 1998) showing higher numbers of spring run crayfish (*Procambarus paludosus*), grass shrimp (*Palaemonetes paludosus*), and total fishes in water hyacinth (treatment) as compared to strap leaf sag communities. Rasp elimia snail (*Elimia floridensis*) populations are considerably higher in strap leaf sag.

Habitat Values of Water Lettuce and Hydrilla

Detailed habitat assessments in a springs ecosystem are not available for either water lettuce or hydrilla. However, as suggested by Carr (1994), it may be reasonable to assume that the similar structure of water lettuce and water hyacinth is likely to provide habitat for a similar faunal species assemblage. Schmitz *et al.* (1993) note that water lettuce supports high concentrations of *Hyalella azteca*, and Evans (2007) anecdotally reports large numbers of spring run crayfish and apple snails in water lettuce harvested from the Ichetucknee River in 2000 – 2001. Similarly, Corrao *et al.* (2006) report high concentrations of apple snails on hydrilla and apple snail eggs on water lettuce at Wacissa Springs. In other ecosystem contexts, hydrilla is known to support large macroinvertebrate populations (Schramm and Jirka 1989) and attract diverse assemblages of water fowl (Johnson and Montalbano 1984; Esler 1990). Dramatically increased manatee utilization of Kings Bay/Crystal River beginning in the 1960s (Kochman *et al.* 1985) coincides

with the introduction and rapid spread of hydrilla, a preferred manatee forage (Campbell and Irvine 1977), in that system.

Non-Target Concerns

As noted by Bartodziej (1992) for water hyacinth-associated amphipod populations and Corrao *et al.* (2006) for apple snails, the effects of habitat loss associated with aquatic plant control on faunal communities in springs is largely unknown. Corrao *et al.* (2006) suggested that direct removal of apple snails during harvest of hydrilla at Wakulla Springs and herbicide suppression of plants containing snail eggs at Wacissa Springs may have had significant negative effects on apple snail populations, but noted that more detailed studies would be necessary to test these observations. Similarly, Evans (2007) observed that harvest of water lettuce from Ichetucknee Springs resulted in direct mortality of several faunal species, including apple snails and spring run crayfish, but also noted that more detailed studies would be necessary to quantify the overall faunal impacts of plant harvest.

Use of copper herbicides has raised significant non-target concerns in Florida springs. Most notably, copper herbicide use in Kings Bay/Crystal River was discontinued in the late 1980s due to the finding of severe accumulation of copper in aquatic sediments (Facemire 1991; Leslie 1992) and the tissues of manatees (O'Shea 1984). More systematic concerns about long-term copper herbicide usage are suggested by Cooke *et al.* (2005), who note that dissolved copper can severely suppress zooplankton grazers and that sediment contamination can have long-term effects on the structure and function of benthic communities. Increased levels of *Lyngbya wollei* often were observed in Kings Bay/Crystal River subsequent to hydrilla herbicide treatments (see Cowell and Botts 1994), which led Evans *et al.* (2007) to hypothesize that toxicological suppression of grazer communities associated with copper herbicide usage may have contributed to subsequent algal overgrowth.

Risk assessments on four grazer species performed by Mastin and Rodgers (2000) indicate 50% lethal concentration dosages² (LC50) at 48 hours for copper herbicides between 0.011 mg/l – 0.029 mg/l for *Daphnia magna*; between 0.158mg/l to 0.433 mg/l for *Hyalella azteca*; between 0.374 and 0.114 mg/l for *Chironomus tetanus*; and between 0.019 and 0.48 mg/l for *Pimephales promelas*. Copper concentrations reported by Haller *et al.* (1983) in the water of Kings Bay following a copper herbicide treatment ranged from 0.002 mg/l to 0.011 mg/l, which is generally lower than the above LC50s (with the exception of *Daphnia magna*) reported by Mastin and Rodgers (2000). Dick (1989), however, reported that poor control of hydrilla using standard dosage rates sometimes led aquatic plant managers to apply significant higher rates of copper in Kings Bay/Crystal River than those monitored by Haller *et al.* (1983). Copper's toxicity to organisms in dissolved form generally decreases as a function of increased hardness due to carbonate-induced precipitation of copper compounds (Mastin and Rodgers 2000). Thus, it can be argued that non-target risks in Florida springs ecosystems from dissolved copper may be mitigated due to the relatively high hardness values in most springs as compared to the water hardness values (48 – 100 mg/l) reported in the Mastin and Rodgers (2000) experiment. Clearly,

² A 50% lethal concentration dose (LC) is the concentration of a chemical that results in 50% mortality of a test organism within 24 to 96 hours.

any future use of copper compounds in Florida springs ecosystems should be implemented cautiously and carefully monitored to minimize the secondary effects on fauna.

Risk assessments and toxicological data for diquat indicate that use of this herbicide may also raise serious non-target concerns for springs fauna. In a risk assessment for diquat conducted for the State of Washington Department of Ecology, Emmett (2002) reports that diquat is “very highly toxic” to *H. azteca*, with a LC50 of 0.048 mg/l, and “highly toxic” to the apple snail (*Pomacea paludosa*) with a LC50 of 0.34 mg/l. Nicholson and Clerman (1974) noted the high sensitivity of *H. azteca* to diquat toxicity in laboratory studies, and suggested that a combination of direct toxicity and the destruction of aquatic plants through herbicide usage were likely mechanisms for drastic *H. azteca* declines observed in New York’s Chautauqua Lake during the 1960s and 1970s. Given that *H. azteca* is an important grazer of *Lyngbya wollei* (Camacho and Thacker 2006), it is reasonable to hypothesize that toxicological suppression of *H. azteca* potentially may be a factor in the increased dominance of *L. wollei* in Florida springs where diquat has been widely used.

Available literature suggests that very little non-target toxicological effects on fauna are associated with fluridone (e.g., Hamelink *et al.* 1986; Haag and Buckingham 1991), 2,4-D (Johnson and Finley 1980), or glyphosate (Langeland 2006) at concentrations used for aquatic plant control. However, Wang *et al.* (1994) does document bioaccumulation of 2,4-D after water hyacinth treatment in some fish species, and a breakdown product of 2,4-D (2,4-dichlorophenol) has been shown to have relatively high toxicity to earthworms (Roberts and Dorough 1984). Relyea (2005) has raised concerns about the effects of the Roundup formulation of glyphosate on amphibians, but Langeland (2006) notes that the toxicological effects reported by Relyea (2005) are associated with an adjuvant in Roundup that is not used in the aquatic-approved formulations of glyphosate (e.g., Rodeo).

Aside from habitat loss and toxicology, the other major concern associated with aquatic plant control is prolonged dissolved oxygen depression as plant biomass decays. Wetland Solutions, Inc. (2006) measured an increase in community respiration of 120% and a reduction of net primary production by 150% in a segment of Rock Springs Run following herbicide treatment of floating and emergent plants in December 2005. It was also noted that the trend of increased respiration continued for approximately two weeks following the herbicide treatment, thereby resulting in “a detectable but temporary impairment of the aquatic community in Rock Springs Run” (Wetland Solutions, Inc. 2006).

Some of the most detailed monitoring of aquatic plant control in a springs ecosystem has taken place over recent years in the Wakulla River. A report by DEP (2002) indicates that the stream condition index and habitat assessment scores at Wakulla River improved after an Aquathol treatment of hydrilla (Figure 9). However, significant non-target concerns were raised after state park biologists observed a significant die-off of spring run crayfish following at least one subsequent Aquathol treatment (DEP 2006). In response to these concerns, DEP (2006) conducted a management experiment in which crayfish were monitored following aquatic plant control. Twenty chambers containing crayfish were deployed immediately prior to herbicide application, and nineteen were retrieved after four days. The remaining chamber was initially missed, but retrieved with a live crayfish after nine days. Another twenty chambers were

deployed nine days after the herbicide application and again retrieved four days later. Data sondes showed that dissolved oxygen dropped from as high as 4.3 mg/l to approximately 2.0 mg/l after the herbicide treatment, and Aquathol exposure was measured at concentrations that ranged from 0.41 mg/l to 2.06 mg/l – levels known to be well under toxicological thresholds for crayfish. Despite these low oxygen levels, only one crayfish death among the forty replicates was observed during the duration of the experiment. Although these results did not support the hypothesis that previously observed crayfish mortality was caused by aquatic plant control, the possibility of drastically reduced crayfish fitness as a result of prolonged dissolved oxygen depression that extended beyond the temporal scope of the experiments could not be ruled out (DEP 2006).

Wakulla Springs Herbicide Study					
Station STORET			Wakulla Springs STMARKSSTORET01		
Station Nickname WAKULLA SP			04/04/02 and 05/06/02		
Sampling Date					
Macroinvertebrate Parameters		4/4/2002	5/6/2002	Chemistry Data	
		4/4/2002	5/6/2002		
SCI	19	21	Ammonia (mg/L)	0.01 U	0.0191
SCI Evaluation	Poor	Good	Nitrate-Nitrite (mg/L)	0.73	0.79 J
Number of Taxa	17	16	TKN (mg/L)	0.06 U	0.06 U
EPT Index	2	0	Total Phosphorus (mg/L)	0.0321	0.052
FL Index	6	8	Color (PCU)	5 U	5 U
% Dominant Taxon	35.42	51.33	Turbidity	0.6	0.35
% Diptera	58.33	81.42	Physical-Chemical Data		
Total number of Chironomidae	9	11	4/4/2002	5/6/2002	
% Filter-Feeders	26.04	31.86	Habitat Assessment	115	130
Periphyton Parameters		4/4/2002	5/6/2002	Specific Conductivity (umhos/cm)	320
% Bacillariophyceae	90.7	89.63	Dissolved Oxygen (mg/L)	5	4.7
% Cyanophyceae	8.59	9.31	pH (SU)	7.45	7.6
% Chlorophyceae	0.72	1.05	Temperature (deg C)	20.6	21.5
Percent Dominant taxon	26.83	25.66			

Figure 9 – Habitat and water quality assessments at Wakulla River before (4/4/2002) and after (5/6/2002) Aquathol treatment of hydrilla (DEP 2002).

RECOMMENDATIONS FOR FURTHER RESEARCH

This chapter opened by asking four sets of questions related to nonnative plants in Florida springs. The first asked to what extent increased nitrate-nitrogen might be a factor in the spread of the invasive plants water hyacinth, water lettuce, and hydrilla, and at what level might invasive plant growth in springs be limited by nitrate-nitrogen. Available literature does not provide a clear answer for determining a concentration of nitrate-nitrogen that would be limiting to nonnative springs, but observations suggests that nitrogen limitation is most likely alleviated at the very low end, and perhaps even close to background, concentrations in Florida springs. Detailed nutrient assay experiments in flowing mesocosms and, in the case of hydrilla, with realistic sediment nutrient concentrations would be necessary to determine more accurate nutrient limitation parameters for nonnative plants in spring systems.

The second question asked about the potential implications of invasive plant proliferation on ecosystem structure and function in springs. Available literature indicates that biomass accumulation, suppression of native plants, and algicidal emissions associated with nonnative

plants may produce feedback mechanisms that together make springs systems more prone to a successional trajectory of overgrowth by nuisance algal taxa. At the same time, scientific studies and observations indicate that the major invasive plants often provide highly attractive habitat for key springs ecosystem fauna and may support some feedbacks that could be expected to reduce algal overgrowth. Detailed habitat assessments, monitoring of sediment accumulation, and multi-year monitoring of vegetational succession patterns in nonnative plant communities would be needed to better understand the relationships between nonnative plants and algal overgrowth.

The third question asked about the potential implications of aquatic plant control on ecosystem structure and function. What emerged from a review of literature was a wide range of concerns about possible algal selection, habitat loss, faunal toxicology, and dissolved oxygen suppression that may be associated with aquatic plant control. With the notable exceptions of circa 1980s work conducted by several agencies in Kings Bay/Crystal River due to concerns over copper herbicide contamination (Haller *et al.* 1983; O'Shea *et al.* 1984, Facemire 1991) and more recent work in Wakulla Springs associated with concerns over crayfish mortality after Aquathol applications (DEP 2005), there has been very little monitoring of the overall ecosystem consequences of aquatic plant control in springs ecosystems. To better understand the overall ecosystem effects of aquatic plant control in springs communities, detailed monitoring programs that measure key variables such as dissolved nutrients, dissolved oxygen, biomass deposition, and floral and faunal community structure should be monitored as a matter of course before and after major aquatic plant control operations.

As for the fourth question: are there opportunities for alternative management of invasive plants that may assist in the restoration of desired ecosystem functions in highly degraded springs and spring run ecosystems? Given the notorious history of these plants recounted above, the mere suggestion that there may be anything “good” or even redeemable about water hyacinth, water lettuce, or hydrilla in the context of springs ecosystems is undoubtedly controversial from the outset. However, discussions among ecological restoration practitioners indicate an increasing willingness to consider the proposition that, given the diverse realities of modern environmental change (e.g., climate change, nutrient enrichment, toxic contamination, and global species mixing), more adaptive approaches to nonnative species control should be considered (D'Antonio and Meyerson 2002; Ewel and Putz 2004; Gobster 2005). From an adaptive management perspective, the overriding questions might be: Are nonnative species management efforts directly leading to an even worse set of problems (e.g., succession into an even more undesirable ecosystem state), and, if so, how might future efforts be adjusted in the face of these emergent problems?

Assuming that the most prominent ecological concerns facing many springs ecosystems is the proliferation of nuisance algae such as *Lyngbya wollei*, an adaptive management question implied from several lines of evidence presented above is the extent to which aquatic plant control may be a contributing factor in this proliferation. A complementary question is how alternative methods of aquatic plant management could potentially help mitigate nuisance algae and/or restore habitat for desirable species.

But before exploring such alternatives in more detail, an initial boundary must be set that distinguishes between “prevention” and “control” when managing nonnative species. Clearly,

none of the nonnative plants should be intentionally introduced into springs where they have not been present historically, and precautionary steps to prevent their introduction and/or spread into new systems should remain a high management priority. In addition, early detection and eradication efforts aimed at preventing newly discovered nonnative plant populations from becoming irreversibly established are also clearly justified. Instead, the opportunity for adaptive reflection is within those springs systems where nonnative plant species are extant and considered to be permanently established.

Alternative Management of Floating Plants

Establishment of selective biocontrol organisms often is regarded as the most sustainable long-term method for controlling water hyacinth, water lettuce, and other nonnative plants. A successful biocontrol organism should greatly reduce the potential for invasive overgrowth, which in theory should lessen, or even render unnecessary, the use of chemical herbicides and/or harvester machines over time (Center 1996; Dray *et al.* 2001). In practice, however, aquatic plant control methods in Florida have rarely been adjusted at a large scale in response to biocontrol introductions (Haller 1996). For springs in which current aquatic plant control methods may be a significant disturbance factor that selects for algal overgrowth, increased use of floating plant biocontrol organisms may be a promising alternative aquatic plant management strategy.

Interestingly, observations by Odum (1957) suggest that attack by an unknown insect (or insects) historically was an important control mechanism for water lettuce in Silver Springs. New research studies would be needed to determine whether or not such natural control mechanisms for water lettuce are currently at work in springs systems where water lettuce is established, or if the water lettuce moth (*Spodoptera pectinicornis*), an introduced biocontrol organism (Dray *et al.* 2001), is having significant control effects.

Center *et al.* (2005) found that herbivory by water hyacinth weevils (*Neochetina eichhorniae* and *N. bruchi*) greatly reduced the competitiveness of water hyacinth in relation to water lettuce. While water hyacinth's superior competitive abilities led to complete displacement of water lettuce, weevil herbivory allowed for competitive parity in which water lettuce could persist and, in some cases, become dominant. Bartodziej and Leslie (1998) evaluated the effects of water hyacinth weevil (*Neochetina eichhorniae*) on water hyacinth populations in the St. Marks River, and calculated that baseline weevil populations reduced the rate of water hyacinth expansion by approximately 10% over the course of a growing season. Bartodziej and Leslie (1998) also reported that augmentation of weevils successfully reduced population to an even greater extent, but estimated a prohibitively high augmentation cost of \$40,000 per acre, or approximately 100 times the cost of chemical control. No field studies or augmentation estimates for water hyacinth moth (*Sameodes albiguttalis*), another effective biological control agent for water hyacinth in Florida (Center 1984), were given by Bartodziej and Leslie (1998). Revised studies of weevil and moth herbivory on water hyacinth population dynamics in Florida springs, particularly if paired with detailed study of regular aquatic plant treatment sites and provisional "no aquatic plant management" control sites, could potentially provide useful information for adjusting the intensity of aquatic plant treatment programs.

A more controversial alternative management strategy for floating plants is experimental utilization of these plants in support of ecosystem recovery in highly degraded springs ecosystems. Both of these plants are well known for their luxury uptake of nitrogen (Aoi and Hayashi 1996; Ho and Tsang 1998), and also are known for their ability to suppress algal production through direct shading, nutrient competition, allelopathy, and grazer habitat feedbacks (Joyce 1985; Aliotta *et al.* 1991; Cohen 1993; Ho and Tsang 1998; Kim *et al.* 2001; Jin *et al.* 2003). Mahujcharyawong and Ikeda (2001) detail an ambitious use of water hyacinth for nutrient remediation in Thailand's Tha-Chin River, and St. Johns River Water Management District recently has commissioned a project to better understand the nitrogen reduction implications of allowing for greater colonization of water hyacinth and water lettuce in Lake George (SJRWMD 2006). Detailed ecosystem surveys by Bartodziej and Leslie (1998) in the St. Marks River clearly indicate the high habitat value of water hyacinth to a diverse variety of native springs fauna, and observations suggest that similar habitat values are likely associated with water lettuce. In springs with large numbers of resident and wintering manatees, it is reasonable to suspect that an increased availability of water hyacinth, which is known as a nutritious and sometimes preferred manatee forage source (Lomolino 1977), might reduce herbivory pressure that can adversely affect desirable native submersed plant populations (Hauxwell *et al.* 2004). Studies could include small scale pilot projects that study the ecosystem effects of variable water hyacinth and water lettuce coverage levels in springs, particularly in those now affected by severe algal overgrowth. Comparisons among springs ecosystems with no aquatic control of floating plants (e.g., St. Marks River) and widespread control of floating macrophytes (e.g., Wekiva River) may also be valuable.

Alternative Management of Hydrilla

Alternative management of hydrilla poses more apparent concerns than water hyacinth and water lettuce, as the disruptions associated with hydrilla in some springs systems (e.g., Wakulla River) may actually be more severe than nuisance algae. In addition, the submersed growth habit makes hydrilla inherently harder to contain than the floating plants for the purposes of phytoremediation. However, hydrilla's apparent ability to evolve resistance to fluridone (Michel *et al.* 2004) and concerns that it may do the same for endothall (Jones and Beardall 2004) may force alternative management strategies.

The most serious problem associated with hydrilla in Florida springs is not that it provides poor wildlife habitat; rather, the major concern is its ability to form extensive topped out canopies that competitively exclude native plant species and radically diminish the recreational desirability of springs systems. Thus, the suggestion by Cuda *et al.* (2002) that herbivory by *Cricotopus lebetis*, an aquatic midge of unknown origin discovered in Kings Bay/Crystal River in 1992, may effectively prevent hydrilla from topping out is potentially of great importance for other springs ecosystems affected by hydrilla. Similar to the field observations of stunted hydrilla in Kings Bay given by Cuda *et al.* (2002), Van *et al.* (1998) found that hydrilla's competitiveness with *Vallisneria americana* was severely reduced in experimental treatments containing biocontrol organisms *Hydrillia pakistanae* and *Bagous hydrillae*. Increased experimentation with release of such biocontrol organisms clearly should be a priority for Florida springs ecosystems affected by well-established hydrilla populations.

Surprisingly, recent research in the Potomac River has identified significant positive correlations between hydrilla colonization and long-term recovery of native plants, including *Vallisneria americana* (Rybicki and Landwehr 2007). Cowell and Botts (1994) found that hydrilla coverage in Kings Bay had a significant negative relationship to coverage by *Lyngbya wollei*, perhaps indicating that hydrilla – particularly if overgrowth is controlled by constant herbivory by insects and, in some cases, manatees – could, similar to the Potomac River (Rybicki and Landwehr 2007), have valuable functional benefits in terms of guiding community succession away from filamentous algae and toward increased submersed plants in some springs systems. In springs ecosystems now affected by large hydrilla populations, management experiments might be set up to comparatively monitor the successional consequences of different control strategies (e.g., biocontrol, herbicides, manual removal, native plant restoration, and various combinations of these) over time.

CONCLUSION

There is little question that nonnative plant invasions have had profound effects on the aquatic environments of Florida, including many springs, over the past several decades. While it is reasonable to suspect that nitrate-nitrogen enrichment of springs may have contributed to overgrowth by nonnative aquatic plants, current studies provide insufficient information for making a definitive determination of nitrate-nitrogen concentrations that would effectively limit water hyacinth, water lettuce, or hydrilla growth in springs. Scientific literature suggests that both nonnative plant overgrowth and aquatic plant control techniques to suppress such overgrowth have the potential to serve as severe disturbances that could promote succession to algal dominated states in springs ecosystems. Because it is extremely unlikely that nonnative plant species can be entirely eliminated from systems in which they are established, the chapter argues that it may be beneficial to consider alternative and adaptive management strategies for nonnative plants, particularly in the context of springs and spring runs where algal overgrowth is now the primary management concern. Priorities for more adaptive aquatic plant management include: 1) intensive monitoring of ecosystem and successional impacts associated with current aquatic plant control methods; 2) increased research and experimentation with biocontrol organisms; and 3) careful experimentation with ecosystem recovery methods that utilize the nutrient uptake, algal suppression, and habitat values of floating plants.

REFERENCES

- Aliotta G., P. Monaco, G. Pinto, A. Pollio, and L. Previtera. 1991. Potential allelochemicals from *Pistia stratiotes* L. *Journal of Chemical Ecology* 17:2223-2234.
- Aoi, T. and T. Hayashi. 1996. Nutrient removal by water lettuce (*Pistia stratiotes*). *Water Science and Technology* 34(7-8):407-412.
- Barko, J.W. and R.M. Smart. 1986. Sediment-related mechanisms of growth limitation in submersed macrophytes. *Ecology* 67(5): 1328-1340.
- Bartodziej, W. 1992. Amphipod contribution to waterhyacinth [*Eichhornia crassipes* (Mart.) Solms] decay. *Florida Scientist* 55(3):103-111.
- Bartodziej, W. and A.J. Leslie. 1998. The aquatic ecology and water quality of the St. Marks River, Wakulla County, Florida, with emphasis on the role of water hyacinth: 1989-1995 studies. Bureau of Invasive Plant Management, TSS 98-100. Tallahassee: Department of Environmental Protection. Obtained on 12/05/07 from Web Link – www.dep.state.fl.us/lands/invaspec/2ndlevpgs/pdfs/stmarks.pdf.
- Bartodziej, W. and G. Weymouth. 1995. Waterbird abundance and activity on waterhyacinth and egeria in the St. Marks River, Florida. *Journal of Aquatic Plant Management* 33:19-22.
- Bayne, D.R. 2005. Giant lyngbya: A pond-owner's nightmare. *Southern Ponds Wildlife* 4(2):20-23.
- Bicudo D. D. C., B. M. Fonseca, L. M. Bini, L. O. Crossetti, C. E. D. M. Bicudo, and T. Araujo-Jesus. 2007. Undesirable side-effects of water hyacinth control in a shallow tropical reservoir. *Freshwater Biology* 52:1120-1133.
- Boswell, C., N.C. Sharma, and S.V. Sahi. 2002. Copper tolerance and accumulation potential of *Chlamydomonas reinhardtii*. *Bulletin of Environmental Contamination and Toxicology* 69(4):546-553.
- Brenner, M., L.W. Keenan, S.J. Miller, and C.L. Schelske. 1999. Spatial and temporal patterns of sediment and nutrient accumulation in shallow lakes of the Upper St. Johns River Basin, Florida. *Wetlands Ecology and Management* 6(4):221-240.
- Buckman and Company. 1930. A Report on an Investigation of the Water Hyacinth made for the City Commission of Jacksonville, Florida. Jacksonville: Buckman and Company.
- Buker, G.E. 1982. Engineers vs. Florida's green menace. *The Florida Historical Quarterly* 40(4):413-427.

- Bureau of Invasive Plant Management. 2007. Status of the aquatic plant maintenance program in Florida waters: Annual report fiscal year 2005-2006. Tallahassee: Florida Department of Environmental Protection. Obtained on 01/07/08 from Web Link – <http://www.dep.state.fl.us/lands/invaspec/2ndlevpgs/pdfs/aquatics05-06.pdf>.
- Camacho, F.A., and R.W. Thacker. 2006. Amphipod herbivory on the freshwater cyanobacterium *Lyngbya wollei*: Chemical stimulants and morphological defenses. *Limnology and Oceanography* 51(4):1870-1875.
- Campbell, H.W. and A.B. Irvine. 1977. Feeding ecology of the West Indian manatee *Trichechus manatus* Linnaeus. *Aquaculture* 12(3):249-251.
- Canfield, D.E. and M.V. Hoyer. 1988. Influence of nutrient enrichment and light availability on the abundance of aquatic macrophytes in Florida streams. *Canadian Journal of Fisheries and Aquatic Sciences* 45(8):1467-1472.
- Carr, A. 1994. *A naturalist in Florida: A celebration of Eden*. New Haven: Yale University.
- Center, T. D. 1984. Dispersal and variation in infestation intensities of the waterhyacinth moth (*Sameodes albiguttalis*, Lepidoptera: Pyralidae) in peninsular Florida. *Environmental Entomology* 13:482-491.
- Center, T.D. 1996. Biological control of water hyacinth in the United States. Pp. 165-173 in R. Charudattan, R. Labrada, T.D. Center, and C. Kelly-Begazo (eds.), *Strategies for Water Hyacinth Control: Report of a Panel of Experts Meeting*. Rome: FAO.
- Center, T.D., T.K. Van, F.A. Dray Jr., S.J. Franks, M.T. Rebelo, P.D. Pratt, and M.B. Rayamajhi. 2005. Herbivory alters competitive interactions between two invasive aquatic plants. *Biological Control* 33:173-185.
- Clugston, J.P. 1963. Lake Apopka, Florida: A changing lake and its vegetation. *Quarterly Journal of the Florida Academy of Sciences* 26(2):169-174.
- Cohen, M.A. 1993. Pondscaping with aquatic and marginal plants. *Tortuga Gazette* 29(6):6-7. Obtained on 04/15/08 from Web Link - <http://www.tortoise.org/general/pondplan.html>.
- Cooke, G.D., E.B. Welch, S.A. Peterson, and S.A. Nichols. 2005. *Restoration and management of lakes and reservoirs*. Boca Raton, FL: Taylor and Francis.
- Corrao, N.M., P.C. Darby, and C.M. Pomory. 2006. Nitrate impacts on the Florida apple snail, *Pomacea paludosa*. *Hydrobiologia* 568:135-143.
- Cowell, B.C. and P.S. Botts. 1994. Factors influencing the distribution, abundance, and growth of *Lyngbya wollei* in Central Florida. *Aquatic Botany* 49:1-17.

- Cowell, B.C. and C.J. Dawes. 2004. Growth and nitrate-nitrogen uptake by the cyanobacterium *Lyngbya wollei*. *Journal of Aquatic Plant Management* 42:69-71.
- Cuda, J.P., B.R. Coon, Y.M. Dao, and T.D. Center. 2002. Biology and laboratory rearing of *Cricotopus lebetis* (Diptera: Chironomidae), a natural enemy of the aquatic weed hydrilla (Hydrocharitaceae). *Annals of the Entomological Society of America* 95(5):587-596.
- D'Antonio, C.D. and L.A. Meyerson. 2002. Exotic plant species as problems and solutions in ecological restoration: A synthesis. *Restoration Ecology* 10(4):703-713.
- DEP. 2002. Ecosummary: Wakulla Springs herbicide application study 04/04/02 and 05/06/02. Tallahassee: Department of Environmental Protection. Obtained on 03/02/07 from Web Link - <ftp://ftp.dep.state.fl.us/pub/labs/lds/reports/564.pdf>.
- DEP. 2005. An investigation of the potential for acute toxicity to the crayfish, *Procambarus peninsulanus*, caused by the application of the herbicide, Aquathol, at Wakulla Springs State Park. Biology Section, Bureau of Laboratories, Division of Resource Assessment and Management. Tallahassee: Department of Environmental Protection. Obtained on 03/02/07 from Web Link - <ftp://ftp.dep.state.fl.us/pub/labs/lds/reports/5841.pdf>.
- Dick, T.H. 1989. Crystal River: A 'no-win' situation. *Aquatics* 11(2):10-13.
- Doyle, R.D. and R.M. Smart. 1998. Competitive reduction of noxious *Lyngbya wollei* mats by rooted aquatic plants. *Aquatic Botany* 61: 17-32.
- Dray, F.A., T.D. Center and G.S. Wheeler. 2001. Lessons from unsuccessful attempts to establish *Spodoptera pectinicornis* (Lepidoptera: Noctuidae), a biological control agent of water lettuce. *Biocontrol Science and Technology* 11:301-316.
- Dubose, C., K. Langeland and E. Philips. 1997. Problem freshwater algae and their control in Florida. *Aquatics* 19(1):4,6,8-11.
- Eggler, W.A. 1953. The use of 2,4-D in the control of water hyacinth and alligator weed in the Mississippi Delta, with certain ecological implications. *Ecology* 34(2):409-414.
- Emmett, K. 2002. Final supplemental environmental impact statement for diquat dibromide. Publication Number 02-10-052. Olympia: Washington State Department of Ecology. Obtained on 12/05/07 from Web Link - <http://www.ecy.wa.gov/pubs/0210052.pdf>.
- Esler, D. 1990. Avian community response to hydrilla invasion. *Wilson Bulletin* 102(3):427-440.
- Evans, J.M. 2007. Algae, exotics, and management response in two Florida springs: Competing conceptions of ecological change in a time of nutrient enrichment. Ph.D. Dissertation. Gainesville: University of Florida.

- Evans, J.M., A.C. Wilkie, J. Burkhardt and R.P. Haynes. 2007. Rethinking exotic plants: Using citizen observations in a restoration proposal for Kings Bay, Florida. *Ecological Restoration* 25(3):199-210.
- Ewel, J.J. and F.E. Putz. 2004. A place for alien species in ecosystem restoration. *Frontiers in Ecology and the Environment* 2(7):354-360.
- Facemire, C.F. 1991. Copper and other contaminants in Kings Bay and Crystal River, Florida sediments: Implications for impact on the West Indian manatee. Publication Number VB-89-4-109A. Arlington, VA: United States Fish and Wildlife Service.
- Florida Springs Task Force. 2000. Florida's springs: Strategies for protection and restoration. Tallahassee: Department of Environmental Protection.
- Friedman, H.J. 1987. A watery jungle: Or why there is an aquatic plant management society today. *Journal of Aquatic Plant Management* 25:70-73.
- Garcia-Villada, L., M. Rico, M. Altamirano, L. Sanchez-Martin, V. Lopez-Rodas and E. Costas. 2004. Occurrence of copper resistant mutants in the toxic cyanobacteria *Microcystis aeruginosa*: Characterisation and future implications in the use of copper sulphate as an algacide. *Water Research* 38:2207-2218.
- Glomski, L.A.M., K.V. Wood, R.L. Nicholson and C.A. Lembi. 2002. The search for exudates from Eurasian watermilfoil and hydrilla. *Journal of Aquatic Plant Management* 40:17-22.
- Gobster, P.H. 2005. Invasive species as ecological threat: Is restoration an alternative to fear-based resource management? *Ecological Restoration* 23(4):261-270.
- Gopal, B. 1987. *Water hyacinth*. New York: Elsevier.
- Grimshaw, H.J. 2002. Nutrient-release and detritus production by herbicide-treated freely floating aquatic vegetation in a large, shallow subtropical lake and river. *Archiv fur Hydrobiologica* 153(3):469-490.
- Gross, E.M. 2003. Allelopathy of aquatic autotrophs. *Critical Reviews in Plant Science* 22(3 & 4):313-339.
- Gu, B. 2006. Environmental conditions and phosphorus removal in Florida lakes and wetlands inhabited by *Hydrilla verticillata* (Royle): Implications for invasive species management. *Biological Invasions* 8(7):1569-1578.
- Haag, K.H. and G.R. Buckingham. 1991. Effects of herbicides and microbial insecticides on the insects of aquatic plants. *Journal of Aquatic Plant Management* 29:55-57.

- Haller, W.T. 1996. Operational aspects of chemical, mechanical, and biological control of water hyacinth in the United States. Pp. 137-148 in R. Charudattan, R. Labrada, T.D. Center, and C. Kelly-Begazo (eds.), *Strategies for Water Hyacinth Control: Report of a Panel of Experts Meeting*. Rome: FAO.
- Haller, W.T., J.V. Shireman and D.E. Canfield. 1983. Vegetative and herbicide monitoring study in King's Bay, Crystal River, Florida. Contract No. DACW17-80-C-0062. Jacksonville, FL: United States Army Corps of Engineers.
- Hamelink, J.L., D.R. Buckler, F.L. Mayer and D.U. Palawski. 1986. Toxicity of fluridone to aquatic invertebrates and fish. *Environmental Toxicology and Chemistry* 5(1):87-94.
- Hauxwell, J., C.W. Osenberg and T.K. Frazer. 2004. Conflicting management goals: manatees and invasive competitors inhibit restoration of a native macrophyte. *Ecological Applications* 14(2):571-586.
- Ho, T.B. and J.S.H. Tsang. 1998. Free-floating hydrophytes for treatment of wastewaters. Pp. 77-101 in B.C. Rana (ed.), *Damaged Ecosystems and Restoration*. River Edge, NJ: World Scientific.
- Holm, L.G., D.L. Plucknett, J.V. Pancho and J.P. Herberger. 1977. *The world's worst weeds: Distribution and biology*. Honolulu: University of Hawaii Press.
- Jin, Z.H., Y.Y. Zhuang, S.C. Dai and T.L. Li. 2003. Isolation and identification of extracts of *Eichhornia crassipes* and their allelopathic effects on algae. *Bulletin of Environmental Contamination and Toxicology* 71:1048-1052.
- Johnson, F.A. and F. Montalbano. 1984. Selection of plant communities by wintering waterfowl on Lake Okeechobee, Florida. *Journal of Wildlife Management* 48(1):174-178.
- Johnson, W.W. and M.T. Finley. 1980. *Handbook of acute toxicity of chemicals to fish and aquatic invertebrates*. Resource Publication 137. Washington: United States Department of the Interior, Fish and Wildlife Service.
- Jones, R.M. and H. Beardall. 2005. Florida hydrilla management summit: Facilitator's summary report. December 6 – 7, Orlando, Florida. Conflict Resolution Consortium. Obtained on 11/20/07 from Web Link - www.floridadep.net/lands/invaspec/2ndlevpgs/pdfs/SummitReportEdit10-06.pdf.
- Joyce, J.C. 1982. Effect of gibberellic acid and 2,4-dichlorophenoxyacetic acid on waterhyacinth, *Eichhornia crassipes* (Mart.) solms. Ph.D. Dissertation. Gainesville: University of Florida.
- Joyce, J.C. 1985. Benefits of maintenance control of water hyacinth. *Aquatics* 7(4):11-13.

- Kim, Y., W.J. Kim, P.G. Chung and W.O. Pipes. 2001. Control and separation of algae particles from wastewater effluent by using floating aquatic plant root mats. *Water Science and Technology* 43(11):315-22.
- Kochman, H.I., G.B. Rathbun and J.A. Powell. 1985. Temporal and spatial distribution of manatees in Kings Bay, Crystal River, Florida. *The Journal of Wildlife Management* 49(4):921-924.
- Kulshreshta, M. and B. Gopal. 1983. Allelopathic influence of *Hydrilla verticillata* (L.f.) Royle on the distribution of *Ceratophyllum* species. *Aquatic Botany* 16(2):207-209.
- Langeland, K.A. 1996. *Hydrilla verticillata* (L.F.) Royle (Hydrocharitaceae), the perfect aquatic weed. *Castanea* 61(3):293-304. Obtained on 11/02/07 from Web Link - <http://plants.ifas.ufl.edu/hydcirc.html>.
- Langeland, K.A. 2006. Safe use of glyphosate-containing products in aquatic and upland areas. SS-AGR-104. Gainesville: University of Florida, IFAS Extension. Obtained on 12/05/07 from Web Link - <http://edis.ifas.ufl.edu/pdf/AG/AG24800.pdf>.
- Leslie, A.J. 1992. Copper-herbicide use patterns in Florida waters. Tallahassee: Department of Natural Resources. Obtained on 02/12/07 from Web Link - <http://www.dep.state.fl.us/lands/invaspec/2ndlevpgs/pdfs/cuconfnc.pdf>.
- Lomolino, M.V. 1977. The ecological role of the Florida manatee (*Trichechus manatus latirostris*) in water hyacinth-dominated ecosystems. M.S. Thesis. Gainesville: University of Florida.
- Loper, D.E., W.M. Landing, C.D. Pollman A.B. Chan Hilton. 2005. Degradation of water quality at Wakulla Springs: Assessment and recommendations. Report of the peer review committee on the workshop: Solving water quality problems in the Wakulla springshed of north Florida, May 12-13, 2005. Obtained on 11/12/07 from Web Link - www.1000friendsofflorida.org/FL_Panhandle_Initiative/SPRINGS/WakullaPeerReportFinal.pdf.
- Lopez-Rodas, V., A. Flores-Moya, E. Maneiro, N. Perdigones, E. Marva, M.E. Garcia and E. Costas. 2007. Resistance to glyphosate in the cyanobacterium *Microcystis aeruginosa* as a result of pre-selective mutations. *Evolutionary Ecology* 21(4):535-547.
- Mahujcharyawong, J. and S. Ikeda. 2001. Modelling of environmental phytoremediation in eutrophic river – the case of water hyacinth harvest in Tha-chin River, Thailand. *Ecological Modelling* 142:121-134.
- Maltby, H. 1963. Effects of erosion on farm lands and river front along the St. Johns River. *Hyacinth Control Journal* 2:5.

- Mangas-Ramirez, E. and M. Elias Gutierrez. 2004. Effect of mechanical removal of water hyacinth (*Eichhornia crassipes*) on the water quality and biological communities in a Mexican reservoir. *Aquatic Ecosystem Health and Management* 7(1):161-168.
- Mastin, B.J. and J.H. Rodgers, Jr. 2000. Toxicity and bioavailability of copper herbicides (Clearigate, Cutrine-Plus, and Copper sulfate) to freshwater animals. *Archives of Environmental Contamination and Toxicology* 39:445-451.
- Michel, A., R.S. Arias, B.E. Scheffler, S.O. Duke, M.D. Netherland and F.E. Dayan. 2004. Somatic mutation-mediated evolution of herbicide resistance in the nonindigenous invasive plant hydrilla (*Hydrilla verticillata*). *Molecular Ecology* 13:3229-3237.
- Mossler, M.A. and K.A. Langeland. 2006. Florida Crop/Pest Management Profile: Aquatic Weeds. IFAS Extension Publication PI-138. Gainesville: University of Florida. Obtained on 11/20/07 from Web Link - http://www.orange.wateratlas.usf.edu/upload/documents/Florida_Crop_Pest_management_Aquatic_Weed.pdf.
- Munch, D.A., D.J. Toth, C. Huang, J.B. Davis, C.M. Fortich, W.L. Osburn, E.J. Philips, E.L. Quinlan, M.S. Allen, M.J. Woods, P. Cooney, R.L. Knight, R.A. Clarke, S.L. Knight. 2006. Fifty-year retrospective study of the ecology of Silver Springs, Florida. Publication Number: SJ2007-SP4. St. Johns River Water Management District, Palatka, FL.
- Nicholson, S.A. and R.J. Clerman. 1974. Toxicity of diquat to the Crustacean amphipod *Hyaella* from Chautauqua Lake. *Environmental Letters* 7(3):215-227.
- O'Shea, T.J., J.F. Moore and H.I. Kochman. 1984. Contaminant concentrations in manatees in Florida. *Journal of Wildlife Management* 48(3):741-748.
- Odum, H.T. 1957. Trophic structure and productivity of Silver Springs, Florida. *Ecological Monographs* 27(1):55-112.
- Okay, O.S. and A. Gaines. 1996. Toxicity of 2,4-D acid to phytoplankton. *Water Research* 30(3):688-696.
- Penfound, W.T. and T.T. Earle. 1948. The biology of the water hyacinth. *Ecological Monographs* 18(4):447-472.
- Pennington, T.G., J.G. Skogerboe and K.D. Getsinger. 2001. Herbicide/copper combination for improved control of *Hydrilla verticillata*. *Journal of Aquatic Plant Management* 39:56-58.
- Peterson, H.G., C. Boutin, K.E. Freemark and P.A. Martin. 1997. Toxicity of hexazinone and diquat to green algae, diatoms, cyanobacteria and duckweed. *Aquatic Toxicology* 39(2):111-134.

- Phillippy, C.L. 1966. A progress report on the use of sulphuric acid treatment for elodea control. *Hyacinth Control Journal* 5:15-17.
- Phlips, E.J., P. Hansen and T. Velardi. 1992. Effect of the herbicide diquat on the growth of microalgae and cyanobacteria. *Bulletin of Environmental Contamination and Toxicology* 49(5):750-756.
- Reddy, K.R. and J.C. Tucker. 1983. Productivity and nutrient uptake of water hyacinth, *Eichhornia crassipes*: I. Effect of nitrogen source. *Economic Botany* 37(2):237-247.
- Relyea, R.A. 2005. The lethal impact of Roundup on aquatic and terrestrial amphibians. *Ecological Applications* 15(4):1118-1124.
- Roberts, B.L. and H.W. Dorough. 1984. Relative toxicity of chemicals to the earthworm *Eisenia foetida*. *Environmental Toxicology and Chemistry* 3:67-78.
- Rybicki, N.B. and J.M. Landwehr. 2007. Long-term changes in abundance and diversity of macrophyte and waterfowl population in an estuary with exotic macrophytes and increasing water quality. *Limnology and Oceanography* 52(3):1195-1207.
- St. Johns River Water Management District (SJRWMD). 2006. Agenda request for Governing Board meeting, May 9, 2006. Obtained on 11/04/06 from Web Link - sjr.state.fl.us/governingboard/pdfs/2006/gb0605/gb0605_019.pdf.
- Schardt, J. 1997. Maintenance control. Pp. 229-243 in D. Simberloff, D.C. Schmitz, and T.C. Brown (eds.), *Strangers in Paradise: Impact and Management of Nonindigenous Species in Florida*. Washington: Island Press.
- Schmitz, D.C., J.D. Schardt, A.J. Leslie, F.A. Dray, Jr., J.A. Osborne and B.V. Nelson. 1993. The ecological impact and management history of three alien aquatic plant species in Florida. Pp. 173-194 in B.N. McKnight (ed.), *Biological pollution: The control and impact of invasive exotic species*. Indianapolis: Indiana Academy of Science.
- Schmitz, D.C., D. Simberloff, R.H. Hofstetter, W. Haller and D. Sutton. 1997. The ecological impact of nonindigenous plants. Pp. 39-61 in D. Simberloff, D.C. Schmitz, and T.C. Brown (eds.), *Strangers in Paradise: Impact and Management of Nonindigenous Species in Florida*. Washington: Island Press.
- Schramm, H.L. and K.J. Jirka. 1989. Effects of aquatic macrophytes on benthic invertebrates in two Florida lakes. *Journal of Freshwater Ecology* 5(1):1-12
- Scott, T.M., G.H. Means, R.P. Meegan, R.C. Means, S.B. Upchurch, R.E. Copeland, J. Jones, T. Roberts and A. Willet. 2004. *Springs of Florida*. Bulletin No. 66. Tallahassee: Florida Geological Survey.

- Simberloff, D. 1997. The biology of invasions. Pp. 3-17 in D. Simberloff, D.C. Schmitz, and T.C. Brown (eds.), *Strangers in Paradise: Impact and Management of Nonindigenous Species in Florida*. Washington: Island Press.
- Smart R.M., J.W. Barko, D.G. McFarland. 1994. Competition between *Hydrilla verticillata* and *Vallisneria americana* under different environmental conditions. Technical Report A-94-1. Vicksburg, MS: United States Army Corps of Engineers, Waterways Experiment Station.
- Solberg, K.L. and K.F. Higgins. 1993. Effects of glyphosate herbicide on cattails, invertebrates, and waterfowl in South Dakota wetlands. *Wildlife Society Bulletin* 21(3):299-307.
- Spencer, D. and C. Lembi. 2005. Spatial and temporal variation in the composition of filamentous algae present in California rice fields. Project No. 5325-22000-019-04. United States Department of Agriculture, Agricultural Research Service. Obtained on 02/14/07 from Web Link - http://www.ars.usda.gov/research/projects/projects.htm?accn_no=408890.
- State of Florida Division of Administrative Hearings. 1993. *Ameraquatic, Inc., Applied Aquatic Management, Inc., Aquatic Systems, Inc., Boliden Intertrade, Inc., and Applied Biochemists, Inc., Petitioners, vs. Department of Natural Resources, Respondent*. Case No. 93-1629RP. Tallahassee, FL. Obtained on 04/19/07 from Web Link - <http://www.doah.state.fl.us/ros/1993/93-1629.PDF>.
- Stevenson, R.J., A. Pinowska, and Y.K. Wang. 2004. Ecological condition of algae and nutrients in Florida springs. Contract Number WM 858. Tallahassee: Florida Department of Environmental Protection.
- Stevenson, R.J., A. Pinowska, A. Albertin and J.O. Sickman. 2007. Ecological condition of algae and nutrients in Florida springs: The synthesis report. Contract Number WM 858. Tallahassee: Florida Department of Environmental Protection.
- Stoddard, A.A. 1989. The phytogeography and paleofloristics of *Pistia stratiotes* L. *Aquatics* 11:21-24.
- Stuckey, R.L. and D.H. Les. 1984. *Pistia stratiotes* (water lettuce) recorded from Florida in Bartram's travels, 1765-74. *Aquaphyte* 4(2):6.
- Terrell, J.B. and D.E. Canfield, Jr. 1996. Evaluation of the effects of nutrient removal and the "Storm of the Century" on submersed vegetation in Kings Bay – Crystal River, Florida. *Journal of Lake and Reservoir Management* 12(3):394-403.
- Tilghman, N.J. 1963. The St. Johns River hyacinth story. *Hyacinth Control Journal* 2:13-14.

- United States Army Corps of Engineers. 1973. Final Environmental Statement, Aquatic Plant Program, State of Florida. EIS-FL-73-1488-F. Jacksonville: United States Army Corps of Engineers.
- Van, T.K., W.T. Haller and G. Bowes. 1976. Comparison of the photosynthetic characteristics of three submersed plants. *Plant Physiology* 58(6):761-768.
- Van, T.K., G.S. Wheeler and T.D. Center. 1998. Competitive interactions between hydrilla (*Hydrilla verticillata*) and Vallisneria (*Vallisneria americana*) as influenced by insect herbivory. *Biological Control* 11(3):185-192.
- Van, T.K., G.S. Wheeler and T.D. Center. 1999. Competition between *Hydrilla verticillata* and *Vallisneria americana* influenced by soil fertility. *Aquatic Botany* 62(4):225-233.
- Wang, Y., C. Jaw, and Y. Chen. 1994. Accumulation of 2,4-D and glyphosate in fish and water hyacinth. *Water, Air, and Soil Pollution* 74(3-4):397-403.
- Webber, H.J. 1897. The Water Hyacinth and its Relation to Navigation in Florida. U.S. Department of Agriculture, Division of Botany. Washington: Government Printing Office.
- Weiner, J.A., M.E. DeLorenzo and M.H. Fulton. 2007. Atrazine induced species-specific alterations in the subcellular content of microalgal cells. *Pesticide Biochemistry and Physiology* 87(1):47-53.
- Wetland Solutions, Inc. 2006. Pollutant Load Reduction Goal (PLRG) Analysis for the Wekiva River and Rock Springs Run, Florida. Final Phase 2 Report. Palatka: St. Johns River Water Management District.
- Weldon, L.W. and R.D. Blackburn. 1967. Water lettuce – nature, problem, and control. *Weeds* 15:5-9.
- Wilson, J.R., N. Holst and M. Rees. 2005. Determinants and patterns of population growth in water hyacinth. *Aquatic Botany* 81(1): 51-67.
- Wong, P.K. 2000. Effects of 2,4-D, glyphosate and paraquat on growth, photosynthesis and chlorophyll-a synthesis of *Scenedesmus quadricauda* Berb 614. *Chemosphere* 41(1-2):177-182.

Effects of Nutrients on Spring Ecosystems

Robert L. Knight,^{1,2} and Sky K. Notestein¹

¹ Wetland Solutions, Inc.

² Department of Environmental Engineering Sciences, University of Florida

Summary

The relationship between nutrients and spring ecosystem structure and function primarily focuses on the state-wide increase in spring nitrate concentrations derived from anthropogenic sources and the concurrent observed visual decline of these ecosystems. However, the apparent correlation between increased nitrate loading and declining aesthetic appearance of spring ecosystems has only anecdotally provided evidence for a causative relationship. Organism-level studies, focused on single species of algae, vascular plants, aquatic macroinvertebrates, and primary and secondary consumers, have produced mixed results that do not currently present a clear or consistent link between nutrient availability and population structure in springs. Firm conclusions linking rising spring nitrogen concentrations and changes to individual components of biotic communities remain illusive, in some measure due to the immense complexity of spring ecosystems and the large number of external forcing functions (energy and matter inputs) that shape their structure and functions.

General systems theory predicts that any significant change in an important external factor (*e.g.*, nitrate nitrogen delivery in ground water feeding a spring) should result in a significant change in the target system (in this case the spring ecosystem), as long as the system of interest is highly adapted and operating at its maximum potential. If this type of cause and effect relationship holds for nutrients and springs, then measurements of whole ecosystem responses over a gradient of nitrate nitrogen concentrations should be an especially productive approach to applied research. Springs data presented and reviewed in this chapter reveal a significant correlation between rising nitrate concentrations and declining ecosystem primary production and photosynthetic efficiency. While this possible cause and effect relationship is based on detailed data from only a limited number of springs and their associated spring runs, so far this relationship has proven consistent.

While an inverse correlation between nitrate concentration and primary productivity appears counter-intuitive based on typical single plant species responses to increasing nutrients, it can be explained based on the subsidy-stress hypothesis that has been supported by a variety of ecosystem and organism-level studies. While low nitrate levels may be optimal for ecosystem productivity in pristine springs, higher nitrate levels appear to have the opposite effect of reducing overall primary productivity. It can be theorized that spring ecosystem responses to nutrient increases integrate the observed complexity of their hundreds of important plants and animals. In their natural, moderate to low nutrient state, springs may be adapted for optimal

efficiency of light utilization and maximum ecosystem metabolism (Maximum Power Theory). Rising nutrient concentrations may result in the competitive advantage of “weedy” algae and plant species that can capture light and spatial resources through higher rates of net productivity but lower gross productivity. Continuing elevated nutrient concentrations in concert with differential grazing pressure, reductions in flow, or loss of other top-down control mechanisms may be linked to observed plant community shifts from adapted submersed aquatic plants with sparse but highly productive periphyton communities to systems dominated by benthic and attached filamentous algae. Data are also presented which link elevated nitrate concentrations with alterations in the reproductive functioning of amphibians and fish. These complex interactions between increased nutrients and algae, decreased dissolved oxygen due to lowered primary productivity, and altered grazer populations illustrate the importance of employing an ecosystem perspective when examining the multiple factors potentially affecting springs.

It is the conclusion of this review that an ecosystem approach is essential for future research efforts to provide a greater understanding of the relative interactions between the myriad physical, chemical, and biological fluxes present in springs and their normal responses to rising nutrient levels. In summary these recommended applied research activities might include the following:

- Detailed baseline investigations of the “normal” or “existing” ecosystem-level structure and response of a broad sample of first and second magnitude springs to key forcing functions, including sunlight, flow, and nutrient levels. These studies need to be fairly long-term (multiple years of repeated measures) and conducted over a representative sample of springs with a range of forcing functions including discharge rates, groundwater chemistry, nutrient concentrations, and recreational intensities;
- Multivariate statistical analysis of these baseline data to look for significant and repeatable patterns between independent and dependent variables such as nutrient concentrations and photosynthetic efficiency;
- Design of *in situ* complex (multi-species) mesocosm studies to allow replication of spring plant community responses to a range of nutrient conditions under realistic and relevant spring environmental conditions;
- Whole-spring manipulation studies (if necessary) to test the effects of possible management techniques such as controlling levels of springshed nutrient loading, human recreational activities, alternative control methods for invasive species, and estimation of optimal consumer carrying capacities (e.g., manatee density).

There exists a wide-spread recognition of the environmental and economic importance of artesian springs in Florida. A generous commitment of public dollars and a focused and logical research agenda will be critical to pulling these precious but threatened natural resources back from their current declining path.

ECOSYSTEM STRUCTURE

Primary Producers

The paradigm of eutrophication is that nutrient enrichment (nitrogen and or phosphorus primarily) will result in an increase in biomass in primary producers often with negative ecological and economic consequences (Cloern 2001, Nixon 1995, Rabalais 2002). Although this view assumes that nutrients are the primary limiting factor for algae and vascular plants, and not some other factor such as light or grazing, observations from a variety of aquatic systems broadly support this assertion. For marine and estuarine systems, nitrogen is typically identified as the nutrient limiting primary production. The effects of nitrogen on marine and estuarine systems, the pathways for nitrogen transport between land and aquatic habitats, and the positive correlation between nitrogen and primary production and often secondary production (*i.e.* fishery yields) have been widely reviewed (*e.g.* Hecky and Kilham 1988, Howarth 1988, Rabalais 2002). However in freshwater systems, phosphorus is the nutrient more commonly implicated as limiting for primary production and has been highly correlated with phytoplankton and fisheries biomass, especially in lakes (Bachmann *et al.* 1996, Canfield 1983, Hoyer and Canfield 1991).

Among streams and rivers, a consistent limiting nutrient for primary production does not appear to be the case (*e.g.* Tank and Dodds 2003) likely because of distinct regional differences and because the abundance and rates of primary producers represent an integration of physical, chemical, and biological conditions. Examples of the variability of stream primary producers include a cross-system analysis of temperate streams in which Dodds *et al.* (1997) established that both total nitrogen and total phosphorus in the water column were significantly related to benthic algal biomass, while Francoeur's (2001) meta-analysis of 237 nutrient enrichment studies in temperate streams found that 16% indicated a nitrogen (N) response, 18% indicated a phosphorus (P) response, 23% required N and P be added together for a response, and 43% had no response to N or P.

It is important to remember that spring runs and other lotic (flowing water) ecosystems can transform inorganic nutrients into organic material, thus preventing or reducing the downstream export of inorganic nutrients. However, these lotic ecosystems can become saturated with respect to relatively conservative inorganic nutrients such as phosphorus and recalcitrant forms of organic nitrogen and in some instances may not be able to further assimilate inorganic forms through uptake, microbial utilization, and denitrification. It is unclear at what concentration or loading rate saturation can occur, but likely is dependent on whether it is an acute or chronic nutrient load and on the magnitude of other limiting chemical constituents or forcing functions such as light availability. Once saturation occurs, nitrogen export to downstream ecosystems will increase proportionally to nitrogen loading (Bernot and Dodds 2005). Whether saturation of nitrogen or phosphorus has occurred in Florida spring ecosystems remains uncertain in most cases and is obviously a function of individual spring biogeochemistry. In at least one case within portions of the Wekiva River system, which is fed by Wekiwa and Rock Springs (WSI 2007a) there is evidence that phosphorus saturation may have occurred (as evidenced by zero or negative assimilation rates).

It is important to remember that thresholds exist for the capacity of all aquatic ecosystems to productively assimilate increased nutrient loads and that if these thresholds are exceeded, harmful ecological consequences may occur. Our use of this concept has origin in the paper by E. P. Odum *et al.* (1979), titled: *Perturbation Theory and the Subsidy-Stress Gradient*, in which the model of “too much of a good thing” is examined in the context of ecosystem response to perturbation (Figure 1). An example of a subsidy-stress gradient is the productivity of hardwood forested swamps in response to flooding, in which forested swamp productivity was observed to increase under seasonal flooding conditions but to decline under permanent flooding (Conner and Day 1992). With regard to spring ecosystems, it is likely that a variety of physical, biological, and chemical inputs may operate individually or simultaneously within subsidy-stress gradients. For instance, stream velocity can replace nutrients and remove waste products at low velocities, but is capable of scouring at high velocities, and grazing of primary producers may promote algal productivity at moderate levels but a reduction in primary production at higher levels. Knight (1980) examined and described several examples of the subsidy-stress gradient in research at Silver Springs, including the effects of herbivorous snails, carnivorous fish, and a trace metal (elemental cadmium) on primary productivity in stream mesocosms.

It is hypothesized in this chapter that nutrients also function along a subsidy-stress gradient in aquatic ecosystems. At extremely low concentrations overall system productivity of plant and animal life is low; as nutrient concentrations increase, so too does primary and secondary productivity, but at some point, productivity may decrease. Within aquatic ecosystems, nutrient subsidy-stress gradients are likely to have unique performance curves for primary producers by functional group, *i.e.* algae vs. vascular plant, or even by species within these groups. Considering this, when monitoring ecosystems for impairment or the effects of nutrient gradients, whole ecosystem measures may produce diametrically opposite results than single-species studies and will be more informative for documenting overall ecosystem impairment than measures of individual functional groups.

Algae

Pseudo-phytoplankton – The development of plankton in lotic ecosystems is largely prevented due to inadequate water resident times (Hynes 1970). A more accurate term is pseudo-phytoplankton, which is a mix of sloughed material from periphytic primary producers. Once entrained in the water column, this material will either be consumed, settle out or if it remains in suspension continue to grow through cellular division. The factors which affect pseudo-phytoplankton include the abundance of periphytic primary producers, light, nutrients, temperature, and velocity. In flowing water systems, stream discharge or velocity will influence their rate of delivery downstream. Given that phytoplankton populations can double in as little as one to two days, the relationship between stream flow and phytoplankton abundance is likely to be inversely correlated (Allan 1995). However, should declines in spring discharge rates occur to the point that water residence time is greater than about three days, the development of true phytoplankton communities could occur in the spring run, as was suggested by Frazer *et al.* (2002) in their examination of limiting nutrients in several spring ecosystems using traditional phytoplankton bioassay methods.

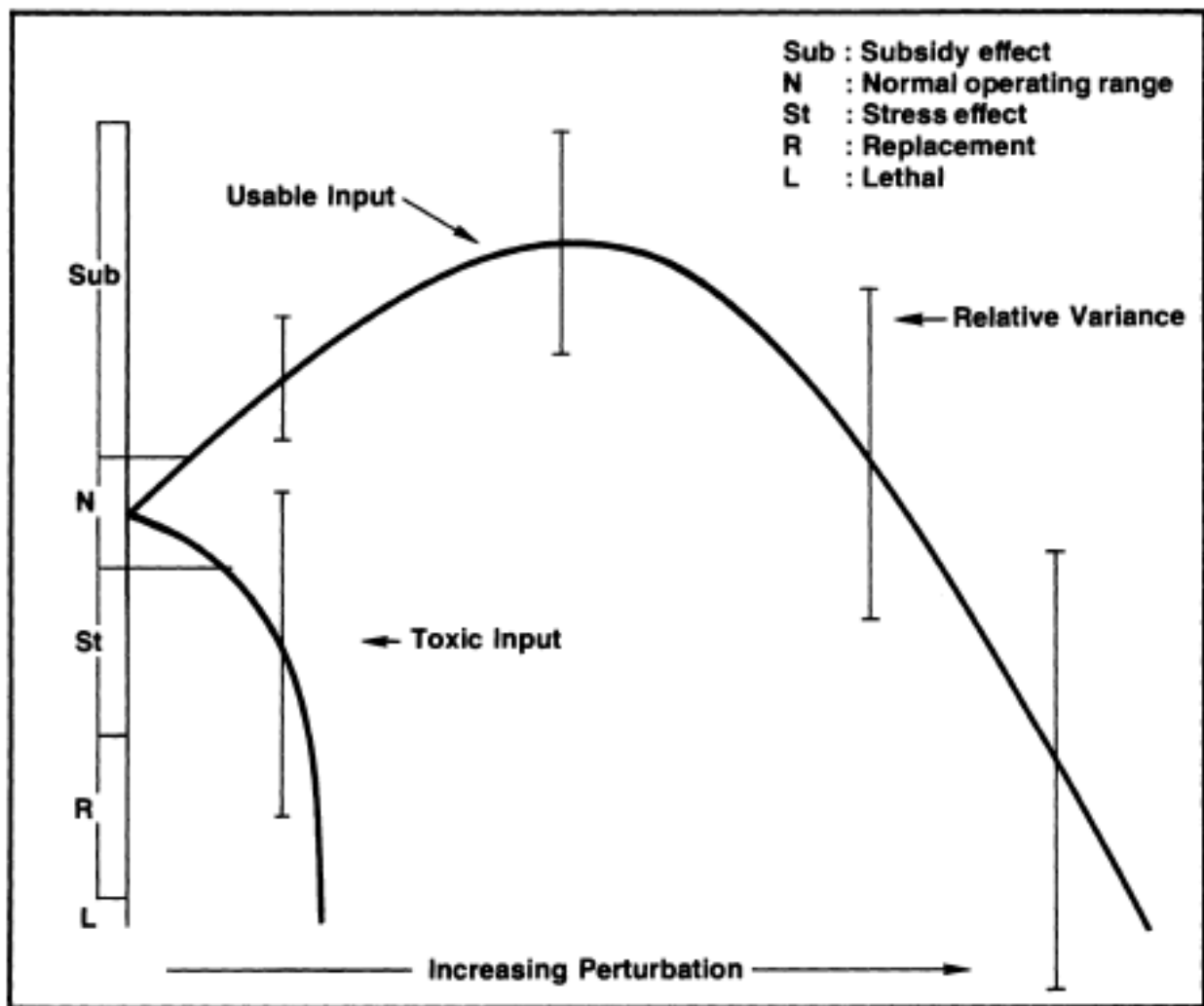


Figure 1 – A hypothetical example of two types of inputs and their resulting ecosystem perturbations due to increasing input levels. Nutrients and nitrate in particular could be viewed as an example of a usable input (top curve), which have a subsidy effect on ecosystem productivity to a point beyond which stress is incurred (from E. P. Odum *et al.* 1979).

A limited number of studies are available which have examined pseudo-phytoplankton collected from spring ecosystems and their response to manipulations of ambient nutrient levels. Frazer *et al.* (2002) conducted nutrient addition bioassay of pseudo-phytoplankton collected from several locations of the Chassahowitzka, Crystal, Homosassa, and Weeki Wachee Rivers. These samples were allowed to grow under near-optimal light and temperature conditions under a variety of nutrient treatments. These treatments included a control (without any additional nutrient additions), nitrogen (N) addition (0.4 mg $\text{NO}_3\text{-N/L}$), phosphorus (P) addition (0.04 mg $\text{PO}_4\text{/L}$), silica (Si) addition (0.4 mg Si/L), N+P addition (0.4 mg $\text{NO}_3\text{-N/L}$ + 0.04 mg $\text{PO}_4\text{/L}$), and N+P+Si (0.4 mg $\text{NO}_3\text{-N/L}$ + 0.04 mg $\text{PO}_4\text{/L}$ + 0.4 mg Si/L). For those pseudo-phytoplankton samples collected at the upper spring run, bioassays with additional nutrients did not produce an increase in growth compared to controls with ambient nutrient levels in 61% of the experiments, suggesting that the majority of locations were not nutrient limited. In the balance of experiments, 19% were phosphorus limited, 10% were nitrogen limited and 10% were co-limited

by nitrogen and phosphorus. Given that all four of these spring ecosystems are supplied by waters with elevated nitrate concentrations relative to historic values, it is not surprising that nutrients did not appear to be limiting in majority of the experiments. This observation was supported by the average ($n=8$) ambient concentrations of nitrate where pseudo-phytoplankton were collected: Chassahowitzka was 0.39 mg/L, Crystal was 0.03 mg/L, Homosassa was 0.42 mg/L, and Weeki Wachee was 0.53 mg $\text{NO}_3\text{-N/L}$. Crystal River, the spring ecosystem with the lowest ambient levels of nitrate, had a pseudo-phytoplankton community which was most responsive to nitrate additions as it exhibited nitrogen limitation in 75% of the experiments. The data from the Frazer *et al.* (2002) study suggest that when spring run nitrate concentrations exceed approximately 0.4 mg/L, nitrogen limitation is unlikely.

A second springs' study utilizing a pseudo-phytoplankton bioassay from material collected from Kings Bay, which contains multiple spring vents, was completed by Saindon (2005). This researcher compared pseudo-phytoplankton growth rates for experimentally manipulated nitrate and soluble reactive phosphorus concentrations at two sites, which had ambient nitrate concentrations of 0.083 and 0.039 mg N/L and ambient soluble reactive phosphorus concentrations of 0.011 and 0.006 mg P/L. Saindon (2005) observed significant differences between sites in the relative growth rates of pseudo-phytoplankton, and that maximum biomass was influenced by both nutrient ratios and nutrient concentrations, but that growth rates "did not determine the maximum achieved biomass, just how long it took to reach that biomass". An important conclusion from Saindon's (2005) work was that maximum pseudo-phytoplankton biomass could be maintained at very low ambient nutrient concentrations when the N:P (by weight) ratios were either very low ($\text{N:P} < 3$) or very high ($\text{N:P} > 27$) and that when the N:P (by weight) ratios were between 3 and 27, maximum pseudo-phytoplankton biomass appeared to increase with increasing nutrient availability. By way of comparison, historical N:P ratios for spring waters were reported by Odum (1957a) and Odum *et al.* (1953) and were generally below 7:1 (by weight) but not always, suggesting that historically most springs had the potential for nitrogen limitation. By way of comparison, N:P ratios can be reported by weight or by atomic (*i.e.* molar) ratio, the commonly reported Redfield ratio for N:P of 16:1 is expressed in atomic units and represents an N:P ratio of approximately 7:1 by weight (Redfield *et al.* 1963, Duarte 1992).

Filamentous and Benthic Macroalgae - These categorical terms include macroalgae commonly viewed as nuisance species and associated with declines in aesthetics of many springs such as *Lyngbya* or *Vaucheria*. It is important to note that *Lyngbya* or *Vaucheria* are indigenous genera of macroalgae and that Florida spring ecosystems have (or had) a natural diversity of macroalgae (Whitford 1956). The mere presence of these species is not an indicator of decline, but an overabundance or monoculture of macroalgae especially in conjunction with a loss of native submersed vascular species may be cause for concern.

A comprehensive synthesis report on macroalgae inhabiting Florida springs in relation to nutrients was recently completed by Stevenson *et al.* (2007). The macroalgae study included sampling from 29 different Florida springs and multiple laboratory approaches to elaborate on prior related work (Stevenson *et al.* 2004). Results for the Stevenson *et al.* (2007) report suggest that macroalgal taxa may not respond to nutrients uniformly, as the abundance of *Vaucheria* spp. in spring ecosystems was positively correlated to nitrogen and phosphorus concentrations with a

clear threshold increase at 0.59 mg total nitrogen/L; however, the abundance of *Lyngbya wollei* was not correlated to either nitrogen or phosphorus water concentrations in surveyed springs, although it was related to sediment phosphorus concentrations and indices of human activities within 1,000 m of the sampling site. Several possible explanations for the lack of better correlations between ambient nutrient concentrations and macroalgae abundance are that other factors limit and influence the standing crop. Principally, instantaneous field measures are incapable of incorporating prior environmental conditions which have caused the current state. Other important forcing functions affecting macroalgae were not measured as well, for instance in spring runs with strong flow and heavy recreational use, macrophytes can easily be dislodged and swept downstream preventing the accumulation of substantial coverage or biomass. Another alternative is that some other factor, such as light, is primarily limiting, and hence nutrient supply can only be secondarily limiting. The phenomenon in which light supply appears to be the primarily limiting factor was observed by Canfield and Hoyer (1988) as well as Frazer *et al.* (2006) in their studies on the abundance of macrophytes in spring runs. The role that grazing plays on determining the standing crop of filamentous algae, particularly *Lyngbya sp.* is largely unknown as well.

Cowell and Dawes (2004) determined that increased populations of *Lyngbya* in the Rainbow River (nitrate > 1.0 mg/L) may be due to increased nitrate concentrations. *Lyngbya wollei* growth was stimulated by nitrate additions in the laboratory although no biomass increase was observed above about 1 mg/L of nitrate nitrogen. They concluded that based on their lab studies nitrate nitrogen concentrations would need to be reduced to below 0.3 mg/L in order to significantly reduce *Lyngbya* biomass. This research confirms that increased nitrate levels can increase benthic algal biomass, at least in the short term.

Stevenson *et al.* (2007) also conducted *in situ* bioassays of *Vaucheria* and *Lyngbya* in three different microcosm designs each with a matrix of nitrogen and phosphorus treatments maintained under relatively optimal growth conditions. From these experiments it appears nutrient concentrations affect the growth rate and ultimately the abundance of macroalgae as growth occurred in most nutrient treatments, even at very low nutrient concentrations, yet fastest growth rates occurred in high nutrient concentrations and were approximately two or more times greater than under low nutrient concentrations. Based on the bioassay experiments, it was preliminarily estimated that to initiate a reduction in the abundance of *Vaucheria* in Florida springs total nitrogen and total phosphorus concentrations would have to be less than 0.59 and 0.026 mg/L, respectively; while *Lyngbya* reductions would require total nitrogen and total phosphorus concentrations lower than 0.25 and 0.033 mg/L, respectively (Stevenson *et al.* 2007). These conclusions suggest that the response of macroalgae to nutrients is complex, that both nutrient ratio and concentration are important, and that growth rate (or grazing rate) can have a large impact on ultimate biomass (*i.e.* standing crop).

Periphyton and Epiphytes – These are terms for another category of primary producers which are commonly thought to respond to nutrient enrichment of spring water through an increase in their coverage, biomass, and/or occurrence of weedy species. It is possible that these weedy species may escape top-down controls by grazers, reduce the light energy available to their vascular plant hosts, and ultimately have the potential to modify the spring ecosystem plant community. One study to directly examine nutrient effects on periphyton abundance in a spring

fed system was completed by Notestein *et al.* (2003) as an *in situ* bioassay in the Chassahowitzka River, a spring run in coastal Citrus County, Florida. This study added nitrate, phosphate, and a combination of nitrate and phosphate to the upstream end of flow-through tubes containing glass microscope slides in the spring run. This experimental design allowed the amount of periphyton colonizing glass microscope slides to be compared between nutrient treatments and with a control treatment over a one month period. Increased epiphyte abundance (as measured by chlorophyll per unit area) was observed following the addition of phosphorus, as well as phosphorus in combination with nitrogen, when compared to the control (no nutrient addition treatment). The results suggested that phosphorus was the primary nutrient limiting periphyton abundance in the upper spring fed portion of this system, however nitrate additions supported additional periphyton growth over the control treatment and therefore nitrogen appeared to be secondarily limiting (Notestein *et al.* 2003). The Chassahowitzka spring system had elevated nitrate concentrations, approximately 0.45 mg/L at the time of the study, so the finding that phosphorus (approximately 0.016 mg/L) was limiting is consistent with the elevated N:P nutrient ratios (28:1 by weight) observed during the study period. The observation that additional nitrate could stimulate periphyton abundance, even though nitrogen was not the primary limiting nutrient, suggests that a nutrient need not be absolutely limiting for it to have a biological effect in a spring ecosystem.

In stream systems outside of Florida, there have been numerous publications on the relations between periphyton abundance and nutrients (*e.g.* Dodds *et al.* 1997, Francoeur 2001). Interestingly, there do not appear to be consistent trends or factors which control periphyton abundance in stream systems, which may be the case with Florida's spring systems as well. As the following interstate examples show, increased nutrient concentrations can influence periphyton abundance, but the responses to nutrient additions are frequently variable. Nitrogen alone may stimulate periphyton abundance (Crawford 1979, Mosisch *et al.* 1999) but often only when accompanied by increased light availability from removing riparian shading or adding artificial light (Busch 1978, Gregory 1980, Hill and Harvey 1990). The addition of phosphorus, both on its own and in combination with nitrogen, has been shown to increase periphyton abundance (Elwood *et al.* 1981, Peterson *et al.* 1993, Bothwell 1985). Other essential elements including carbon supplied by organic sources such as sucrose (Warren *et al.* 1964) or carbon supplied via inorganic forms such as carbon dioxide and bicarbonate (Dickman 1973 and Crawford 1979) have also been shown to increase periphyton abundance. Another factor that interacts with periphyton abundance is grazing (Steinman *et al.* 1991, Hill *et al.* 1992). In a recent study, grazers were shown to control periphyton abundance at a variety of ambient nutrient levels, while in the absence of grazers there was a significant positive correlation between periphyton and nutrients (nitrogen and phosphorus simultaneously added, Chen *et al.* 2007). These examples show that periphyton abundance in streams can be influenced by nutrients and other ecological controls originating from the bottom up (*i.e.* light availability) or top down (*i.e.* grazers controls) and suggest that the factors controlling periphyton abundance in Florida's spring systems needs further research, likely at the level of *in situ* complex mesocosms that can colonize with realistic populations and diversity of algae and invertebrates.

Vascular Plants

Studies of two Florida springs systems, the Chassahowitzka (Notestein 2001) and the Ichetucknee (Kurz *et al.* 2004), involved measuring the abundance of submersed vascular macrophytes and the concentration of water column nutrients. Chassahowitzka had ambient water column nitrate concentrations of approximately 0.45 mg/L and phosphate concentrations of 0.016 mg/L; while Ichetucknee had approximately 0.55 mg/L nitrate and 0.04 mg/L phosphate in the water column. These measurements are elevated compared to historic concentrations. Neither study showed a correlation between surface water nutrient concentrations and the growth rate and/or abundance of submersed aquatic macrophytes, which appears to be consistent with research from other non-spring fed stream systems. For example, Peltier and Welch (1969) experimented with *Potamogeton pectinatus*, and observed that nitrate concentrations above 0.44 mg/L and phosphate concentrations above 0.03 mg/L did not significantly increase growth, nor was there a correlation between the field growth of *P. pectinatus* or *Najas sp.* when inorganic nitrogen concentrations were 0.2 to 0.3 mg/L and phosphate concentrations were 0.03 to 0.08 mg/L. Mulligan and Baranowski (1969), studied several macrophytes including *Myriophyllum spicatum* under greenhouse conditions, and found that optimum growth could be achieved with 0.1 mg/L nitrogen and 0.02 mg/L phosphorus, values which are equal to or greater than historic concentrations for many Florida springs. In a study of 17 Florida streams, many of them spring fed, Canfield and Hoyer (1988) concluded that at concentrations above 0.3 mg/L nitrogen and 0.03 mg/L phosphorus, the potential for nutrient limitation of submersed aquatic vegetation was unlikely. Therefore, in many of the spring ecosystems with current average surface water nitrate concentrations exceeding these values, particularly for nitrate, the point of nutrient limitation may have already been passed. Because rooted aquatic macrophytes are known to derive much of their nutrient supply from the interstitial pore water of the substrate (Bristowe and Whitcombe 1971, Carignan and Kalff 1980, Chambers *et al.* 1989) and that these pore-water nutrient concentrations are often much higher than the overlying waters (Stevenson *et al.* 2007), it is likely that vascular macrophyte nutrient demand can be met from sediments and helps explain the lack of correlation between water column nutrient concentrations and submersed vascular macrophytes.

Much concern over the apparent reduction from the historical abundance of submersed vascular plants in spring ecosystems exists, and is warranted due to the important habitat and the food web contributions these primary producers make (see Chapters 1 and 4). As noted in the section on periphyton above, the potential causes for declines in submersed vascular plant abundance could include resource competition from periphyton or filamentous and benthic algae, overgrazing by consumers, physical disturbance from recreation, and/or disease; it is likely that causative mechanisms responsible for declines in submersed vascular plant abundance are system specific and may not be universal. An additional explanation of reduced submersed vascular plant abundance, which could be related to elevated nitrate concentrations, was provided by Boedeltje *et al.* (2005) who reported that high water column concentrations of nitrates (> 7 mg/L, a value higher than that observed in 98% of Florida springs) can significantly reduce the growth of ammonia-preferring rooted submersed species such as *Potamogeton alpinus*. Boedeltje *et al.* (2005) hypothesized that nitrate dominated nitrogen assimilation may lead to strong metabolic disturbances affecting the levels of organic anions within those species adapted to ammonia uptake by the roots (such as *P. alpinus*). This may explain the observed

reduction in growth under high water column nitrate concentrations, although further experiments are needed to assess potential negative effects on other species.

Primary Consumers

Invertebrates

Nitrate pollution in Florida springs has been implicated as a possible reason for the apparent decline in populations of the Florida apple snail (*Pomacea paludosa*). To explore this hypothesis, Corrao *et al.* (2006) correlated snail density with nitrate concentration measurements in six Florida springs and conducted laboratory studies to examine short-term acute impacts of nitrate on adult and juvenile apple snails. They observed no correlation between apple snail densities and ambient nitrate concentrations. LC₅₀ levels (the concentration at which 50% mortality occurred) could not be determined despite nitrate concentrations >500 mg/L (Corrao *et al.* 2006). Although juvenile apple snail growth was affected in two trials with nitrate concentrations of 504 and 622 mg/L, respectively, the EC₅₀ (the effective concentration of a compound where 50% of its maximal effect is observed) for these apple snails generally exhibited little to no response to these nitrate concentrations which are orders of magnitude greater than those found in Florida springs. The authors suggested that perhaps other factors, such as habitat structural changes due to non-indigenous plant invasions, might explain the observed declines in apple snail abundance (Corrao *et al.* 2006).

Studies on the effects of nitrate on invertebrates outside of Florida vary considerably, with changes in survival of caddisfly (*Hydropsyche occidentalis*) demonstrated at concentrations starting around 2.2 mg/L (Camargo and Ward 1995), while juvenile marine shrimp (*Penaeus monodon*) tolerate nitrate concentrations > 2,000 mg/L (Tsai and Chen 2002), and no mortalities were observed in juvenile Australian crayfish (*Cherax quadricarinatus*) exposed to nitrate concentrations up to 1,000 mg/L (Meade and Watts 1995) suggesting that the impact of nitrate must be assessed on a case by case basis.

Vertebrates

Studies examining the effects of nitrate on the reproduction and development of two vertebrate species found in Florida spring ecosystems, have been made for the Southern toad (*Bufo terrestris*) by Edwards *et al.* (2006) and the Eastern mosquitofish (*Gambusia holbrooki*) by Edwards and Guillette (2007). These researchers reported that nitrate concentrations in the range of 4 to 30 mg/L had the ability to alter endocrine physiology of these amphibians and fish. In laboratory experiments utilizing reverse osmosis water enriched with nitrate, Southern toad tadpoles metamorphosed earlier as nitrate concentration increased while in experiments utilizing spring water, tadpoles reared in high nitrate (30 mg/L) delayed metamorphosis, suggesting that water source was a factor besides nitrate concentration affecting *Bufo* development (Edwards *et al.* 2006). In their study of adult male mosquito fish collected from springs with varying nitrate concentrations, Edwards and Guillette (2007) observed that nitrate concentration (up to 5 mg/L) were significantly correlated with decreased total sperm counts, although other characteristics such as pH and temperature also affected physiological condition of the mosquito fish, again suggesting that nitrate alone may not have been responsible.

Secondary Consumers

Fish

Most fish utilizing spring ecosystems fall in the category of secondary and or higher level consumers. Walsh and Williams (2003) examined fish and mussel species diversity in sixteen Florida springs and spring runs. For the purposes of this review, their data were compared to ambient nitrate nitrogen concentrations reported from fifteen of those springs. Although there were trends for lower fish and mussel species numbers with higher nitrate levels, they were not significant. Fish species diversity appears to be relatively constant at Silver Springs, as evidenced by the following: Hubbs and Allen (1943) reported thirty-five species in the 1940s, Walsh and Williams (2003) collected twenty-nine species in 2002, and Munch *et al.* (2006) observed thirty-three species in 2004-05. Although the number of fish species doesn't appear to have declined in correlation with increased nitrate, the biomass of fishes in Silver Springs has declined precipitously over the past 50 years (estimated 96% reduction since the 1950's Odum study). The observed decline in fish biomass at Silver Springs (primarily channel catfish and striped mullet) may be hypothesized to be indirectly affected by elevated nitrate concentrations and their apparent contribution to plant community changes and resulting lower overall ecosystem net productivity during this 50-year period. However, at the trophic level of consumers such as herbivorous and omnivorous fish, the list of possible environmental stressors is lengthy, including limited access by riverine and marine species due to the construction of the Rodman Reservoir and dam in 1968 (Munch *et al.* 2006). This discussion illustrates the need to consider the complexity of spring ecosystems when designing experimental studies and drawing conclusions from incomplete data sources.

Higher-Level Consumers

Ecosystem level changes that have the potential to affect higher level consumers as a result of nitrate enrichment are largely hypothetical. If elevated nitrate concentrations cause qualitative or quantitative changes in primary producers, these could be reflected in quantitative changes in higher trophic levels including fish (catfish, gar, sunfish, bass, and pickerel), reptiles (alligators, softshell and snapping turtles), birds, and mammals (otters and manatees). Another potential impact to higher level consumers could be nitrate toxicity resulting in methemoglobinemia or "blue-baby" syndrome. This syndrome is known to affect mammals; hence there may be a reasonable risk of impacting manatees which are known to drink spring water. A novel hypothesis has been presented to explain the apparently high number of perinatal deaths (*i.e.* stillborn manatee calves) which account for 22% percent of all manatee deaths between 1992 and 2000 (USFWS 2001). Dr. W.T. Haller (UF professor, personal communication 2004) has suggested that if pregnant manatee feed on hydrilla which has elevated tissue concentrations of nitrate or drink nitrate rich spring water their developing *in-vitro* calves may be susceptible to methemoglobinemia. This hypothesis warrants testing given the potential of impacting a threatened species due to nitrate contamination of ground water and spring ecosystems in Florida.

Humans

A number of springs are utilized as a source for commercially bottled water (*e.g.* Gainer Springs in Bay County, Ginnie Springs in Alachua County, and Silver Springs in Marion County (Scott *et al.* 2002)). Given the widespread occurrence and generally increasing magnitude of nitrate contamination in Florida's springs, there may be the potential of spring water utilized for human consumption to approach or even exceed current USEPA drinking water standards of 10 mg/L. The USEPA (2007) has good information concerning the effects of nitrate on human health (*e.g.* <http://www.ead.anl.gov/pub/doc/nitrate-ite.pdf>, accessed December 2007). According to this USEPA source, nitrate is a normal component of the human diet, with the average daily intake from all sources estimated at 75 milligrams. In healthy adults, about 5% is converted to nitrite by bacteria in saliva and additional bacterial conversion of nitrate takes place inside the alimentary tract and the stomach. A pH of the gastric fluid greater than five promotes the growth of nitrate-reducing bacteria and increases the conversion of nitrate to nitrite. This is especially a concern for infants, whose gastrointestinal systems normally have a higher pH than those of adults. Nitrites and the compounds they can form with proteins (*e.g.* nitrosamines), have been implicated in causing stomach cancer, but evidence remains inconclusive. Although nitrates alone are relatively nontoxic, their conversion to nitrite in the human digestive system can in turn react with hemoglobin in the blood and creating methemoglobin, a form of the protein hemoglobin that is unable to transport oxygen. This results in a decreased capacity of the blood to transport oxygen causing a condition known as methemoglobinemia. Although some amount of methemoglobin in blood is common, levels of 10% can cause the skin and lips to take on a bluish tinge (cyanosis), levels above 25% can cause weakness and a rapid pulse, and levels above 50 to 60% can cause loss of consciousness and death. It appears that infants are much more sensitive than adults to nitrates/nitrites, as essentially all deaths from nitrate/nitrite poisoning have occurred in infants; however adults are susceptible to long-term exposure to lower levels of nitrates and nitrites which can cause diuresis (an increase in the amount of urine, and starchy deposits and hemorrhaging of the spleen). Given the potential for human health impacts, the USEPA has designated a drinking water standard of 10 mg/L for nitrate and 1 mg/L for nitrite. At this time, only a minority (< 2%) of Florida springs currently have nitrate concentrations greater than 10 mg/L.

ECOSYSTEM FUNCTION

Community Metabolism

We define the term community metabolism to include the characterization of the primary producers (autotrophs) and consumers (primary, secondary, etc. heterotrophs and decomposers) which collectively comprise the living component of spring ecosystems (see Chapter 1). Because primary producers generate oxygen through photosynthesis and both producers and consumers use oxygen through respiration, the measurement of oxygen (or carbon dioxide) dissolved in the water can serve as a proxy for community metabolism. In addition, the ability to characterize changes in oxygen per unit area and per unit time allow rates of change in metabolism to be estimated further strengthening this techniques' ability to document ecosystem responses. An example of the daily cycle in dissolved oxygen (DO) is shown in Figure 2, which

shows average daily DO change at Silver Springs, Florida over three different time intervals separated by about 50 years.

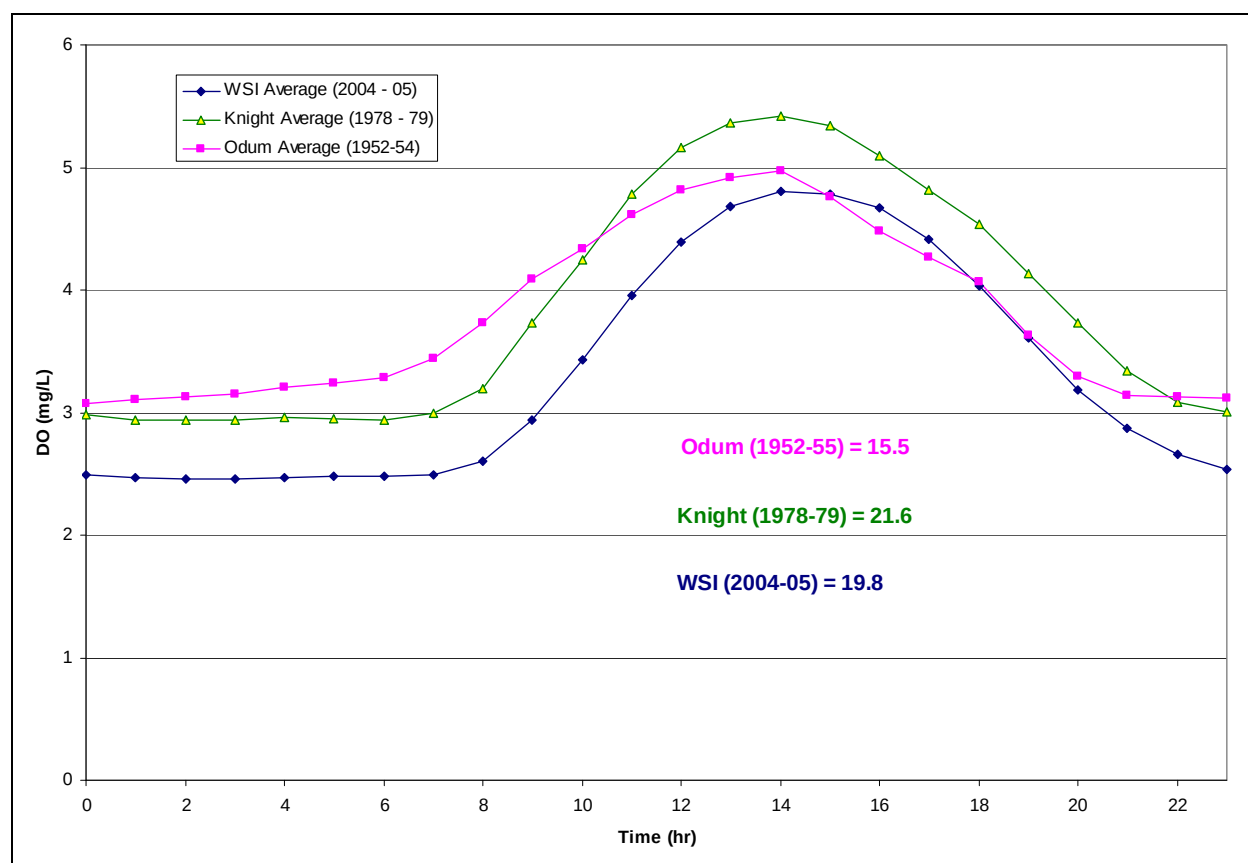


Figure 2 – Comparison of Silver Springs average diurnal oxygen curves at the 1,200-m downstream station with the resultant estimated gross primary productivity in units of ppm-hrs. Higher total GPP estimates for Knight (1978-79) and WSI (2004-05) are a result of increased wetted area in Silver Springs Run above the 1,200-m station due to the addition of the Back Channel Extension in the late 1970s. Estimated GPP rates corrected for the total aquatic area declined from about 15.7 to 15.6 g O₂/m²/d in the 1950s and the late 1970s, to about 11.2 g O₂/m²/d during 2004/2005 (from Munch et al. 2006).

Gross and Net Productivity

Odum (1957a) measured nitrate and gross primary productivity (GPP) in eleven Florida springs in 1955, which reveal a weak but negative relationship between nitrate concentration and GPP ($R^2 = 0.14$). The recent findings of lower GPP in Silver Springs at higher nitrate nitrogen concentrations are consistent with the patterns revealed by Odum's earlier research (Table 1). A more recent study of community metabolism has been completed as part of the Wekiva River Pollutant Load Reduction Goal evaluation conducted by the St. Johns River Water Management District, in which spring runs from the Wekiva River System with high nitrate levels were compared to spring runs with minimal nitrate levels (WSI 2007a). The Wekiva River and Rock Springs Run were found to have higher nitrate nitrogen concentrations (averaging 0.69 and 0.84

mg/L respectively) compared to the reference streams located in the Ocala National Forest (Juniper Creek – 0.05 mg/L and Alexander Springs Creek – 0.02 mg/L). Within the spring runs, the upstream nitrate concentrations in the Wekiva River and in Rock Springs were significantly higher than downstream concentrations (Wekiva – 1.1 vs. 0.36 mg/L; Rock Springs Run – 1.1 vs. 0.55 mg/L, respectively). Gross primary productivity and PAR efficiency were found to be significantly lower in all of these spring-fed streams with higher nitrate nitrogen concentrations (Figure 3 and Table 2, WSI 2007a). This trend is consistent with the observations made at Silver Springs during the fifty-year retrospective study described by Munch *et al.* (2006).

Table 1. A comparison of gross primary productivity (GPP) over a fifty-year time period for Silver Springs (from Munch *et al.* 2006).

Odum (1957b)		Knight (1980)		Munch <i>et al.</i> (2006)	
Date	GPP (gO ₂ /m ² /d)	Date	GPP (gO ₂ /m ² /d)	Date	GPP (gO ₂ /m ² /d)
2/19/1953	12.4	8/31/1978	19.3	Feb-04	8.2
3/7/1953	14.0	10/5/1978	13.6	Mar-04	11.4
3/25/1953	17.5	12/13/1978	7.8	Apr-04	13.2
1/7/1954	10.1	3/7/1979	10.7	May-04	13.9
5/23/1954	24.4	4/15/1979	16.8	Jun-04	12.7
7/12/1955	12.1	5/16/1979	23.4	Jul-04	13.6
8/11/1955	19.7	6/19/1979	20.7	Aug-04	12.3
		7/17/1979	11.2	Sep-04	10.9
		8/15/1979	17.1	Oct-04	11.7
				Nov-04	9.8
				Dec-04	8.5
				Jan-05	8.6
				Feb-05	11.1
				Mar-05	10.8
Average	15.7		15.6		11.2

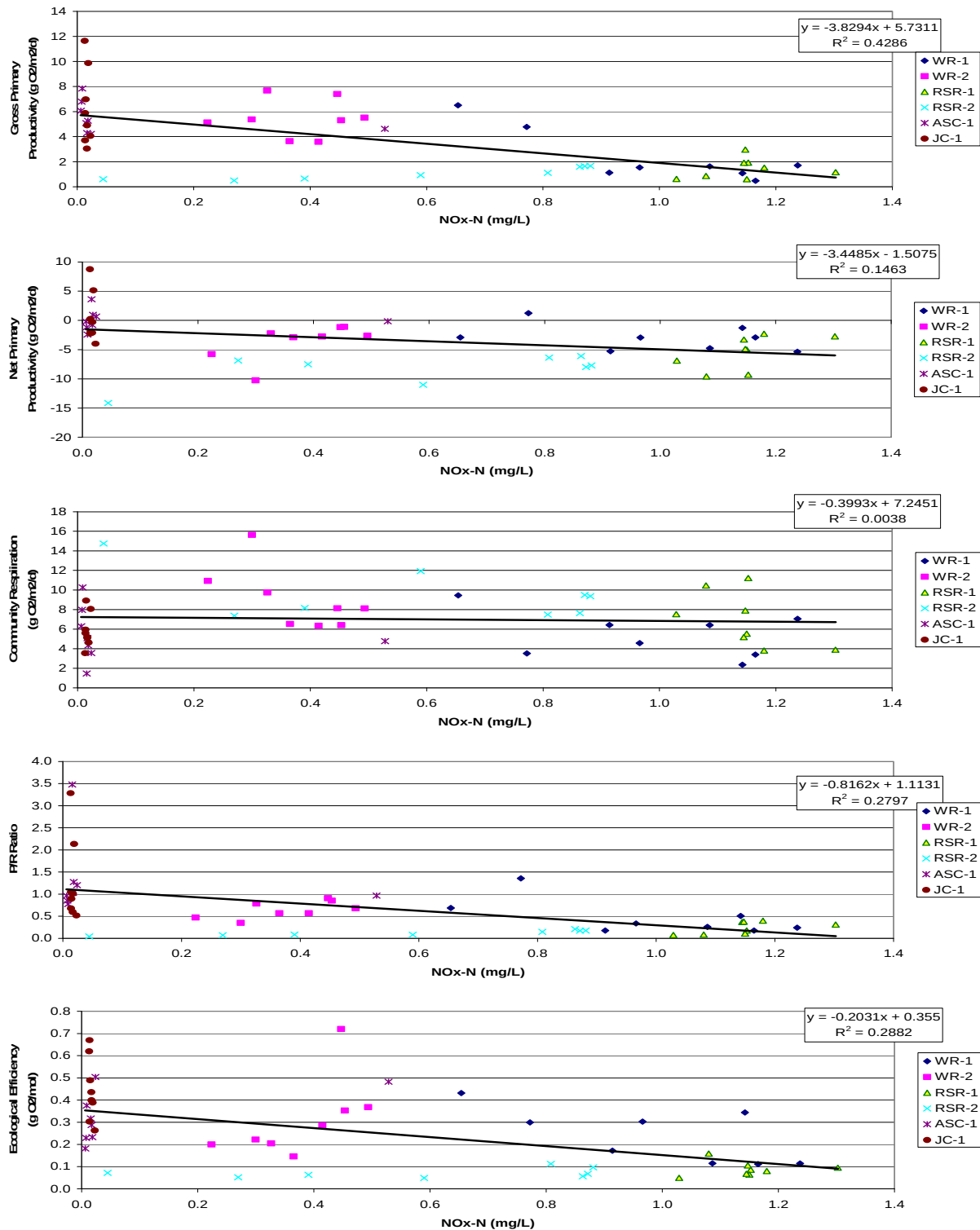


Figure 3 – The relationship between nitrate and community metabolism parameters from six spring run segments, ASC is Alexander Springs Creek, JC is Juniper Creek, RSR is Rock Springs Run (1 is upstream, 2 is downstream), WR is Wekiva River (1 is upstream, 2 is downstream). Eight sampling events for each spring segment (from WSI 2007a).

Table 2. Summary comparison of ecological indices between the spring run segments from Wekiwa Springs and Rock Springs and the reference spring runs from, Alexander Springs and Juniper Springs (from WSI 2007a).

Parameter	Units	Wekiwa Springs			Rock Springs			Reference Springs		
		SEG 1	SEG 2	Average	SEG 1	SEG 2	Average	Alexander Springs	Juniper Springs	Average
Dissolved Oxygen	mg/L	1.93	6.81	4.37	5.67	6.40	6.03	5.54	6.81	6.17
pH	s.u.	7.47	7.71	7.59	7.84	7.67	7.76	7.97	7.82	7.90
Specific Conductance	$\mu\text{S}/\text{cm}$	316	426	371	242	257	250	898	1,645	1,272
Total Nitrogen	mg/L	1.20	1.36	1.28	1.31	1.15	1.23	0.25	0.17	0.21
Nitrate + Nitrite N	mg/L	1.01	0.364	0.686	1.13	0.554	0.841	0.051	0.024	0.038
Total Phosphorus	mg/L	0.130	0.118	0.124	0.095	0.101	0.098	0.049	0.024	0.037
Soluble Reactive Phosphorus	mg/L	0.120	0.105	0.112	0.084	0.084	0.084	0.041	0.016	0.028
Community GPP	g $\text{O}_2/\text{m}^2/\text{d}$	2.12	5.39	3.76	1.41	1.00	1.20	5.71	5.67	5.69
Community NPP	g $\text{O}_2/\text{m}^2/\text{d}$	-3.50	-3.78	-3.64	-5.85	-8.59	-7.22	-0.39	-0.52	-0.46
Community Respiration	g $\text{O}_2/\text{m}^2/\text{d}$	5.62	9.18	7.40	7.26	9.58	8.42	6.10	6.19	6.15
P/R ratio	unit less	0.44	0.63	0.54	0.23	0.11	0.17	1.16	0.96	1.06
Community GPP Efficiency	g O_2/mol	0.22	0.29	0.26	0.09	0.09	0.09	0.31	0.45	0.38
Community GPP Efficiency	%	6.06	3.57	4.82	1.87	3.63	2.75	1.82	3.05	2.44

Factors influencing stream metabolism have been estimated in eight streams from several biomes in North America by Mulholland *et al.* (2001). These streams were not spring runs, but were relatively free from human disturbance and had dissolved inorganic nitrogen concentrations less than 0.15 mg/L and soluble reactive phosphorus concentrations of 0.014 mg/L or less. These streams had GPP estimates ranging from less than 0.1 to 15 g $\text{O}_2/\text{m}^2/\text{d}$, community respiration (CR) estimates ranging from about 2.0 to 11.1 g $\text{O}_2/\text{m}^2/\text{d}$, and photosynthetically active radiation (PAR) efficiencies ranging from 0.042 to 0.45 g O_2/mol . Mullholland *et al.* (2001) reported that GPP and NPP were not correlated with either dissolved inorganic nitrogen or soluble reactive phosphorus concentrations but were significantly correlated with PAR, although CR was correlated with soluble reactive phosphorus concentrations.

Other estimates of primary production from spring ecosystems include those made by Duarte and Canfield (1990a), who published plant community and productivity data for thirty-one Florida springs. Productivity data were not directly comparable to data collected by Odum (1957a, b), Knight (1980), WSI (2006), or Munch *et al.* (2006) as they were based on a short term, rapid assessment technique rather than on a full diurnal cycle. Still Duarte and Canfield (1990a)

observed no correlation between total nitrogen (which was mostly in the form of nitrate) or total phosphorus with the biomass or productivity of submersed aquatic vegetation (SAV) in the spring runs they examined. SAV standing crop and maximum daily productivity were correlated with degree of shading by shoreline vegetation. These results suggest that light may have been the primary limiting factor during their study.

Respiration

Changes in community respiration are likely to be influenced by nutrients if nutrients are influencing the abundance or productivity of primary producers. Changes in primary producers would in turn affect the consumer or decomposer community and hence the respiration of this part of the ecosystem. The practical differentiation of autotrophic versus heterotrophic respiration is not feasible in field studies. From Florida spring studies that have compared community respiration rates to water column nutrient concentrations, it appears that a negative correlation does exist (*i.e.* Munch *et al.* 2006; Figure 3, WSI 2007a), but the correlation is weak. Community respiration was also observed to increase downstream in the Wekiva River and in Rock Springs Run as nitrate concentrations decreased. Community respiration also declined at Silver Springs at the same time nitrate nitrogen concentrations were increasing (Munch *et al.* 2006).

Productivity/Respiration Ratio

The productivity/respiration (P/R) ratio is commonly used to classify ecosystems as either autotrophic ($P/R > 1$) or heterotrophic ($P/R < 1$) depending on whether they are net producers or net consumers of organic matter (Odum 1956). Florida spring ecosystems were noted by Odum (1956) to have P/R ratios greater than one, indicating net production of organic matter. Estimates from Silver Springs illustrate that during the winter of 1952/1953 and March 1954, this ecosystem had P/R ratios of 2.9 and 7.0 respectively. The effects of elevated nitrate concentrations on the P/R ratio are revealed by the results of Munch *et al.* (2006), in that period-of-record (February 2004 to March 2005) average P/R ratio at Silver Springs was estimated as 1.06, with the monthly maximum P/R ratio being 1.26 in June 2004 and a minimum monthly average of 0.73 in February 2004. In a comparison of spring run segments with nitrate concentrations ranging from natural ambient levels (< 0.05 mg/L) to elevated levels (> 1.0 mg/L), P/R ratios were found to decline significantly in relation to increasing nitrate concentrations (Figure 3, WSI 2007a). This negative correlation suggests that the P/R ratio can be used to evaluate nutrient impairment of spring ecosystems.

Photosynthetic Efficiency

The efficiencies of photosynthetic primary producers have been measured most comprehensively at Silver Springs, where Odum (1957b) reported an average value of $1.09 \text{ g O}_2/\text{mol of PAR}$ (ranging from 0.79 to 1.53), while Knight (1980) reported an average value of $1.06 \text{ g O}_2/\text{mol of PAR}$ (ranging from 0.61 to 1.50), and Munch *et al.* (2006) reported an average value of $0.95 \text{ g O}_2/\text{mol of PAR}$ (ranging from 0.07 to 2.71). The Munch *et al.* (2006) period-of-record average photosynthetic efficiency of $0.95 \text{ g O}_2/\text{mol}$, is equivalent to an estimated PAR efficiency of 7.6% using estimated conversion factors and PAR efficiency was observed to vary seasonally with the

highest monthly average value of 10.5% (1.30 g O₂/mol) measured in December 2004 and the lowest value of 5.5% (0.68 g O₂/mol) measured in June 2004. These estimates of photosynthetic efficiency at Silver Springs indicate a slight reduction in the magnitude of this parameter over the past 50 years although differences in the number of estimates make it difficult to determine if this change is significant and if it has any relation to increasing nitrate concentrations. Photosynthetic efficiency estimates for other spring ecosystems have recently been made for Alexander, Juniper, Rock, and Wekiwa Springs with average values of 0.32, 0.45, 0.09, and 0.26 g O₂/mol of PAR respectively (Figure 3, WSI 2007a). These estimates were derived from a similar number of daily measures collected during the same time periods and illustrate a reduction in photosynthetic efficiency correlated with increasing nitrate concentrations.

Community Metabolism Conclusions

As the previous examples illustrate, traditional measures of describing community structure which use biomass metrics allow few generalizations about the response of primary producers to elevated nutrient conditions in stream systems. This dilemma supports the use of ecosystem-level metabolism functional measures, such as GPP, NPP, P/R ratio and photosynthetic efficiency, which integrate the overall functional response of the ecosystem components and may reduce variance caused by site-specific conditions. The observations summarized in this chapter of reduced primary productivity and ecological efficiency in correlation with increasing nutrients may have multiple explanations.

First, Florida's spring run ecosystems were likely adapted to naturally lower ambient nutrient conditions and higher nutrient levels could represent an imbalance or stress; this explanation follows the subsidy-stress hypothesis of Odum *et al.* (1979). Support for this concept was provided in an ecosystem-level metabolism study of Silver Springs, where ecosystem production and efficiency were also reduced in inverse proportion to rising nitrate nitrogen concentrations (Munch *et al.* 2006).

A second possible mechanism that might help to explain a decline in ecosystem primary production could be reduced macrophyte photosynthesis resulting from increased epiphytic algae growth and shading as a result of elevated water column nutrients. While epiphytic growths can reduce the light energy available to host plants, some research found these effects were primarily observed at low light levels and did not affect host photosynthetic rates at typical midday intensities. As spring waters are generally clear and light transmission is excellent (Duarte and Canfield 1990b), epiphytic reductions in light availability to vascular plants may not reach the level of causing host plant death. In an experimental manipulation of epiphytes and light levels, Asaeda *et al.* (2004) noted that both epiphytic algae and low light reduce growth and production; plants tended to optimize low light-created shade by changing their physiology and morphology, but were unable to do the same when epiphytic algae-created shade occurred on the leaf surface.

A third alternative explanation to reduced primary productivity in macrophytes in relation to elevated nitrate concentrations was provided by Boedeltje *et al.* (2005) who reported high water column nitrate nitrogen concentrations can significantly reduce the growth of ammonia-preferring species such as *Potamogeton alpinus*, because the uptake and reduction of nitrate has a much higher energy and carbon requirement than ammonia uptake and assimilation (Runge

1986, Marschner 1995). Boedeltje *et al.* (2005) hypothesized that nitrate-dominated nitrogen assimilation may lead to strong metabolic disturbances in species adapted to ammonia uptake by the roots (such as *P. alpinus*) resulting in the observed reduction in growth under high water column nitrate concentrations, although further experiments are needed to assess potential negative effects on species found in the springs of Florida.

Although the causative mechanisms which result in reduced primary productivity and ecological efficiency in correlation with increasing water column nutrient concentrations (especially nitrate and perhaps phosphorus) remain unknown; the averages, extremes, and seasonal patterns for these ecological measures are becoming more apparent as additional ecosystem metabolism data are being collected in Florida's springs. Year-to-year measures of ecosystem metabolism are remarkably consistent compared to structural measures such as plant or fish populations and provide a valuable database for comparison to other springs, spring runs, and streams in Florida.

HUMAN AND AESTHETIC USES

Visitor Satisfaction

There are little or no published data that relate recreational satisfaction from Florida springs to their trophic status. It is readily apparent that people prefer to swim in clear, clean water rather than turbid, colored, or phytoplankton-rich waters. It is likely that highly abundant macrophytes discourage water recreation as well. This presents a dilemma, in that, native benthic vascular plants represent a natural and ecologically important component of spring ecosystems. Species such as *Vallisneria americana* or *Sagittaria kurziana* are typically not viewed as nuisance solely due to their presence.

Economic Impacts

As detailed in Chapter 1, the number of visitors attending the springs in Florida and their cumulative economic impact is substantial enough to impact local economies. If recreational attendance were to decline due to real or perceived diminished appeal of a spring system, there would be associated declines in the economic impacts generated. Preservation of spring ecosystems should not be based solely on an economic basis, unless considerations for environmental services are factored in as well, but they provide support towards these systems protection. At this time insufficient quantitative public use data exist from most springs to develop correlations with increasing nutrient concentrations.

Effects of Eutrophication on Human Recreation

The type of recreation will obviously influence tolerance for the presence of SAV, with water dependent recreation perhaps having lower tolerance levels than non water dependent contact activities. SAV can attract waterfowl, wading birds, and other wildlife which would affect perceptions of persons engaged in observation of wildlife as well. Limited data on recreational satisfaction in relation to primary producers exists, but Holland and Cichra (1994) reported that what respondents liked best about their trip to Rainbow River was: clear, clean water (35%), scenery (19%), quiet, relaxing (17%), and seeing wildlife and fish (11%) and that what

respondents liked least about their trip: rainy weather (13%), motorboat noise (12%), vegetation and algae in water (10%), and river float too long (10%). These results suggest that while water clarity is very important, there is tolerance for submersed aquatic vegetation among the surveyed recreationalists, possibly because this vegetation may have been viewed as a natural component of a healthy ecosystem. Declines in water clarity as a result of reductions in stream flow with corresponding increases in water residence time and phytoplankton abundance would likely be associated with decreased recreational satisfaction. Similarly, increases in the abundance of vascular plants or macroalgae are likely to be viewed negatively by recreational users of spring ecosystems, given that people do not like to swim through or stand in vegetation. If the abundance of filamentous algae increases as a result of eutrophication in a spring ecosystem, there would likely be a decline in recreational user satisfaction. Real or perceived declines in the aesthetics of a spring ecosystem as a result of eutrophication would likely result in less human recreational use and visitation, with resulting declines in the economic impact. It is important to note that human uses of the terms, such as *natural* or *healthy*, are subjectively defined, and that an educational component aimed to identify these biases would serve both the managers and users of springs and other ecosystems.

DISCUSSION

In the past century, many of Florida's spring ecosystems have experienced changes which include declines in discharge, increases in conductivity, increased recreation, and colonization by non-indigenous species. However, the widespread increase in nitrate concentrations during this time period continues to be one of the key elements that spring ecosystems have had to adjust to, and it has been hypothesized that the increasing concentration of that form of nitrogen is a principal causative factor for observed changes in ecosystem metabolism. Strong (2004) examined temporal trends in water quality characteristics in 109 Florida springs. Parameters that were generally found to be increasing were specific conductance, alkalinity, hardness, and nitrate. Only pH concentrations were observed to be declining. There were no apparent trends in phosphorus concentrations. Mean nitrate concentrations in spring samples generally increased from about 0.43 mg/L before 1977 to about 1.13 mg/L since 1990. Strong's (2004) study suggests that state-wide trends for declining water quality of springs are occurring. An illustration showing the range of nitrate plus nitrite concentrations ($\text{NO}_x\text{-N}$ mg/L, although nitrite is generally a minimal component of these aggregate values) for 130 Florida springs compiled from 2006 Florida Geological Survey data is shown in Figure 4. This figure presents the wide range of $\text{NO}_x\text{-N}$ concentrations that Florida springs exhibit and suggests that 83% of the surveyed springs have $\text{NO}_x\text{-N}$ concentrations greater than 0.1 mg/L, which is a commonly assumed background level for groundwater nitrate levels in Florida.

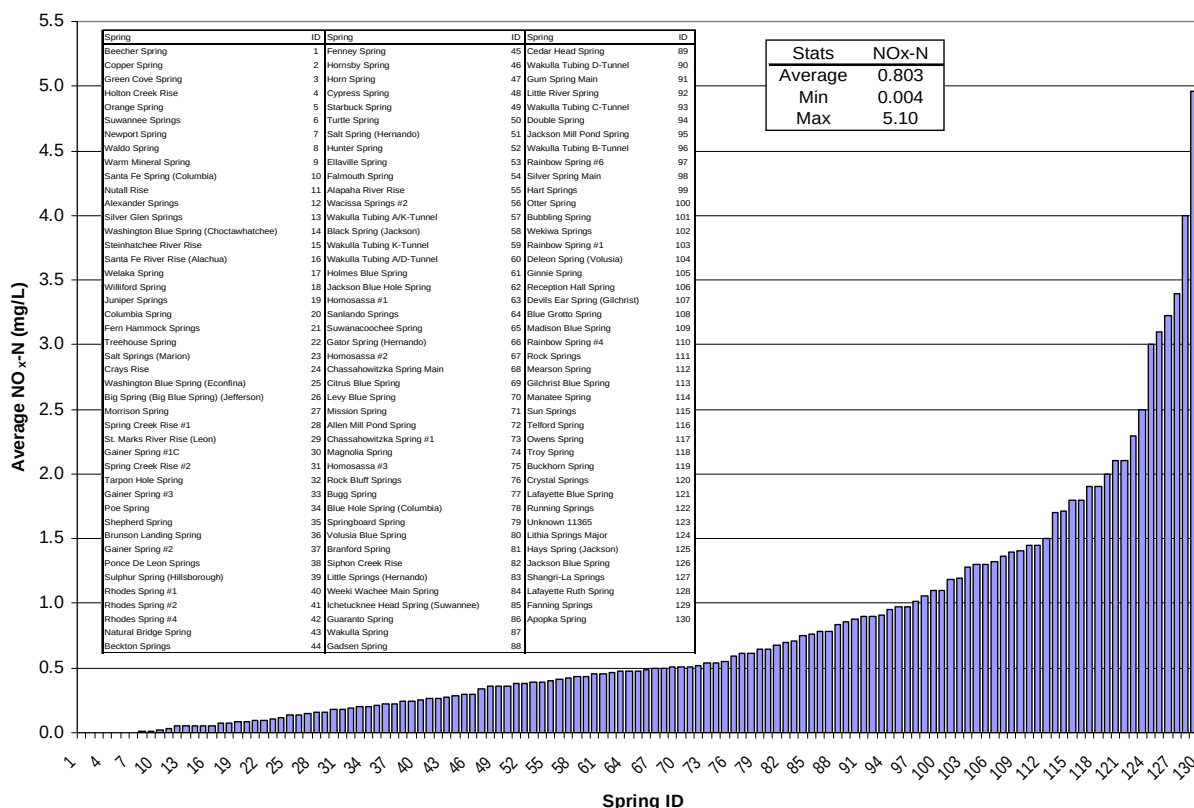


Figure 4 – Illustrates the average NO_x-N concentrations (mg/L) for 130 Florida springs (data from Florida Geological Survey, Scott et al. 2004).

A similar illustration showing the range of total phosphorus concentrations (TP mg/L), for 130 Florida springs compiled from 2006 Florida Geological Survey data is shown in Figure 5. Although total phosphorus (the aggregate of all forms of phosphorus) data are presented, in the case of groundwater, this total phosphorus is almost entirely composed of dissolved inorganic forms of phosphorus such as orthophosphate or soluble reactive phosphorus. This figure suggests that the total phosphorus concentrations of spring water are less variable than the wide range of NO_x-N concentrations that Florida springs exhibit. Groundwater phosphorus concentrations are largely a function of the associated geology and many of the higher phosphorus values are observed from springs which overlie natural phosphatic deposits.

Of these 130 springs, 80% have total phosphorus concentrations greater than 0.025 mg/L, a value which has been defined as a break point separating mesotrophic and eutrophic lakes (Table 3, Forsberg and Ryding 1980). Although other indices of trophic status exist (*e.g.* the Florida Trophic State Index created by the Florida Department of Environmental Protection), their application to lotic systems has been problematic. This is principally due to the index's inability to incorporate macrophytes and benthic algae that are not accounted for by standard methods which measure water column chlorophyll content in non-flowing systems.

Stats	TP
Average	0.084
Min	0.008
Max	1.90

Spring	ID	Spring	ID	Spring	ID	Spring	ID
Spring	1	Spring	27	Spring	53	Spring	89
Weeki Wachee Main Spring	2	Wakulla Tubing C-Tunnel	28	Rhodes Spring #4	54	Otter Spring	90
Little Springs (Hernando)	3	Juniper Springs	29	Wacissa Springs #2	55	Welaka Spring	91
Guarato Spring	4	Wakulla Tubing B-Tunnel	30	Nuttall Rise	56	Hart Springs	92
Gainer Spring #3	5	Gilchrist Blue Spring	31	Natural Bridge Spring	57	Rock Springs	93
Washington Blue Spring (Econfina)	6	Mearson Spring	32	Reception Hall Spring	58	Bugg Spring	94
Gainer Spring #2	7	Hunter Spring	33	Blue Hole Spring (Columbia)	59	Crays Rise	95
Gator Spring (Hernando)	8	Homosassa #3	34	Crystal Springs	60	Siphon Creek Rise	96
Green Cove Spring	9	Manatee Spring	35	Lafayette Blue Spring	61	Fenney Spring	97
Hays Spring (Jackson)	10	Ponce De Leon Springs	36	Alexander Springs	62	Sulphur Spring (Hillsborough)	98
Magnolia Spring	11	Unknown 11365	37	Brantford Spring	63	Poe Spring	99
Salt Springs (Marion)	12	Brunson Landing Spring	38	Steinhatchee River Rise	64	Wekiwa Springs	100
Black Spring (Jackson)	13	Cum Spring Main	39	Mission Spring	65	Alapaha River Rise	101
Gadsden Spring	14	Homosassa #2	40	Lithia Springs Major	66	Holton Creek Rise	102
Springboard Spring	15	Rainbow Spring #6	41	Ellaville Spring	67	Suwannee Springs	103
Washington Blue Spring (Choctawhatchee)	16	Fern Hammock Springs	42	Telford Spring	68	Starbuck Spring	104
Newport Spring	17	Salt Spring (Hernando)	43	Sun Springs	69	Big Spring (Big Blue Spring) (Jefferson)	105
Warm Mineral Spring	18	Wakulla Spring	44	Deleon Spring (Volusia)	70	Sanlando Springs	106
Willford Spring	19	Rainbow Spring #1	45	Fanning Springs	71	Rainbow Spring #4	107
Jackson Mill Pond Spring	20	Jackson Blue Hole Spring	46	Suwanacoochee Spring	72	Santa Fe Spring (Columbia)	108
Jackson Blue Spring	21	Shangri-La Springs	47	Volusia Blue Spring	73	Treehouse Spring	109
Double Spring	22	Wakulla Tubing D-Tunnel	48	Hornstby Spring	74	Santa Fe River Rise (Alachua)	110
Turtle Spring	23	Wakulla Tubing K-Tunnel	49	Owens Spring	75	Columbia Spring	111
Chassahowitzka Spring #1	24	Apopka Spring	50	Shepherd Spring	76	Silver Glen Springs	112
Little River Spring	25	Cedar Head Spring	51	Rock Bluff Springs	77	Homosassa #1	113
Cypress Spring	26	Citrus Blue Spring	52	Waldo Spring	78	Beecher Spring	114
Beckton Springs	27	Wakulla Tubing A/K-Tunnel	53	Orange Spring	79	Buckhorn Spring	115

292

Table 3. Lake trophic state classification system based on Forsberg and Ryding (1980).

Trophic State	Chlorophyll (mg/L)	Total Phosphorus (mg/L)	Total Nitrogen (mg/L)	Water Clarity (ft)
Oligotrophic	< 0.003	< 0.015	< 0.40	> 13.1
Mesotrophic	0.003 – 0.007	0.015 – 0.025	0.40 – 0.60	8.2 - 13.1
Eutrophic	0.007 – 0.04	0.025 – 0.10	0.60 – 1.50	3.3 – 8.2
Hypereutrophic	> 0.04	> 0.10	> 1.50	< 3.3

The best evidence suggesting a decline in the health of Florida's spring ecosystems comes from studies that have been conducted over a half-century time period in Silver Springs. Both the direct measurements and the estimated system metabolism analyses indicate that the Silver Springs ecosystem may be considerably less productive than it was fifty years ago (Munch *et al.* 2006). This appears to be a consequence of lowered gross primary productivity and efficiency of light utilization. This result appears to be counter-intuitive to the observation that nutrient levels (nitrate nitrogen) which support plant growth have increased in Silver Springs. It is generally thought that an increase in nutrients will stimulate both gross and net primary productivity in aquatic ecosystems (Wetzel 2001). However, spring ecosystems are characterized by flowing waters which continually re-supply nutrient demands of primary producers. H.T. Odum (1957a) theorized that prior to modern anthropogenic impacts, Florida's springs existed as a balanced aquatic ecosystem which had evolved to maximize community metabolism, and the relatively recent increase of nutrients in the form of nitrate may have resulted in a stress rather than a subsidy (E.P. Odum *et al.* 1979). The subsidy-stress hypothesis may be the best model to describe the response of spring ecosystems to increasing nitrate concentrations; however, controlled field experiments need to be made in order to test this hypothesis.

One of the most comprehensive examinations of the effects of nitrate on spring ecosystem structure and function is the 50-year retrospective study of Silver Springs by Munch *et al.* (2006). The key findings from that study are reproduced here:

- *Sagittaria kurziana* remains the dominant submersed aquatic plant species in Silver Springs and represents one of the main physical features of the ecosystem.
- Biomass estimates for submersed aquatic plants in the summer season were not significantly different from estimates made by Odum in the early 1950s. However, estimates for winter biomass were 31% lower than Odum's, who reported no seasonal difference in submersed aquatic plant biomass.
- Biomass estimates for the epiphyte community in the summer were approximately three-fold higher than those reported by Odum, while winter values were not significantly different between the two studies.
- The largest disparity between the Munch *et al.* (2006) estimates of primary producer community biomass and those of Odum from the 1950s was the substantial increase in biomass for the benthic algal mat community. While Odum discounted the importance of algal mats, in terms of biomass, the Munch *et al.* (2006) study indicated that this primary producer category had biomass estimates similar to those observed for epiphytes and

submersed aquatic plants. However, it is important to note that these estimates may not be an accurate indicator of primary productivity attributable to benthic mats, since mat biomass includes large proportions of bacteria, fauna, dead algae, and other detrital material.

- Total species richness for birds, fish, and reptiles in the Munch *et al.* (2006) study were similar to historical records at Silver River.
- Estimated annual average fish live-weight biomass in the Munch *et al.* (2006) study has declined in Silver Springs since Odum's study in the early 1950s by about 96%; and by 61% since Knight's 1978-79 study (Knight 1980). These declines in biomass were primarily due to large reductions in a few species (channel catfish, mullet, and gizzard shad), while the remaining fish species were found in similar abundance across the fifty-year span. It is likely that declines in channel catfish, mullet, and gizzard shad abundance are the result of diminished access to the St. Johns River and the Atlantic Ocean due to the Kirkpatrick (AKA Rodman) Dam
- Annual average gross primary productivity (GPP) declined from about 15.6 grams oxygen per square meter per day ($\text{g O}_2/\text{m}^2/\text{d}$) in the 1950s and late 1970s to about 11.2 $\text{g O}_2/\text{m}^2/\text{d}$ during the current study, a decline of about 27%.
- Community respiration also declined from about 14.8 $\text{g O}_2/\text{m}^2/\text{d}$ during the earlier studies to about 10.9 $\text{g O}_2/\text{m}^2/\text{d}$ during the Munch *et al.* (2006) study, a 26% reduction.
- The resulting net community primary productivity declined from about 1.0 $\text{g O}_2/\text{m}^2/\text{d}$ in the 1950s, to 0.80 $\text{g O}_2/\text{m}^2/\text{d}$ in the late 1970s, to about 0.42 $\text{g O}_2/\text{m}^2/\text{d}$ during the Munch *et al.* (2006) study, a decline of about 59% over the past fifty years.
- The production to respiration (P/R) ratio remained relatively consistent between the three studies, ranging from about 1.11 during Odum's study in the 1950s to about 1.06 during Knight's study in the late 1970s, and 1.06 in the Munch *et al.* (2006) study.
- Ecological efficiency declined from about 1.09 gram of oxygen per mol ($\text{g O}_2/\text{mol}$) of Photosynthetically Active Radiation (PAR) during Odum's study to about 0.94 $\text{g O}_2/\text{mol}$ of PAR during the Munch *et al.* (2006) study, a decline of about 13%.
- Average particulate export rates were found to be 72% lower during the Munch *et al.* (2006) study compared to data published by Odum (1957). These particulates are a representation of the net system productivity, and their decline strengthens the evidence that overall productivity has declined in Silver Springs.

The Munch *et al.* (2006) study observed that the percentage of developed lands within the springshed (5 mile radius) was positively correlated with actual nitrate concentrations and spring discharge was found to be inversely correlated with nitrate. The resulting correlation models were used in turn to predict future nitrogen loading to the Silver Springs ecosystem if the future land use development estimates for 2055 are realized (Table 4).

Table 4. Modeled changes in the nitrogen concentration of Silver Springs water based on projected changes in land use and corresponding nitrogen loading rates (Munch et al. 2006).

Year	Observed Spring Flow	MODFLOW Simulated Spring Flow	Observed Nitrogen Load (lbs/yr)	Land Use/Land Cover Model Est. N Load (lbs/yr)	Observed Spring N Concentration (mg/L)	Land Use/Land Cover Model Est. N Concentration (mg/L)	N Concentration Change (Model Predictions, %)
1957	640.0	716.5	94,416.0	399,054.10	0.10	0.38	N/A
1979	778.0	710.8	814,898.6	802,633.06	0.71	0.76	102.75
1995	720.0	708.3	955,962.0	1,036,198.93	0.90	0.99	29.56
2005	680.0	687.6	1,057,606.7	1,120,813.63	1.07	1.10	11.42
2055	N/A	687.6	N/A	1,760,000.00	N/A	2.02	84.00

The apparent decline in ecosystem metabolism and efficiency observed in Silver Springs over the past fifty years may be the result of a several ecosystem-level factors working in concert or at odds. Four possible hypotheses were offered to explain these observations (Munch *et al.* 2006):

- Decreased usable solar radiation is reaching the level of submersed aquatic plants in Silver Springs due to increased shading by a growing tree canopy (natural wetland forest succession) along the river and this reduced input of solar energy may have lowered GPP and PAR efficiency.
- GPP may have declined as areas of optimal submersed aquatic vegetation growth (*Sagittaria kurziana* beds with adapted periphytic algae) have been replaced with benthic algal mats, possibly due to increasing nitrate nitrogen concentrations, flow decreases, or physical factors related to human uses.
- Decreases in flow rate and water velocities due to natural climatic conditions or consumptive groundwater uses may have reduced the previous subsidy needed for maximum plant/periphyton growth and higher GPP and PAR efficiency.
- Decreased top-down consumer control of the primary producers and lowered GPP is resulting from lower fish/consumer populations below optimal grazing densities, possibly due to obstruction of fish migration by the Kirkpatrick Dam, or lower minimum daily dissolved oxygen concentrations, or due to indirect effects of nitrate on consumers. The role of striped mullet (*Mugil cephalus*) in the top-down control of the periphytic growths on submersed vascular plants in Silver Springs was reported by Allen (1946, p. 32), who wrote: “*These attractive fish are very prominent, always swimming about, forever feeding on algae off the blades of underwater grasses [Sagittaria kurziana]. They start at one end of the blade of grass, sucking up food as they slowly swim up toward the other end.*”

Overall, the Munch *et al.* (2006) study indicates that multiple factors may have resulted in the observed ecosystem changes at Silver Springs over the past 50 years. These factors include reductions in the volume of spring discharge, increases in riparian shading, reductions in the abundance of herbivorous fish, and increases in nitrate concentration and load. The authors of

the Munch *et al.* (2006) study suggest that the corresponding increases in nitrate concentration over this time period cannot exclusively be responsible for this degradation, but that nitrate pollution has likely contributed to this decline. Given the anticipated future increases in nitrate pollution, additional concern due to this factor remains warranted. Support for the concept that nitrate can act as both a subsidy at low concentration and a stressor at high concentrations has been provided by the WSI (2007a) study in the Wekiva River and Rock Springs Run which observed negative correlations between measures of ecosystem productivity and nitrate concentrations. Based on these lines of available evidence, nitrate alone may not be the sole factor negatively impacting Florida spring ecosystems, but it is the single most important water quality parameter that has changed during the period of observed declines in spring ecosystem structure and function.

RECOMMENDATIONS FOR FURTHER RESEARCH

Despite a wide variety of springs' research, there remains a significant knowledge gap between the real and perceived threats that nitrate pollution plays on the ecology of spring ecosystems. This situation is not unique to Florida, as Bernot and Dodds (2005, p. 442) observed that for North American streams: "*There is a great need for long-term studies of nitrogen additions in lotic ecosystems and clear distinctions need to be made between ecosystem responses to short-term or periodic increases in nitrogen loading and alterations in ecosystem functions due to chronic nitrogen loading.*" In addition to the general research questions to be answered, Florida's springs represent important cultural and economic resources which also provide real-time windows into the condition of Florida's most essential natural resource – high-quality groundwater.

With these caveats in mind, we suggest that nutrients are not the only stressors of concern in spring ecosystems. Recent work in the headwater areas of Wekiwa and Rock springs indicates that ecosystem metabolism can be negatively impacted by high levels of human recreation and by flow reductions (WSI 2007a, 2007b). Many, if not most, of Florida's springs are threatened by these additional stressors as well as by invasions from non-indigenous plant and animal species, aquatic weed management activity, erosion and deposition of sediments, and increasing stormwater inflows from surrounding urbanized areas. Future research to be conducted should attempt to effectively understand the separate and synergistic effects of these multiple forcing functions and the associated responses of our spring ecosystems.

With the multiple stressors affecting spring ecosystems, any metric used to monitor their health should to the fullest extent possible be integrative. The single best way to characterize these systems would be through estimates of community metabolism and its constituent parameters: gross primary productivity, net primary productivity, community respiration, productivity to respiration ratios, and photosynthetic efficiency. These metrics can be relatively easily estimated using upstream-downstream changes in dissolved oxygen concentrations and have the best ability to describe ecosystem level functions, and their value is enhanced when combined with measures of fauna and flora abundance and water chemistry, other typical single-component ecosystem metrics.

Proposed Research Priorities

The following springs' research priorities are suggested:

- Recognize the importance of the collection of water quality samples, particularly for dissolved oxygen (diel changes) and nitrates, on a periodic schedule, from major springs. Continue the collection of discharge estimates from major springs (all first and second magnitude and a representative sample of springs with lower discharge rates), as declining discharge represents a major threat to springs. These types of data are regularly collected by local, state, and federal agencies, but improvements in the spatial and temporal sampling could be realized as well as improved assembly, analysis, and reporting of the resulting data.
- Continue to expand and refine the development of Land Use and Land Cover (LULC) datasets, which in conjunction with improved infrared and color imagery, will greatly increase the relative accuracy in the LULC classifications for springsheds. In conjunction with accurate estimates of nitrogen loading per LULC category, assessment of springshed land use changes on the nutrient concentration of associated spring discharge could be made. Thus, rather than solely reacting to spring pollution after the source is in place, the ability to predict and as a result to limit or prevent springshed pollution would be enhanced.
- Better utilize current technology of *in situ* data loggers in a representative set of major springs ecosystems so as to provide regular or continuous records of changing water quality conditions, including temperature, dissolved oxygen, pH, and specific conductance (and other parameters including nutrients as instruments and technologies become available). These measures, particularly if made in conjunction with levels of ambient solar radiation and spring discharge would allow the direct estimation of ecosystem metabolism and photosynthetic efficiency. Given the inter-specific range of physical and chemical conditions that Florida springs currently exhibit, simultaneous estimates of ecosystem metabolism would allow development of a response surface for comparison to changing environmental conditions (forcing functions). For example, multivariate analysis could be applied to determining the relative importance of a number of forcing functions on ecosystem metabolism, including identification of the concentration or intensity of each variable (*e.g.*, nitrate) as it transitions from a subsidy to a stressor.
- Quantify invertebrate, vertebrate, and floral diversity and abundance on a three-to-five year schedule at 1st and 2nd magnitude springs so that trends in these ecosystem components can be observed. This sampling should be conducted on springs that are also being monitored for ecosystem metabolism and should be scheduled on a monthly basis for at least one year during each three-to-five -year period so as to elucidate seasonal trends.
- Conduct *in situ* mesocosm experiments which quantify the role that bottom-up processes (*i.e.* nutrient limitation) versus top-down processes (*i.e.* herbivore grazing) have on the growth and abundance of primary producers, particularly epiphytes and filamentous algae. The primary question to be answered is whether future increases or decreases in nutrient concentrations will result in responses by the primary producer community.

- Better monitor and inventory human use activities in a representative group of important springs on a routine basis so that optimal (as opposed to high) levels of human recreation can be maintained without degradation of the springs' resource. Human recreation levels or uses which are identified to be impairing spring health or degrading spring aesthetics should be modified through adaptive management strategies. The most successful example of this balance may be Ichetucknee Springs State Park which annually accommodates hundreds of thousands of in water recreationalists while maintaining sustainable populations of submersed macrophytes.

Recommendations

Based on the synthesis of information provided concerning the effects of nutrients on springs in Florida, the following recommendations are provided:

- It is recommended that the Florida Department of Environmental Protection (DEP) Springs Initiative continue funding applied research under field conditions in order to develop a consistent base of scientific knowledge for spring ecosystems. A critical need exists to establish a comprehensive baseline database for a large number of artesian spring ecosystems, including their ecosystem metabolism, trophic structure, and key forcing functions. A substantial increase in the annual funding for this research is justified by the ecological and economic importance of artesian springs in Florida.
- It is recommended that counties with significant springs' resources utilize existing governmental agencies to develop springs protection plans that address such components as land development regulations and land acquisition, along with other groundwater and spring protection measures in order to prevent further and, if possible, reverse the observed increases in nitrate-nitrogen concentrations. Regulatory programs and tax incentives should be utilized to reduce nitrogen loads to the artesian groundwater in karst areas of the state. These actions have the ability to reduce other ground water pollutants introduced through anthropogenic activities and would contribute to high quality ground water recharge which would be widely beneficial.
- It is recommended that the DEP with support from the Florida Legislature develop applicable standards that define nutrient impairment in artesian springs. Springs that meet these impairment metrics should be moved as quickly as possible into the state's Total Maximum Daily Load (TMDL) program. Nitrate concentrations significantly above historical spring levels could be used as a criterion for listing under the Impaired Waters Rule. For springs that are above recommended thresholds for nitrate nitrogen concentrations, these TMDLs could provide a basis for enhanced nitrogen-removal standards for municipal and on-site wastewater facilities as well as for stormwater management systems and the active and pro-active enforcement of nitrogen mass loading limits by existing and future point and non-point sources in the affected springsheds.

REFERENCES

- Allan, J.D. 1995. Stream Ecology, Structure and function of running waters. Chapman and Hall. 388 pp.
- Allen, E.R. 1946. Fishes of Silver Springs, Florida. No publisher. Copyright E. Ross Allen, Silver Springs, Florida. 36 pp.
- Asaeda, T., M. Sultana, J. Manatunge, and A. Ablimit. 2004. Colonization and growth of epiphytic algal communities on *Potamogeton perfoliatus* under two different light regimes. New Zealand Journal of Marine and Freshwater Research 38: 585–594.
- Bachmann, R.W., B.L. Jones, D.D. Fox, M.V. Hoyer, L.A. Bull, and D.E. Canfield, Jr. 1996. Relations between trophic state indicators and fish in Florida (USA) lakes. Canadian Journal of Fisheries and Aquatic Sciences 53: 842-855.
- Bernot, M.R. and W.K. Dodds. 2005. Nitrogen retention, removal, and saturation in lotic ecosystems. Ecosystems 8: 442-453.
- Boedeltje, G.A., J.P. Smolders, and J.G.M. Roelofs. 2005. Combined effects of water column nitrate enrichment, sediment type and irradiance on growth and foliar nutrient concentrations of *Potamogeton alpinus*. Freshwater Biology 50(9): 1537-1547.
- Bothwell, M.L. 1985. Phosphorus limitation of lotic periphyton growth rates: An intersite comparison using continuous flow troughs (Thompson River System, British Columbia). Limnology and Oceanography 30: 527-554.
- Bristowe, J.M. and J. Whitcombe. 1971. The role of roots in the nutrition of aquatic vascular plants. American Journal of Botany 58: 8-13.
- Busch, D.E. 1978. Successional changes associated with benthic assemblages in experimental stream. Ph.D. Thesis. Oregon State University. Corvallis, OR. 91 pp.
- Camargo, J.A. and J.V. Ward. 1995. Nitrate (NO₃-N) toxicity to aquatic life: a proposal of safe concentrations for two species of nearctic freshwater invertebrates. Chemosphere 31: 3211-3216.
- Canfield, Jr., D.E. 1983. Prediction of chlorophyll *a* concentrations in Florida lakes: The importance of phosphorus and nitrogen. Water Resources Bulletin 19(2): 255-262.
- Canfield, D.E., Jr. and M.V. Hoyer. 1988. Influence of nutrient enrichment and light availability on the abundance of aquatic macrophytes in Florida streams. Canadian Journal of Fisheries and Aquatic Sciences 45: 1467-1472.
- Carignan, R. and J. Kalff. 1980. Phosphorus sources for aquatic weeds: water or sediments. Science 207: 987-988.

- Chambers, P.A., E.E. Prepas, M.L. Bothwell, and H.R. Hamilton. 1989. Roots versus shoots in nutrient uptake by aquatic macrophytes in flowing waters. *Canadian Journal of Fisheries and Aquatic Sciences* 46: 435-439.
- Chen, C., D. Yin, B. Yu, and H. Zhu. 2007. Effect of Epiphytic Algae on Photosynthetic Function of *Potamogeton crispus*. *Journal of Freshwater Ecology* 22(3): 411-420.
- Cloern, J.E. 2001. Review. Our evolving conceptual model of the coastal eutrophication problem. *Marine Ecology Progress Series* 210: 223-253.
- Conner, W.H. and J.W. Day. 1992. Water level variability and litterfall productivity of forested freshwater wetlands in Louisiana. *American Midland Naturalist* 128: 237-245.
- Cowell, B.C. and C.J. Dawes. 2004. Growth and nitrate-nitrogen uptake by the cyanobacterium *Lyngbya wollei*. *Journal Aquatic Plant Management* 42: 69-71.
- Corrao, N.M., P.C. Darby, and C.M. Pomory. 2006. Nitrate impacts on the Florida apple snail, *Pomacea paludosa*. *Hydrobiologia* (568): 135-143.
- Crawford, J.K. 1979. Limiting nutrients in streams: A case study of Pine Creek, Pennsylvania. Ph.D. Thesis. Pennsylvania State University. State College, PA. 139 pp.
- Dickman, M. 1973. Changes in periphytic algae following bicarbonate additions to a small stream. *Journal of the Fisheries Research Board of Canada* 30: 1882-1884.
- Dodds, W.K., V.H. Smith, and B. Zander. 1997. Developing nutrient targets to control benthic chlorophyll levels in streams: a case study of the Clark Fork River. *Water Research* 31: 1738-1750.
- Duarte, C.M. 1992. Nutrient concentration of aquatic plants: patterns across species. *Limnology and Oceanography* 37(4): 882-889.
- Duarte, C.M. and D.E. Canfield, Jr. 1990a. Macrophyte standing crop and primary productivity in some Florida spring-runs. *Water Resources Bulletin* 26(6): 927-934.
- Duarte, C.M. and D.E. Canfield, Jr. 1990b. Light absorption in Florida springs. *Florida Scientist* 53: 118-122.
- Edwards, T.M., K.A. McCoy, T. Barbeau, M.W. McCoy, J.M. Thro, and L.J. Guillette, Jr. 2006. Environmental context determines nitrate toxicity in Southern toad (*Bufo terrestris*) tadpoles. *Aquatic Toxicology* 78: 50-58.
- Edwards, T.M. and L.J. Guillette. 2007. Reproductive characteristics of male mosquitofish (*Gambusia holbrooki*) from nitrate-contaminated springs in Florida. *Aquatic Toxicology* 85: 40-47.

- Elwood, J.W., J.D. Newbold, A.F. Trinble, and R.W. Stark. 1981. The limiting role of phosphorus in a woodland stream ecosystem: Effects of P enrichment on leaf decomposition and primary producers. *Ecology* 62: 146- 158.
- Forsberg, C. and S. Ryding. 1980. Eutrophication parameters and trophic state indices in 30 Swedish waste-receiving lakes. *Archives of Hydrobiology* 89: 189-207.
- Francoeur, S.N. 2001. Meta-analysis of lotic nutrient amendment experiments: detecting and quantifying subtle responses. *Journal of the North American Benthological Society* 20: 358-368.
- Frazer, T.K., E.J. Phlips, S.K. Notestein, and C. Jett. 2002. Nutrient Limiting Status of Phytoplankton in Five Gulf Coast Rivers and Their Associated Estuaries. Final Report. Southwest Florida Water Management District. Brooksville, FL.
- Frazer, T.K., S.K. Notestein and W.E. Pine, Jr. 2006. Changes in the Physical, Chemical and Vegetative Characteristics of the Homosassa, Chassahowitzka and Weeki Wachee Rivers. Final Report. Southwest Florida Water Management District. Brooksville, FL.
- Gregory, S.V. 1980. Effects of light, nutrients and grazing on periphyton communities in streams. Ph.D. Thesis. Oregon State University. 150 pp.
- Hecky, R.E. and P. Kilham. 1988. Nutrient limitation of phytoplankton in freshwater and marine environments: a review of recent evidence on the effects of enrichment. *Limnology and Oceanography* 33: 796–822.
- Hill, W.R. and B.C. Harvey. 1990. Periphyton responses to higher trophic levels and light in a shaded stream. *Canadian Journal of Fisheries and Aquatic Sciences* 47: 2307-2314.
- Hill, W.R., H.L. Boston, and A.D. Steinman. 1992. Grazers and nutrients simultaneously limit lotic primary productivity. *Canadian Journal of Fisheries and Aquatic Science* 49: 504-512.
- Holland, S.M. and C.E. Cichra. 1994. Human and environmental dimensions of the recreational use of Blue Run and Rainbow Springs State Park, Dunnellon, Florida. Final Report. Submitted to the Florida Department of Natural Resources, Division of Recreation and Parks. 275 pp.
- Howarth, R.W. 1988. Nutrient limitation of net primary production in marine ecosystems. *Annual Review of Ecology and Systematics* 19: 898–910.
- Hoyer, M.V. and D.E. Canfield, Jr. 1991. A phosphorus-fish standing crop relationship for streams? *Lake and Reservoir Management* 7(1): 25-32.
- Hubbs, C.L. and E.R. Allen. 1943. Fishes of Silver Springs. *Proceedings of the Florida Academy of Sciences* 6: 110-130.
- Hynes, H.B.N. 1970. The ecology of running waters. University of Toronto Press. Toronto.

- Knight, R.L. 1980. Energy Basis of Control in Aquatic Ecosystems. Ph.D. Dissertation. University of Florida. 200 pp.
- Kurz, R.C., D.C. Woithe, S.K. Notestein, T.K. Frazer, J.A. Hale, and S.R. Keller. 2004. Mapping and Monitoring Submerged Aquatic Vegetation in Ichetucknee Springs – 2004. Final Report. Prepared for Suwannee River Water Management District. pp. variously numbered.
- Marschner, H. 1995. Mineral Nutrition of Higher Plants. pp. 232–242. Academic Press, San Diego, CA.
- Meade, M.E. and S.A. Watts. 1995. Toxicity of ammonia, nitrite, and nitrate to juvenile Australian crayfish, *Cherax quadricarinatus*. Journal of Shellfish Research 14: 341-346.
- Mosisch, T.D., S.E. Bunn, P.M. Davies, and C.J. Marshall. 1999. Effects of shade and nutrient manipulation on periphyton growth in a subtropical stream. Aquatic Botany 64(2): 167-177.
- Mulholland, P.J., C.S. Fellows, J.L. Tank, N.B. Grimm, J.R. Webster, S.K. Hamilton, E. Martí, L. Ashkenas, W.B. Bowden, W.K. Dodds, W.H. McDowell, M.J. Paul, and B.J. Peterson. 2001. Inter-biome comparison of factors controlling stream metabolism. Freshwater Biology 46: 1503-1517.
- Mulligan, H. and A. Baranowski. 1969. Growth of phytoplankton and vascular aquatic plants at different nutrient levels. Proceedings- International Association of Theoretical and Applied Limnology 17d: 802-810.
- Munch, D.A., D.J. Toth, C. Huang, J.B. Davis, C.M. Fortich, W.L. Osburn, E.J. Philips, E.L. Quinlan, M.S. Allen, M.J. Woods, P. Cooney, R.L. Knight, R.A. Clarke, S.L. Knight. 2006. Fifty-year retrospective study of the ecology of Silver Springs, Florida. Publication Number: SJ2007-SP4. St. Johns River Water Management District, Palatka, FL.
- Nixon, S.W. 1995. Coastal marine eutrophication: A definition, social causes, and future concerns. Ophelia 41: 199-219.
- Notestein, S.K. 2001. Physical, Chemical, and Vegetative Characteristics of the Chassahowitzka River. M.S. Thesis. University of Florida. Gainesville, FL. 86 pp.
- Notestein, S.K., T.K. Frazer, M.V. Hoyer, and D.E. Canfield, Jr. 2003. Nutrient Limitation of Periphyton in a Spring-Fed, Coastal Stream in Florida, USA. Journal of Aquatic Plant Management: 41: 57-60.
- Odum, E.P., J.T. Finn, and E.H. Franz. 1979. Perturbation theory and the subsidy-stress gradient. BioScience 29: 349-352.
- Odum, H.T. 1956. Primary Production in Flowing Waters. Limnology and Oceanography 1: 102-117.

- Odum, H.T. 1957a. Primary Production Measurements in Eleven Florida Springs and a Marine Turtle-Grass Community. *Limnology and Oceanography* 2: 85-97.
- Odum, H.T. 1957b. Trophic structure and productivity of Silver Springs, Florida. *Ecological Monographs* 27(1): 55-112.
- Odum, H.T., O. Galindo, B. Parrish, R. Pinkerton, W.C. Sloan, and L.A. Whitford. 1953. Productivity of Florida Springs Factors controlling marine invasion in Florida fresh waters. Third semi-annual report to the Biology Division, Office of Naval Research 3: 134-156.
- Peltier, W.H. and E.B. Welch. 1969. Factors affecting growth of rooted aquatics in a river. *Weed Science* 11(4): 412-416.
- Peterson, B.J., L. Deegan, J. Helfrich, J.E. Hobbie, M. Hullar, B. Moller, T.E. Ford, A. Hershey, A. Hiltner, G. Kepphut, M.A. Lock, D.M. Fiebig, V. McKinley, M.C. Miller, J.R. Vestal, R. Ventullo, and G. Volk. 1993. Biological responses of a tundra river to fertilization. *Ecology* 74(3): 653-672.
- Rabalais, N. 2002. Nitrogen in aquatic ecosystems. *Ambio* 31: 102-112.
- Redfield, A.C., B.H. Ketchum, and F.A. Richards. 1963. The influence of organisms on the composition of sea-water. p. 26-77, v. 2. *In* M.N. Hill, E.D. Goldberg, C. O'D. Iselin, and W.H. Munk (Eds.). *The sea*. Interscience, London.
- Runge, M. 1986. Physiology and ecology of nitrogen nutrition. *In*: *Physiological Plant Ecology III: Responses to the Chemical and Biological Environment*. O.L. Lange, P.S. Nobel, C.B. Osmond & H. Ziegler, (Eds.), pp. 163-200. Springer-Verlag, Heidelberg-NewYork.
- Saindon, D. 2005. Quantifying the magnitude of nutrient limitation on phytoplankton in Kings Bay, Florida, USA. M.S. Thesis. University of Florida. Gainesville, FL. 41 pp.
- Scott, T.M., G.H. Means, R.C. Means, and R.P. Meegan. 2002. First magnitude springs of Florida. Open File Report No. 85. Florida Geological Survey. Tallahassee, FL. 138 pp.
- Scott, T.M., G.H. Means, R.P. Meegan, R.C. Means, S.B. Upchurch, R.E. Copeland, J. Jones, T. Roberts, and A. Willet. 2004. Springs of Florida. Bulletin No, 66. Florida Geological Survey. Tallahassee, FL. 677 pp.
- Steinman, A.D., P.J. Mulholland, and D.B. Kirschtel. 1991. Interactive effects of nutrient reduction and herbivory on biomass, taxonomic structure, and P uptake in lotic periphyton communities. *Canadian Journal of Fisheries and Aquatic Sciences* 48: 1951-1959.
- Stevenson, R.J., A. Pinowska, and Y.K. Wang. 2004. Ecological condition of algae and nutrients in Florida springs. Prepared for the Florida Department of Environmental Protection. Tallahassee, FL.

- Stevenson, R.J., A. Pinowska, A. Albertin, and J.O. Sickman. 2007. Ecological condition of algae and nutrients in Florida springs: The Synthesis Report. Prepared for the Florida Department of Environmental Protection. Tallahassee, FL. 58 pp.
- Strong, W.A. 2004. Temporal Water Chemistry Trends within Individual Springs and within a Population of Florida Springs. M.S. Thesis. University of Florida. Gainesville, FL. 54 pp.
- Tank, J. and W.K. Dodds. 2003. Responses of heterotrophic and autotrophic biofilms to nutrients in ten streams. *Freshwater Biology* 48: 1031-1049.
- Tsai, S.J. and J.C. Chen. 2002. Acute toxicity of nitrate on *Penaeus monodon* juveniles at different salinity levels. *Aquaculture* 213: 163-170.
- United States Environmental Protection Agency (USEPA). 2007. Nitrate web page fact sheet. Found at: <http://www.ead.anl.gov/pub/doc/nitrate-ite.pdf> Accessed December 2007.
- United States Fish and Wildlife Service (USFWS). 2001. Florida Manatee Recovery Plan, (*Trichechus manatus latirostris*), Third Revision. U.S. Fish and Wildlife Service. Atlanta, Georgia. 144 pp. + appendices.
- Walsh, S.J. and J.D. Williams. 2003. Inventory of fishes and mussels in springs and spring effluents of north-central Florida State Parks. Final Report submitted to the Florida Park Service. Gainesville, FL. 91 pp.
- Warren, C.E., J.H. Wales, G.E. Davis, and P. Doudoroff. 1964. Trout production in an experimental stream enriched with sucrose. *Journal of Wildlife Management* 28: 617-660.
- Wetland Solutions, Inc (WSI). 2006. Phase 2 Final Report. Pollutant Load Reduction Goal (PLRG) Analysis for the Wekiva River and Rock Springs Run, Florida. Report prepared for the St. Johns River Water Management District, Palatka, FL. 269 pp.
- Wetland Solutions, Inc (WSI). 2007a. Phase 3 Final Report. Pollutant Load Reduction Goal (PLRG) Analysis for the Wekiva River and Rock Springs Run, Florida. Report prepared for the St. Johns River Water Management District, Palatka, FL. 418 pp.
- Wetland Solutions, Inc (WSI). 2007b. Human Use and Ecological Water Resource Values Assessments of Rock and Wekiwa Springs (Orange County, Florida) Minimum Flows and Levels. Report prepared for the St. Johns River Water Management District, Palatka, FL. 285 pp.
- Wetzel, R.G. 2001. *Limnology: Lake and River Ecosystems*. Third edition. San Diego: Academic Press.
- Whitford, L.A. 1956. The Communities of Algae in the Springs and Spring Streams of Florida. *Ecology* 37(3): 433-442.

Managing Nutrient Inputs to Florida Springs: The Legal Framework

*Richard Hamann
Center for Governmental Responsibility
Levin College of Law
University of Florida*

Summary

The legal framework for managing the nutrient pollution of Florida springs is potentially as broad as the scope of human activities that contribute nutrients to the springshed. Regulations on the discharge of wastewater are key elements. The federal Clean Water Act and Safe Drinking Water Act provide a set of mandates and incentives for state programs. The focus of the Clean Water Act is protecting surface waters through the regulation of point source discharges under the National Pollutant Discharge Elimination System (NPDES). Discharges to groundwater may be regulated under this program if there is a “significant nexus” to the quality of navigable surface waters. The Safe Drinking Water Act protects public water supplies by establishing minimum criteria for drinking water quality and requiring states to regulate the underground injection of pollutants. Groundwater quality standards for nutrients are thus focused on the protection of public health. Florida has been delegated NPDES permitting authority by the Environmental Protection Agency (EPA) and implements an Underground Injection Control (UIC) program that is consistent with the SDWA. In addition, Florida regulates certain sources of nutrient pollution that do not fall within the direct jurisdiction of the federal program, such as nonpoint sources, agricultural discharges, and additional discharges to groundwater.

The regulatory program requires discharges to achieve effluent limitations based on the application of specified levels of technology or to achieve water quality standards, whichever is more stringent. Domestic wastewater treatment plants are generally only required to use secondary treatment, except in areas where the Legislature has required advanced wastewater treatment (AWT). Concentrated Animal Feeding Operations (CAFO) are currently regulated under state rules pending the adoption by EPA of a new federal rule. Those stormwater dischargers subject to NPDES permitting are required to reduce the discharge of pollutants to the Maximum Extent Practicable.

Florida’s surface water quality standards must be reviewed and approved by EPA every three years. They consist of designated uses, narrative and numeric criteria for each of those uses, and moderating provisions. There is also a general limitation on the degradation of any waters and a prohibition on the degradation of designated Outstanding Florida Waters (OFW). A narrative nutrient standard prohibits altering nutrient concentrations “so as to cause an imbalance in natural populations of aquatic flora or fauna.” Numeric standards can also be developed, most commonly as Total Maximum Daily Loads (TMDL).

TMDLs can be adopted by either EPA or the Florida Department of Environmental Protection (DEP). Florida's process begins with determining whether a particular waterbody is "impaired" based on "objective and credible data, studies and reports" demonstrating it does not meet water quality standards for a specific criterion, such as nitrogen or phosphorus. If there is sufficient data demonstrating the concentration of the specific pollutant causing the impairment, it can be added to the verified list. A TMDL is then calculated and the load reasonably and equitably allocated to the various sources and basins contributing pollutants. The DEP then assembles a group of stakeholders to develop a Basin Management Action Plan (BMAP) to develop strategies for implementing the adopted TMDL. NPDES permits may be revised as necessary to implement the BMAP. Other dischargers may be required to reduce their discharge "to the maximum extent practicable". Nonpoint sources must demonstrate compliance by either implementing Best Management Practices (BMP) or conducting water quality monitoring. There are additional powerful incentives for implementing BMPs. BMPs for nonagricultural sources may be adopted as rules by the DEP or a water management district. Only the Florida Department of Agriculture and Consumer Services (DACS) has the authority to adopt them for agricultural sources, although they must be verified by the DEP or a water management district.

Stormwater is a significant source of pollutants that can be regulated as a point source, because much of it is collected into pipes or channels, or as a nonpoint source, because much of it comes from diffuse sources and activities. The NPDES program regulates many of the larger stormwater systems and stormwater associated with industrial activities. Systems subject to NPDES permitting must be periodically reviewed and ways to reduce pollution must be considered in permit renewals. Most stormwater systems in Florida, however, are either unpermitted, regulated or regulated under an Environmental Resource Permit program or its predecessor. The emphasis of ERP permitting is on the design and construction of stormwater systems. Although they must be operated and maintained, there is no program for periodic review for compliance or enhancements. Because even systems that are constructed in compliance with the current standards discharge more pollutants than previously assumed, the DEP is now developing a unified stormwater rule. Many local governments also have their own stormwater programs.

Septic tanks and other Onsite Treatment and Disposal Systems (OSTDS) are another major potential source of nutrient pollution. The Department of Health (DOH) has adopted regulations for the construction and siting of septic tanks and drainfields. However, these systems are inefficient at removing nitrogen, a nutrient of concern in springsheds. In some areas where nutrients are a concern, such as the Florida Keys, performance-based systems have been required. Local governments can adopt more stringent requirements.

Local governments are required to periodically revise and implement comprehensive plans that can provide a framework for local springs protection. Local comprehensive plans and land development regulations can limit the intensity and design of land development to limit the contribution of nutrients to springs. They can provide for improved stormwater and wastewater management. The Florida Legislature has specifically required local governments in the Wekiva Study Area to amend their comprehensive plans to enhance springs protection. It has also limited the ability of local governments to regulate agricultural land uses and the conversion of

agricultural land to urban uses. Local governments are liable for compensating landowners who show an “inordinate burden”. A Consumer Fertilizer Task Force has recommended new restrictions on the ability of local governments to regulate the application of fertilizers.

REGULATION OF DISCHARGES

Clean Water Act

The Federal Water Pollution Control Act Amendments of 1972³ created one of our nation’s most comprehensive environmental statutes. It was enacted in response to widespread water pollution, including nutrient overenrichment, and the failure of the states and weak federal institutions to remedy it. The goal of the FWPCA was to “protect and restore the chemical, physical and biological integrity of the nation’s waters⁴” through a combination of research, planning, construction and regulation. The Act was amended in 1977 and renamed the Clean Water Act⁵ (CWA), but the fundamental structure and policies have remained intact for over 35 years.

The CWA prohibits any discharge of pollutants that is not authorized by a permit or otherwise in compliance with the Act⁶. Discharges may be authorized through a permit issued by EPA or a state under a program called the National Pollutant Discharge Elimination System (NPDES)⁷. The issuance of a permit depends on compliance with the most stringent effluent limitations based on either technology or water quality. Technology-based effluent limitations require the use of specified levels of technology for the prevention or removal of pollutants regardless of the impacts to water quality. Water quality-based effluent limitations impose additional limits on discharges to prevent violations of state water quality standards.

Not every source of nutrients to springs, however, qualifies as a regulated discharge under the definitions and exemptions of the CWA. A discharge is defined as “any addition of any pollutant to navigable waters from any point source”⁸. Nutrients certainly fall within the definition of a pollutant and many common sources of nutrients fit the definition of a “point source ” as a “discernible, confined and discrete conveyance” of pollutants⁹. Point sources might include wastewater treatment plants, industrial sources, concentrated animal feeding operations, or stormwater systems. Agricultural stormwater and irrigation return flows are expressly exempted from regulation, even though they might have the physical characteristics of a point source¹⁰. A spring itself might be considered a point source under this definition if it served to directly convey pollutants to navigable waters.

³PL 92-500, codified at 33 U.S.C. §§1251-1387 (2007).

⁴33 U.S.C. §1251(a) (2007).

⁵PL 95-217, Section 1.

⁶33 U.S.C. §1311(a) (2007).

⁷Id., §1342.

⁸Id., §1362(12).

⁹Id., §1362(14).

¹⁰Id.

Although the term “navigable waters” was defined in the Act as “waters of the United States¹¹”, the extent to which discharges to groundwater are subject to the CWA is not clear¹². Several judicial opinions held that Congress intended to exclude groundwater from the scope of regulation under this statute¹³. Other decisions have found jurisdiction over groundwater that is hydrologically connected to surface waters¹⁴.

The Supreme Court’s recent decision in *Rapanos v. United States*¹⁵ has further confused the scope of CWA jurisdiction in a case involving the discharge of dredged or fill material to wetlands. A plurality held that there was no jurisdiction over waters that were not relatively permanent streams or standing bodies of water and connected wetlands. One concurring justice, with the deciding vote, held that jurisdiction required a “substantial nexus” to waters that are navigable¹⁶. In interpreting these opinions, the 11th Circuit Court of Appeals recently held there might be no CWA jurisdiction over a discharge of pipe processing wastewater to a perennial stream that connected to navigable waters¹⁷. A “mere hydrologic connection” was insufficient. A “significant nexus” must be proved in a new trial, presumably by showing how the discharge could significantly affect the chemical, physical or biological integrity of the navigable waters.

A similar test would have to be met for any discharge of nutrients to groundwater to be subject to CWA regulation. There would have to be a relatively direct hydrologic connection to navigable waters and there would have to be proof that the discharge significantly affected the quality of

¹¹33 U.S.C. §1362(7)

¹²See generally, Thomas L. Casey, III, Reevaluating “Isolated Waters”: Is Hydrologically Connected Groundwater “Navigable Water” Under the Clean Water Act?, 54 Ala. L. Rev. 159 (2002).

¹³*Rice v. Harken Exploration Co.*, 250 F.3d 264 (5th Cir 2001); *Village of Oconomowoc Lake v. Dayton Hudson Corp.*, 24 F.3d 962, 965 (7th Cir. 1994); *Town of Norfolk v. United States Corps of Engineers*, 968 F.2d 1438, 1451 (1st Cir. 1992); *Exxon Corp. v. Train*, 554 F.2d 1310, 1322 (5th Cir. 1977); *Umatilla Water Quality Protective Ass’n, Inc. v. Smith Frozen Foods, Inc.*, 962 F.Supp. 1312, 1318 (D. Ore. 1997); *Kelley v. United States*, 618 F. Supp. 1103 (W.D. Mich. 1985).

¹⁴*U.S. Steel Corp. v. Train*, 556 F.2d 822, 852 (7th Cir. 1977); *Coldani v. Hamm*, 2007 U.S. Dist. LEXIS 62644 (E.D.Cal. 2007); *Idaho Rural Council v. Bosma*, 2001 U.S. Dist. LEXIS 9519 (D. Idaho 2001); *Washington Wilderness Coalition v. Hecla Min. Co.*, 870 F.Supp. 983, 990-991 (E.D. Wash. 1994); *Sierra Club v. Colorado Refining Co.*, 838 F.Supp. 1428, 1434 (D. Colo. 1993); *Williams v. PipeLine Co. v. Bayer Corp.*, 964 F.Supp. 1300, 1320 (S.D. Iowa); *Idaho Rural Council v. Bosma*, 143 F.Supp.2d 1169, 1180 (D. Idaho 2001); *McClellan Ecological Seepage Situation (MESS) v. Weinberger*, 707 F. Supp. 1182, 1196 (E.D.Cal.1988); *Friends of Santa Fe County v. LAC Minerals, Inc.*, 892 F. Supp. 1333, 1357 (D. New Mexico 1995).

¹⁵126 S.Ct. 2208 (2006).

¹⁶The requisite nexus could be shown if the subject wetlands “either alone or in combination with similarly situated lands in the region, significantly affect the chemical, physical, and biological integrity of other covered waters more readily understood as ‘navigable’”. 126 S Ct. 2248. Those effects cannot be “speculative or insubstantial” *Id.*

¹⁷*U.S. v. Robison*, 505 F.3d 1208 (11th Cir 2007).

those surface waters. The 9th Circuit Court of Appeals recently found such a significant nexus in a case involving the discharge of wastewater to a pond adjacent to a river¹⁸. Because the wastewater seeped into the river through a groundwater connection, affected the quality of the surface water and had a significant ecological connection through bird, mammal and fish populations, it was a regulated water¹⁹.

State Discharge Permitting

The DEP has assumed primary responsibility from EPA for implementation of the NPDES permitting program²⁰. For discharges to groundwater that do not have a sufficiently close connection to a surface water, however, only state law applies. Florida's regulatory authority over discharges that affect groundwater is more extensive than that of the federal Clean Water Act. The Florida Air and Water Pollution Control Act prohibits the construction or operation without a permit of any stationary installation reasonably expected to be a source of water pollution²¹. An "installation" is any "structure, equipment or facility which may emit . . . water contaminants. . ."²² "Pollution" is "the presence in the . . . waters of the state of any substances, contaminants, . . . or manmade or human-induced impairment of . . . waters, or alteration of the chemical, physical, biological, or radiological integrity of . . . water in quantities or at levels which are or may be potentially harmful or injurious to human health or welfare, animal or plant life, or property or which unreasonably interfere with the enjoyment of life or property, including outdoor recreation unless authorized by applicable law."²³ Finally, "waters" "include, but are not limited to, rivers, lakes, streams, springs, impoundments, wetlands, and all other waters . . . including underground waters"²⁴. The distinction in federal law between "point" and "nonpoint" sources and between "navigable waters" and groundwater is thus not very significant in Florida²⁵. The state, unlike EPA, has clear authority to regulate virtually any discharge to any water.

Several sections of Florida statutes authorize the DEP to adopt rules and issue permits for

¹⁸N.Cal. Riverwatch v. City of Healdsburg, 496 F.3d 993 (9th Cir. 2007).

¹⁹496 F.3d 1000-1001.

²⁰Fla. Stat. §303.0885 (2007); Rule 62-620, FAC. DEP assumed NPDES authority for industrial and domestic wastewater discharges in 1995 and stormwater discharges in 2000. See generally, Terry Cole, National Pollutant Discharge Elimination System Program, Ch. 12.2, Florida Environmental and Land Use Law (June 2007).

²¹Fla. Stat. §403.087(1) (2007).

²²Id., §403.031(1).

²³Id., §403.031(7)

²⁴Id., §403.031(13)

²⁵If a discharge is regulated under Florida law, but not subject to the Clean Water Act, however, then certain provisions adopted to allow the state to qualify for NPDES permitting do not apply. Id., §403.0885(2). For example, non-NPDES discharge permits can be issued for up to ten years, whereas NPDES permits are limited to five years. Id., §403.087(3). Unlike most other state permits, NPDES permits are not subject to issuance by default if the state fails to take action within ninety days. Id., 403.0885(3).

sources of pollution²⁶. If wastewater is discharged directly to groundwater via a well, then an Underground Injection Control (UIC) permit is required²⁷. Generally, dischargers are required to provide “reasonable assurance” that water quality standards will not be violated and that appropriate levels of treatment are being implemented. The rules applicable to certain significant sources are set forth below.

Domestic Wastewater

Domestic wastewater must generally receive a minimum of secondary treatment before it is discharged. Additional treatment may be required to meet water quality standards, depending on where the effluent is discharged. Discharges to groundwater can be made through a variety of systems, with different levels of public access²⁸. Treated wastewater is increasingly in demand for irrigation of areas where the public has access, e.g. golf courses and lawns. For dischargers to groundwater through sprayfields or rapid infiltration basins, the practical limit on nitrogen has generally been set by the Maximum Contaminant Level (MCL) for drinking water of 10 mg/l measured at the edge of the site or zone of discharge.

Advanced wastewater treatment has been required in areas where the Legislature has determined that the risks of regulatory uncertainty and delay should be reduced in favor of imposing the most protective requirements. For example, wastewater discharged to such estuaries as Sarasota Bay, Tampa Bay, Charlotte Harbor and their tributaries must meet advanced waste treatment standards²⁹. Special requirements have recently been imposed on domestic wastewater discharges in the Wekiva Study Area that may serve as a model for other areas contributing recharge to springs³⁰. These requirements were based on recommendations developed pursuant to the Wekiva Parkway and Protection Act³¹. The DEP first determined that 0.2 mg/l should be adopted as an initial target for nitrogen concentrations at the spring vents, based on unimpacted reference sites. The DEP also mapped the recharge areas according to their relative vulnerability.

²⁶Id., §§403.061(14), .087(2), (5), .088(2) (2007). The rules governing permitting are at Fla. Admin. Code r. 62-4 (2007).

²⁷Fla. Admin. Code r. 62-528 (2007).

²⁸Rule 62-610 provides different criteria depending on whether treated water feeds a reuse system or is applied to the land in slow or high rate systems with restricted or open access.

²⁹Fla. Stat. §403.086(1)© (2007). For nutrients, the AWT standard is Total Nitrogen, 3 mg/l and Phosphorus, 1 mg/l. Id., §403.086(4).

³⁰Fla. Admin. Code r. 62-600.550 was adopted April 13, 2006.

³¹Chapter 2004-384, Laws of Florida codified at Fla. Stat. §369.318(1) (2007). The Wekiva Study Area was delineated by the Florida Legislature, Id. §369.316, and includes large parts of the springsheds of Rock Spring, Wekiwa Spring and other springs feeding the Wekiva River. For the basis of recommendations specific to wastewater discharge see Florida Department of Environmental Protection, A Strategy for Water Quality Protection: Wastewater Treatment in the Wekiva Study Area (December 2004). For background information on the various planning and coordination activities related to the Wekiva Study Area see <http://www.dca.state.fl.us/fdcp/dcp/wekiva/wekivaact/index.cfm> (visited December 14, 2007).

The rule thus adopted three protection zones, with the Primary Protection Zone considered “Most Vulnerable”. The rule prohibits new or expanded sprayfields or rapid infiltration basins and absorption fields within the Primary Protection Zone³². Large existing facilities are limited to 3.0 mg/l Total Nitrogen. Increasing concentrations of nitrogen are allowed in areas of less vulnerability, for systems that have lower rates of application and for smaller systems whose costs of additional treatment are much higher. Dischargers can qualify for relief from these requirements by making “an affirmative demonstration, based on relevant water quality data, physical circumstances, or other credible information, that the discharge of reclaimed water is protective of surface and ground water quality with respect to the target nitrate-nitrogen level of 0.2 mg/l, as N, for the spring vent. . . .”³³

Industrial Discharges and Concentrated Animal Feeding Operations (CAFO)

Industrial wastewater is any regulated wastewater that is not domestic wastewater³⁴. Industrial dischargers must comply with technology-based effluent limitations developed for various industrial categories and adopted as rules, as well water quality-based effluent limitations³⁵. New sources must meet new source performance standards (NSPS). Existing sources are required to implement the best available technology economically achievable (BAT). For conventional pollutants such as Biological Oxygen Demanding materials (BOD5) or Total Suspended Solids (TSS), a less stringent effluent limitation is applicable, termed best conventional pollutant control (BCT).

Concentrated Animal Feeding Operations (CAFO) are a particular type of industrial discharger that generates substantial quantities of nutrients³⁶. The national regulations adopted by EPA have been challenged by both industrial and environmental interests³⁷. Final revisions have not yet been adopted³⁸. Florida will be required to implement the final federal rules, but meanwhile such facilities are governed by rule 40 C.F.R. pt. 412. Facilities that are not subject to NPDES permitting are governed by rule 62-670, F.A.C.³⁹

³²Fla. Admin. Code r. 62-600.550(4)(a)(2007). Technically these are termed “rapid-rate or restricted access slow-rate land application systems”.

³³Id., 62-600.550(7). This provision appears to allow the discharger to demonstrate that the discharge will achieve compliance with the target goal, not to challenge the goal itself.

³⁴Id., 62-660.200(2)(e).

³⁵Id., 62-660.400. DEP has adopted by reference the rules developed and adopted by EPA under the Clean Water Act.

³⁶ See generally, James H. Andreasen, Concentrated Animal Feeding Operations: A Program in Transition, *Natural Resources and Environment* 45 (Spring 2007). CAFOs produce 500 million tons of manure annually. Id. at 45.

³⁷*Waterkeeper Alliance v. U.S. Env’tl Protection Agency*, 399 F.3d 486 (2d Cir. 2005).

³⁸71 Fed. Reg. 37744 (June 30, 2006). The existing rules are at 40 C.F.R. pt 412.

³⁹The application of the rule, however, has been affected by court order in *Save Our Suwannee v. Fla. Dept. of Env’tl Protection*, ER FALR 04:181, Case No. 2001-CA-001266 (Fla. 2d Cir. Ct Mar. 5, 2004). See Susan L. Stephens, *Florida’s Waters: Significant Cases in the Works*, Section Reporter (March 2005). Environmental and Land Use Law Section, The Florida Bar. Available at <http://www.eluls.org>, visited February 23, 2008. DEP is

WATER QUALITY STANDARDS

Florida has established classifications and standards for both ground and surface water⁴⁰. One of the primary regulatory criteria for any discharge is that it not cause or contribute to violations of water quality standards⁴¹.

Groundwater Quality Standards

The DEP generally regulates discharges of pollutants to groundwater and has established a scheme of groundwater classification and standards.⁴² The standards for groundwater are primarily designed to protect human health⁴³. For example, all groundwater must be “free from” substances in concentrations which are carcinogenic, mutagenic, teratogenic, or toxic to human beings⁴⁴. The only protection for non-human organisms in the groundwater is for plants, animals and organisms native to the soil that are responsible for treating the discharge. A groundwater discharge is also prohibited from causing violations of the acute toxicity standard for surface water if it reaches the surface⁴⁵, cannot cause a nuisance, and cannot interfere with the reasonable beneficial use of adjacent waters. A nutrient discharge that causes the growth of algae resulting in allergic reactions by recreational users could violate these criteria. The difficulties of proving a causal relationship, however, are substantial.

Other standards applicable to groundwater depend on the classification. Generally, the groundwater that discharges to springs is likely to be Class G-II and for this classification the most important standard is the maximum contaminant levels (MCL) for drinking water⁴⁶. The only nutrient listed in the MCL is nitrate/nitrite which is limited to 10 mg/l⁴⁷. Groundwater quality standards thus protect spring discharges against only the highest levels of nutrient contamination..

engaged in rulemaking to revise rule 62-670 and adopt new rules for certain types of animal feeding operations. See draft rules 62-620, 62-621.500(3) & (3)(a).

⁴⁰Florida, like other states, must review its surface water quality standards every three years and submit any changes to EPA for review and approval. 33 U.S.C. §1313; 40 CFR Part 131.

⁴¹Fla. Admin. Code r.62-4.030, -4.070, -4.240(4) (2007).

⁴²See generally, Cynthia Christen, Groundwater Protection: An Overview, Ch 11.1, Florida Environmental and Land Use Law (Feb 2002).

⁴³Fla. Admin. code ch 62-520 (2007).

⁴⁴Id., 62-520.400(1)(b).

⁴⁵Rule 62-302.200(1) is the acute toxicity standard.

⁴⁶Rules 62-520.420; 62-550.310 (primary);62-550.320 (secondary). The federal Safe Drinking Water Act (SDWA), 42 U.S.C. §§300f-300j-26 (2007), requires states to regulate the quality of water delivered for human consumption through water supply systems. EPA adopts Maximum Contaminant Levels (MCL) as minimum criteria for drinking water. The SDWA also requires the states to regulate the discharge of pollutants to underground sources of water and MCLs have become commonly used to limit the contamination of groundwater and provide criteria for the remediation of contaminated sites.

⁴⁷Fla. Admin. Code r. 62-550.310 and Table 1. The level can be up to 20 mg/l under some circumstances.

Surface Water Quality Standards

Once groundwater reaches the surface at a spring, however, surface water quality standards apply and a discharge of nutrients to groundwater cannot be permitted if it would cause or contribute to a violation of surface water quality standards⁴⁸. Florida's surface water quality standards include a policy statement on nutrients⁴⁹. It states,

The Department finds that excessive nutrients (total nitrogen and total phosphorus) constitute one of the most severe water quality problems facing the State. It shall be the Department's policy to limit the introduction of man-induced nutrients into waters of the State. Particular consideration shall be given to the protection from further nutrient enrichment of waters which are presently high in nutrient concentrations or sensitive to further nutrient concentrations and sensitive to further nutrient loadings. Also, particular consideration shall be given to the protection from nutrient enrichment of those presently containing very low nutrient concentrations: less than 0.3 milligrams per liter total nitrogen or less than 0.04 milligrams per liter total phosphorus.

Water quality standards have two components, a classification of the designated use and standards applicable to that class of water. In addition, there are both a general nondegradation standard and special criteria applicable to Outstanding Florida Waters (OFW). The “moderating provisions” are also considered part of state water quality standards⁵⁰.

Most spring discharges in Florida will be Class III waters, whose designated use is “Recreation, Propagation and Maintenance of a Healthy, Well-Balanced Population of Fish and Wildlife”. A discharge cannot interfere with the designated use⁵¹. A discharge of nutrients that interfered with recreational swimming, for example, or the propagation of wildlife, would violate this criterion. In addition, a discharge cannot interfere with an existing use, which “may be different or more extensive than the designated use”⁵².

There are both minimum water quality standards, applicable to all classes, and numeric and narrative standards specific to each class. The minimum criteria prohibit discharge components which produce nuisance or toxic conditions⁵³. To the extent that nutrient discharges could have such effects, they would violate the minimum standards. In that case they would also be likely to

⁴⁸ Id., 62-4.070; 62-302.300(15).

⁴⁹ Id., 62-302.300(13)

⁵⁰ The moderating provisions include exemptions from water quality standards, Rule 62-4.243, mixing zones, rule 62-4.244 and site specific alternative criteria, rule 62-302.800.

Dischargers who are violating water quality standards can also continue to operate under the terms of an administrative order, apply for a variance or seek reclassification of the affected waters. See generally, Jennifer L. Fitzwater, Relief from Florida Water Quality Criteria, 12.4, Florida Environmental and Land Use Law (August 2003).

⁵¹ Fla. Stat. §403.021 (2007); Fla. Admin. Code r. 62-302.300(11), (14) (2007).

⁵² Id., 62-302.300(14). A discharger can, however, show that a particular use is not attainable and overcome this prohibition.

⁵³ Fla. Admin. Code r. 62-302.500(1).

violate the specific narrative standards for nutrients.

There is a general prohibition on any substances, including nutrients, “in concentrations which result in the dominance of nuisance species”⁵⁴. The narrative standard specific to nutrients states, “In no case shall nutrient concentrations of a body of water be altered so as to cause an imbalance in natural populations of aquatic flora or fauna.”⁵⁵ Determining the point at which an alteration of nutrient concentrations causes an imbalance can be extraordinarily difficult and conflicted. For example, in 1988 the United States sued the State of Florida and the South Florida Water Management District, alleging that operation of the water management system in South Florida caused an imbalance of flora and fauna⁵⁶. In 1992 the lawsuit was settled⁵⁷, but it was not until 2004 that a numeric criterion for phosphorus was finally adopted⁵⁸.

Florida’s nondegradation policy and implementing rules also control nutrient discharges. In addition to protecting existing and designated uses, the policy prohibits any degradation of water quality by a new discharge or the expansion of an existing discharge unless the degradation is “necessary or desirable under federal standards and under circumstances which are clearly in the public interest”⁵⁹. Degradation, for these purposes, includes “Man-induced nutrient enrichment (total nitrogen or total phosphorus). . .”⁶⁰. Factors for determining whether a discharge is clearly in the public interest are set forth at rule 62-4.242(1). Nutrient enrichment can be allowed by the DEP after considering and balancing these factors.

A related nondegradation standard protects waters that are designated as Outstanding Florida Waters (OFW) and thus entitled to the highest levels of protection⁶¹. Many of Florida’s springs are designated as OFWs in Rule 62-302.700, F.A.C.. The standard applies to discharges or activities that are located within the boundaries of an OFW or that contribute to significant degradation of the OFW. Existing ambient water quality cannot be lowered as a result of the proposed activity or discharge⁶². The term “existing ambient water quality” is defined as the water quality that could reasonably have been expected, based on the best scientific information

⁵⁴Id., 62-302.530(46).

⁵⁵Id., 62-302.530(47)(b).

⁵⁶United States v. S. Fla. Water Management Dist., Case No. 88-1886 (S.D. Fla.).

⁵⁷United States v. S. Fla. Water Management Dist., 847 F.Supp. 1567 (S.D.Fla.1992).

Enforcement of the resulting consent decree has been similarly controversial. U.S. v. S.F.W.M.D., 373 F.Supp.2d 1338 (S.D. Fla. 2005).

⁵⁸ Fla. Admin. Code r. 62-302.540 (2007). For a comprehensive review of the issues and process see Miccosukee Tribe of Indians v. Dept of Env’tl Protection, Final Order, DOAH Case No. 03-2872RP (June 17, 2004). Approval of the standards by EPA was also challenged. Miccosukee Tribe of Indians v. U.S., 2006 WL 648055 (S.D. Fla. 2006).

⁵⁹Fla. Admin. Code r. 62-302.300(17)(2007).

⁶⁰Id., 62-302.530 (47) (a) (Table).

⁶¹Id., 62-302.700, 62-4.242(2). A slightly more stringent rule applies to Outstanding National Resource Waters, which are given additional protection against degradation to the extent required by federal rule 40 C.F.R. 131.12. Fla. Admin. code r. 62-4.242(2)(3)(2007).

⁶²Id., 62-4.242(2)(a)2. The activity must also be “clearly in the public interest”. Id. Note that the rule contains numerous exceptions and qualifications to these requirements.

available, to have existed during the baseline year for the particular OFW (i.e. the year prior to designation) or the year prior to a permit application⁶³.

Specific numeric nutrient standards can be established in several ways. The Legislature required the DEP to establish a numerical criterion for phosphorus in the Everglades⁶⁴. Rule 62-40 provides for the development by water management districts or local governments of pollutant load reduction goals as part of watershed management plans or basin-specific criteria development⁶⁵. Most numeric criteria, however, are being developed as Total Maximum Daily Loads (TMDL), discussed below. The DEP also has an ongoing project to develop numeric criteria for nutrients that can be applied throughout the state⁶⁶.

TOTAL MAXIMUM DAILY LOADS

The Clean Water Act required the states to assess their waters to identify those areas where compliance with technology-based effluent limitations is not sufficient to achieve water quality standards⁶⁷. For those waters, the state is required to establish a total maximum daily load (TMDL) for relevant pollutants at a level sufficient to meet the standards or EPA is required to establish one. EPA and the states effectively ignored this requirement until citizen groups had prevailed in a number of lawsuits to force compliance with the statutory mandate⁶⁸. The result in Florida was a 1999 consent decree requiring EPA to establish TMDLs for almost 2000 waterbodies by 2011⁶⁹. The Florida Legislature responded by enacting the Florida Watershed Protection Act⁷⁰, which established a process for developing and implementing TMDLs by the state. Florida now has a very comprehensive process for assessing waterbodies, establishing TMDLs and developing Basin Management Action Plans (BMAP) to address water quality violations⁷¹. TMDLs and BMAPs are being developed to address nutrient pollution in many areas. Whenever the state fails to develop a TMDL that meets federal criteria or the requirements of the consent decree, then EPA must establish one⁷². The Florida Legislature has directed the DEP to take action to develop and implement TMDLs for several specific waterbodies, including

⁶³Id., 62-4.242(2)©

⁶⁴Fla. Stat. §373.4592(2)(m), (4)(e)(2007). The statute provided for a default standard of 10 ppb to be used if the scientific uncertainties could not be resolved sufficiently to adopt a rule by 2004. Id., §373.4592(4)(e)2.

⁶⁵Fla. Admin. Code r. 62-40.210 (20), .430 (2007). The Districts are authorized to develop strategies for meeting water quality standards in Surface Water Improvement and Management (SWIM) plans. Fla. Stat. §373.453(2)(e) (2007).

⁶⁶<http://www.dep.state.fl.us/water/wqssp/nutrients/index.htm>.

⁶⁷33 U.S.C. §1313(d) (2007).

⁶⁸OLIVER A. HOUCK, THE CLEAN WATER ACT TMDL PROGRAM: LAW, POLICY AND IMPLEMENTATION (2d Ed. 2002). Environmental Law Institute, Washington.D.C. ISBN 1-58576-038-2.

⁶⁹Florida Wildlife Federation v. Carol Browner, Case No. 4:98CV356-WS (N.D.Fla.).

⁷⁰Fla. Stat. § 403.067 (2007).

⁷¹DEP TMDL documents are available at <http://www.dep.state.fl.us/water/tmdl/index.htm>.

⁷²EPA TMDL documents are accessible at <http://www.epa.gov/OWOW/TMDL/>.

Lake Okeechobee and its tributaries⁷³, the Caloosahatchee⁷⁴, the St Lucie⁷⁵ and the Wekiva⁷⁶. Legislation has been proposed to require the development of TMDLs for additional springs⁷⁷.

Impaired Waters

For the purpose of developing TMDLs, the DEP has assigned all of the state's watersheds to one of five groups, which it reviews every five years. The cycle begins by determining whether there is sufficient quality data to prove that a particular waterbody is "impaired", as defined in the impaired waters rule⁷⁸, to justify placement on the planning list for further evaluation and assessment. A waterbody is impaired if there is "objective and credible data, studies and reports" demonstrating that it does not meet water quality standards for a specific criterion⁷⁹. The rule establishes stringent quality standards for the data that can be used in this assessment. If numeric criteria have been established, then narrative or biological criteria cannot be used as the basis for showing impairment unless the DEP demonstrates the numeric criteria are not adequate⁸⁰. If impairment is based on narrative or biological criteria, "the specific factors concerning particular pollutants shall be identified prior to a total maximum daily load being developed for those criteria. . .⁸¹" For interpreting the narrative nutrient criteria, the rule sets forth specific guidance:

Trophic state indices (TSIs) and annual mean chlorophyll a values shall be the primary means for assessing whether a water should be assessed further for nutrient impairment. Other information indicating an imbalance in flora or fauna due to nutrient enrichment, including, but not limited to, algal blooms, excessive macrophyte growth, decrease in the distribution (either in density or areal coverage) of seagrasses or other submerged aquatic vegetation, changes in algal species richness, and excessive diel oxygen swings, shall also be considered⁸².

Specific nutrient criteria are also specified for streams⁸³, lakes⁸⁴ and estuaries⁸⁵.

⁷³Fla. Stat. §§ 373.4595(1)(e)-(h), (l), ©, (4) (2007).

⁷⁴Id., § 373.4595(5).

⁷⁵Id., § 373.4595(l), ©, (4).

⁷⁶Id., § 369.318(1), (8).

⁷⁷Proposed Florida Springs Protection Act, SB 2394 (02/28/2008). Earlier proposed legislation also relied on a modified TMDL process. See e.g., SB 2368 (03/08/2005), 2005 Regular Session, The Florida Senate. Use of the TMDL program to protect Florida springs was proposed by students in the Conservation Clinic at the University of Florida Levin College of Law. See http://www.law.ufl.edu/conservation/springs_narrative.shtml (visited April 22, 2008).

⁷⁸Fla. Admin. Code r. 62-303 (2007).

⁷⁹Fla. Stat. § 403.067(3)(b) (2007).

⁸⁰Id., ©.

⁸¹Id.

⁸²Fla. Admin. Code r. 62-303.350(1) (2007).

⁸³Id., 62-303.351.

⁸⁴Id., 62-303.352.

The Verified List

The next step is to determine whether to list the waterbody on the “verified list”. For a water to be placed on this list due to nutrient enrichment, the DEP must have five years of data sufficient to develop a site-specific threshold for when an imbalance in flora or fauna occurs or to apply the generic thresholds for streams, lake and estuaries⁸⁶. To add a water to the verified list, the DEP must be able to “specify the pollutant or pollutants causing the impairment and the concentration of the pollutant(s) causing the impairment.”⁸⁷ For waters impaired by nutrients, the DEP must identify whether it is limited by nitrogen, phosphorus or both⁸⁸. Even if the water meets these criteria, it cannot be added to the verified list if the DEP determines that “existing or proposed technology-based effluent limitations and other pollution control programs under local, state, or federal authority are sufficient to result in the attainment of applicable water quality standards” in the future, with “reasonable progress” by the next cycle⁸⁹. The verified list must be submitted to EPA for review and approval and is subject to challenge in state administrative courts as a final order⁹⁰.

Calculation and Allocation

The development of a TMDL is the next step in the process for those waterbodies that reach the verified list. For each pollutant specified in the verified list, the DEP must calculate the amount that can be received from all sources without exceeding water quality standards⁹¹. In calculating the TMDL, the DEP must account for seasonal variations and “include a margin of safety that takes into account any lack of knowledge concerning the relationship between effluent limitations and water quality⁹².” The calculated load must then be allocated to the various sources contributing pollutants. The DEP may allocate loadings between point and nonpoint sources, among basins and among sources. The allocation must be “reasonable and equitable” and based on consideration of ten listed factors⁹³. TMDLs are adopted as rules by the Secretary. Detailed allocations may be left to the Basin Management Action Plan.

⁸⁵Id., 62-303.353. Open coastal waters are also included.

⁸⁶Id., 62-303.450.

⁸⁷Id., 62-303.710(1).

⁸⁸Id., 62-303.710(4).

⁸⁹Id., 62-303.600. An example of such a case is the Suwannee River Partnership. Ayşin Dedekorkut, *Suwannee River Partnership: Representation Instead of Regulation*, Ch 2 in JOHN T. SCHOLTZ AND BRUCE STIFTEL, EDS., *ADAPTIVE GOVERNANCE AND WATER CONFLICT: NEW INSTITUTIONS FOR COLLABORATIVE PLANNING* (2005). Resources for the Future, Washington, D.C. ISBN 1-933115-18-1.

⁹⁰Winston K. Borkowski, *Total Maximum Daily Loads in Florida— The New Millennium*, 12.5-5 in *Florida Environmental and Land Use Law* (June 2007).

⁹¹Fla. Stat. § 403.067(6)(a)2 (2007).

⁹²Id.

⁹³Id., §403.067(6)(b).

Basin Management Action Plans (BMAP)

Basin Management Action Plans (BMAP) are the foundation for implementation of an adopted TMDL. BMAPs are intended to integrate existing water management strategies to achieve water quality standards and equitably allocate pollutant reductions. They must include an implementation schedule, a basis for evaluating the plan's effectiveness, feasible funding strategies and mechanisms to address future increases in pollutant loading. Phased implementation is allowed. Credits may be granted to sources that reduced pollutant loads prior to development of the BMAP. The plan must include provisions for monitoring water quality and revising the plan in response to the results⁹⁴.

The BMAP may include such nonregulatory measures as public works construction, land acquisition, education, waste minimization, pollution prevention, interagency agreements and further planning⁹⁵. The BMAP must also affect permitting. NPDES permits may be reopened to incorporate conditions to implement the plan⁹⁶. If the NPDES permit regulates stormwater discharges, the obligation of the permittee is to implement "best management practices or other management measures" "to the maximum extent practicable."⁹⁷ For other permitted, nonagricultural dischargers, the pollutant reduction actions in the BMAP must be implemented "to the maximum extent practicable."⁹⁸

Nonpoint sources are also subject to the BMAP, thus bringing many of them within a regulatory framework for the first time. Nonpoint dischargers identified in the BMAP must demonstrate compliance by either implementing best management practices (BMP) or conducting water quality monitoring⁹⁹. A further incentive for implementing BMPs is that the discharger cannot be required to implement measures by "permit, enforcement action, or otherwise. . ."¹⁰⁰ BMPs provide a presumption of compliance with state water quality standards and release from liability for reimbursement of the Water Quality Assurance Trust Fund for contamination-related expenses¹⁰¹. BMPs thus set a maximum limit on regulatory requirements.

Mandatory BMPs must be adopted as rules by the DEP, a water management district or the Department of Agriculture and Consumer Services (DACS)¹⁰². The DEP and the water management districts have authority to adopt BMPs for "nonagricultural, nonpoint pollutant sources" and DACS has authority to adopt them for "agricultural pollutant sources". The

⁹⁴Id., §403.067(7)(a)5.

⁹⁵Id., §403.067(7)(b)1.b-f.

⁹⁶Id., §403.067(7)(b)2.a.

⁹⁷Id., §403.067(7)2.b.

⁹⁸Id., §403.067(7)2.b.f.

⁹⁹Id., §403.067(7)(b)2.g.

¹⁰⁰Id., §403.067(7)(b)2.i.

¹⁰¹Id., §403.067(7)(c)3. The shield also extends to research projects that are developing or demonstrating BMPs. Id.

¹⁰²Id., §403.067(7)©. The term "BMP" means what this section actually refers to as "interim measures, best management practices, or other measures necessary to achieve the level of pollution reduction established by the department. . ." Id.

effectiveness of all BMPs must be verified at representative sites by the DEP¹⁰³. An initial verification based on “best professional judgement” that BMPs are “reasonably expected to be effective” must be made by the DEP before BMPs are adopted as rules¹⁰⁴. If water quality problems persist despite the implementation of BMPs, they must be reevaluated and, if modifications are warranted, they must be implemented within a reasonable time period¹⁰⁵.

STORMWATER

Stormwater conveys nutrients to both ground and surface waters, and one of the objectives of stormwater regulation has been to control those inputs. In Florida, stormwater may be regulated by any combination of the DEP, a water management district or a local government, depending on where in the state the discharge is located, the date the discharge was permitted, the activity generating the stormwater and other permits that may be required for the facility.

Florida first enacted a comprehensive stormwater rule in 1982 to regulate the construction of new stormwater systems¹⁰⁶. Florida’s water management districts also exercised authority over the construction and operation of surface water management systems under Part IV of the Water Resources Act of 1972. To streamline permitting and eliminate duplication, the regulation of stormwater in most areas of the state today has been consolidated into an Environmental Resource Permit (ERP), issued by either the DEP or a water management district¹⁰⁷. Older permitting criteria still apply, however, to many existing developments or ongoing vested development activities. A further complexity stems from the phasing in of requirements for some stormwater dischargers to obtain NPDES permits. In order to achieve more uniformity in stormwater regulation and greater effectiveness in controlling nutrients, the DEP has begun the process of developing a new statewide stormwater rule¹⁰⁸.

The Water Resource Implementation Rule sets forth the goals for stormwater permitting¹⁰⁹. In addition to controlling pollution, the program is intended to maintain and restore salinity and flow regimes and groundwater recharge. It established the policy that if a stormwater system is designed to meet the criteria of the relevant rules, there is a rebuttable presumption that it will

¹⁰³Id., 403.067(7)(c)3

¹⁰⁴Id.

¹⁰⁵Id., 403.067(7)(c)4

¹⁰⁶Fla. Admin. Code r. 62-35 (2007). The Department of Environmental Regulation (DER), DEP’s predecessor, implemented the rule.

¹⁰⁷The division of responsibility between DEP and the water management districts is governed by operating agreements. ERP permitting authority may also be delegated to local governments. Many local governments also regulate stormwater under their own authorities. Stormwater utilities have become a popular means of paying for stormwater system maintenance and improvements.

¹⁰⁸DEP is proposing to develop Rule 62-347. A draft is not yet available. See http://www.dep.state.fl.us/water/rules_dr.htm#erp (visited 12-20-07). See also Chad Kennedy, DEP, Florida’s Unified Stormwater Rule Status, Presentation to Lake Okeechobee WRAC, November 2007 (Powerpoint slides available at sfwmd.gov).

¹⁰⁹Fla. Admin. Code r. 62-40.431(2)(a) (2007).

not cause or contribute to violations of state water quality standards and will achieve an 80% reduction in the average annual loading of pollutants. For stormwater discharges to Outstanding Florida Waters (OFW), the goal is a 95% reduction. Each of the water management districts has rules regulating the construction and operation of stormwater systems¹¹⁰. The criteria adopted by the Districts vary significantly, but all rely on a combination of retention, detention and filtration to meet the pollutant load reduction goals. A recent review of the criteria and site conditions, however, determined that current permitted designs only remove 40-50% of the nutrients¹¹¹. There may thus be no rational basis as to nutrients for the presumption.

A problem with the current criteria relevant to springs protection is that the goals for pollutant removal are intended to protect surface water quality. The retention of stormwater that recharges groundwater may contribute to achieving pollutant reduction goals for discharge to surface water, but it does so at the cost of transferring nutrients to the groundwater system. Only the St Johns River Water Management District has adopted any special criteria for groundwater protection. In a Sensitive Karst Area designated for parts of Alachua and Marion Counties special criteria apply to the construction and maintenance of stormwater basins to minimize the potential for the development of sinkholes or solution pipes to convey stormwater directly to the underlying aquifer¹¹². These criteria primarily help to maintain whatever treatment is provided by the system as designed and constructed. Deficiencies in treatment capability are somewhat addressed by requirements for additional soil in stormwater basins. In the Wekiva Recharge Area, special basin criteria require the retention of three inches of runoff on certain soils, but do not enhance the removal of pollutants conveyed to groundwater¹¹³.

ERP permits apply to both construction and operation of the permitted system. Once a system is permitted, and constructed as designed, however, the operation of the system is licensed in perpetuity. Provisions for continuing inspection and maintenance are relatively weak. Most importantly, there are no means for requiring older systems to be upgraded to incorporate additional pollution control measures¹¹⁴. The NPDES stormwater permitting system addresses that deficiency for a limited class of stormwater systems and, for discharges to nutrient impaired waters, the Basin Management Action Plans (BMAP) of the TMDL program may provide a means for requiring increased pollutant reductions.

¹¹⁰ St Johns River Water Management District, Id., 40C-42 (stormwater), 40C-41 (basin criteria), 40C-44 (agricultural surface water); South Florida Water Management District, Basis of Review for Environmental Resource Permit Applications (July 22, 2007); Northwest Florida Water Management District, Id., 62-346; Southwest Florida Water Management District, Id., 40D-4, 40, 400 and Basis of Review; Suwanee River Water Management District, Id., 40B-4.

¹¹¹ Harvey H. Harper and David M. Baker, Evaluation of Current Stormwater Design Criteria within the State of Florida (June 2007). Final Report to Florida Department of Environmental Protection, DEP Contract No. S0108.

¹¹² Fla. Admin. Code r. 40C-41.063(7) (2007).

¹¹³ Id., 40C-41.063(3)(a).

¹¹⁴ The general prohibition on causing or contributing to violations of water quality standards may still apply to permitted systems, but that is difficult to enforce.

NPDES Stormwater Permitting

Many of the facilities that collect and convey stormwater to navigable waters clearly meet the federal definition of a “point source”. Nevertheless, because such systems often collect pollutants generated by many other sources and are controlled by government entities, Congress and EPA delayed requiring NPDES permits for many years. In 1990 EPA began to phase in a regulatory program¹¹⁵. Phase I required NPDES permits for larger municipal separate storm sewer systems (MS4), large construction sites and some industrial sites. In 1999, Phase II extended the program to smaller municipalities and construction sites¹¹⁶. Authority to implement the program has been delegated to the DEP, which has adopted NPDES stormwater rules¹¹⁷. These rules require monitoring, the development of a Stormwater Management Program (SWMP) and the reduction of pollutants discharged to the Maximum Extent Practicable¹¹⁸. Because MS4 stormwater permits cannot be issued for longer than 5 years¹¹⁹, permit renewal provides an opportunity not currently available through the ERP program to require improved performance and correction of problems.

SEPTIC TANKS

Septic tank and drainfield systems, a type of Onsite Sewage Treatment and Disposal System (OSTDS), are used to treat the wastewater of approximately 1/3 of Florida’s population and are a major source of artificial groundwater recharge.¹²⁰ OSTDS are regulated by the Department of Health under authority intended to ensure they do not “adversely affect the public health or significantly degrade the groundwater or surface water¹²¹.” Traditional septic systems can be installed in subdivisions of up to four lots per acre, provided the lots are also served by a public water supply and other criteria are met; if there is no public water supply, the minimum lot size is one half acre. Septic systems must be sized according to the projected load and meet standards for the quality of the soils, depth to the water table, and setbacks from wells and surface water bodies. Generally, there must be 42 inches of suitable soils below the bottom of the drainfield¹²² and it must be at least two feet above the wet season water table¹²³. The drainfield must be set back at least 75 feet from a permanent surface water and 15 feet from a swale or retention area. These standards provide for treatment of wastewater by the soil, which is generally very effective in removing pollutants, with the exception of nitrogen. The criteria can be substantially relaxed for lots in older subdivisions¹²⁴. Variances may also be granted to relieve hardships where there is no reasonable alternative for waste disposal and the onsite system will not

¹¹⁵55 FR 47990 (Nov. 16, 1990).

¹¹⁶64 FR 68722 (Dec 8, 1999).

¹¹⁷Fla. Admin. Code r.62-624 (2007) (MS4).

¹¹⁸Id., 62-624.500.

¹¹⁹Id., 62-624.300(5).

¹²⁰Florida Department of Health, Nitrogen Impact of Onsite Sewage Treatment and Disposal Systems in the Wekiva Area 1-20, 3 (June 30, 2007).

¹²¹Fla. Stat. §381.0065(1) (2007). Fla. Admin. Code r. 64E-6 provides standards for OSTDS.

¹²²Id., 64E-6.006(1).

¹²³Id., 64E-6.006(2)

¹²⁴Fla. Stat. §381.0065(4)(g)(2007).

adversely affect health or “significantly degrade the groundwater or surface waters¹²⁵.”

Alternatives to traditional systems that are designed by engineers to meet specified performance standards must be approved¹²⁶. Alternatives include aerobic treatment systems and so-called performance-based treatment systems. The owner of such a system must have a maintenance contract with an approved entity and an operating permit from the County Health Department¹²⁷. Whenever a central sewer system becomes available, the owner of an OSTDS can be required to connect to it¹²⁸.

More restrictive criteria for OSTDS have been adopted by statute for the floodways of the Suwannee and Aucilla Rivers¹²⁹ and the Florida Keys¹³⁰. Recommendations for improved regulation of OSTDS have been made for systems installed in the Wekiva Study Area¹³¹.

Local governments can adopt more stringent regulations on construction, performance, setbacks or maintenance of OSTDS through local comprehensive plans and land development regulations. For example, in the Green Swamp Area of Critical State Concern, two counties have adopted ordinances requiring periodic maintenance. Wakulla County requires higher levels of nitrogen removal by installation of performance-based systems.

LAND USE PLANNING AND REGULATION

The loading of nutrients to a spring is closely related to the type, intensity and design of land uses in the springshed. Regulatory programs affect land use, but do not provide the kind of comprehensive planning and control of land use that is required to manage nutrient inputs. Florida’s growth management system emphasizes the development and implementation of local government comprehensive plans to control land use.

Florida’s Local Government Comprehensive Planning and Land Development Regulation Act¹³² (hereinafter “Growth Management Act”) requires every local government in the state to adopt, periodically revise and implement a local comprehensive plan. The local comprehensive plan must be “consistent” with the goals, objectives and policies of the State Comprehensive Plan¹³³ and the strategic regional policy plan of the relevant Regional Planning Council¹³⁴. The Florida

¹²⁵Id., §381.0065(4)(h).

¹²⁶Id., §381.0065(4)(j).

¹²⁷Id., §381.0065(4)(j)4.

¹²⁸Id., §381.00655.

¹²⁹Id., §381.0065(4)(t)(2007). The regulatory floodway is defined to include the 10 year floodplain.

¹³⁰Fla. Admin. Code r. 64E-6.017-.0182 (2007).

¹³¹Florida Department of Health, Nitrogen Impact of Onsite Sewage Treatment and Disposal Systems in the Wekiva Area 1-20, 16-17 (June 30, 2007).

¹³⁰Fla. Stat. ch. 163, Pt. II (2007).

¹³³Id., ch 187.

¹³⁴Consistency of the local comprehensive plan with the state comprehensive and the strategic

Department of Community Affairs (DCA), which oversees the process at the state level, has adopted criteria in Rule 9J-5 for making such determinations. The Act requires that local land development regulations be consistent with and implement the goals, objectives and policies of the adopted comprehensive plan¹³⁵. It also requires that land development be consistent with the adopted plan¹³⁶.

A local government's comprehensive plan must incorporate various elements potentially relevant to protecting springs and springsheds. Four of the most pertinent elements are: a Future Land Use Element; a Sanitary Sewer, Solid Waste, Drainage, Potable Water, and Natural Groundwater Recharge Element; a Conservation Element; and an Intergovernmental Coordination Element. The Future Land Use element must include protections for potable water wellfields and protection of environmentally sensitive lands¹³⁷. The Sanitary Sewer, Solid Waste, Drainage, Potable Water, and Natural Groundwater Recharge Element requires identification of natural drainage features/groundwater recharge areas, assessment of current land use regulations related to these issues, and objectives and policies for implementation of land use regulation to protect drainage and recharge functions¹³⁸. The Conservation Element must identify natural resources, including groundwater, and incorporate objectives and policies to conserve such resources¹³⁹. Finally, the Intergovernmental Coordination Element requires analysis of current intergovernmental coordination, specific objectives for future coordination, and policies addressing each objective¹⁴⁰. This element could serve a crucial role in encouraging the intergovernmental coordination necessary for effective protection of springsheds that lie in more than one local government. Coordination also must exist to adequately account for springs protection during water supply planning and under water management district regulatory programs. Sources of water supply adequate to provide for planned growth must be identified. Furthermore, when the Department of Community Affairs (DCA) gives assistance to local governments with their comprehensive plan, DCA must consider, among other things, groundwater recharge.

Local governments must evaluate and update their comprehensive plans every seven years¹⁴¹. This evaluation includes consideration of water management district regional water supply plans

regional policy plan exists if the local plan is compatible with and furthers those plans. It is "compatible" if it does not conflict and it "furthers" a plan if it takes "action in the direction of realizing" the goal or policies of the plan. *Id.*, § 163.3177(10)(b).

Consistency with regional water supply plans is also effectively required. *Id.*, § 3177(6).

¹³⁵*Id.*, § 163.3194, .3202.

¹³⁶*Id.*, § 163.3194(1).

¹³⁷*Id.*, § 163.3177(6)(a) (2006). Fla. Admin. Code r. 9J-5.006 (2007).

¹³⁸ Fla. Stat. § 163.3177(6)© (2007). Fla. Admin. Code r. 9J-5.011(2007).

¹³⁹ Fla. Stat. § 163.3177(6)(d) (2007). Fla. Admin. Code r. 9J-5.013 (2007).

¹⁴⁰ Fla. Stat. § 163.3177(6)(h) (2007). Fla. Admin. Code r. 9J-5.015 (2007).

¹⁴¹ Fla. Stat. § 163.3191 (2007).

and any groundwater issues identified as “major”¹⁴². Water management districts, the DEP, and DCA all have an opportunity to comment on draft evaluations of local government comprehensive plans, thus giving them a chance for input to help protect springs. Only the DCA, however, has the authority to determine that an amendment is not in compliance with the Act¹⁴³. The DCA and the DEP have published a handbook for local governments to use in developing policies for springs protection¹⁴⁴. The DCA is also developing a model land development code for springs protection¹⁴⁵.

The state has assumed a stronger role in supervising local land use decisions in certain areas of the state. The Governor and Cabinet, sitting as the Administration Commission, is authorized to designate “areas of critical state concern” in order to promote protection of and reverse deterioration of water resources in those areas¹⁴⁶. The statute authorizing areas of critical state concern specifically refers to environmental resources and aquifer recharge areas¹⁴⁷. Local comprehensive plans and land development regulations must be consistent with Principles for Guiding Development adopted by the Administration Commission¹⁴⁸. The protection of water quality has clearly been an important goal for designating ACSC such as the Florida Keys, Big Cypress, and Green Swamp¹⁴⁹. While designation as an area of critical state concern could help preserve springs, only five percent of the state can be so designated, thus limiting the usefulness of this tool in its current form.

The Florida Legislature can also specifically compel local governments to adopt policies to protect certain springs. In the Wekiva Parkway and Protection Act, the Legislature required each local government within the Wekiva Study Area to amend appropriate elements of its comprehensive plan to implement a master stormwater management plan and “establish land use strategies that optimize open space and promote a pattern of development on a jurisdiction-wide basis that protects the most effective recharge areas, karst features, and sensitive natural habitats including Longleaf Pine, Sand Hill, Sand Pine, and Xeric Oak Scrub¹⁵⁰.” Legislation proposed to protect Silver and Rainbow Springs would require local governments to “adopt local land

¹⁴²Id., §163.3191(1)© (2007).

¹⁴³Id., §163.3184 (2007). DCA’s determination is, however, subject to challenge before an administrative law judge and an ultimate determination, based on that record, by the Administration Commission.

¹⁴⁴Fla. Dept. of Env’tl Protection and Fla. Dept. of Community Affairs, Protecting Florida’s Springs: Land Use Planning Strategies and Best Management Practices (November 2002). Available at <http://www.dca.state.fl.us/fdcp/dcp/publications/index.cfm> (visited Jan 8, 2008).

¹⁴⁵<http://www.dca.state.fl.us/fdcp/DCP/springs/index.cfm> (visited Jan. 8, 2008).

¹⁴⁶Fla. Stat. §380.05 (2007)..

¹⁴⁷Id., §380.05(2)(a) (2007).

¹⁴⁸Id., § 380.05(1)(b)2

¹⁴⁹<http://www.dca.state.fl.us/fdcp/dcp/acsc/index.cfm> (visited Feb 13, 2007).

¹⁵⁰Fla. Stat. §369.321(3) (2007).

development regulations and other local requirements to minimize harmful impacts to the springs¹⁵¹.”

State statutes can also limit the authority of local governments to plan and regulate for springs protection. For example, agricultural activities do not fall within the scope of “development” for the purposes of comprehensive plans and thus are not regulated by comprehensive plans¹⁵². Local governments may not enforce new regulations for agricultural activities already regulated by or subject to best management practices promulgated by DEP, the Department of Agriculture and Consumer Services (DACS), a water management district, or a federal entity¹⁵³. Thus, while agriculture is a significant contributor of nutrients to springs and springsheds in many areas of the state, counties and municipalities have limited authority to improve their regulation of agricultural practices.

Local governments have also been prohibited from restricting the density of residential and commercial development in so-called “agricultural enclaves¹⁵⁴,” and cannot impose an “inordinate burden” on any landowner without payment of compensation¹⁵⁵.

One area of current controversy concerns the authority of local governments to regulate the use of fertilizers within their jurisdictions. Many local governments have adopted or proposed regulations to limit nonagricultural fertilizer use¹⁵⁶. Apparent concern for regulatory overreaching and confusion led the 2007 Legislature to create a Consumer Fertilizer Task Force¹⁵⁷. Among the charges to the was the following:

Recommending methods to ensure local ordinances are based on best available data and science and to achieve uniformity among local government ordinances where possible, unless local ordinance variations are necessary to meet mandated state and federal water quality standards¹⁵⁸.

The Task Force report recommends legislation to authorize local governments to regulate fertilizer use by adopting a specified “model ordinance”¹⁵⁹. Local governments could adopt more

¹⁵¹Proposed legislation 10-16-07, adding section 369.406(1), F.S.

¹⁵²Fla. Stat. § 380.04 (2007), referred to by Id., §163.3164(6).

¹⁵³Id., §§ 163.3162, 823.14(6); J-II Investments v. Leon Cty., 908 So. 2d 1140 (Fla. 1st DCA 2005).

¹⁵⁴Fla. Stat. §§163.3162(5), (33) (2007).

¹⁵⁵Id., §§70.001-.80.

¹⁵⁶See the undated compilation of “local fertilizer use ordinances” at <http://consensus.fsu.edu/Fertilizer-Task-Force/legislation.html> (visited April 22, 2008).

¹⁵⁷S. 10, Ch. 2007-232, Laws of Florida, codified at Fla. Stat. §576.092 (2007).

¹⁵⁸Id., §576.092(2)(a)4.

¹⁵⁹Florida Department of Agriculture and Consumer Services, Florida Consumer Fertilizer Task Force, Final Report to the 2008 Florida Legislature, Appendix # 4 (January 15, 2008)

stringent limitations only under the following conditions:

- They have verified impaired waters and are facing existing or possible TMDL requirements (under state and federal laws); or
- They have verified harm to human health or harm to the environment that warrants additional consumer fertilizer requirements; or
- That they will improve water quality or prevent future impacts of consumer fertilizers on the environment¹⁶⁰. The 2008 Legislature is considering bills to implement the Task Force recommendations¹⁶¹.

Available at <http://consensus.fsu.edu/Fertilizer-Task-Force/index.html> (visited April 22, 2008).

¹⁶⁰ Id.

¹⁶¹ S2352 and H1267, 2008 Regular Session, Florida Legislature.

Synthesis of Nutrients and Springs: Knowns, Unknowns, Research Priorities and Management Implications

*Mark T. Brown
Center for Environmental Policy and
Department of Environmental Engineering Sciences
University of Florida*

Summary

This summary of the state of the knowledge related to nutrient effects on spring ecosystems and biota draws from the proceeding seven chapters of this report. It represents a synthesis of the most important findings; greater details can be found within each of the chapters. This synthesis chapter is organized into three parts:

- 1) a summary of the “knowns” regarding nutrient effects on springs and spring biota,
- 2) the unknowns and suggestions for future research, and
- 3) suggestions for a research and adaptive management program for spring ecosystems in Florida.

Florida springs are undergoing change. It is clear that nutrient loads within springsheds, particularly nitrate-N, from anthropogenic sources are increasing. These loads have apparently increased the quantities of nitrogen in shallow and deep ground waters. Nitrogen, but not phosphorus, concentrations in the discharges of many springs have increased in the past several decades. There are numerous other biotic and abiotic factors that have also changed in some, but not all springs, such as increased recreational use, decreased discharges, decreased O₂ concentrations in discharges, increased aquatic weed control, invasive species, and increased salinities. By themselves or in combination, these factors may explain the changes Florida's springs have experienced in the last several decades.

There is a general consensus in the management community that nitrate-N is an important cause of change in spring ecosystems and biota. In summary, control of nitrate-N appears warranted, indeed critical, since nitrate-N has been linked to many detrimental impacts in both ecological and human systems (obviously this is true of all watersheds, not just the karst regions of Florida). The fact that nitrate-N is likely to be nearly conservative in the groundwater, and since much of the increased loads are believed to be of human origin, suggests that efforts to control nitrate loads should be focused at the springshed scale and focus on its control prior to delivery to the soil and ultimately to the aquifer.

Few studies have been able to provide a threshold value for nitrate-N at which impacts begin. The literature suggests that in addition to nitrate-N, discharge and dissolved oxygen, which show short-term and perhaps long-term correlation with nitrogen should receive more attention in the

future as potential causes of ecosystem change in springs. Other stressors in combination or separately may be important causes of change in spring ecosystems as well.

After reviewing the literature, an adaptive management and research program that faces these uncertainties directly and uses them to learn and change is proposed. This proposal combines management interventions with targeted monitoring to make them more useful as scientific experiments that form the basis for learning and adaptive change. We call for a grand experiment through the creation of Adaptive Springshed Action Programs (ASAPs) as a way of developing a statewide response to the declines in ecosystem health observed of many springs. The proposed ASAPs will develop an environment within which meaningful research, education, social learning, and management can occur for the betterment of Florida's spring ecosystems.

INTRODUCTION

This review of the literature was conducted in response to a request by the Florida Springs Initiative of the Florida Department of Environmental Protection (DEP) for a summary and interpretation of the available information on the effects of nutrients on spring organisms and systems. DEP's mandate was to prepare a review of what is known about the interactions between nutrients and springs, what information gaps exist that inject substantial uncertainty into management and restoration of springs, and what policy and research could be used to address these gaps. This summary of knowledge related to nutrient effects on spring ecosystems and biota represents a synthesis of the most important findings from the literature related to Florida springs along with important findings studies in other aquatic systems.

To address the complexity of spring ecosystems, we developed a multi-chapter review conducted by several units at the University of Florida (UF) and Wetland Solutions, Inc.. The UF Water Institute provided project management, and other groups were responsible for different chapters in the literature review:

1. Springs as Ecosystems – Wetland Solutions Incorporated
2. Springshed Nutrient Loading, Transport and Transformations – UF –School of Forest Resources and Conservation
3. Biogeochemical Processes and Implications for Nutrient Cycling – UF –Department of Soil and Water Science
4. Nutrient Effects on Spring Flora and Fauna – UF Department of Fisheries and Aquatic Sciences
5. Invasive Aquatic Plants and Aquatic Plant Control in Florida Springs – UF –School of Forest Resources and Conservation
6. Effects of Nutrients on Spring Ecosystems – Wetland Solutions Incorporated
7. Managing Nutrient Inputs to Florida Springs: The Legal Framework – UF –Center for Governmental Responsibility
8. Synthesis of Nutrients and Springs – UF –Center for Environmental Policy

This chapter, organized into three parts, summarizes the details from other chapters in an attempt to synthesize knowledge regarding effects of nutrients; recommends additional research for discussion with a broad group of stakeholders; and outlines an approach to future policy and management.

PART 1 - NUTRIENTS and SPRINGS: State of the knowledge

Fate, Transport, and Transformation: *What we know*

There is growing evidence that nitrate concentrations are increasing in the water discharging from springs (Chapter 2). Indeed, increasing nitrate concentrations in freshwater is not just a Florida or karst problem, but rather a global problem. Human populations have altered the global nitrogen cycle and other biogeochemical cycles through land use changes, fertilizer use, fossil fuel combustion and other pathways. With population and land use change comes nutrient

enrichment. Florida's karst region has experienced unprecedented population growth and changes in land use over the past several decades, with a consequent transfer of nutrients to the relatively unprotected groundwater.

Among the nutrients of concern, nitrogen, particularly nitrate, appears to be most problematic in Florida's karst region. There are four primary reasons for greater concern about nitrate-N than phosphorus. First, increases in concentrations of nitrate-N are nearly omnipresent in areas where anthropogenic loading to the land's surface has occurred. Second, once in the ground water, nitrate-N appears to be transported as a conservative solute, with denitrification apparently being negligible (Chapter 2). Third, although Florida's geology is naturally rich in phosphorus, there does not appear to be a trend of increasing phosphorus concentrations in spring discharges (Chapter 2, 4, and 6). Second, because springs are naturally rich in phosphorus, the majority of Florida springs may be historically nitrogen limited (Chapter 3, 6).

Given the importance of nitrate-N and its role as a driver of primary production in many aquatic systems, for better or for worse, the loading, fate, transport, and transformation of N appear to be the aspect of springs that has received the most study. Some general principles and caveats have emerged from this work (Chapter 2):

- Emphasis on nitrate-N loading has been prioritized because of strong evidence for anthropogenic enrichment on groundwater N in the karst environment of North Florida while contemporaneous evidence for broad-scale enrichment of P has not been accumulated.
- Because there is no geologic store of N, all of the nitrogen emerging in spring vents was deposited on the land surface.
- Where data exists, evidence suggests that overall, the increases in loading have resulted in 10 to 350 fold increases in concentrations of nitrate-N in spring discharges over the past 50 years. As a consequence of these increases in groundwater nitrate-N concentrations, downstream nitrate-N loads are increasingly rapidly in many watersheds. For example, a two to three-fold increase in nitrate export to the Gulf by the Suwannee River has been documented over the past 5 years.
- Delineation of springsheds has direct bearing on loading calculations but delineation is not an exact science.
- The underground reservoir from which spring flow derives may be extremely large, and hence nominal residence times can be long and extremely variable between springs.
- Some aging measurements of water emerging from springs suggest, on average, it has spent between 10 and 30 years in the subsurface, but that a significant portion of water (30-70%) has residence times less than 4 years. Relative age contributions can vary from spring to spring.
- Biological fixation of nitrogen has not been taken into account in most loading studies; an omission that may account for as much as 30 to 35% of the contemporary nitrogen budget.
- Based on differences between N loads applied to the land within springsheds and N in spring discharges, attenuation within springsheds appears to be significant

(~90%), but this apparent attenuation may be the result of lag times between application and emergence.

- Estimates of nitrate and total nitrogen loading in various Florida springsheds suggest that over half the apparent loads to the land surface result from fertilizer application on either urban or agricultural lands. Additional loads result from livestock manure and wastewater septic systems. Atmospheric N deposition is generally less than 10% in most studies, but it can account for as much as 26% in some rural springsheds.
- Isotopic characteristics of nitrate-N emerging from springs appears to provide evidence of mixed sources (i.e., mineral fertilizers, organic wastes), but use of isotopes for management purposes requires flowpath tracking and consideration of transformations along the flow path.

Biogeochemical transformations of nutrients in spring systems (Chapter 3) have been little studied. What we know of elemental cycling and nutrient transformations is gleaned from the general literature on lotic environments:

- In general, transformations are most prominent in biofilms, algal mats, and the hyporheic sediments resulting from a variety of processes including: organic matter decomposition, nitrogen fixation, nitrification /denitrification, iron reduction, and sulfate reduction, among others. While these processes have been studied in other lotic environments, there is very little information regarding these processes in spring systems.
- In their historical natural state, most Florida springs contain high levels of bioavailable phosphorus (P) (Soluble Reactive Phosphorus [SRP] levels of between 30-60 ppb),
- There are suggestions that once established, algal mats may play a significant role in nutrient transformations and eventual nutrient storage, making reversal of current conditions where algae dominate spring primary producers problematic.

In summary, control of nitrate-N appears warranted, indeed critical, since nitrate-N has been linked to many detrimental impacts in both ecological and human systems (obviously this is true of all watersheds, not just the karst regions of Florida). The fact that nitrate-N is likely to be nearly conservative in the groundwater, and since much of the increased loads are believed to be of human origin, suggests that efforts to control nitrate loads should be focused at the springshed scale and focus on its control prior to delivery to the soil and ultimately to the aquifer. Given that springsheds are heterogeneous surfaces of topography, soils, and vegetation, with subsurface confining layers that are not ubiquitous, detailed land use planning should figure prominently in controlling loads. Best Management Practices (BMPs) in confined regions are of value (although, there is some disagreement on the effectiveness of BMPs), but in unconfined regions where groundwater recharges rapidly and there is little opportunity to store and treat stormwater on the surface, BMPs alone may be insufficient to prevent groundwater nitrate enrichment.

Effects of Nutrients on Spring Organisms and Systems: *What we know*

There is no question that Florida's spring ecosystems are undergoing change. An apparent increase in the dominance of filamentous algae in many springs, losses of desirable submerged aquatic vegetation (SAV, e.g., native vascular species such as *Vallisneria americana* or

Sagittaria kurziana), increases in invasive vegetation forms, and anecdotal evidence of the disappearance of grazers and higher order animals all point to significant structural and functional changes in spring ecosystems. It is a widely held belief that these observed changes are the result of anthropogenic enrichment of nutrient levels in groundwater discharges and the consequent eutrophication of the spring ecosystem. Certainly, the correlative evidence (in the time domain) points in that direction, yet the apparent correlation between increased nitrate loading and increases in filamentous algae in spring ecosystems has only anecdotally provided evidence for a causative relationship between these phenomena (Chapters 4 and 6). Further, the belief that increased algal biomass has led to the displacement of native macrophytes appears to be based largely on extrapolation from laboratory studies or qualitative observations (Chapter 4). Overall, this review of the literature suggests, that there is little direct evidence linking increases in filamentous algae observed in many springs with increased nitrate delivery to spring systems (Chapter 4). This is not to say that causality does not exist, only that direct quantifiable evidence has yet to be demonstrated.

These changes in springs parallel a eutrophication progression scheme proposed for shallow and relatively open coastal systems (see Duarte 1995). This scheme suggests that increased delivery of dissolved nutrients to aquatic systems will favor production of fast-growing algae that extract their nutrients primarily from the water column. These algae may ultimately out-compete and displace slower growing vascular plants that rely primarily on nutrients in sediment and require more light. In the scheme, algal growth can create feedback loops that exacerbate the shift to algal dominance and decouple the system from nutrient concentrations in the water column. For example, increased organic matter or eutrophication can lead to decreased oxygen levels that can stress vascular plants and displace or kill grazers that might control algae. Although the changes in Florida springs appear consistent with this scheme, other information from spring systems raises questions, including: 1) the possibility that flux of nutrients in springs is a more potent driver of primary productivity than water-column concentrations, 2) the potential that flux obviates nutrient limitation for most flora even at historical and low concentrations, and 3) the possibility that the observed parallels to the eutrophication scheme initially arose from changes to limiting factors other than nutrients, such as light (Odum *et al.* 1953; Odum 1957) or 4) the possibility that top-down effects such as loss of higher trophic level organisms have had a cascading effect on vegetative community structure.

Effects on Flora and Fauna

The general pattern that emerges from the review of the literature related to primary producers in Florida springs (Chapter 4) can be summarized as follows:

- Few studies of nutrient limitation for algae exist, and the available results indicate that, if limitation exists, both nitrogen and phosphorus limitation can occur.
- There are no experimental studies that unequivocally demonstrate any submersed vascular plant in a Florida, spring-fed system is consistently limited by either nitrogen or phosphorus.
- There are a number of empirical investigations that suggest the potential for a negative effect of epiphytes or macroalgae on vascular plants in Florida's spring systems, although none clearly demonstrated it or clarified causal mechanisms.

- Algal mat assemblages may be limited by the availability of dissolved inorganic carbon, in Florida's springs.
- Algal mat thickness in Florida's springs was weakly and positively correlated with nitrogen and phosphorus concentrations, but cover and biomass were not significantly correlated with nutrient concentrations.
- Empirical data suggest that there is no statistically significant link between surface water nutrients and production of macrophytes at this time; however, light availability, especially as mediated by riparian shading, has been implicated as a limiting factor for SAV growing in Florida's spring-fed streams.
- The literature suggests that nitrate concentrations currently observed in the water column of many springs should not limit the growth rates of algae comprising benthic mats. However, this does not preclude the possibility of nitrogen limitation in large, well-developed algal mats, where access to nutrients may be impacted by diffusion rates and nutrient gradients within the mat.
- The possibility that phosphorus may be a limiting factor for algal growth in some springs has been highlighted by recent observations of high N/P ratios in plant and algal samples from several Florida springs.
- Specific conductance (salinity) has been shown to affect the structure of vegetative assemblages in several of Florida's coastal, spring-fed systems, perhaps masking the effects of nutrient enrichment.
- There is some evidence from a survey of springs in Florida that a negative relationship exists between dissolved oxygen concentrations and benthic algal coverage.

Nutrients can affect fauna in springs through direct toxicity and indirect effects mediated by vegetation. In essence, effects can be generated in three primary ways: 1) toxicity, 2) changes to trophic webs, and 3) changes in habitats. The literature indicates:

- Nitrate levels in 92% of 130 Florida springs have been reported to average less than 2 mg L^{-1} ; a value that is lower than most concentrations reported to cause effects on animals (Munch *et al.* 2006). However, nitrate concentrations exceed levels of concern in some springs, and they may reach levels of concern for short periods in other springs, especially after the application of safety factors.
- Invertebrate assemblages vary among different vegetated and unvegetated habitats, which suggests that changes in the types and amounts of vegetation (e.g., replacing rooted, vascular plants with algal mats) may lead to changes in invertebrate assemblages.
- Differences in invertebrate assemblages were correlated with dissolved oxygen concentrations, which points to the importance of factors beyond nutrients.
- Fish assemblages and standing stocks vary among different habitats, which suggests that changes in habitats may lead to changes in fish assemblages.
- Evidence of changes in fish assemblages based on repeated surveys in springs that have experienced increases in nitrate concentrations (e.g., Silver and Wekiva) is equivocal, with significant potential for confounding of drivers.
- Fish biomass and phosphorus concentrations were related in a nonlinear manner, with increases in fish biomass being correlated with increased phosphorus concentrations only for lower initial concentrations.
- Nonlinear interactions among fauna, flora and abiotic drivers are found in other aquatic systems, and they may operate in Florida's springs.

Thus, the effects of nutrients on flora and fauna in springs are likely to arise through interrelated and interacting mechanisms. The outcomes bear directly on the sustainable use and management of spring ecosystems.

Effects on Invasive Plants and Invasive Plant Effects on Springs

The literature from lake ecosystems demonstrates a positive relationship between nutrient levels and growth potential for non-native “invasive” plants. As a result, there is widespread concern that increases in nitrate-N in springs may be a primary factor driving invasive plant overgrowth. However, the available literature suggests that maximum stimulation of invasive plant growth by nitrate-N is likely to occur at the very low end of concentrations in Florida springs and thus the nutrient increases experienced in recent years may not portend increased likelihood of plant invasion. For instance, productivity measurements of *Eichhornia crassipes* (water hyacinth) and *Pistia stratiotes* (water lettuce) suggest that maximum growth potential was possible at nitrate-N concentrations characteristic of historical background concentrations, but that the reason they did not take over may have been the result of downstream export rather than nutrient limitation.

Overall the interrelationships between invasive plants and spring ecosystems can be summarized as follows:

- Available scientific studies have not definitively determined a concentration of nitrate-N in springs that would effectively limit growth of *E. crassipes*, *P. stratiotes*, or *Hydrilla verticillata* (hydrilla).
- There is evidence that growth of *H. verticillata* and its ability to out-compete *Vallisneria spiralis* (native tape grass) increases as a function of increased sediment N (albeit from tank experiments rather than *in situ* experiments).
- Field surveys in Florida lakes indicate a marginally significant relationship between dissolved total N and the extent of *H. verticillata* occurrence.
- In one long-term study of ecological communities associated with *E. crassipes* in the St. Marks River, faunal habitat values were demonstrated to be similar to that provided by native plant communities.
- Contrary to other ecosystem contexts in which large mats of *E. crassipes* have been clearly shown to depress DO, coverage by *E. crassipes* in the flowing waters of the St. Marks River did not result in significant oxygen profile differences as compared to *Sagittaria kurziana* (strap-leaf sag) or other native plant communities.
- The literature suggests that aquatic plant control techniques (e.g. herbicide applications or mechanical harvesters) that are used to suppress plant overgrowth have the potential to serve as severe disturbances that could promote succession towards algal dominated springs ecosystems.

Ecosystem Scale Effects

Frequently the changes observed in spring ecosystems are described as driven by “bottom-up” or “top-down” control processes (or combinations of both). Bottom-up control describes processes that originate at the bottom of the trophic ladder and are driven generally by exogenous forcing functions such as, light, flow regime, temperature, or nutrient availability that act to control growth and productivity of primary producers. Top-down control, on the other hand, originates

at the higher end of the trophic ladder and generally takes the form of endogenous effects like changes in grazing pressure, seed dispersal, and other controlling feedbacks from within. However, the exogenous versus endogenous effects should not be taken to mean that top-down only implies factors originating within the ecosystem. In fact exogenous drivers like the removal of top carnivores or the loss of grazers can ultimately result in top-down cascades of impacts.

Detailed study of two spring ecosystems, Silver Springs and the Rock Creek, Wekiva Spring complex, suggests that there is evidence for ecosystem scale effects of nitrate-N enrichment. Using a subsidy stress theory to explain the decline in gross primary production (GPP), it is suggested that increases in nitrate-N act to increase productivity for a time, but then act as a stress to depress productivity above a certain threshold (Chapter 6). One study presents compelling evidence for a decrease in overall productivity in Silver Springs from values measured in a 1950 study as compared to today. This declining ecosystem productivity documented at Silver Springs was highly correlated with increasing nitrate nitrogen concentrations during the 50-year period of available data. Declining spring flows, increased shading by riparian trees, and altered fish populations were also observed to be correlated with declining ecosystem production at Silver Springs and could offer alternate or cumulative explanations of the observed ecosystem changes. The second study conducted in the Wekiva River and Rock Springs Run also found an inverse correlation between nutrient (total nitrogen and total phosphorus) concentrations and ecosystem metabolism. These spring run ecosystems also had other significant environmental stresses caused by humans, including decreases in discharge, intensive exotic plant management efforts, and disturbance due to recreational activities. Studies of whole ecosystem responses to nutrients that would result in direct evidence that increased nutrient levels alone could result in decreased ecosystem productivity and/or photosynthetic efficiency are not available (Chapter 6).

The Legal Framework

The legal framework for managing spring ecosystems exists primarily as a collection of regulations for the discharge of wastewaters through the National Pollutant Discharge Elimination System (NPDES). Additionally, certain sources of nutrient pollution that do not fall within the direct jurisdiction of the federal program, such as nonpoint sources, agricultural discharges, and additional discharges to groundwater are regulated by Florida through various programs (Chapter 7). Narrative nutrient standard for surface waters prohibits altering nutrient concentrations “so as to cause an imbalance in natural populations of aquatic flora or fauna.” Numeric standards can also be developed, as Total Maximum Daily Loads (TMDL), however, development of TMDLs for a particular waterbody requires that it be “impaired”. Local comprehensive plans and land development regulations can be developed to limit the intensity of land development to minimize potential nutrients contributions to springs. They can also provide for improved stormwater and wastewater management.

Overall, the current framework for managing spring ecosystems is focused on water quality with little or no ability to manage holistically or adaptively. Springs management would benefit from a framework that includes options for integrating program initiatives of a variety of agencies and programs including: Florida Department of Environmental Protection, Florida Department of Health, DEPs Bureau of Invasive Plant Management, Florida Water Management Districts,

Florida Fish and Wildlife Conservation Commission, and local citizens representing important stakeholders.

PART 2: SPRINGS RESEARCH PRIORITIES

We present recommendations for research before we discuss management implications of the findings of this literature review, because what we don't know has serious implications for how and why we manage ecosystems. The management of complex, coupled human and natural systems, like Florida's springs, necessarily requires an "adaptive" approach, an approach that sees management as an evolving process rather than an end in itself. Management requires knowing, and while we can never know everything, a baseline of knowledge is always a good idea prior to meddling. Therefore, a concerted effort to more thoroughly study and understand springs and their springsheds is warranted.

Florida's 700+ springs are important resources that are undergoing significant change. They are under assault from a variety of stressors including reduced flows, increased nutrients (principally nitrate-N), human disturbance, changes in specific conductance, decreasing oxygen levels, invasions of non-native species, and so forth. While key elements of spring ecosystems resemble key elements of other lotic systems, Florida spring systems are unique, (indeed, even individual spring systems often differ in key elements) making generalizations using key principles and across all springs to be dangerous at best.

Our review of the available literature has shown that we do not have a systematic understanding of historic changes, fundamental processes, or mechanisms of ecosystem function sufficient to definitively manage springs and their contributing areas. Yet manage we must in the face of significant uncertainty. It is with this uncertainty in mind that we make the following recommendations regarding research needs. There are many areas of research that if undertaken would yield important information that should lead to better understanding of spring ecosystems. While we present these suggestions one at a time, it is our concerted belief that the research approach should be a systematic one. An approach that incorporates many of the individual suggestions into a holistic comparative, cross scale, cross stressor study of a half dozen springs. Obviously the springs need be carefully chosen.

Nutrient Fate, Transport, and Transformation: *What we don't know*

Some of the most fruitful research that will improve understanding of past changes and potentials for future management of spring ecosystems can be found in elucidating factors affecting fate, transport and transformation of nutrients at the scale of the springshed. We offer the following research objectives:

- Explicit accounting of nutrient budgets is essential to understanding attenuation in springsheds (or lack thereof). Developing nutrient and water budgets for springsheds has already begun to yield a clear picture of source importance and will continue to help setting realistic target load reduction strategies. It is a critical factor necessary in the development of TMDLs for spring sheds. As part of a systematic research program, continued development of spatially explicit models of nutrient and water budgets is

strongly encouraged to better understand the reasons for the observed attenuation between springsheds and vent.

- Understanding the effective springsheds and flow-paths is essential to establishing baseline conditions and for targeting management for individual springs. The link between discharge and age is an important research need because of its implications for regulatory minimum flows and levels and for better understanding of the time lags between management action and water quality response. Detailed studies that elucidate spatial variability in recharge and resulting spring discharge are needed for management of individual springs.
- Indications are that Florida's karst geology does not have an unlimited capacity for P sorption and that future phosphorus release is a potential area of concern. As such, this should be an area of active research, with the primary objective to determine the degree of sorption saturation along principal groundwater flow-paths.
- Indications are that there may be significant spatial and temporal variability in DO of spring water that may be related to larger scale springshed dynamics (e.g., organic matter loading of ground waters, ground water age). Research is needed to determine if declines in DO or variability in DO levels are related to the increase in the dominance of filamentous algae in many springs, either through negative impacts on grazers, or impacts on SAV respiratory functions.

Within-system nutrient dynamics are not well understood and there is a general lack of data on characterization of spring systems for biogeochemical purposes. We propose the following studies that will elucidate biogeochemical pathways and processes, enhancing spring management in the long run

- Our understanding of nutrient dynamics in Florida spring systems resembles a black box approach, where changes in water column nutrients provide evidence that biogeochemical transformations are taking place within the hyporheic, detrital, and epiphytic zones, but with little understanding of how or what rate these transformations are occurring.
- Carbon (C) sources and distribution play a key role in structuring the biogeochemistry of the spring system; therefore, better understanding is needed regarding the sources and processing of C in spring systems and especially the role of aquatic plant management in the distribution and fate of C within particular systems.
- The role of internal nutrient supply and relative bioavailability of various nutrient forms stored in sediments and water column is important to document as are the fluxes between sediment, vegetation, and water column.
- Research is needed to understand the fate of nitrogen within the spring system. This would include understanding of biotic uptake processes (algal/macrophyte uptake), importance of different N sources (NH_4^+ , NO_3^- , DON), and the occurrence, rates and importance of biological N_2 -fixation. Whole spring run N budgets should be performed to better isolate these processes.

Nutrient Effects on Flora and Fauna: *What we don't know*

The effects of nutrients on spring flora and fauna always will be uncertain for two primary reasons: 1) we cannot afford the amount of science that would come close to eliminating uncertainty and 2) unforeseen and unforeseeable responses will arise as emergent properties of these complex systems. In support of sustainable use and management of springs systems, we recommend a targeted research program comprising inventories, baselines, diagnostic studies and other scientific approaches, with choices driven primarily by management questions derived from human values. Given these relationships, input from diverse stakeholders becomes a requirement during development of both “answerable” questions, e.g., questions with well-defined scopes and appropriate levels of precision, and detailed research projects designed to provide useful answers. Issues that arose during this review serve as starting points for such discussions. Key unknowns and examples of research directions are:

- A lack of understanding regarding the roles of various types of flora in nutrient budgets hampers management decisions regarding assimilation of nutrients and setting of numeric criteria for nutrient loads or concentrations; and it can be addressed by diagnostic studies to determine assimilation of nutrients by vascular plants, macroalgae, epiphytes, microphytobenthos or microalgae found in sediments, and other types of flora.
- A lack of understanding regarding the links among nutrients and other drivers of primary productivity hampers efforts to predict impairment, such as overgrowth or shading of vascular plants by algae, set criteria to reverse impairment, or make decisions about restoration; and it can be addressed by diagnostic studies that determine how nutrients, other drivers, and interactions among drivers affect or limit production, competition, and other relationships among periphyton, macroalgae and vascular plants.
- A lack of understanding regarding the form and magnitude of faunal responses to changes in vegetated habitats hampers efforts to predict impairment, such as loss of grazers or valued species, set criteria to reverse impairment, or make decisions about restoration; and it can be addressed by diagnostic studies to 1) elucidate changes in composition and function of faunal assemblages related to changes in habitats and 2) determine palatability of flora to grazers, rates of grazing, and the form and magnitude of predation by primary consumers in an effort to identify flora, grazers, and trophic links to be protected or restored by management actions.
- A lack of understanding regarding the population and assemblage effects of ammonia and nitrate toxicity hampers efforts to set criteria and safety factors; and it can be addressed by diagnostic studies to identify and elucidate the toxic effects of ammonia and nitrate beyond physiological and individual levels of organization (e.g., population and assemblage effects) in an effort to determine threshold levels, safety factors and the need for management actions.

Invasive Plants and Springs: *What we don't know*

It is surprising that more research has not been conducted on the impacts of aquatic weed and invasive plant management on spring ecosystems in general and specifically as it relates to changes in trophic structure, nutrient cycling, and ecosystem productivity. The pervasive nature of these management techniques should provide strong incentive for a more holistic approach to understanding their short and long term effects. The study of spring ecosystems offer ample

opportunities to investigate the role of invasive plants and the possible detrimental effects of their management in the changes that are occurring within spring ecosystems. We offer the following research topics related to invasive plants and their management in spring systems.

- Diagnostic studies (nutrient and organic matter budgets and cycling as well as flora and fauna community structure) before and after aquatic plant control in springs ecosystems are needed to better understand and characterize the effects on sediment nutrient accumulation and ecosystem succession.
- Since the available literature suggests that even historically characteristic nutrient concentrations at Florida springs could support invasive plant growth, research into growth dynamics is needed to better target management interventions.
- The seemingly opposing views in the literature that invasive plants cause irreparable change to aquatic systems at all trophic levels and studies and observations that indicate major invasive plants often provide highly attractive habitat for key springs ecosystem fauna and may support some feedbacks that could be expected to reduce algal overgrowth needs further study. Are there circumstances that would potentially warrant the use or existence of invasive and/or non-native plants as a management intervention?
- Finally, given the wide range of concerns about possible algal selection, habitat loss, faunal toxicology, and dissolved oxygen suppression that may be associated with aquatic plant control, a significant diagnostic program of study is warranted. This should include detailed *in situ* studies of the above under differing aquatic plant control regimes (including both mechanical and chemical treatment). The funds for such studies should be included in aquatic plant control budgets as a matter of course.

Ecosystem Scale Effects: *What we don't know*

Spring ecosystems are exceedingly complex, but potentially understandable based on theories derived from the study of general systems. They do not possess a singularity that would suggest that there is a one to one correspondence between a stressor (such as nitrate concentrations) and a response (such as algal or plant growth and abundance). We know that springs, like other ecosystems, have feedback and control pathways that make predicting cause and effect relationships somewhat problematic. Yet that is exactly what management interventions require. Given X intervention, we expect Y result. Unfortunately the result is often Z; something we did not intend at all.

Ecological monitoring of the multi-level effects of stressors on ecosystems is important for understanding the full implications of management interventions. It is not sufficient to monitor only the target of a particular intervention, because frequently the target is not the true indicator of the problem we are trying to address with the intervention or the element that responds the quickest, or responds at all. Whole system monitoring is essential if management is to learn from past and refine future interventions. With this in mind we offer the following “whole ecosystem” research agenda.

- A critical need exists to establish a comprehensive baseline database for a large number of spring ecosystems, including their range of ecosystem metabolism, trophic structure,

and key forcing functions. Data need to be collected at a spatial and temporal resolution to facilitate separation of transient behaviors from long-term trends.

- Elucidating changes in primary production, ecological efficiency, species composition, and succession, that result from changes in forcing functions such as nutrient concentrations, dissolved oxygen, salinity, temperature, and shading are necessary if we are to understand ecosystem management interventions. This can be accomplished through in-situ whole system studies in a variety of springs.
- Elucidating effects of changes in herbivory, which could lead to primary producer effects that appear similar in symptom to nutrient effects is an important area of research since the strength of bottom-up vs. top-down effects is a central question to be answered.
- *In-situ* mesocosm experiments are also needed that involve controlled manipulation of one or more environmental forcing functions (temperature, discharge, carbon dioxide concentration, nutrient concentrations, oxygen concentration, specific conductance or salt contents, and grazing pressure) and the responses of individual species and trophic levels. Any changes in individual organisms could then be related to changes in ecosystem structure and functioning and coupled with whole ecosystem studies (above) might help to elucidate feedbacks and heuristic potentials.
- Indicators and assessment tools for spring ecosystems are essential. Understanding change requires indices that are sensitive enough to detect change. DEP's Stream Condition Index has been developed and used to assess a wide variety of stream ecosystems of Florida, yet we are uncertain if it is applicable in its present form to Spring ecosystems. Research is needed to develop appropriate indices of biotic integrity for spring ecosystems.

Summary of Research Recommendations

During one of the public meetings that preceded the final production of this document, an attendee expressed extreme frustration because “we scientists” were pontificating on the cause while the patient was sick and dying on the operating table...a particularly vivid and apropos analogy and one that has stuck with us. To carry the analogy a bit further...we have the luxury of multiple sick patients, multiple potential diseases, and relatively low-risk of clinical trial error as a result of the ecological changes now being experienced by a diversity of Florida's springs. We propose using this opportunity to explore the causes and long-term implications of these changes. Therefore we propose that a number of smaller springs be selected that represent a variety of stressors acting separately and in combination as a means of testing various hypotheses regarding the impacts of stressors on spring ecosystems and biota. Tests might involve, for instance, choosing springs with low versus high DO, presence and absence of grazers, low versus high nitrate-N, absence versus presence of recreation and so forth; then changing environmental conditions such as nitrate-N concentrations or DO concentrations in springs to support grazers, etc. These experiments should be accompanied by sufficiently fine-grained monitoring, both spatially and temporally, to discriminate the effects of manipulations from other potential interactions. The experiments also need to be carried out over sufficient lengths of time to elucidate the possibility for alternative stable states and hysteresis effects in which, even after long periods of time, the state of the spring system may be determined by its history. In other words removing a stressor may not be sufficient to “restore” a spring ecosystem to a former state

as there may be considerable lag in spring ecosystems between removal of a stressor and the effect of its removal.

In addition to the above, we suggest a relatively intense monitoring campaign in a like number of springs that is designed to elucidate spatial variability and temporal dynamics of stressors and impacts. Most of the current spring monitoring data has a resolution that makes discriminating spatial variability impossible and lacks the temporal sensitivity to account for potential pulse events that may have significant impact (low DO/nitrogen/high salinity events, for example).

Scanning through the list of research suggestions, it is apparent that answers to the many uncertainties surrounding Florida Spring management will not come quickly. A sustained research program will necessarily require a sustained source of funding. Here we suggest a simple source of funding that is tied directly to the resource and that is independent of water management district funding or state tax dollars....a source of funding that with appropriate social marketing can be thought of as a positive contribution to natural resource management instead of a tax. The term social marketing in this context means that through a marketing campaign we would enlist the cooperative buy-in of those affected as a contribution rather than imposing a tax.

The proposed source of funding is a “One-cent contribution” for sustainable springs research and management from each bottle of water sold in Florida. According to the International Bottled Water Association, total U.S. sales of bottled water volume surpassed 8.82 billion gallons, in 2007. That translates into an average of 104 single-serve bottles per person per year. With 18.68 million people in Florida, that equals 1.94 billion bottles of water sold in Florida in 2007. If one cent per bottle were contributed toward springs research, the sale of bottled water in Florida would generate \$19.4 million/yr (this does not include tourism sales of bottled water which could easily push the total available funding to nearly \$21 million per year). If marketed correctly this could result in a sustainable source of funding for research and management of Florida’s spring ecosystems, obviously some of the most important natural resources the State possesses. The authors recognize that this is no easy sell, for the first reaction to the proposed funding source is that it looks like a tax. However, we emphasize that it is not a tax, we do not solicit legislative intervention to impose a tax, rather we believe that if presented correctly to the bottling industry they would be extremely willing to add a sentence on their bottling labels indicating that with the sale of each bottle of water they are contributing to research that will ultimately lead to sustainable management of Florida’s springs.

PART 3: RECOMMENDATIONS for SPRINGS POLICY and MANAGEMENT

There is no question that Florida’s springs are important, unique resources and as with most natural resources in Florida, they are under considerable pressure from changes in environmental drivers, direct human use, and indirect alteration of the chemical and physical environment in which they exist. Equally apparent is the fact that many Florida springs are exhibiting change in biological components. While exact causes are uncertain, in the previous sections, we document numerous stressors that might be grouped into at least four general classes: physical disruption, changes in quantity of discharges, changes in chemical composition of discharges, and changes in populations of higher trophic organisms which have top-down cascade effects on lower

trophic levels. It is quite possible but highly unlikely that the observed changes in biological indicators in some springs may be caused by a single stressor. More probable is the possibility that springs exhibiting change are affected by combinations of stressors, acting in a cumulative manner. In some systems, management interventions can be tailored to a particular stressor and the trajectory of change it produces. However, it is unlikely at this time that our ability to understand causality between stressors and indicators in spring ecosystems is sufficient to allow such a fine grain approach to management. Thus, it is our opinion that a holistic (or systems) approach to management is required.

A systems approach is nothing new; there has been a call for an ecosystem approach to management of natural resources for some time (Agee and Johnson 1987). Defined as the integration of ecological, social, and economic objectives for the planning and management of natural resources, early attempts at *ecosystem management* sought to maintain and enhance biological diversity and ecosystem integrity (Grumbine, 1994). The focus on integration of these ecological objectives with the simultaneous attainment of social and economic objectives is what distinguished ecosystem management from earlier natural resource management approaches.

Recognizing the often pathological insistence of managers to stick to one narrative and one management scheme with little or no flexibility for new information, resulted in a call for an approach that addressed not only a whole systems approach to management but an adaptive one as well (Holling, 1978; Walters, 1986).

The Springs Initiative: Protecting Florida's Springs

In 2001, the Department of Environmental Protection (DEP) made springs protection a priority through the establishment of the Florida Springs Initiative (FSI). Since then, DEP committed several million dollars to fund scientific research, water quality and biological monitoring, education and outreach, landowner assistance projects, and springs restoration (FSI, 2007). In the six years since its establishment, the FSI has accomplished much in the four areas of its responsibility:

- *Research and monitoring;*
- *Landowner assistance in the form of planning, management, and restoration;*
- *Restoration/protection activities and educational outreach in state parks; and*
- *Environmental education and outreach.*

Cited as an “adaptive management approach” the resources and staff of the FSI are tailored to future management activities based on the past experiences of the program (FSI, 2007). While FSI’s approach involves change and might be called adaptive in the sense that the FSI tailors future activities to what has been “learned” from past activities, it is not Adaptive Management (AM) by the strict characterization suggested by the Resilience Alliance (RA, 2008) and others (Holling, 1978, 1986; Gunderson et al. 1995; Habron, 2003; Folke et al. 2005). A casual understanding of Adaptive Management leads to the belief that monitoring management activities and occasionally changing them constitutes an Adaptive Management approach. Contrary to this commonly held belief, AM is much more than simply changing future activities based on past experience. This is not criticism of the current approach of the FSI, only

clarification since the following proposals for policy and management of Florida's springs revolve around an AM strategy. We believe that the complexity of the issues as well as the complexity of the springs' social ecological system, comprised of a multitude of actors from microbes to state government, requires a true AM approach. What follows then, are suggestions for establishing an AM program and framework for Florida springs.

Adaptive Management: An Approach to Springs Protection

An adaptive approach to natural resource management involves exploring alternative ways to meet management objectives, predicting the outcomes of alternatives based on the current state of knowledge, implementing one or more of these alternatives, monitoring to learn about the impacts of management actions, and then using the results to update knowledge and adjust management actions (Murray and Marmorek, 2004). AM is a dynamic process that requires learning and adapting. This means that an AM program incorporates, as an integral part of the program, management interventions that are developed and carried out as scientific experiments. Through the experiments, the AM team learns about the systems but more importantly, they are learning whether the intervention is likely to result in the desired objective. As an experiment, the management intervention must be monitored and data that is gathered must be analyzed to yield information that can direct management. Finally, the management team must be flexible enough to incorporate new information and adjust management if the experiment suggests that adjustment is necessary. A main organizational principle of AM is that it requires partnerships of policymakers, managers, scientists, and other stakeholders who learn together how to create and maintain sustainable resource systems. In other words, AM is a social as well as a scientific process.

A Tragedy of the Commons

Unlike Hardin's (1968) over simplified dilemma of the commons involving herders use of rangelands, Florida's springs are nestled in a complex world of physical, ecological, economic and political realities. As such, Hardin's twofold institutional arrangement for protection, either centralized government or private property, cannot work to protect the "springs commons" over the long run in the face of over exploitation. The complexity of springs issues do not lend themselves to traditional single focus resource management that uses informed- trial-and-error of applying management interventions, watching the impacts, seeing what works, and then adjusting future interventions according to observations. Nor does their resolution lie in either private ownership or top-down government control. Instead, the complexity of issues and causes must be addressed in an informed process of Adaptive Management that is inclusive, holistic and responsive.

The springs' commons have a multitude of players: from herders, to agriculturalists, to boaters, to government, to scientists each with their own understanding of the issues, causes, impacts, solutions and futures of Florida's springs. The adaptive management framework not only must include all these stakeholders, but must have the capacity for social learning (Bandura 1963), or the ability for the entire framework to learn and exchange information that is linked to management decisions. Thus, central to the AM framework for springs is the development of a social fabric that is inclusive and that can address links between institutions, communities,

knowledge, science, and power (Stringer et al. 2006). This requires that information flows be horizontal, among groups, as well as vertical, among institutional levels.

Managing in the Face of Uncertainty

The National Research Council (2004) defines adaptive management as a process that promotes flexible decision-making that can be adjusted in the face of *uncertainties* as outcomes from management actions and other events become better understood. The careful monitoring of outcomes both advances scientific understanding and helps adjust policies or operations as part of the iterative learning process. AM is not an end in itself or a trial and error process, but rather a means to more effective decisions and enhanced benefits through learning while doing.

Springs are complex, coupled natural and social systems, sometimes called social ecological systems. Their complexity leads to uncertainty about the exact structure of the system, the relationships between components, and causes and effects of actions, all of which lead to significant uncertainty regarding the outcomes of management decisions. In the face of some ecological change (or crisis), the approach most often used is to develop an informed trial and error approach to management that first tries the most obvious intervention. The intervention generally is the result of a rigid idea of cause and effect, which leads to relatively inflexible management in the face of new information and often results in effects that were counter to expected, sometimes called “ecological surprises”. The alternative is the generation of several hypotheses for the observed change and then interventions based on the hypotheses and designed as scientific experiments. If posed correctly and followed up with sufficient monitoring, management interventions become the basis for learning, and if the management framework is sufficiently flexible, the basis for adaptive change.

In the face of changing springs ecosystems, the causes of which are somewhat uncertain, we must learn as we manage. The opportunity to impose an adaptive management framework on the process so that research generates new knowledge and information that flows directly from management decisions is irresistible and too good to pass up. Thus, we suggest a springs management framework that faces uncertainty head on and uses it to learn and change, instead of avoiding risk and uncertainty and preserving the management system. There is a fundamental difference in approach between management that is adaptive and Adaptive Management; the former stresses preservation of the status quo, avoidance of risk, and concern with the costs of management. The latter accepts change and the uncertainty that comes with it, and is willing to fund the processes necessary to avoid ignorance.

Adaptive Springshed Action Programs (ASAPs)

What is required are new institutions and institutional frameworks as well as new science and experimental frameworks. As a grand experiment, we propose the creation of up to six Adaptive Springshed Action Programs (ASAPs). Called Action Programs instead of management programs, we wish to stress that these programs are more than management. They are new management, research, and education structures that incorporate institutional verticality (i.e., state, regional, and local institutions) along with a horizontal group structure of socio-economic stakeholders, managers, and scientists organized as a working group to adaptively manage the

spring and its springshed. They are akin to BMAPs but contrary to the BMAP/TMDL program, waters do not have to be declared impaired in order to implement an ASAP. All their implementation requires is the acceptance that a spring ecosystem is changing, a belief that through appropriate management it is possible to affect positive change, a willingness to implement interventions as scientifically valid experiments, the ability to monitor, collect and analyze data, and finally the readiness to change interventions should the data suggest it is appropriate to do so.

The springsheds should be chosen to represent a cross-section of geographical, ecological, physiological, sociological, and political settings. As a first cut, we suggest the following eleven spring systems, from which six could be chosen:

- ***Silver and Rainbow Springs in Marion County*** – two of the state’s largest and most economically important springs with rising nitrate concentrations
- ***Ocala National Forest Springs (Alexander, Juniper, and Silver Glen)*** – three of the State’s most protected springs that are currently unaffected by any nutrient increases or flow reductions
- ***Wakulla Springs*** – an important north Florida spring with a history of springshed interventions to reduce nitrate-N.
- ***Kings Bay/Crystal River Complex*** – a complex of springs with a long history of management interventions related to invasive species
- ***Homosassa Springs Complex*** – a system with significant baseline data and a recent loss of flora
- ***Chassahowitzka Springs Complex*** – a system adjacent to the Homosassa system with a similarly comprehensive baseline and less development in its springshed
- ***Weeki Wachee Springs*** – on the west coast of Florida the springshed has undergone significant development in the last two decades
- ***Ichetucknee Springs*** – a long history of recreational use with several different spring boils with differing chemistry and a newly urbanizing landscape
- ***Wekiwa /Rock Springs Complex*** – a highly urbanized springshed, with decreased discharged volumes, intense recreational use and important regulatory initiatives for protection
- ***Suwannee River Springs (Fanning and Manatee)*** – springs in an agricultural landscape with the highest nitrate N concentrations in the state
- ***Wacissa River Springs*** – springs in a relatively undeveloped rural landscape with minimal nutrient impacts

By choosing several spring systems simultaneously, we suggest that communication between spring ASAPs is just as important to management, learning, and science as within ASAP communication. Frameworks for communication between them must be facilitated, encouraged, and even required. Since each spring systems is a test case in a broader study of adaptive management it is imperative that cross system communication, comparison and ultimately learning take place.

Part of ASAP framework should be workshops that build a collaborative space for discussions between the policy, science, user, and manager groups. These discussions should focus, using a

“systems approach”, on elucidating leading problems and issues within each of the spring systems, developing hypotheses concerning the causes of problems and effects of interventions, and develop scenarios about the future. These workshops should be a common form of participant interaction, feedback and formalization of the reflective/iterative processing of information that is required of the adaptive process. A deeper understanding of the resource issues, management options, and future scenarios are likely outcomes.

The current bag of spring management tools (PLRGs, TMDLs, BMAPs, MFLs etc.) is appropriate and usable within the context of the ASAPs. Ultimately whatever tools are used, the allocation of responsibility for reducing impacts on springs (whether impacts are from nutrients, reduce discharges or human disturbance) will require negotiation. Who pays and how much are part of reducing impacts. The proposed ASAPs represent a democratic, responsive bottom-up management structure that can garner support and allocate responsibility without heavy-handed top-down regulation.

It should be noted that the ASAP approach suggested here is in addition to the needed research proposed in the previous section of this chapter. There needs to be multiple layers to understanding and managing spring ecosystems with efforts at the large scale to control things that matter at that scale and science at the small scale to better understand which interventions are most likely to yield desired ecological effects. These are not mutually incompatible, and are likely wholly complementary. The research proposed in the previous section is designed to provide baseline information about spring ecosystems and responses of spring ecosystems to stressors. The ASAP program suggested here is a novel approach to management that includes science and the ability to test hypotheses concerning appropriate management interventions for problems believed to be at the root of changes in spring ecosystems. The proposed approach to management is similar to, and in fact could use the existing spring working groups as a starting point. So far, the working groups seem to be less about management and more about exchanging information, as suggested in the following statement by a participant in spring working groups:

"Springshed working groups provide a marvelous opportunity for collaboration, exchange of ideas, and general education. As someone who has participated in a number of different working groups, my impression is that while there is clear success in bringing stakeholders together and sharing information, there is much room for improvement in terms of facilitating bottom-up discussion about how to process and use this information moving forward. All too often, working group meetings are characterized by a series of presentations that are not followed by serious discussion, synthesis, and argument among stakeholders about the information presented, much less the articulation of different ideas about how to proceed in the face of this information. Exchange of information is undoubtedly a good thing, but we need to come up with better ways to take advantage of multi-stakeholder expertise in progressively evaluating the big picture at each spring and adapting the research and policy agenda over time. The interest and energy to do this is there. What we need is a formal recognition that critical dialogue, collaborative development of research and management priorities, and collaborative evaluation of research and management results should be integral parts of the working group model."

Our proposal for the ASAPs would build on the working groups model, develop overall management goals and objectives, and then initiate a round of management interventions to test hypotheses concerning the causes of current apparent declines in spring ecosystem condition.

The social framework of the ASAP team should include a tripartite of individuals from government, science, and the citizenry at large. The ASAP team should be empowered to make management decisions and direct the relevant agencies to carry out the interventions. For instance, they may direct the appropriate agency to limit recreational use, or eliminate spraying of aquatic weeds as part of an overall management strategy to restore SAV vegetation in a spring run. The appropriate agencies as members of the ASAP team would develop the necessary policy and implementation strategy.

In summary, the key difference between the ASAPs and the current springs working groups is related to membership, organization, and empowerment. Through agreements between agencies, the ASAP will be empowered to take action after developing a program that includes goals and objectives, management interventions that are testable and capable of being validated through collection of data, the collection and synthesis of that data, and finally, real time reflection on whether the interventions are succeeding. The DEP's springs initiative could coordinate the ASAPs. We propose the DEP utilize a neutral facilitator whose primary job would be the development of consensus between the tripartite members of each ASAP.

Adaptive Spring and Springshed Research

Research within the AM context is designed for the purpose of producing results that may be applied to and answer management questions. Just as this concept of research differs from "basic research" (investigations of a phenomenon without reference to particular human needs and wants) the science that drives the AM research is different. Science within the context of AM differs radically from classical notions of "pure science" as it must respond to often-conflicting group demands of managers, politicians, citizens, developers, environmentalists, and users. It must be able to operate under conditions of complexity, uncertainty and risk, and generally be applied over large spatial and temporal scales. In addition AM research must cross many ecological and organizational boundaries increasing its complexity and the lead time required for accomplishing its objectives. Thus, the payoff from AM research should be measured over the course of years, not months. Often this is difficult for the management and policy arena to accept. Frequently policy makers want answers before science has even formulated the question, wishing for a synthesis of available information with inductive inference to the particular case in point. Managers want to move forward with scientific certainty that their intervention will achieve the desired result. Science is left wanting; wishing for the time to do the research, synthesize the results, and answer the questions.

The research within each of the ASAPs should ultimately be formulated by their participants, as they each have their particular ecological issues, management potentials, and socio-economic constraints. Overall, our understanding of Florida spring systems would benefit from cross system comparison. It is important that the science/research component foster the development of broad integrative studies that bring policy and management into focus and generate the kinds

of knowledge and understanding that will inform and develop better management as well as social learning rather than just the accumulation of more information. In the absence of the ASAP system and the integrative program of study it would foster, the individual research questions given in the preceding section of this chapter remain as important research priorities. Most are significant questions about the controlling factors of ecological change in spring ecosystems. However, the creation of ASAPs and the opportunities for real time research, education, management and social learning that they will afford is truly a grand experiment and the most important opportunity provided by the crises of ecological change now being experienced by Florida's springs.

REFERENCES

- Agee, J.K. and D.R. Johnson. 1987. Ecosystem management for parks and wilderness. University of Washington Press, Seattle.
- Bandura, A. 1963. *Social learning and personality development*. Holt, Rinehart, and Winston, New York, New York, USA.
- Duarte, C.M. 1995. Submerged aquatic vegetation in relation to different nutrient regimes. *Ophelia* 41: 87–112.
- Florida Springs Initiative (FSI) 2007. Florida Springs Initiative, Program Summary and Recommendations, 2007. Florida Department of Environmental regulation, Tallahassee Florida. Obtained on 03/01/08 from Web Link - <http://www.dep.state.fl.us/springs/reports/files/FSIreport2007FINAL.PDF>
- Folke, C., T. Hahn, P. Olsson and J. Norberg. 2005. Adaptive governance of social-ecological systems. *The Annual Review of Environment and Resources*. 30:8.1-8.33.
- Grumbine , R.E. 1994. What Is Ecosystem Management? *Conservation Biology* 8(1): 27-38
- Gunderson L., C.S. Holling and S.S. Light. 1995. Barriers and bridges to the renewal of ecosystems and institutions. New York: Columbia University Press.
- Gunderson L., and C.S. Holling, editors. 2001. *Panarchy: understanding transformations in human and natural systems*. Washington (DC): Island Press.
- Hardin, 1968. The Tragedy of the Commons. *Science* 162(1968):1243-1248.
- Habron, G., (2003). Role of Adaptive Management for Watershed Councils. *Environmental Management* 31(1):29-41
- Holling, C.S. 1978. *Adaptive environmental assessment and management*. J. Wiley, London, U.K.
- Holling, C.S. 1986. The resilience of terrestrial ecosystems; local surprise and global change. In: Clark WC, Munn RE, editors. *Sustainable development of the biosphere*. Cambridge (England): Cambridge University Press. 292–317.
- Levin, S. 1999. *Fragile Dominion: Complexity and the Commons*. Perseus Publishing.
- Munch, D.A., D.J. Toth, C. Huang, J.B. Davis, C.M. Fortich, W.L. Osburn, E.J. Phlips, E.L. Quinlan, M.S. Allen, M.J. Woods, P. Cooney, R.L. Knight, R.A. Clarke and S.L. Knight. 2006. Fifty-year retrospective study of the ecology of Silver Springs, Florida. Publication Number: SJ2007-SP4. St. Johns River Water Management District, Palatka, FL.

- Murray, C. and D.R. Marmorek. 2004. Adaptive management: A science-based approach to managing ecosystems in the face of uncertainty. In: N.W.P. Munro, T.B. Herman, K. Beazley and P. Dearden (eds.). Making Ecosystem-based Management Work: Proceedings of the Fifth International Conference on Science and Management of Protected Areas, Victoria, BC, May, 2003. Science and Management of Protected Areas Association, Wolfville, Nova Scotia. Obtained on 03/01/08 from Web Link - http://www.essa.com/downloads/AM_paper_Fifth_International_SAMPAA_Conference.pdf
- National Research Council. 2004. Adaptive Management for Water Resources Planning, The National Academies Press. Washington, DC.
- Odum, H.T., O. Galindo, B. Parrish, R. Pinkerton, W.C. Sloan and L.A. Whitford. 1953. Productivity of Florida Springs Factors controlling marine invasion in Florida fresh waters. Third semi-annual report to the Biology Division, Office of Naval Research 3: 134-156.
- Odum, H.T. 1957. Primary Production Measurements in Eleven Florida Springs and a Marine Turtle-Grass Community. *Limnology and Oceanography* 2: 85-97.
- Olsson, P., C. Folke and F. Berkes. 2004. Adaptive co-management for building resilience in socio-ecological systems. *Environmental Management*. 34: 75-90.
- Resilience Alliance (RA). 2008. Key Concepts: Adaptive Management Web resource downloaded 03/01/08 from: <http://www.resalliance.org/600.php>.
- Stringer, L. C., A. J. Dougill, E. Fraser, K. Hubacek, C. Prell and M.S. Reed. 2006. Unpacking “participation” in the adaptive management of social–ecological systems: a critical review. *Ecology and Society* 11(2): 39. [online] URL: <http://www.ecologyandsociety.org/vol11/iss2/art39/>
- Walters, C. 1986. Adaptive management of renewable resources. New York: Macmillan.