

Fate of Effluent-Borne Contaminants beneath Septic Tank Drainfields Overlying a Karst Aquifer

Brian G. Katz,* Dale W. Griffin, and Peter B. McMahon U.S. Geological Survey

Harmon S. Harden Florida State University

Edgar Wade and Richard W. Hicks Florida Department of Environmental Protection

Jeffrey P. Chanton Florida State University

Groundwater quality effects from septic tanks were investigated in the Woodville Karst Plain, an area that contains numerous sinkholes and a thin veneer of sands and clays overlying the Upper Floridan aquifer (UFA). Concerns have emerged about elevated nitrate concentrations in the UFA, which is the source of water supply in this area of northern Florida. At three sites during dry and wet periods in 2007–2008, water samples were collected from the septic tank, shallow and deep lysimeters, and drainfield and background wells in the UFA and analyzed for multiple chemical indicators including nutrients, nitrate isotopes, organic wastewater compounds (OWCs), pharmaceutical compounds, and microbiological indicators (bacteria and viruses). Median $\text{NO}_3\text{-N}$ concentration in groundwater beneath the septic tank drainfields was 20 mg L^{-1} ($8.0\text{--}26 \text{ mg L}^{-1}$). After adjusting for dilution, about 25 to 40% N loss (from denitrification, ammonium sorption, and ammonia volatilization) occurs as septic tank effluent moves through the unsaturated zone to the water table. Nitrogen loading rates to groundwater were highly variable at each site ($3.9\text{--}12 \text{ kg N yr}^{-1}$), as were N and chloride depth profiles in the unsaturated zone. Most OWCs and pharmaceutical compounds were highly attenuated beneath the drainfields; however, five OWCs (caffeine, 1,7-dimethylxanthine, phenol, galaxolide, and tris(dichloroisopropyl)phosphate) and two pharmaceutical compounds (acetaminophen and sulfamethoxazole) were detected in groundwater samples. Indicator bacteria and human enteric viruses were detected in septic tank effluent samples but only intermittently in soil water and groundwater. Contaminant movement to groundwater beneath each septic tank system also was related to water use and differences in lithology at each site.

ABOUT ONE IN FOUR households in the United States uses a septic tank for wastewater disposal (USEPA, 2003). Conventional septic tanks are the most commonly used systems and consist of a tank that allows solids to settle out and septic tank effluent (STE) to flow to a drainfield where it percolates downward through soil and the unsaturated zone toward the water table. Various biogeochemical processes occur beneath the drainfield that can modify and attenuate certain chemical and microbiological constituents in the STE. Numerous studies have assessed the impacts of STE on groundwater quality, with particular emphasis on the transformation and fate of nutrients (Wilhelm et al., 1994; Aravena and Robertson, 1998; Hinkle et al., 2008), bacteria and viruses (DeBorde et al., 1998; Rose et al., 2000; Darby and Leverenz, 2004), organic wastewater contaminants (e.g., Hinkle et al., 2005; Swartz et al., 2006; Conn et al., 2006), and pharmaceuticals (Seiler et al., 1999; Godfrey et al., 2007; Carrara et al., 2008). Subsurface pathways of nutrients and wastewater organic compounds (including pharmaceuticals and personal care products) are increasingly recognized as a problem for aquifers (e.g., Barnes et al., 2008; Focazio et al., 2008).

Reasonable estimates of the nitrogen (N) flux from septic tanks to groundwater exist, but this flux is mitigated to an unknown degree by physical, chemical, and microbiological processes occurring in the shallow subsurface and in the unsaturated zone above the water table. Apparent loss or attenuation of N beneath septic tank drainfields has been observed in varied hydrogeologic settings (e.g., Robertson et al., 1991; Ptacek, 1998; Seiler, 2005; Hinkle et al., 2008). Apparent N loss has been attributed to several processes, including ammonia volatilization, sorption of ammonium (NH_4^+) and organic N on soil particles, denitrification, and dilution from infiltrating rainfall and mixing with ambient groundwater. Without knowing the amount of N, phosphorus, and organic wastewater compounds stored in the unsaturated zone beneath on-site waste disposal sites, it is not possible to

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*Corresponding author (bkatz@usgs.gov).

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5585 Guilford Rd., Madison, WI 53711 USA

B.G. Katz and D.W. Griffin, U.S. Geological Survey, Florida Water Science Center, 2639 N. Monroe St., Tallahassee, FL 32303; P.B. McMahon, U.S. Geological Survey, Colorado Science Center, Lakewood, CO 80225; H.S. Harden and J. P. Chanton, Florida State Univ., Dep. of Oceanography, Tallahassee, FL 32306; E. Wade and R.W. Hicks, Florida Dep. of Environmental Protection, Tallahassee, FL 32399. Supplemental material available online for this article. Assigned to Associate Editor Lakshinder Hundal.

Abbreviations: bls, below land surface; cfu, colony-forming units; DOC, dissolved organic carbon; KN, Kjeldahl nitrogen; OWCs, organic wastewater compounds; RT-PCR, reverse transcriptase–polymerase chain reaction; STE, septic tank effluent; UFA, Upper Floridan aquifer; WKP, Woodville Karst Plain.

accurately model the movement of contaminants to groundwater and springs from these systems.

A steady increase in nitrate-nitrogen ($\text{NO}_3\text{-N}$) concentrations ($0.25\text{--}0.9\text{ mg L}^{-1}$) during the past 30 yr in Wakulla Springs, a large regional discharge point for water from the Upper Floridan aquifer (UFA), has increased concerns about groundwater contamination in the Woodville Karst Plain (WKP) in northern Florida (Katz et al., 2004). There are an estimated 20,000 septic tanks in the WKP (Fig. 1), an area highly susceptible to groundwater contamination due to numerous sinkholes and a relatively thin layer of highly permeable sands and clays overlying the karstic UFA. Although septic tanks have been presumed to be a significant source of N to the unconfined groundwater system (Chelette et al., 2002), little direct information exists on the impact of STE on groundwater quality. Studies in other mantled karst systems have shown that septic tank systems contributed to elevated NO_3 concentrations in groundwater (e.g., Panno et al., 2006; Harden et al., 2003, 2008). Chemicals in many household products can enter the subsurface from STE in more concentrated amounts, such as optical brighteners (Murray et al., 2007). Pharmaceutical compounds have been found in shallow zones of the UFA in areas where septic tanks are presumably affecting groundwater quality (Katz and Griffin, 2008; Katz et al., 2009).

Our study had two main objectives: (i) to estimate N loading to groundwater from septic tanks in the WKP and (ii) to determine the attenuation of microorganisms, organic wastewater compounds (OWCs), and pharmaceutical compounds in the subsurface beneath septic tank drainfield sites in the WKP. Multiple chemical indicators are used to elucidate processes controlling the transport and fate of nutrients, OWCs, and pharmaceutical compounds as effluent moves downward

from septic tank drainfields to the groundwater system. In addition, fecal indicators and enteroviruses are used to examine the movement of microorganisms beneath the drainfield sites. The multitracer approach used in this study can be applied to a variety of locations in different soil types to improve model predictions of impacts from NO_3 and other contaminants from septic tanks on groundwater quality.

Description of Study Area and Sites

The study area (approximately 1100 km^2) lies within the WKP and is located in southern Leon and Wakulla Counties (Fig. 1). The WKP is characterized by numerous wet and dry sinkholes, conduit networks, and disappearing streams (Rupert and Spencer, 1988). The study area is mostly rural, with low-density residential areas (most lot sizes $>0.4\text{ ha}$). In the WKP, the UFA is overlain by a thin veneer of highly porous quartz sand with highly variable amounts of silt and clay (Fig. 1). Streams flowing into this area flow into sinkholes and disappear, and other streams originate in the WKP from spring discharge. Land-surface altitudes in the WKP are generally less than 15 m above sea level. The climate is humid subtropical with an average annual air temperature of 19.5°C and average annual precipitation of 161 cm (1971–2000), measured at the National Weather Service station at the Tallahassee Regional Airport (<http://cdo.ncdc.noaa.gov/ancsum/ACS>). The largest amount of monthly rainfall typically occurs in June, July, and August, and the smallest monthly amount in occurs April, October, and November. During August 2007 through July 2008, rainfall was about 28 cm below average. Recharge to the UFA in the study area is about 46 cm yr^{-1} (Davis, 1996), and groundwater flow in the UFA generally is from north to south (Fig. 1) based on previous potentiometric maps (Chelette et al., 2002).

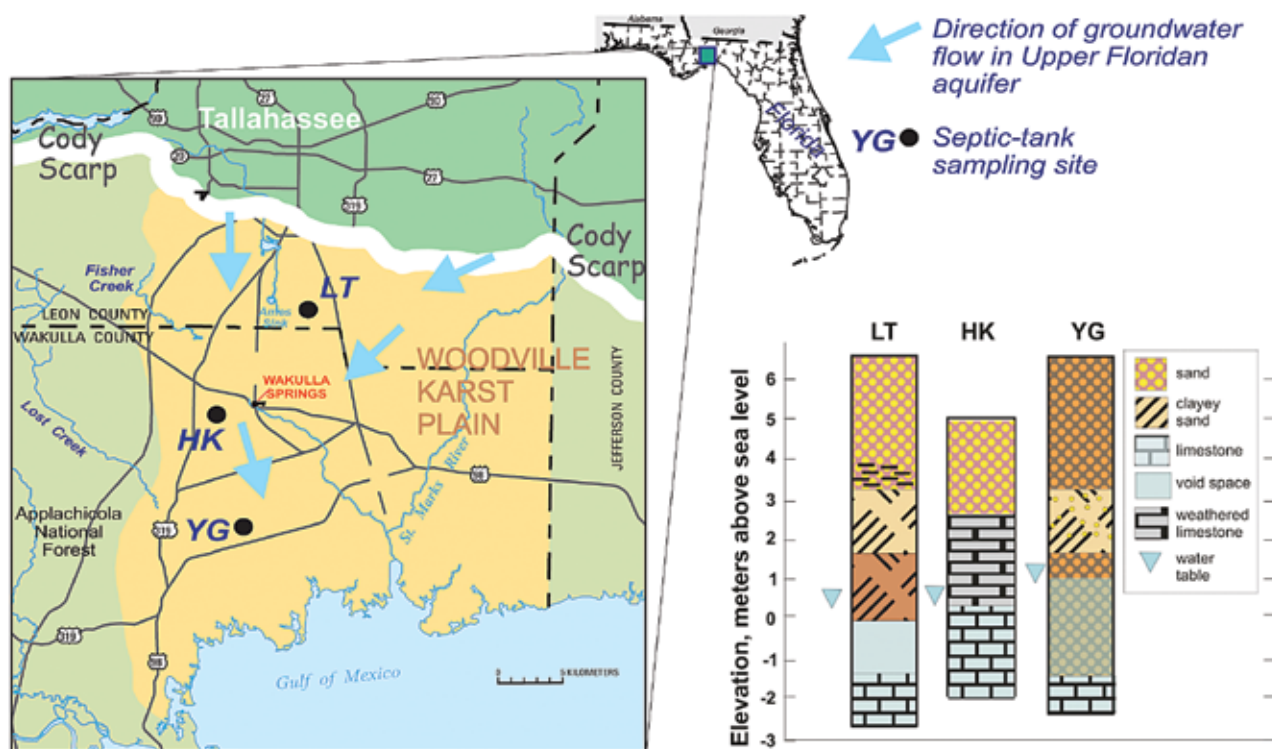


Fig. 1. Location map showing septic tank sites and generalized lithology at each site.

Site Characteristics

The three sites selected for this study (Fig. 1) represent a range of residences and water usage that likely are representative of septic tank systems in the WKP. Water meters were installed at each house, and the septic tank at each site was pumped before the start of the study. Drainfield pipes are located at approximately 0.6 m below land surface. The northernmost site (LT) had two to three adult residents who had lived in the house since it was built in 1987; the household used the original septic tank and drainfield. Average daily water use at the LT site was 394 L d⁻¹. No fertilizers had been applied by the current residents of the house. Depth to groundwater ranged from 3.0 to 3.6 m during the study.

The HK site had four residents (two adults and two teenage children), and the septic tank had been in use for approximately 30 yr. Average daily water use during the study period was 1630 L d⁻¹, although water discharge to the septic system was reduced in early 2008 through the use of water conservation measures. The septic tank was installed in the mid 1970s, and the drainfield was repaired or replaced on three occasions. The original drainfield, consisting of terra cotta pipe into a gravel bed, was extended in 1984. The extension was two gravel-filled trenches with perforated black plastic pipe. That drainfield failed in 2005 and was replaced with infiltrators in February 2005. Due to excessive loading of water, that drainfield failed in December 2007 and was replaced in January 2008 by the current one, which also has infiltrators. The turf over the new septic tank drainfield (approximately 80 m²) was seeded with rye and given a few handfuls of fertilizer in January 2008. In May 2008, it was seeded with a summer grass mix, and about 2 kg of fertilizer (10–10–10) was added. In addition, <2 kg of 10–10–10 fertilizer was applied to a garden (about 70 m²) next to the new drainfield. Depth to the water table ranged from 2.6 to 2.7 m during the study.

The YG site had two adult residents that have lived in the household for 4 yr. The house was built around 2003. The original septic tank system was in use at the time of the study. Average daily water use was 610 L d⁻¹. No fertilizers had been applied by the residents of the house. Depth to the water table ranged from 4.1 to 4.4 m during the study.

Subsurface Lithology

All three sites have variable amounts of sands and clays that overlie limestone of the Upper Floridan aquifer. Soils have low slopes (0–5%), have low organic matter content (<2%), and are classified as Alpin sand and Blanton fine sands (thermic, coated Typic Quartzipsamments), Alpin fine sands, and Ortega sands (thermic, uncoated Typic Quartzipsamments) at the LT, HK, and YG sites, respectively (Allen, 1991). Based on observations of core material collected during well installation, there are important differences between the lithology of subsurface material at the three sites (Fig. 1). Sand comprises the upper 2 to 3 m of the subsurface at each site and overlies clayey sand at the LT and YG sites but overlies weathered limestone at the HK site. Depth to limestone was variable at each site; the greatest depth to limestone was at the YG site (Fig. 1). Particle size analyses of samples from various depth intervals (from land surface to 123 cm below land surface) at each site indicate vari-

ous mixtures of very fine to coarse sand and an increasing percentage of silt and clay with depth at each site.

Materials and Methods

The sampling design at each site (Supplemental Fig. S1) consisted of two sets of lysimeters, a background well located upgradient from the septic tank drainfield, a well beneath the drainfield, and STE. A sampling port was installed by a septic tank contractor in the pipe that connects the septic tank to the drainfield to allow sampling of the STE.

Four suction-cup lysimeters were installed by hand auger beneath the drainfield at each of the three sites to collect pore water samples moving in the unsaturated zone. Details about lysimeter construction are included in Supplemental Fig. S1. Each of the shallow lysimeters had a total length of 110 cm and collected soil water samples from a depth of 92 to 118 cm below land surface. At this depth the shallow lysimeters were immediately below the bottom of the drainfield. Each of the deep lysimeters had a total length of 186 cm, sampling from a depth of 168 to 194 cm below land surface. To obtain samples, a suction of 60 kPa was applied to the lysimeters for a period of about 24 h before sample collection. Nitrogen gas was used to apply a pressure of 5 to 10 kPa to force the water into a collection vessel.

Drainfield and background wells were installed at each site using a direct push rig. These wells consisted of a 1.9-cm-diameter PVC casing with a 1.5-m-length prepacked screen that was placed below the water table. A peristaltic pump was used to purge three well volumes and to collect water samples for analyses.

Water Samples

Water samples were collected at each site on three occasions: December 2007, March 2008, and July 2008. On each occasion, samples were collected from the STE, the shallow and deep lysimeters, the drainfield well, and the background well. Two lysimeter samples from each depth were combined to obtain the required volume of sample for laboratory analyses. Sample collection and preservation methods are described in the National Field Manual for the Collection of Water-Quality Data (U.S. Geological Survey, 1999). Specific conductance, pH, dissolved oxygen, and temperature were measured in water samples in the field. Major ions, nutrients, boron, and dissolved organic carbon (DOC) were analyzed at the U.S. Geological Survey National Water Quality Laboratory (USGS NWQL) in Denver, Colorado (Fishman and Friedman, 1989; Patton and Truitt, 1992; Brenton and Arnett, 1993; Fishman, 1993; Patton and Truitt, 2000).

Stable isotopes of N, oxygen, and hydrogen were used to help differentiate between sources of N in water samples and to evaluate N transformation processes. Nitrogen isotope analyses of dissolved NH₄⁺ (δ¹⁵N-NH₄) were performed at the USGS Stable Isotope Laboratory in Reston, Virginia, using continuous-flow isotope ratio mass spectrometry (Brenna et al., 1997; Hannon and Böhlke, 2008) and are reported in parts per thousand (‰) relative to N₂ in air. The 2-sigma (σ) uncertainty of δ¹⁵N-NH₄ analyses is 0.8‰.

The stable isotope composition of NO₃ (δ¹⁵N-NO₃ and δ¹⁸O-NO₃) in water samples was analyzed at the USGS Stable Isotope Laboratory in Reston, Virginia, by bacterial conversion

of NO_3 to nitrous oxide and subsequent measurement on a continuous flow isotope ratio mass spectrometer (Sigman et al., 2001; Casciotti et al., 2002; Coplen et al., 2004). Values of $\delta^{15}\text{N}\text{-NO}_3$ are reported in ‰ relative to N_2 in air (Mariotti, 1983). For samples with $\text{NO}_3\text{-N}$ concentrations $\geq 0.06 \text{ mg L}^{-1}$, the 2σ uncertainty of N isotopic results is 0.5‰; for samples with NO_3 concentrations $< 0.06 \text{ mg kg}^{-1}$ as N, it is 1‰. Values of $\delta^{18}\text{O}\text{-NO}_3$ are reported in ‰ relative to Vienna Standard Mean Ocean Water (reference water) and normalized on a scale such that Standard Light Antarctic Precipitation reference water is -55.5‰ (Coplen, 1988; Coplen, 1994). For water samples with $\text{NO}_3\text{-N}$ concentrations $\geq 0.06 \text{ mg L}^{-1}$, the 2σ uncertainty of oxygen isotopic data is 1.0‰, and for samples with $\text{NO}_3\text{-N}$ concentrations $< 0.06 \text{ mg L}^{-1}$, it is 2‰.

Water samples were analyzed for various groups of OWCs (Supplemental Table S1) to assess the movement of these compounds into groundwater beneath septic tank drainfields. The OWCs included fragrances and flavorants, flame retardants, antioxidants, fuel-related compounds, detergent metabolites, plasticizers, disinfectants, solvents and preservatives, polynuclear aromatic hydrocarbons, pesticides, plant and animal steroids, and caffeine. Samples were collected using protocols to avoid field contamination of the sample (U.S. Geological Survey, 1999) because several compounds are present in commonly used products, including soaps, fragrances, insect repellants, and beverages. Water samples were filtered in the field through 0.7- μm nominal pore size glass fiber filters, chilled and maintained at 4°C , and shipped overnight to the laboratory. Samples were analyzed at the USGS NWQL for 63 compounds using capillary-column gas chromatography/mass spectrometry methods (Zaugg et al., 2002; Burkhardt et al., 2006; Zaugg and Leiker, 2006). Quality assurance information for OWCs is included in Supplemental Table S1.

Water samples were collected and analyzed for 16 pharmaceutical compounds at the USGS NWQL (Cahill et al., 2004). Supplemental Table S2 includes a list of these compounds (selected prescription and over-the-counter drugs and certain degradates/metabolites) along with laboratory quality assurance information for these compounds.

Subsurface Material Samples

Core samples of unsaturated zone material were collected beneath the septic tank drainfields (in between drain lines) using direct push techniques. This technique resulted in minimal disturbance to subsurface material due to the small-diameter holes created by the rig because no cuttings are produced, and greater sample recovery can be achieved compared with other methods. Subsamples of oven-dried (105°C) core material from discrete depth intervals were analyzed for exchangeable NH_4^+ in a solution extracted with 2 mol L^{-1} KCl. Ammonium was analyzed colorimetrically using the salicylate method (Nelson, 1983; McMahon et al., 2006). Nitrate and other anions (nitrite, chloride, bromide, and sulfate) were analyzed in a solution extracted using deionized water (McMahon et al., 2006). Replicate samples were run after every fifth environmental sample to assess the effects of field and laboratory procedures on measurement variability.

Microbiology Analyses

Microbiological samples were collected in sterile 1.0-L bottles and stored on ice until processed. Samples were analyzed for the presence of fecal indicator bacteria in duplicate in 5.0 μL (septic effluent) to 200-mL volumes. Samples were processed using membrane filtration per Standard Method (SM) 9222D (American Public Health Association, 1998). Indicator sample results are expressed in the text and tables as the number of colony-forming units (cfu) per 100.0 mL of water (average of the duplicates).

Samples also were screened for enteroviruses (polio, coxsackie A, coxsackie B, echoviruses, etc.) using 50.0- to 100.0-mL volumes (volume dependent on particle load) following a modified reverse transcriptase–polymerase chain reaction (RT-PCR) and dot blot protocol (Lipp and Griffin, 2004). The modification was direct concentration of water samples with Centriprep YM-50 centrifugal filter devices (i.e., no acidification or membrane filtration–based preconcentration) following the Centriprep protocol in 15-mL increments to a final volume of $\sim 500.0 \mu\text{L}$. RNA was purified from one half of the Centriprep concentrate using Qiagen's RNeasy Kit to a final eluent volume of $30 \mu\text{L}$ ($7 \mu\text{L}$ was used for RT-PCR). The combined enterovirus RT-PCR–dot blot results are expressed as presence (+) or absence (–). Negative and positive controls were used with all prokaryote and virus assays.

For screening of soil samples for microbial indicators and viruses, 10 mL of sterile water was added to $\sim 5.0 \text{ g}$ of soil and shaken overnight on a table top rotator at room temperature. On the following day, samples were centrifuged at 1500 rpm for 2 min, and 4.5-mL aliquots ($\times 2$) were used for membrane filtration following SM 9222D. Indicator sample results are expressed as the number of cfu per gram of soil (average of the duplicates). RNA was extracted from $\sim 2.0 \text{ g}$ of soil using the RNA PowerSopil Total RNA Isolation Kit (MO BIO, Carlsbad, CA). Kit protocol was followed, and $7 \mu\text{L}$ of eluent was used for RT-PCR.

Results and Discussion

Distribution of Nitrogen Species in Septic Tank Effluent, Soil Pore Water, and Groundwater

Concentrations of N species varied considerably among and within sites during the three sampling periods (Fig. 2). Kjeldahl nitrogen (KN) comprised essentially 100% of the total N in the STE at each site. About 80 to 94% of the total N consists of NH_4^+ , which is slightly higher than the range of 75 to 85% in previous studies (McCray et al., 2005). Kjeldahl nitrogen concentrations in the STE were lowest at the HK site ($17\text{--}39 \text{ mg L}^{-1}$) and ranged from 42 to 65 mg L^{-1} and from 53 to 58 mg L^{-1} at the YG and LT sites, respectively. High and low KN concentrations in STE were not consistent temporally among the three sites (Fig. 2). Nitrate was the dominant form of N in water samples from the shallow lysimeters, deep lysimeters, and the drainfield well at each site, with median $\text{NO}_3\text{-N}$ concentrations comprising 94, 95, and 99% of the total N, respectively. This is consistent with other studies that show nearly complete and rapid nitrification in septic system effluent within short distances from the distribution lines (Wilhelm

et al., 1994; Ptacek, 1998; Barringer et al., 2006). Ammonium and organic N comprised almost 44% of the total N in water from the HK drainfield well in December 2007, indicating that the drainfield was not functioning properly. The homeowner replaced the clogged drainfield with a new drainfield in January 2008, and a new set of lysimeters and a drainfield well were installed.

Median $\text{NO}_3\text{-N}$ concentrations were higher in the July 2008 water samples from the shallow and deep lysimeters and from drainfield wells at the three sites than in samples from December 2007 and March 2008. Median chloride concentrations also increased in the July 2008 samples from the deep lysimeters and drainfield wells from the three sites but decreased in the shallow lysimeters. Because the median chloride and KN concentrations in STE were lower in the July 2008 samples than in the December 2007 and March 2008 samples, it is likely that the chloride and $\text{NO}_3\text{-N}$ that were stored beneath the drainfield lines moved deeper due to increased rainfall and recharge during late spring and early summer. The higher median $\text{NO}_3\text{-N}$ concentration in groundwater samples from July 2008 also could be biased high due to fertilizer application at the HK site (see below).

Isotope Ratios of Ammonium, Nitrate, and Water

Values of $\delta^{15}\text{N-NH}_4^+$ in STE samples showed little variation among sites and temporally, ranging from 4.4 to 4.9‰, from 4.5 to 5.3‰, and from 5.0 to 5.5‰ at the HK, YG, and LT sites, respectively. These values are similar to those (4.2–5.1‰) for STE from a study of septic tank systems and packed bed sand filters (Hinkle et al., 2008). Values of $\delta^{15}\text{N-NO}_3^-$ in water samples were more variable and ranged from <2‰ (YG background well) to 13.4‰ (old drainfield well at HK site) (Supplemental Table S3). The low $\delta^{15}\text{N-NO}_3^-$ values (<6.0‰) correspond to values observed elsewhere, where NO_3^- in groundwater is recharged beneath land receiving inorganic fertilizers (Kendall and Aravena, 2000). Previous studies have found that $\text{NO}_3\text{-N}$ concentrations and $\delta^{15}\text{N-NO}_3^-$ values were highly variable in groundwater from sites throughout the WKP and could be attributed to several sources, including inorganic fertilizer applied to lawns, gardens, cropland, and turfgrass, and organic wastes from domestic wastewater and animal wastes (Katz et al., 2004). The HK homeowner indicated that fertilizer was applied to new grass planted on top of the new drainfield before the collection of the July 2008 samples. Fertilizer applied upgradient from the YG site may have resulted in the low $\delta^{15}\text{N-NO}_3^-$ signature in the background well, as the homeowner indicated that no fertilizer had been applied recently.

Additional information about processes affecting the transformation of N species can be gleaned from N and oxygen isotopes of NO_3^- . Values of $\delta^{15}\text{N-NO}_3^-$ and $\delta^{18}\text{O-NO}_3^-$ increase systematically in water samples from shallow and deep lysimeter samples at the LT and YG sites and plot along trend lines with a slope of 0.5, which is consistent with denitrification (Fig. 3). This process is related to the ratio of enrichment of oxygen to N in NO_3^- , which has been shown to be close to 1:2 (Aravena and Robertson, 1998; Kendall and Aravena, 2000). Additional evidence for this ratio of enrichment of oxygen to N in NO_3^- is based on a comparison of plotted values of $\delta^{18}\text{O-}$

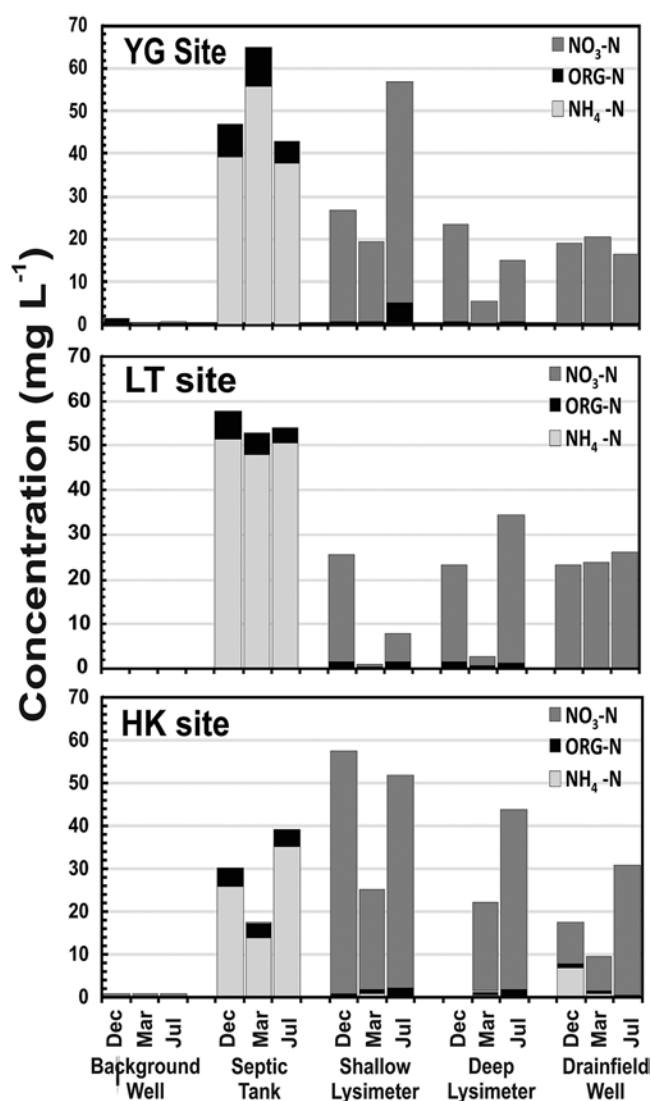


Fig. 2. Plots showing concentrations of nitrogen species in water samples from the background well, septic tank, lysimeters, and drainfield well at each site. Nitrogen species include nitrate ($\text{NO}_3\text{-N}$), organic nitrogen (ORG-N), and ammonium ($\text{NH}_4\text{-N}$).

H_2O and $\delta^{18}\text{O-NO}_3^-$ (Supplemental Fig. S2 and Table S3). The higher $\delta^{15}\text{N-NO}_3^-$ and $\delta^{18}\text{O-NO}_3^-$ values in the LT deep lysimeter site could be related to higher clay content in the subsurface, which could create conditions (perched-water; slower water movement, low-dissolved-oxygen microsites) more favorable to denitrification. Problems with ponding and poor drainage over time at the old HK drainfield likely resulted in an enriched $\delta^{15}\text{N-NO}_3^-$ and $\delta^{18}\text{O-NO}_3^-$ signature in the December 2007 sample from the drainfield well; however, similarly high isotopic values were not seen in the shallow lysimeter at this time. Mixed redox conditions at the water table at the old HK drainfield site likely were present in December 2007, as indicated by elevated NH_4^+ , NO_3^- , and dissolved oxygen concentrations (Table 1). The July samples at the new HK drainfield site clearly show the influence from the application of synthetic fertilizer, with low $\delta^{15}\text{N-NO}_3^-$ values <6‰. Elevated $\delta^{15}\text{N-NO}_3^-$ (8–10‰) and $\delta^{18}\text{O-NO}_3^-$ (5–6.5‰) values for water from the HK background well may indicate the influence from upgradient septic tanks in the area.

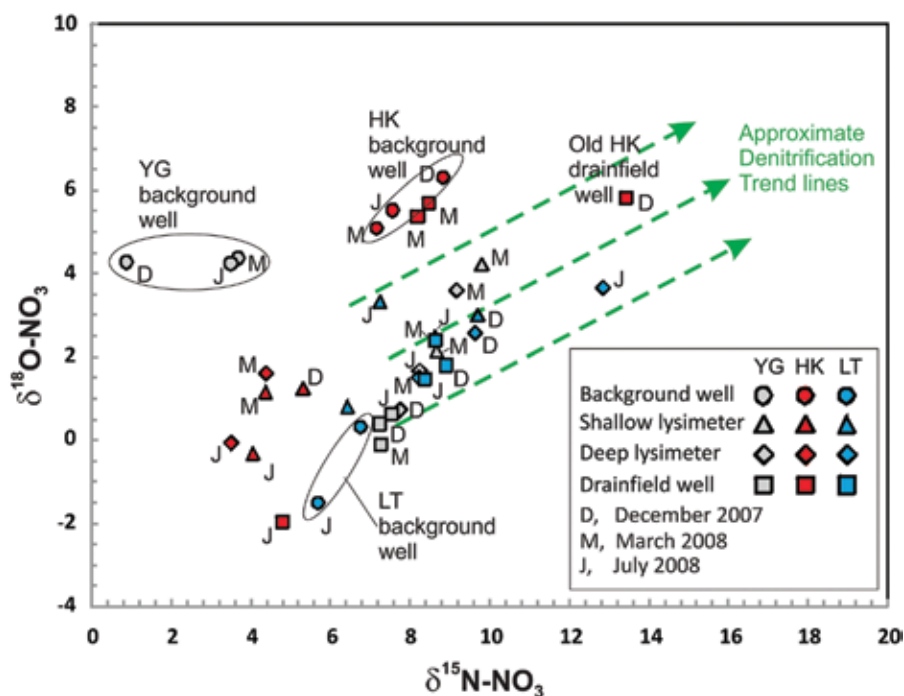


Fig. 3. Plot of nitrate isotope data for water samples from the background well, septic tank, lysimeters, and drainfield well at each site. Values of $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ are given with respect to air N_2 and Vienna standard mean ocean water, respectively, in parts per thousand.

Depth Profiles of Nitrogen Species and Chloride in Unsaturated Zone Material

Analyses of N species and chloride in soil core material from various depth intervals provide snapshots of N and Cl fluxes to the water table before and after the water samples were collected. Ammonium N concentrations (expressed as mg L^{-1} by accounting for moisture content of the oven-dried samples) were substantially higher in core samples from depths <5 cm at the YG site compared with the two other sites (Fig. 4). At depths >50 cm, $\text{NO}_3\text{-N}$ generally was the dominant N species at the three sites, which corresponds to the oxic conditions measured in soil pore water from lysimeters and in groundwater (top of UFA). Nitrogen concentrations were substantially higher in the July 2008 samples compared with November 2007 samples at all three sites. At the LT site, the highest N (NO_3) concentration (about 110 mg L^{-1}) at the 180-cm depth corresponded to the highest chloride concentration. This depth interval also contains a higher amount of clay ($\sim 5\%$) compared with other depth intervals analyzed for particle size distribution. Depth profiles of chloride concentrations were similar at the YG site between November 2007 and July 2008. In contrast, higher chloride concentrations were measured in core samples beneath the old drainfield compared with those collected beneath the new drainfield at the HK site (Fig. 4). At all three sites, N concentrations in the unsaturated zone generally were higher than concentrations measured in STE but were similar to N concentrations measured in water samples from shallow lysimeters at the YG and HK sites. Concentrations at the LT site were considerably higher in extracts of unsaturated zone material than in water from shallow lysimeters. High variability of N concentrations in soil and unsaturated zone pore water among sites has been reported in other studies (Rosen et

al., 2006; Hinkle et al., 2008). The high variability of N concentrations between the three sites likely is due to a combination of factors, such as N loading, soil characteristics and lithology, and dilution from household activities such as washing clothes and bathing.

Large differences in concentrations of N species and chloride with depth between the November 2007 and the July 2008 samples appear to be related to differences in rainfall and recharge conditions before sampling. In December 2007, the previous 30-, 60-, and 90-d rainfall amounts (7, 13, and 21 cm) were substantially lower than before the March (22, 29, and 36 cm) and July (15, 25, and 27 cm) sampling events. Increased recharge in the spring and early summer of 2008 likely resulted in downward movement of N (NH_4^+ and NO_3). With increased rainfall/recharge, one would expect that concentrations in the unsaturated zone would be lower (i.e., more dilution) than during periods of lower rainfall. However, it is likely that

NH_4^+ and organic N in water retained beneath the drainfields may have been converted to NO_3 as it moved toward the water table. At the LT site, the perched-water conditions created by the presence of higher amounts of clay at lower depths may account for the increase in chloride and N at the 170 cm depth and possibly allowing more water–sediment contact time for NH_4^+ desorption reactions.

Attenuation of Nitrogen beneath Septic Tank Drainfields

Median and mean N (dissolved) concentrations in STE decrease with depth as the STE percolates downward from the drainfield to the water table, as indicated by progressively lower concentrations in shallow lysimeters, deep lysimeters, and drainfield wells. Mean N concentrations ($\pm 1\sigma$) for all samples of STE, shallow lysimeters, deep lysimeters, and drainfield wells were 45 ± 14 , 30 ± 21 , 22.6 ± 16.5 , and $21 \pm 6.8 \text{ mg L}^{-1}$, respectively (Fig. 5). Also, N concentrations decrease with depth to about 25 to 40 mg L^{-1} in pore water samples from the unsaturated zone. Dilution accounts for some of the decrease in N concentrations (15–25%) based on median and mean chloride concentrations, respectively, in STE, water from shallow and deep lysimeters, and drainfield wells (Fig. 5) (assuming that chloride is conservative and that there are no naturally occurring sources of chloride in the unsaturated zone). Nitrogen loss is related to denitrification, sorption of NH_4^+ (includes adsorption and ion exchange) on soil particles, and ammonia volatilization.

Denitrification and Ammonium Volatilization

Decreased N concentrations in soil water and groundwater may result from denitrification or ammonia volatilization. At the YG and LT sites, there were average increases of 3.3 and 3.6‰ between $\delta^{15}\text{N-NH}_4$ in water samples from STE and $\delta^{15}\text{N-NO}_3$

Table 1. Physical properties and concentrations† of major dissolved chemical constituents in water samples from septic tanks, background (back.) wells, shallow (shal.) and deep lysimeters (lys.) and drain-field (drain.) wells at the three studied sites.

Site	Date	Smpl. t#	Temp. °C	Sp. Cond., at 25°C#	Diss. O ₂ #	pH	Amm., as N#	Amm. plus ON, as N#	Nitrate plus nitrite, N	Ortho-phosphate, as P	Ca	Mg	Na	K	Cl ⁻	Sulfate	F ⁻	SiO ₂	B	Alk., as CaCO ₃ #	Bromide	Cl/Br mass ratio	
µg L ⁻¹																							
YG																							
Septic tank	18 Dec 2007	1430	19.0	725	2.2	6.5	39#	47	<0.04	5.8	33	50	1.8	27	9.6	27	E0.12\$	0.14	14	22	293	0.04	680
Septic tank	13 Mar. 2008	1200	23.6	887	1.0	6.6	56	65	<0.04	7.8	46	46	2.2	42	15	41	<0.18	0.12	9.6	253	346	E0.07	591
Septic tank	16 July 2008	1140	20.2	738		6.6	38	42	<0.04	6.2	26	48	1.7	34	9.9	35	4.5	E.09	9.5	191	285	0.05	694
Septic tank	16 July 2008	1145	20.2	738		6.6	38	43	<0.04	6.2	26	50	1.7	35	10	35	4.4	0.1	11	207	287	0.05	692
(DUP#)																							
Back. well	18 Dec. 2007	1200	18.4	20	6.2	8.3	<0.10	1.2	<0.04	0.13	7.1	0.15	0.42	1.8	0.17	2.6	1.1	<0.12	8.5	7.9	<5	<0.02	ND
Back. well	13 Mar. 2008	940	17.8	182	5.3	5.3	<0.02	E0.08	0.2	0.12	1.1	33	0.96	1.8	0.40	2.6	1.3	<0.12	5.8	8.7	84	E0.01	263
Back. well	16 July 2008	930	21.7	225		6.5	<0.02	E0.14	0.39	0.13	0.8	39	1.1	2.8	0.37	5.6	2.5	<0.12	5.3	7.9	103	0.03	187
Drain. well	18 Dec. 2007	1350	21.0	288	5.6	5.7	0.08	0.29	18.7	0.02	2.2	3.7	7.9	29	11	27	7.6	0.14	6.3	200	<5	0.04	665
Drain. well	13 Mar. 2008	1030	20.4	324	4.8	5.0	0.07	0.14	20.5	0.02	1.3	5.4	8.3	29	11	32	7.7	0.17	5.7	164	<5	0.04	805
Drain. well	16 July 2008	1000	24.0	294		5.5	0.13	0.21	16.2	0.02	0.7	4.3	6.8	27	8.9	35	7.1	0.14	5.2	142	<5	0.04	865
Shal. lys.	18 Dec. 2007	1340	17.0	438	5.9	5.7	0.02	0.49	26.2	<0.006	15	42	3.4	26	4.8	31	17	NS	13	31	27	0.03	1043
Shal. lys.	13 Mar. 2008	1130	18.6	439	3.3	5.7	0.11	0.77	18.6	0.02	14	35	1.7	45	5.0	39	22	<0.12	11	186	44	0.04	970
Shal. lys.	17 July 2008	1110	29.6	1450		6.2	0.13	4.9	51.9	0.04	24	105	1.6	195	0.96	196	58	<0.12	14	470	153	0.21	933
Deep lys.	18 Dec. 2007	1400	17.2	421	5.3	5.7	0.04	0.58	22.7	<0.006	NS	NS	NS	NS	NS	31	20	NS	NS	NS	34	E0.02	1560
Deep lys.	13 Mar. 2008	1100	17.2	332	4.0	5.5	E0.02	0.45	4.97	E0.003	14	29	1.4	35	1.1	27	19	<0.12	8.6	100	79	E0.02	1370
Deep lys.	16 July 2008	1050	28.4	467		6.0	0.04	0.61	14.4	0.01	16	35	1.1	53	2.3	40	28	<0.12	12	234	78	0.07	571

Table 1. Continued.

Site	Date	Smpl. t†	Temp. ‡	Sp. Cond., at 25°C‡	Diss. O ₂ ‡	pH	Amm., as N‡	Amm., plus ON, as N‡	Nitrate plus nitrite, N	Ortho-phosphate, as P	DOC‡	Ca	Mg	Na	K	Cl ⁻	Sulfate	F ⁻	SiO ₂	B	Alk., as CaCO ₃ ‡	Bromide	Cl/Br mass ratio
HK																							
Septic tank	19 Dec. 2007	1130	19.0	1050	1.5	6.8	26	30	<0.04	5.4	43	63	15	86	11	136	24	0.21	15	61	257	E0.25	544
Septic tank	12 Mar. 2008	1300	22.2	566	1.7	7.0	14	17	0.2	4.0	22	69	4.6	17	4.3	20	7.1	E0.09	7.6	99	242	0.02	1010
Septic tank	15 July 2008	1200	29.8	725		6.6	35	39	<0.04	7.2	56	56	6.3	26	10.8	30	4.2	0.15	10	115	290	0.05	598
Back. well	19 Dec. 2007	900	21.0	435	1.6	6.2	0.06	0.15	0.37	E0.006	2.1	91	2.3	2.1	0.20	3.1	4.4	0.13	7.6	11	222	<0.04	77
Back. well	12 Mar. 2008	1000	18.9	397	3.5	6.3	<0.02	E0.08	0.53	E0.004	0.9	81	1.9	2.1	0.12	4.3	4.2	<0.12	6.0	8.6	198	E0.02	213
Back. well	15 July 2008	920	25.0	400		6.7	<0.02	<0.14	0.39	0.01	1.2	77	2.1	2.1	0.23	3.4	4.5	E0.07	7.2	12	201	E0.01	339
Drain. well, old	19 Dec. 2007	945	21.0	894	7.3	6.3	6.9	7.6	9.9	0.02	3.1	139	5.7	28	5.1	43	18	E0.09	11	154	338	0.1	427
Drain. well, new	12 Mar. 2008	1110	19.4	560	2.1	6.6	1.00	1.5	8.2	0.11	2.7	93	4.2	11	2.6	18	12	<0.12	6.6	53	211	0.04	453
Drain. well, new\$	12 Mar. 2008	1115	19.4	560	2.1	6.6	0.81	1.2	8.0	0.06	2.6	93	4.1	11	2.5	18	12	<0.12	6.7	54	211	0.03	603
Drain. well, new	15 July 2008	1020	25.4	763		6.5	<0.02	0.26	30	1.0	2.1	105	6.3	29	5.7	46	19	E0.06	11	51	180	0.11	420
Shal. lys.	19 Dec. 2007	1100	15.0	1270	3.0	6.7	0.08	0.81	57	0.87	13	171	20	68	11	103	104	E0.11	13	102	122	0.21	490
Shal. lys.	12 Mar. 2008	1230	18.0	673	5.0	6.9	0.62	1.7	23	0.22	11	98	8.4	22	11	27	21	<0.12	24	130	204	0.05	534
Shal. lys.	15 July 2008	1120	27.0	1080		6.4	0.06	2	50	0.64	30	156	17	9.7	20	9.1	34	E0.07	13	65	288	<0.02	ND
Deep lys.	12 Mar. 2008	1140	18.5	680	4.2	6.9	0.32	1.2	21	0.16	16	93	8.5	19	7.6	27	23	<0.12	17	105	181	0.06	447
Deep lys.	15 July 2008	1050	26.6	783		6.4	<0.02	1.7	42	0.24	40	118	13	10	14	14	27	<0.12	8.7	52	202	<0.02	ND
LT																							
Septic tank	19 Dec. 2007	1730	16.0	1030	1.6	7.1	52	58	<0.04	13	50	46	12	57	21	41	2.4	0.24	25	71	391	E0.05	812
Septic tank	11 Mar. 2008	1300	18.4	923	2.8	7.1	48	53	<0.04	11	49	50	9.7	41	20	35	2.0	0.20	23	57	373	E0.03	1150
Septic tank	17 July 2008	1200	25.7	1100		6.9	51	54	E0.02	6.3	31	49	11	85	18	31	9.2	0.18	14	83	491	E0.04	773
Back. well	11 Mar. 2008	1030	18.8	195	4.9	6.8	<0.02	E0.07	0.11	0.01	1.1	34	2.4	1.5	0.22	2.7	3.5	<0.12	5.6	9.0	92	E0.01	270
Back. well	17 July 2008	910	21.3	193		7.0	<0.02	E0.13	0.08	0.01	1.4	34	2.6	2.0	0.23	2.7	3.4	E0.06	7.3	9.1	93	E0.01	271

Table 1. Continued.

Site	Date	Smpl. t†	Temp. °C	Sp. Cond., at 25°C†	Diss. O ₂ ‡	pH	Amm., as N‡	Amm. plus ON, as N‡	Nitrate plus nitrite, N	Ortho-phosphate, as P	DOC‡	Ca	Mg	Na	K	Cl ⁻	Sulfate	F ⁻	SiO ₂	B	Alk., as CaCO ₃ ‡	Bromide	Cl/Br mass ratio
Drain. well	19 Dec. 2007	1430	20.0	733	6.5	6.9	0.14	0.29	23	0.18	3.1	78	19	55	4.2	27	21	0.22	42	304	252	0.08	335
Drain. well	11 Mar. 2008	1115	19.3	794	5.8	6.9	0.04	0.19	24	0.17	2.4	85	19	46	4.3	29	21	0.13	30	285	254	0.05	584
Drain. well	17 July 2008	1010	21.3	762		6.8	0.03	0.19	26	0.31	1.9	80	20	47	4.4	28	20	0.14	31	210	237	0.05	550
Shal. lys.	19 Dec. 2007	1600	12.0	716	5.5	7.3	0.04	1.5	24	3.3	NS	NS	NS	NS	NS	30	40	0.20	NS	NS	177	<0.02	ND
Shal. lys.	11 Mar. 2008	1200	16.9	312	5.6	7.2	E0.02	0.5	0.47	1.1	13	41	12	3.7	1.8	1.6	10	0.14	12	92	146	<0.02	ND
Shal. lys.	17 July 2008	1130	27.1	942		6.9	<0.02	1.6	6.5	3.1	40	91	25	60	1.6	18	43	0.30	33	182	359	E0.01	1830
Deep lys.	19 Dec. 2007	1620	16.0	724	4.5	7.2	E0.01	1.6	22	3.2	13	69	20	48	11	27	33	0.24	21	59	204	E0.02	1350
Deep lys.	11 Mar. 2008	1230	16.7	365	5.5	7.3	0.02	0.83	1.9	3.1	9.8	45	13	12	3.4	2.6	8.9	0.19	18	39	172	<0.02	ND
Deep lys.	17 July 2008	1100	27.4	1120		6.6	0.03	1.4	33	5.6	20	90	25	79	17	54	53	0.21	25	70	267	0.05	1086

† Concentrations are in mg L⁻¹ unless otherwise noted.

‡ Smpl. t., sample time; Sp. cond., specific conductance; Diss., dissolved; Amm., ammonia; ON, organic nitrogen; DOC, dissolved organic carbon; Alk., alkalinity.

§ E, estimated value between method reporting level and detection limit; NS, no sample collected due to insufficient volume of water; ND, not determined as bromide concentration is below method reporting level.

¶ Duplicate sample.

in lysimeters and the drainfield well samples. These increases in N-isotopic composition, along with the decrease in N at these sites, are consistent with isotopic fractionation resulting from denitrification or volatilization of ammonia. At the HK site, the lower average increases of 1.7‰ (0.4‰ median) between $\delta^{15}\text{N-NH}_4$ in STE samples and $\delta^{15}\text{N-NO}_3$ in lysimeters and the drainfield samples likely were affected by fertilizer applications in April and May to turfgrass above the drainfield. However, samples showed an increase of 8.5‰ between $\delta^{15}\text{N-NH}_4$ and $\delta^{15}\text{N-NO}_3$ in water samples collected from the old drainfield well in December 2007 and an increase of 3.7 to 4.0‰ in the new drainfield well in March 2008 before fertilizer applications.

Denitrification likely occurs directly beneath the drainfield lines in all three systems. Other studies report about 10 to 25% N loss due to denitrification and ammonia volatilization before the leachate leaves the bottom of the drainfield, depending on the initial N concentration in STE (Bauman and Schafer, 1985; Hantzsch and Finnemore, 1992). Septic tank effluent from the three sites has elevated concentrations of DOC, with a median concentration of about 42 mg L⁻¹ (Fig. 5; Table 1). Median concentrations in soil water from lysimeters decrease to about 15 mg L⁻¹, indicating that DOC was consumed (or sorbed) during infiltration. However, water samples generally are oxic, but denitrification can occur in anaerobic microsites beneath septic tank systems in otherwise oxic systems (Koba et al., 1997). Concentrations of DOC in the drainfield well decrease to slightly greater than those in the background wells. Evidence for some denitrification can be seen from enriched values of $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ of NO_3 (Fig. 3). There is a shift toward more enriched values for water samples from shallow and deep lysimeters at the LT and YG sites and for water from the old drainfield well at the HK site. These slightly enriched values of $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ of NO_3 plot along denitrification trend lines with a slope of 0.5 (Kendall and Aravena, 2000).

Sorption of Ammonium

Ammonium strongly sorbs to mineral surfaces, particularly clay minerals (Drever, 1988); however, Hinkle et al. (2008) found essentially complete sorption of NH_4^+ on coarse sand with only 0.4% silt and clay in column experiments. Almost 100% of sorbed NH_4^+ was recovered using 2 mol L⁻¹ KCl in column desorption experiments (Hinkle et al., 2008). Even though soil cores were not collected directly beneath drainfield lines (to prevent damage to the existing system), the cores collected and analyzed for N species between the drainfield lines provide information about NH_4^+ sorption by soils. Based on 2 mol L⁻¹ KCl extracts of core samples, NH_4^+ concentrations ranged from 0.2 to 8.2 $\mu\text{g g}_{\text{soil}}^{-1}$ (~ 5 –190 $\mu\text{eq NH}_4^+ \text{g}_{\text{soil}}^{-1}$) in the November 2007 samples (Fig. 6) below the bottom of the drainfield (depth of about 80–100 cm). Higher amounts of

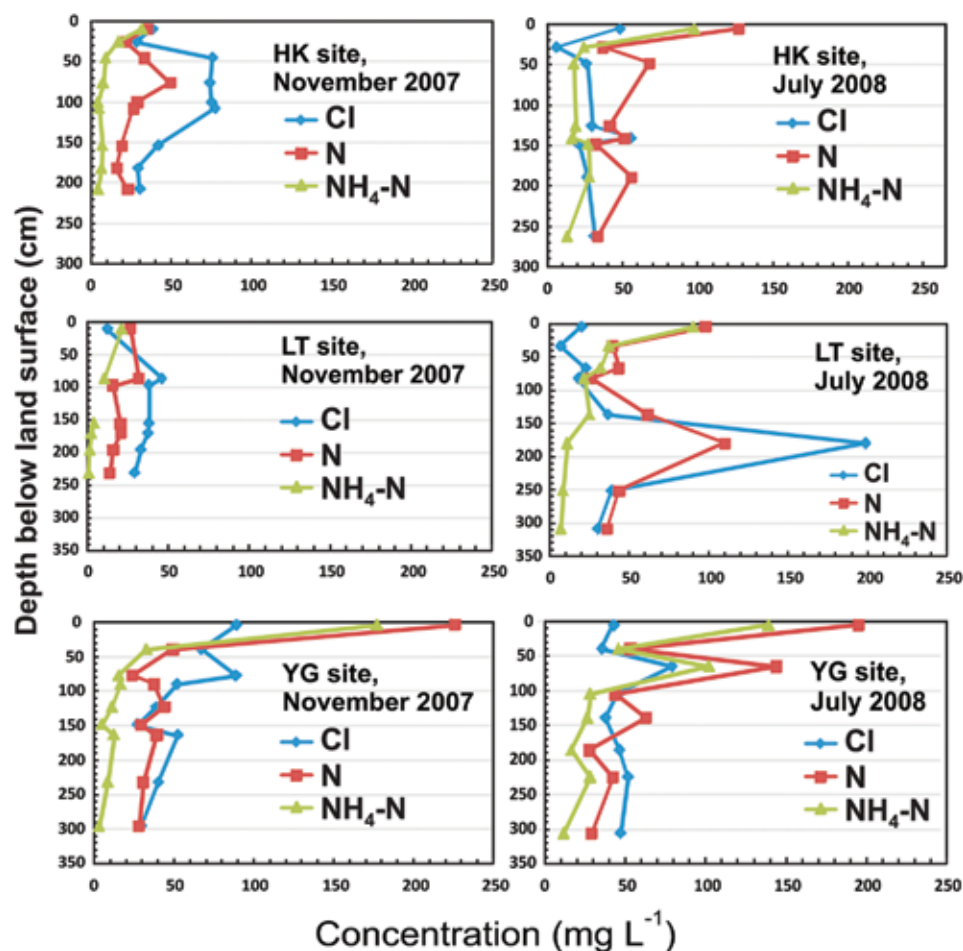


Fig. 4. Depth profiles of ammonium-N, nitrogen (sum of nitrate-N, nitrite-N, and ammonium-N), and chloride in subsurface samples from various depth intervals collected from each site in November 2007 and July 2008.

NH_4^+ were found in KCl extracts of soil material in the July 2008 samples ($2\text{--}10\ \mu\text{g g}_{\text{soil}}^{-1}$). These values fall within the range of total cation exchange capacities for glacial outwash sands ($5\text{--}20\ \mu\text{eq g}^{-1}$; Bohlke et al., 2006) to various types of clays ($28\text{--}8800\ \mu\text{eq g}^{-1}$) (Busenberg and Clemency, 1973). Thus, there would be sufficient opportunity for additional NH_4^+ sorption, particularly with the increasing relative amounts of clay minerals with depth. Also, NH_4^+ sorption by soils was likely greater beneath the new HK drainfield because this material was not at steady state with respect to NH_4^+ sorption. The source of the higher amounts of NH_4^+ in samples from the shallow subsurface ($<100\ \text{cm}$) at the YG site is unknown but may result from ammonia volatilization, nitrification of organic N, or fertilizer applications.

Nitrate-Nitrogen Loading to Groundwater from Septic Tanks

Based on average daily water use at each household (metered) and $\text{NO}_3\text{--N}$ concentrations at the water table (adjusted for dilution), N loading (kg N yr^{-1}) to groundwater ranged from 4.3 to 5.4 at the YG site, 3.9 to 4.3 at the LT site, and 6.6 to 12 at the HK site. The higher loading at the HK site compared with the two other sites results from a higher average daily water use ($\sim 1,630\ \text{L d}^{-1}$) and the larger range in $\text{NO}_3\text{--N}$ concentrations over the three sampling events. The July 2008 $\text{NO}_3\text{--N}$ data from the HK drainfield well were not used to calculate septic tank loads because fertilizer applications in May resulted

in a large increase in NO_3 in water from the drainfield well ($39\ \text{mg L}^{-1}$) (and the lysimeter samples). Annual per capita N loading rates to groundwater at the LT and YG sites are lower than other estimates of $4.5\ \text{kg N yr}^{-1}$ (Cox and Kahle, 1999), which would yield 9 and $13.5\ \text{kg N yr}^{-1}$ for households with two and three people, respectively. Based on septic tank studies in central Florida (Sherman and Anderson, 1991) and Oregon (Morgan et al., 2007), about 9.5 to $9.7\ \text{kg N yr}^{-1}$ per home are released to the drainfield, and it is estimated that an additional 25% reduction in N occurs beneath the drainfield (Anderson et al., 1994; Morgan et al., 2007). The annual N loading for the HK site ($6.6\text{--}12\ \text{kg N yr}^{-1}$) also is lower than the estimated loading to groundwater of $18\ \text{kg N yr}^{-1}$ based on per capita N loading (Anderson et al., 1994; Cox and Kahle, 1999).

Although only three septic tank systems were studied, measured N loading rates to groundwater are consistent with results from other studies. Furthermore, the number of people living in each household, per capita water use, location, and age of the studied septic

tank systems are representative of the area. Given that there are many uncertainties in extrapolating from the studied sites to the approximately 20,000 septic tanks in the WKP, it is estimated that annual $\text{NO}_3\text{--N}$ loading to groundwater from septic tanks in the WKP would range from 78,000 to 240,000 kg. This estimated range of N loading to groundwater can be considered conservative because $\text{NO}_3\text{--N}$ loads from septic tanks in this study are lower than those from other studies (due to lower per capita water use). Even with the conservative estimate of N loading from septic tanks in the WKP, this source represents a substantial contribution compared with the estimated N loading to the land surface (about $2\ \text{million kg N yr}^{-1}$) from other sources (atmospheric deposition, the land application of treated wastewater effluent, commercial fertilizers, livestock, and sinking streams) (Chelette et al., 2002). After N losses are considered for these other sources (e.g., uptake by vegetation, soils, denitrification, and volatilization), the relative contribution from septic tanks would be considerably higher and would represent a significant source of NO_3 to the groundwater system.

Attenuation of Organic Wastewater and Pharmaceutical Compounds

Given the relatively low analytical spike recoveries for several OWCs ($<60\%$) and for surrogate compounds (Supplemental

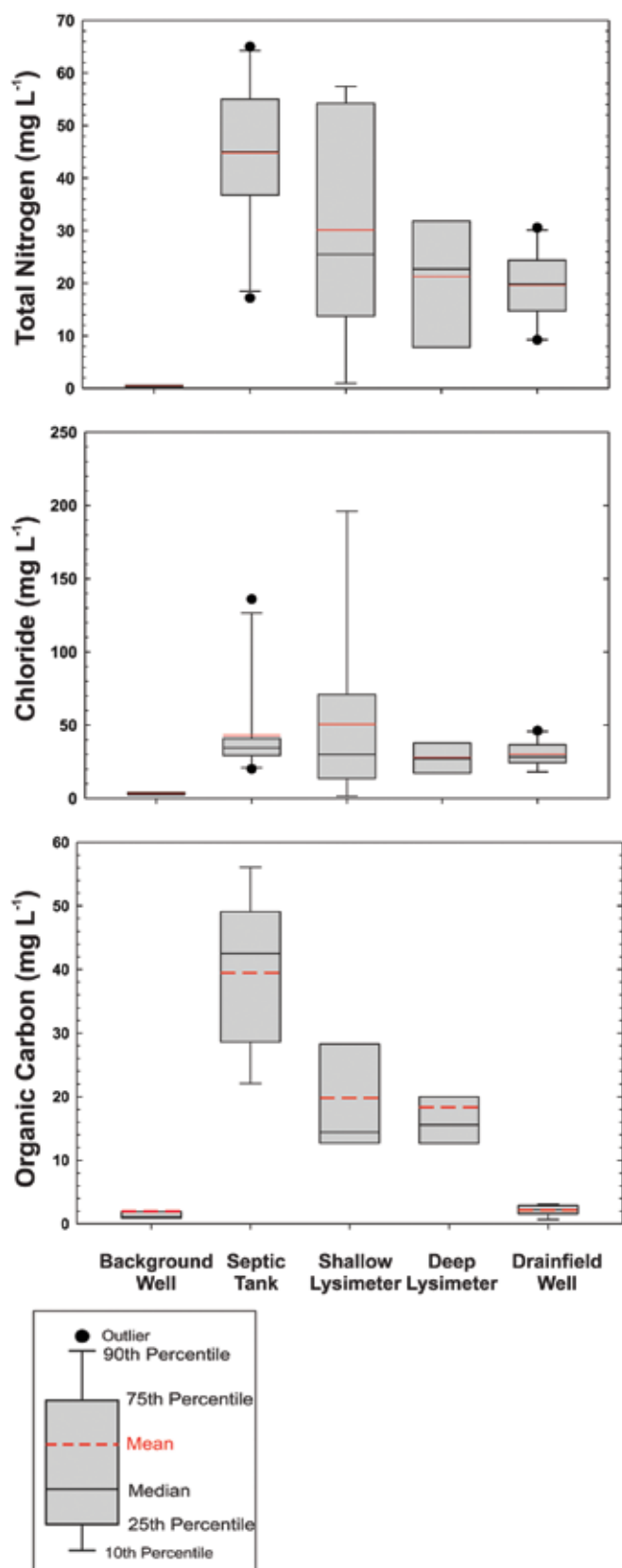


Fig. 5. Boxplots showing concentration distribution of nitrogen, chloride, and dissolved organic carbon in water samples from the background well, septic tank, lysimeters, and drainfield well at each site.

Table S4), detections for individual compounds only were considered when the measured concentrations were at least

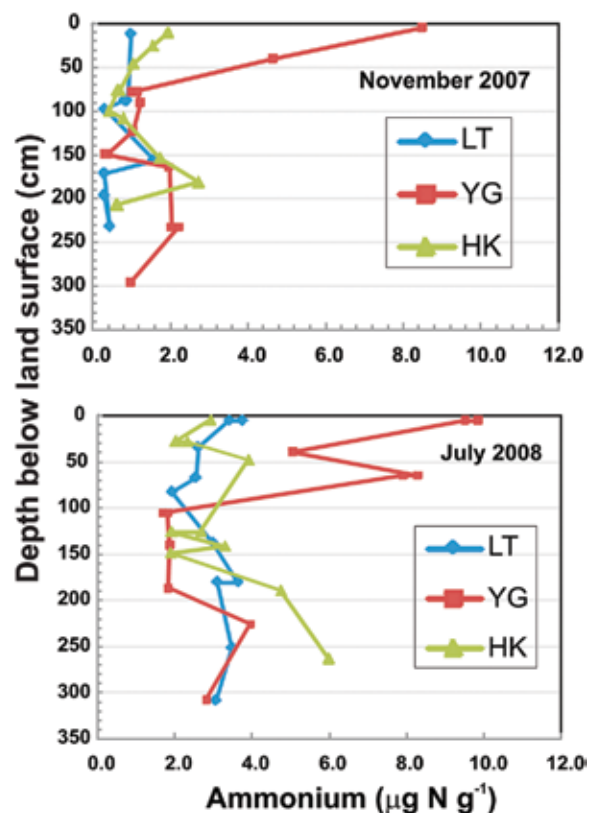


Fig. 6. Depth profile of ammonium in soil samples based on extracts of 2 mol L⁻¹ KCl solution.

three times the method reporting level. No OWCs were detected in blank water samples submitted to the NWQL during the study or in samples from background wells. In STE samples, 25 OWCs were detected out of the 63 compounds analyzed (Supplemental Table S4). The concentrations for most of these compounds were below 10 μg L⁻¹; however, 50% or more STE samples had five compounds with concentrations >10 μg L⁻¹: caffeine, 1,7-dimethylxanthine (caffeine degradate), menthol, p-cresol, and phenol. Concentrations of detergent metabolites and disinfectants (e.g., triclosan) were considerably lower than those found in other studies (e.g., Hinkle et al., 2005; Conn et al., 2006) and may result from uptake by solids and removal by sedimentation in the septic tank (Conn et al., 2006).

Substantial attenuation or removal of OWCs was observed in the subsurface beneath the drainfields. Phenol and cotinine were the only compounds detected in samples from lysimeters (Supplemental Table S4). Five OWCs were detected in the drainfield well at the HK site (caffeine, 1,7-dimethylxanthine, phenol, galaxolide, and tris(dichloroisopropyl)phosphate). Tris(dichloroisopropyl)phosphate was detected twice in samples from the YG site drainfield well. Concentrations of these OWCs in groundwater samples were <1.0 μg L⁻¹. Multiple detections of tris(dichloroisopropyl)phosphate in groundwater samples may indicate that this compound would be useful as an indicator of STE in shallow groundwater. The higher number of OWCs detected in drainfield wells compared with those for shallow and deep lysimeters may be indicative of the inefficiency of lysimeters as collectors of these compounds. Leachate could be moving along preferential pathways that

would lower the effectiveness of using lysimeters to collect OWCs in the unsaturated zone. Another possibility is that some compounds may have been excluded (i.e., removed) during passage through the ceramic cup.

Two pharmaceutical compounds (acetaminophen and sulfamethoxazole) were detected in water samples from septic tanks, lysimeters, and drainfield wells. Median recoveries for these two compounds in spike samples were 78 and 63%, respectively (Supplemental Table S2). Acetaminophen (an over-the-counter analgesic) was detected in eight of nine STE samples in concentrations ranging from 0.18 to 78.2 $\mu\text{g L}^{-1}$ at the HK site (Supplemental Table S5). Sulfamethoxazole (an antibiotic) was detected in only one STE sample (HK site; 0.04 $\mu\text{g L}^{-1}$). This compound was detected in all three water samples from the LT site drainfield well but not in any of the STE samples from this site. Sulfamethoxazole also was detected once in concentrations below the method reporting level in drainfield well water samples from the YG site (0.02 $\mu\text{g L}^{-1}$) and the HK site (0.04 $\mu\text{g L}^{-1}$). Low-level concentrations of these compounds in water samples from lysimeters and shallow groundwater (drainfield wells) are consistent with the movement of sulfamethoxazole from septic systems and its persistence in shallow groundwater in other studies (Godfrey et al., 2007; Carrara et al., 2008). Sulfamethoxazole, which has a low sorption affinity in soils (Cordy et al., 2004; Drillia et al., 2005), has been found in shallow zones of the Upper Floridan aquifer in areas where septic tanks likely have affected groundwater quality (Katz and Griffin, 2008; Katz et al., 2009).

Microbial Indicators and Enteric Viruses

Numbers of fecal coliforms were highly variable temporally in STE samples from each site and among sites (Table 2). For example, fecal coliforms in STE samples from the HK site ranged from 120,000 cfu per 100 mL in July 2008 to 380,000 cfu per 100 mL in March 2008. Fecal coliforms in STE from the LT site ranged from 1.4 million cfu per 100 mL in December 2007 to 7.8 million cfu per 100 mL in July 2008 and from 150,000 in July 2008 to 2.7 million cfu per 100 mL in March 2008 at the YG site. Rapid attenuation of fecal coliforms was observed at all sites; however, occasional detections of fecal coliforms (e.g., high concentrations in the HK drainfield well in March 2008) appear to be related to high rainfall amounts during the previous 30 to 60 d.

Enteroviruses were detected in STE samples from all three sites in December 2007 and in March 2008 but not in any of the July 2008 samples (Table 2). Enteroviruses were detected in an unused domestic well (i.e., an irrigation well) at the HK site, in the LT deep lysimeter in December 2007, in the LT background well and in both YG lysimeters in March 2008, and in the LT shallow lysimeter in July 2008. Sporadic detections and transport of enteroviruses in soil water and groundwater samples beneath the three septic tank drainfields are consistent with other studies (Darby and Leverenz, 2004; DeBorde et al., 1998; Abbaszadegan et al., 1999). The absence of enteroviruses in the July 2008 STE samples may indicate seasonality for this region because previous studies have shown that the enterovirus season runs from June through October in temperate

Table 2. Microbiological data for samples of septic tank effluent, soil water from lysimeters, and water from drainfield and background wells at each site.†

Site†	Fecal coliforms			Enteroviruses		
	Dec. 2007	Mar. 2008	July 2008	Dec. 2007	Mar. 2008	July 2008
	cfu 100 mL ⁻¹ ‡					
HK site						
Background well	0.0	16.8	0.5	–§	–	–
Septic tank effluent	220,000	380,000	120,000	+	+	–
Drainfield well	0.0	tntc¶	6.0	–	–	–
Lysimeter, shallow	0.0	0.0	0.0	–	–	–
Lysimeter, deep	nl	0.0	0.0	nl	–	–
Domestic well used for irrigation	0.5	0.0	3.0	+	–	–
LT site						
Background well	0.0	0.0	0.0	–	+	–
Septic tank effluent	1,450,000	4,660,000	7,800,000	+	+	–
Drainfield well	0.0	0.0	0.0	–	–	–
Lysimeter, shallow	0.0	0.0	0.0	–	–	+
Lysimeter, deep	0.0	0.0	0.0	+	–	–
YG site						
Background well	0.0	0.3	0.3	–	–	–
Septic tank effluent	210,000	2,720,000	150,000	+	+	–
Drainfield well	5.7	0.0	0.0	–	–	–
Lysimeter, shallow	0.0	0.0	0.0	–	+	–
Lysimeter, deep	2.0	0.0	0.0	–	+	–

† Data are for culturable fecal coliform and reverse transcriptase–polymerase chain reaction dot blot detection of human enteroviruses.

‡ cfu, colony-forming units.

§ +, presence; –, absence.

¶ nl, no lysimeter installed on this date; tntc, too numerous to count.

regions and may be continuous in tropical and semitropical environments (Moore, 1982; Melnick, 1989).

Generally there was little relation between detections of fecal coliforms and OWCs and pharmaceutical compounds. In samples where enteroviruses were detected, there were occasional detections of OWCs and pharmaceuticals; for example, in soil water from shallow lysimeters, caffeine was detected at the YG site in March 2008, and phenol was detected at the LT site in July 2008. In soil water from deep lysimeters, cotinine was detected at the YG site in March 2008, and phenol and camphor were detected at the LT site in December 2007. The slightly higher number of detected compounds in the March and July samples may in part be related to increased rainfall and recharge that may enhance the transport of these compounds in the subsurface.

Movement of Chloride and Bromide

Chloride/bromide (Cl/Br) ratios have been used to discriminate between wastewater and other sources of chloride from anthropogenic and naturally occurring contaminants in groundwater (Vengosh and Pankratov, 1998; Panno et al., 2006; Brown et al., 2009). The Cl/Br ratios in samples of STE ranged from 540 to 1150, with a median Cl/Br ratio of 694 ($n = 9$). This median value is similar to the median Cl/Br ratio (769; $n = 29$) reported by Panno et al. (2006) for STE. Groundwater samples from wells beneath the three drainfields had a slightly smaller range of Cl/Br ratios (335–805) and a median of 518 (Supplemental Fig. S3). Based on the small number of samples from this study, it appears that groundwater samples with a Cl/Br range of 400 to 1100 may be useful as a screening tool for evaluating septic tank influence on groundwater quality.

Conclusions

Septic tank effluent represents a substantial source of N loading to groundwater in the WKP, an area in northern Florida that is highly vulnerable to contamination due to a thin veneer of sands and clays overlying a karstic aquifer. Given that measured N loading to groundwater from three studied septic tank systems is consistent with results from other studies and that the studied septic tank systems are representative of other systems in the area, it is estimated that N loading to groundwater from the approximately 20,000 septic tanks in the WKP would range from 78,000 to 240,000 kg N yr⁻¹.

The use of multiple chemical and isotopic indicators provided important information about N transport to groundwater, which was affected by three main processes. The 50% apparent loss of N as drainfield STE moves to the water table is related to (i) dilution, which accounted for only about 10 to 25% of the decrease in N concentrations from STE to groundwater; (ii) denitrification, indicated by a systematic increase in $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ of NO_3^- in soil water from lysimeters; and (iii) sorption of ammonia and retention on soil particles, indicated by the release of NH_4^+ in 2 mol L⁻¹ KCl extracts of soil core samples. Fertilizers applied to lawns and gardens also may represent an important (but unknown) source of N contamination in this area.

For the most part, microbial indicators, viruses, organic wastewater compounds, and pharmaceutical compounds are

highly attenuated or removed as the STE percolates through about 5 to 7 m of unsaturated zone material. Only sporadic detections of fecal coliforms, enteroviruses, organic wastewater compounds, and pharmaceutical compounds were found in soil water from shallow and deep lysimeters and in groundwater (drainfield wells). Higher detections of fecal indicators, enteric viruses, OWCs, and pharmaceuticals were found in groundwater at the site where the depth to the limestone was the shallowest and average daily water use was highest. Enterovirus data from this study are consistent with the movement of viruses from septic tanks found in other studies, indicating that there is a potential for contamination of drinking water supplies from septic tanks and that there is a human health risk in karstic aquifer systems.

Further work is needed to assess the impacts of septic systems on groundwater quality in higher density areas in the karst plain, particularly where limestone is near the land surface, to protect drinking water supplies from on-site waste disposal practices. Current health department regulations require a 23-m separation between a septic tank drainfield and a potable well, which may not be sufficient in areas of higher septic tank density or where the top of the limestone aquifer is near the surface.

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