Constructed Wetland/Filter Basin System as a Prospective Pre-Treatment Option for Aquifer Storage and Recovery and a Potential Remedy for Elevated Arsenic

by

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ABSTRACT

The efficiency to improve the water quality of industrial and municipal wastewater in a constructed wetland/filter basin treatment system was investigated. The wetland system was constructed in a closed phosphate mine used for clay settling and sand tailings in Polk County, Florida. During 18-months of monitoring the chemical/microbiological composition of treated wetland water remained relatively constant, despite significant seasonal variations in temperature, rainfall and humidity. The following changes in water quality between input and output were observed: substantial decrease of water temperature (up to 10 °C), reduction of As, SO_4, F, Cl, NO_3, NO_2, Br, Na, K, Ca, and Mg, change in pH from 9 to 6.5–7, increase of H_2S (up to 1060 μg/L), and a change from positive to negative ORP. There were no exceedances of the primary drinking water standards, volatile organic compounds, synthetic organic compounds, and radionuclides, but a number of exceedances for the secondary drinking water standards (Al, F, Fe, Mn, color, odor, total dissolved solids, and foaming agents). The concentration of fecal and total coliform bacteria in the wetland water was high, but

subsequently reduced during filtration in the filter basin from 30 - 730 and 1000 – 7000 count/100 mL to < 2 and < 100 count/ 100 mL, respectively.

To resolve the complex hydrogeological conditions a combined isotope/chemical mass-balance approach was applied. The results were the following: (1) the composition of water in the wetland varied throughout the period of the study; (2) a change in isotopic composition along the wetland flow path; (3) the wetland contained mainly wastewater (88 - 100 %) during normal pumping operations; however, hurricanes and inconsistent pumping added low conductivity water directly and triggered enhanced groundwater inflow into the wetland of up to 78 %; (4) the composition of water in monitor wells was mostly groundwater dominated; however periodically seepage from a water body to the north was detected; and (5) seepage from adjacent water bodies into the wetland was not identified during operation, which would indicate a potential water loss from the wetland.

To test if the wetland system could be a prospective pre-treatment option for water used in aquifer storage and recovery (ASR) scenarios, a set of bench-scale leaching experiments was carried out using rocks from the Avon Park Formation, the Suwannee Limestone and the Ocala Limestone. Since As in the Floridan Aquifer was mainly present as an impurity in the mineral pyrite the elevated iron and sulfide concentrations in the wetland water were thought to prevent pyrite dissolution. The experiments which covered a range of redox conditions showed that the amount of As released from the aquifer matrix was not perfectly correlated with the bulk rock As concentration, nor the redox state of the water. The following important results were obtained: (1) the highest concentration of As was leached from the Avon Park Formation and the lowest – from the Suwannee Limestone, although the Ocala Limestone had the lowest bulk rock As; (2)

minor to no As was released using native Floridan groundwater; (3) Tampa tap water, which chemically and physically resembled the ASR injection water, caused the As leaching of up to 27 µg/L, which was higher than the As drinking water standard; (4) the wetland and filter basin waters caused the highest release of As (up to 68 µg/L), which was unexpected because those water types were less oxygenated than Tampa tap water and thus should be less aggressive; (5) the in-situ filtration of the wetland water through a 0.2 µm membrane resulted in a reduction of As from 30 µg/L to 16 µg/L; and (5) the UV treatment significantly reduced both fecal and total coliform bacteria, but facilitated the increase of DO in initial waters, a change from negative to positive ORP, and the increase of As concentration in leachates.

The experiments confirmed that perturbations of native aquifer conditions caused the release of As from the Floridan aquifer matrix, although the reaction may not be as simple as the dissolution of pyrite by oxygen, but additionally governed by a complex set of factors including the ORP of the system, SO_4^{2-}/S^2, Fe^{3+}/Fe^{2+}, dissolved organic carbon and microbial activity. In addition, the trend of As leaching could be governed by a set of factors, such as the porosity and permeability of the aquifer matrix influencing the rate and degree of free water saturation, amount of pyrite to be exposed to the preferential water flow paths, limited surface reactivity of pyrite with favored reactions on fractured mineral surfaces, the concentration and the selective leaching of As from individual pyrite crystals.

To characterize and verify the geochemical processes in the column experiments, the Geochemist's Workbench reactive transport models (React and X1t) were developed. Results from the models correlated well to those from the column experiments and

confirmed the following: (1) the water-rock reaction between the aquifer matrix and native groundwater was favorable for pyrite stability preventing the release of As into solution; (2) the injection of oxidizing surface water into reducing native groundwater caused a change in redox potential of the system thus promoting the dissolution of pyrite, and (3) 1D reactive transport model of water-rock reaction between the aquifer matrix and surface water indicated a diverse behavior of As along the column, such as the oxidative dissolution of pyrite, mobilization and simultaneous sorption of As onto neo-formed HFO, followed by the reductive dissolution of HFO and secondary release of adsorbed As, and the potential non-oxidative dissolution of pyrite contributing the additional source of As to the solution.

CHAPTER ONE

INTRODUCTION

The sustainability of water resources is rapidly becoming to be a major concern worldwide. Ujang (2009) characterized water sustainability as the capability of an ecosystem to maintain ecological functions, processes, productivity and biodiversity of water resources for future generations. At the present time, about 35 % of anthropogenic water use is considered unsustainable due to environmental contamination, unsanitary conditions, progressively depleting ground- and surface water resources (Clarke and King, 2004). Access to clean and safe drinking water has developed into a luxury for more than one billion people (Watkins, 2006). Particularly, the excessive groundwater pumping from the Floridan Aquifer, due to growing water demands in highly populated areas of the Florida (Jones and Owen, 2001), causes lowering of the water table, thus affecting spring flows and lake levels, saltwater intrusion along the coast, and land subsidence (Peck et al., 2005). Yearly, about $3x10^{12}$ L of groundwater in Florida is withdrawn by pumping (Scott, 2001a). Therefore, the reduction of water consumption as well as the development of water reuse, reclamation or recycling technologies could provide more sustainable alternative to the extensive groundwater consumption (Alley et al., 1999). The development of constructed wetlands for water treatment is a cost-

effective process, which provide water quality suitable for reuse and thus may become an alternative supply of clean water (House et al., 1999).

1.1. Constructed wetland for water reclamation

Phosphate mining in central Florida annually disturbs about 15-25 km^2 of land through generation of clay settling areas (CSA), open mine pits, phosphogypsum stacks, and tailing sand deposits (FIPR). Of these the CSA and tailing sand deposits are of particular interest to the wetland-based water treatment approach. Generally, constructed wetlands (CWs) are defined as artificial wastewater treatment systems composed of a shallow basin filled with substrate, such as soil or gravel, and planted with vegetation tolerant of saturated soil conditions (EPA, 2000; Davis, 1995). The use of CWs as a cost-effective method for wastewater or stormwater treatment was initiated in 1904 in Australia and became prevalent in the United States during the early 1970s (Cole, 1998). Natural processes in the wetland remove organic, inorganic and microbiological contaminants (Carruthers, 2002; Vrhovsek et al., 1996). Vascular plants play a particularly important role, stabilizing substrates while enhancing permeability, reducing water velocities and thus allow the settling of suspended solids, using nutrients, carbon, and trace elements for plant stem and root systems, and transporting gases between the sediments and atmosphere (Liu et al., 2007; Butler and Dewedar, 1991). In addition, photosynthesis by algae increases the concentration of dissolved oxygen affecting nutrient and metal reactions (Davis, 1995). But more importantly, the stems and roots of plants provide the necessary surface area for growth and adhesion of microorganisms, which facilitate the decomposition of organic material and the recycling of nutrients

(Martin and Moshiri, 1994). Previous studies demonstrated that CWs were advantageous treatment systems for the remediation of acid mine drainage (AMD) due to comparably low cost and maintenance (Stottmeister et al., 2006; Woulds and Ngwenya, 2004; Braun et al., 2003). In general, contaminated mine water is highly acidic and rich in sulfate and metals such as Al, As, Cd, Cu, Fe, Pb, Mn, Ni and Zn (Stottmeister et al., 2006; Ritcey, 1989). The AMD treatment mechanisms in CWs may include metal adsorption on soil matter, accumulation into below- and above-ground plant tissues, and microbial mediated co-precipitation or volatilization of particular metalloids (Stottmeister et al., 2006; Jackob and Otte, 2003).

The reclamation of wastewater and phosphate mining lands using CW technology could prove to be especially important as Florida law requires reclamation of previously mined phosphate lands into wildlife habitat and watershed enhancement (i.e., lakes, wetlands, pasture, and agricultural lands). Wetlands are known to provide excellent opportunities for environmental improvement and restoration through (1) wastewater treatment; (2) water quality improvement and encouragement of water reuse; (3) fish- and wildlife habitat; (4) passive recreation, such as bird watching and photography; (5) active recreation such as hunting; (6) flood storage, and (7) resynchronization of storm rainfall and surface runoff (Davis, 2005; EPA, 1993). Studies showed that extensive groundwater pumping from the Floridan Aquifer causes saltwater intrusion along the coast and lowering of groundwater levels (Peck et al., 2005). Therefore, a significant purpose of CWs in Florida metropolitan areas could be the generation of water that meets drinking water standards to supplement rivers and streams and to satisfy public, industrial, and agricultural water demands. The combination of tailing sand deposits and CSA, which are

post-mining features of phosphate mining, are ideal for the construction of wetland-based water treatment systems. The CSA provides an excellent area for the wetland to develop, while the sand from the tailing sand deposits can be used for filtration prior to extracting the water from the system. With some adaptation this type of water treatment should be applicable to mining sites potentially worldwide.

1.2. Constructed wetland for aquifer storage and recovery (ASR)

One additional application for central Florida could be to use the wetland water to recharge the Floridan Aquifer System, since this water is reducing and thus physicochemically similar to native Floridan groundwater (Lazareva and Pichler, 2010). The injection of wetland water could be essential to the future of aquifer storage and recovery (ASR) as a means of water management in Florida. The principle behind ASR is the storage of treated surplus surface water in a confined aquifer during rainy seasons followed by its recovery during times of need (Arthur et al., 2005; Arthur et al., 2001). The ASR system prevents water loss due to evaporation, which is normally associated with surface water reservoirs and is rapidly developing into the alternative for withdrawing Floridan Aquifer groundwater (Jones and Owen, 2001). In addition, ASR plays a considerable role in environmental restoration, such as the Comprehensive Everglades Restoration Program (CERP) (Arthur et al., 2007). The CERP is an ecosystem restoration/water supply project developing up to 333 ASR wells to restore the Everglades and to supply growing water demands in Florida. Currently, 34 ASR facilities in Florida are in operation and 46 are under construction (FLDEP, 2008).

The ASR storage zone includes confined permeable zones of the Upper Floridan Aquifer System such as the Avon Park Formation, Suwannee and Ocala Limestones, and part of the Hawthorn Group (Missimer, 1997; Scott, 1990; Scott, 1988; Miller, 1986). Generally, native groundwater in these zones is under reducing conditions (Sprinkle, 1989). In order to meet federal regulation, the water to be injected must be treated to meet primary drinking water standards (Arthur et al., 2001). As part of the microbial treatment, ozonation is part of the process, causing the water to become extremely oxygen-rich. As a result, the injection of treated surface waters into reducing native groundwater causes the oxidative dissolution of pyrite (FeS_2), and the mobilization of arsenic (As) with concentrations in recovered water of up to 130 µg/L (Arthur et al., 2005; Arthur et al., 2001). The Maximum Contaminant Level for As in drinking water, established by US EPA on January 23, 2006, is 10 µg/L. The injection water and native groundwater have < 2 µg/L and < 1 µg/L of As, respectively (Jones and Pichler, 2007; Arthur et al., 2001). Studies showed that As in the Florida subsurface is mostly associated with pyrite as a substitute element for sulfur in the FeS_2 structure (Lazareva and Pichler, 2007; Price and Pichler, 2006). The enrichment of As in pyrite in the Avon Park Formation, Suwannee Limestone, and the Hawthorn Group was up to 8260, 11200, and 5820 mg/kg, respectively (Dippold, 2009; Lazareva and Pichler, 2007; Price and Pichler, 2006). Generally, the oxidation of pyrite by O_2 acts as a source of acid, sulfate, iron and arsenic, and can be described by three steps (Evangelou, 1995):

(1) $FeS_2 + 7/2O_2 + H_2O \rightarrow Fe^{2+} + 2SO_4^{2-} + 2H^+$

Fe^{2+} can be further oxidized to Fe^{3+}, which hydrolyzes into hydrous ferric oxides (HFO displayed as $Fe(OH)_3$) to discharge extra amount of acid into the environment (Figure 1):

(2) $Fe^{2+} + 1/4O_2 + H^+ \rightarrow Fe^{3+} + 1/2H_2O$ and

(3) $Fe^{3+} + 3H_2O \rightarrow Fe(OH)_3 + 3H^+$

Consequently, As can be re-sorbed onto HFO if the conditions remain sufficiently oxygenated to promote HFO stability, but released back to native groundwater under reducing conditions. The additional factors affecting the mobility of As may include the following: input and native groundwater chemistry, aquifer matrix chemistry/mineralogy, site hydrogeology, injection water-rock contact time, and amount of cycle tests (Arthur et al., 2005). Poole (2009) reported about the proposed methods of dechlorination that could reduce the oxidation-reduction potential level and deoxygenation that could decrease the dissolved oxygen in the injection water used for ASR in central Florida. The cycle tests showed the positive results for reduction of As leaching with the dechlorination system only.

In order to prevent the oxidation of pyrite and mobilization of As during ASR, the injection of wetland water should be considered. Discharge from a wetland could be the ASR water of choice, because it is often more reducing with high sulfide and low dissolved oxygen levels, which are favorable for the stability of pyrite (Lazareva and Pichler, 2010; Jones and Pichler, 2007). Therefore, in-depth knowledge and understanding of As mobilization from the Floridan Aquifer could be very important to forecast As behavior during anthropogenic physico-chemical changes in Florida and potentially worldwide.

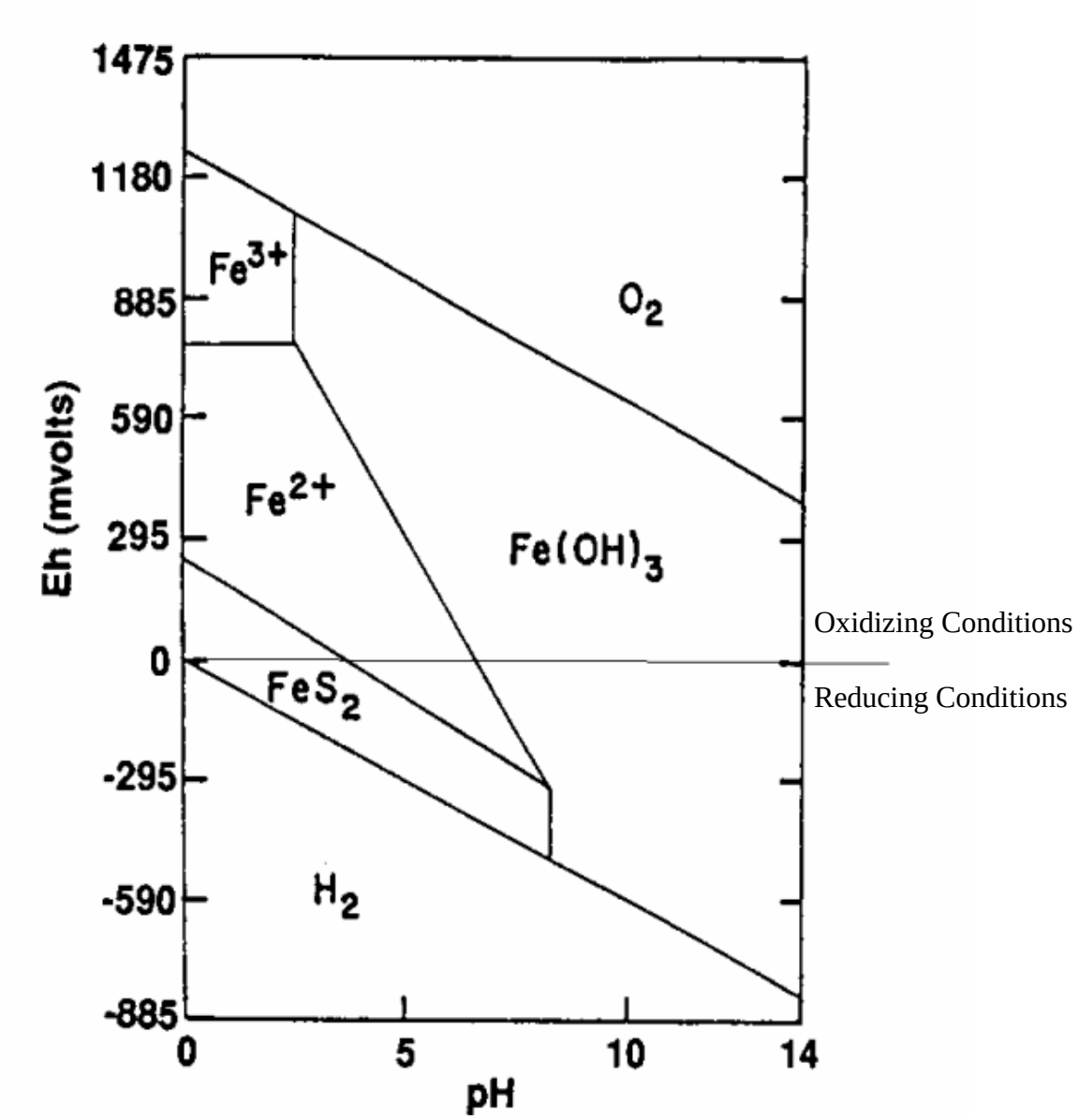

Figure 1. Stability diagram of pyrite and $Fe(OH)_3$ in water at 25ºC and 1 atmosphere total pressure (Modified from Evangelou, 1995).

1.3. Review of arsenic occurrence and toxicity

Arsenic is a well known carcinogen that can lead to a wide range of health problems, such as atherosclerosis, kidney, bladder, colon, skin and lung cancer (Smith et al., 2009; Huang et al., 2008; Pu et al., 2007; Steinmaus et al., 2006; Wu et al., 2006; Chen et al., 2003; Smith et al., 2000; Smith et al., 1992). Over the past several decades As contamination from both natural and anthropogenic sources became one of the most important health issues in many countries across the world (Nriagu, 2002; Thornton, 1999). The elevated concentrations of As in surface- or groundwater were discovered in China, India, Pakistan, Taiwan, Bangladesh, Vietnam, Thailand, Chile, Mongolia, Mexico, Argentina, Canada, and the United States (Brammer and Ravenscroft, 2009; Nriagu, 2002). About 150 million people worldwide are exposed to elevated As contamination concentration in their drinking water (Ravenscroft et al., 2009). A multitude of scientific studies showed that 30 million people in Bangladesh and 6 million inhabitants in West Bengal (India) are chronically exposed to groundwater poisoning with up to 3200 µg/L of As (Nordstrom 2002; Smith et al., 2000; Dhar et al, 1998; Khan et al., 1997).

The average abundance of As in the upper continental crust significantly varies from 1.5 mg/kg (Taylor and McLennan, 1985) to 4.8 mg/kg (average data from Sims et al., 1990; Gao et al., 1998), commonly increasing in igneous and sedimentary rocks, such as coal and shale deposits (Smedley and Kinniburgh, 2002). The average concentrations for shale and river mud are 12.4 and 8.4 mg/kg, respectively (Govindaraju, 1994). The average As for the limestone geostandard GSR-6 is reported as 2.6 mg/kg (Baur and Onishi, 1969). Arsenic-containing pyrite (FeS_2) is perhaps the most common mineral

source of As (Nordstrom 2002). Huerta-Diaz and Morse (1990) detected As concentrations in marine sedimentary pyrites of as much as 9300 mg/kg. Thomas and Sanders (1998) reported that framboidal pyrites contained up to 1000 mg/kg of As. Studies about its occurrence in the Floridan subsurface determined that As is mostly associated with pyrite as a substitute element for sulfur in the FeS_2 structure (Lazareva and Pichler, 2007; Price and Pichler, 2006). The enrichment of As in pyrite in the Avon Park Formation, Suwannee Limestone, and the Hawthorn Group was up to 8260, 11200, and 5820 mg/kg, respectively (Dippold, 2009; Lazareva and Pichler, 2007; Price and Pichler, 2006). Therefore, sedimentary pyrite can be a significant sink and source of As.

Smedley and Kinniburgh (2002) reported that calcium phosphate or apatite can contain up to 1000 mg/kg of As. Soil constituents, such as clays and organic substances, can easily interact with heavy metals such as As via ion exchange or surface adsorption (Manning and Goldberg, 1997; Evangelou, 1995). Clays readily adsorb As because of the oxide- like character of the edges of its grains (Claesson and Fagerberg, 2003). Clays and organic substances have very small particle size, which therefore result in a large surface area per unit volume and ability to adsorb As. Moreover, the potential of humic substances to complex with heavy metals is due to the existence of oxygen-containing functional groups such as carboxyl (COOH), hydroxyl (Oh), and carbonyl (C=O) (Evangelou, 1995). It has been shown that As integrates into sediments by co-precipitation with hydrous ferric oxides (HFO), or is adsorbed onto extremely high surface area of precipitated HFO (Hongshao and Stanforth, 2001; Pichler et al., 1999; Hinkle and Polette, 1999; Evangelou, 1995; Bowell, 1994; Chao and Theobald, 1976).

The cycling of As between different valence states and chemical species in natural waters and soils/rocks is greatly affected by both abiotic and biotic reactions (Inskeep et al., 2002). The essential processes that control As cycling between the solid and aqueous phases are oxidation/reduction, dissolution/precipitation, adsorption/desorption, and biological alterations (Stollenwerk, 2003; Inskeep et al., 2002; Hering and Kneebone, 2002; Zobrist et al., 2000). Arsenic adsorption and desorption reactions are influenced by changes in pH, redox potential and the presence of competing anions. Solid-phase precipitation and dissolution reactions are primarily controlled by pH, redox state and chemical composition (saturation) (Hinkle and Polette, 1999). Behavior, fate, bioavailability, and toxicity of As in the environment vary significantly depending on the chemical species in which As occurs. In the aqueous (mobile) environment such as surface water and groundwater As exists in -III, +III, and +V oxidation states (Hering and Kneebone, 2002; Stottmeister et al., 2006). The most common aquatic forms are the trivalent arsenite (As (III)) and the pentavalent arsenate (As (V)). Organic forms of As include monomethylarsonic (MMA) and dimethylarsinic (DMA) acids and mostly present in seafood. While the inorganic forms are highly toxic, organic species are far less toxic (Le, 2002). It is considered that As (III) is more mobile and more toxic to biota and plants than As (V) (Inskeep et al., 2002). Generally, As (V) is thermodynamically favored in oxic surface waters at Eh greater than -100 mV at pH 8 and greater than Eh 300 mV at pH 4 (Inskeep et al., 2002). Below these redox potentials As (III) is stable either as the H_3AsO_3, As-S complexes, or As (III) solid phases such as As_2S_3 (Inskeep et al., 2002). At the same time, the coexistence of both species is common (Kuhn and Sigg, 1993; Anderson and Bruland, 1991; Mok and Wai, 1990). Important solid phases of As

(V) or As (III) are the Fe, Mn and Ca arsenates, and As (III) sulfides such as orpiment (As_2S_3), and realgar (AsS). Arsenopyrite (FeAsS) is a significant source of As formed under reducing environments (Inskeep et al., 2002). Generally, As (V) displays a strong affinity for most metal hydroxides and clay minerals, forming surface complexes. In contrast, As (III) is selective, demonstrating a strong affinity for iron hydroxides (Inskeep et al., 2002). Both As (III) and As (V) form analogous surface complexes on goethite. Numerous studies reported about the oxidation of As (III) by manganese oxides in waters and lake sediments (Deschamps et al., 2003; Chiu and Hering, 2000). The reduction of As (V) to As (III) is typically observed under microaerobic to anoxic conditions such as in flooded soils, sediments, and aquifers (Masscheleyn at al., 1991). Under reducing conditions, there are two potential pathways for a reductive dissolution of sorbed As: (1) As can be released from the solid (i.e., $Fe(OH)_3$ or $Al(OH)_3$) through reduction to arsenite, or (2) through direct substrate degradation (i.e., $Fe(OH)_3$) (Inskeep et al., 2002). Rochette et al. (2000) reported about the reduction of As (V) by H_2S at a low pH.

Microorganisms are able to facilitate the reduction of As (V) to As (III) and the oxidation of As (III) to As (V) (Salmassi et al., 2002; Jones et al., 2000; Zobrist et al., 2000; Ahmann et al., 1994). A wide variety of microorganisms can reduce aqueous As (V)/oxidize As(III) or adsorbed on $Fe(OH)_3$ or $Al(OH)_3$ as a detoxifying mechanism or a source of energy (Silver et al., 2002; Oremland et al., 2002; Macur et al., 2001; Zobrist et al., 2000; Ghosh et al., 1999; Phillips and Taylor, 1976; Osborne and Ehrlich, 1976). Particularly, an anaerobic microorganism (*Sulfurospirillum barnesii*) is able of both reductive dissolution of Fe (III) oxides and reduction of As (V) to As (III) (Zobrist et al., 2000). High As in the Bangladesh groundwater had been derived from reductive

dissolution of arsenic-rich HFO occurring as a coating on sedimentary grains (Inskeep et al., 2002; Nickson et al., 2000). Typically, the highest concentrations of As in groundwater are found in aquifers with areas high in organic material where greater microbial activity would result in elevated rates of the Fe (III)-oxide reductive dissolution (Inskeep et al., 2002).

1.4. Description of the study area

The constructed wetland /filter basin (CW/FB) treatment system was located on a clay settling area and tailing sand deposits at the Hines Energy Complex, Polk County, Florida (27˚48´N latitude and 81˚52´W longitude) (Figures 2, 3). The CW/FB system was established in 1999 and used for the experimental treatment of industrial wastewater from the Hines Energy electric power generating plant (cooling water), tertiary treated effluent from the city of Bartow, as well as rain and excess surface water. The surface flow wetland was approximately 1 500 m long, 10 m wide, ranged in water depth from 0.5 to 2 m and was constructed in a U-shape. The length-width ratio of the wetland was higher than maximum suggested value of 1:1 to 1:2 (EPA, 2000) due to specific topographic settings of the study area. The area of the wetland was about 12 250 m^2 (Figure 4). The wetland was not lined and the substrate consisted of clay matrix with the decomposing organic matter. Wetland vegetation was allowed to evolve naturally (i.e., not planned and planted) due to comparably high costs and maintenance. It consisted of both native Floridian and non-native species such as water lettuce (*Pistia stratiotes*), carolina willow (*Salix caroliniana*), brazilian pepper (*Schinus terebinthifolius*), water fern (*Salvinia*), baby's tears (*Micranthemum umbrosum),* cattail (*Typha spp.*), willow (*Salix spp.*), and

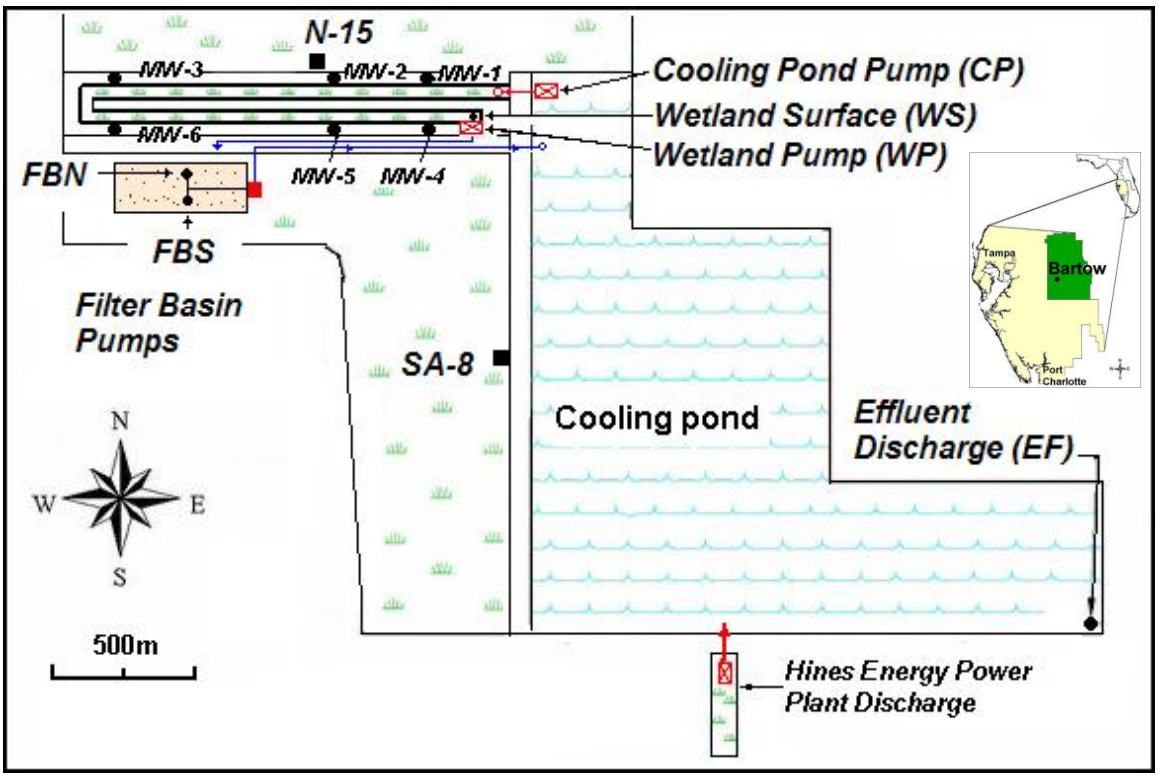

Figure 2. Map of the study area located at the Hines Energy complex (Polk County, Central Florida) including water transfer system from the cooling pond to the U-shaped constructed wetland and filter basin treatment system.

Note: MW-1 to MW-6 – monitor wells; N-15 and SA-8 - water-cropping areas to the north and south of the wetland; FBN and FBS – filter basin north and south pumps.

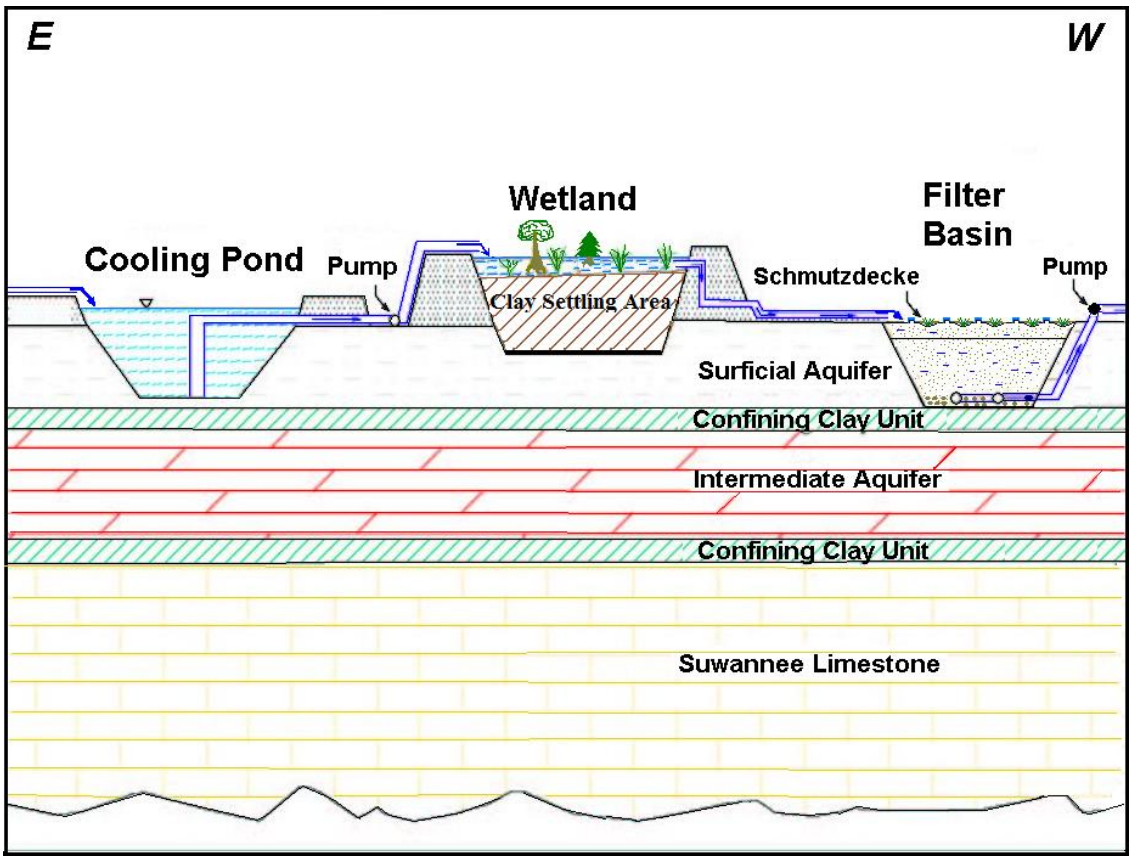

Figure 3. Schematic concept diagram of the constructed wetland/filter basin treatment system.

Note: Schmutzdecke - biological film formed on the sand surface.

Figure 4. Photographs of the constructed wetland treatment system.

common duckweed (*Lemna minor*). The wetland was surrounded by two bodies of water: N-15 to the north and SA-8 to the south. These previously mined and reclaimed phosphate lands are now a water-cropping system to capture, store and reuse stormwater (PEF, 2004). The 6 000 m^2 filter basin (FB) constructed on tailing sands was used to improve the efficiency and reliability of the treatment system. The depth of the FB (i.e., sand bed) was 4 m and the walls and bottom of the FB were lined with a polyethylene cover. The most important feature of the FB was the development of a biologically active layer called the "schmutzdecke" on the tailing sand surface (the top 0.5 – 2 cm) (Figures 3, 5). This reddish-brown slimy biofilm acted as a fine filter of solid particles (mechanical filtration) and a zone of biological action providing the degradation of soluble organics and the potential elimination of pathogens, color and odor contaminants in water (Muhammad et al., 1997; Huisman and Wood, 1974).

Water from the Hines Energy Complex cooling pond (CP) was pumped into the wetland at different rates depending on the season. During the rainy seasons of 2006 and 2007, the hydraulic loading rates into the wetland were around 0.33 and 0.45 L/day/m^2, respectively. During the dry season 2006, it was about 0.61 L/day/m^2. The residence time of water in the wetland was approximately 120 days. At the end of the flow path the water was either pumped back into the CP to control water levels in the wetland, or discharged onto the filter basin surface. Following filtration through the fine sand the water was collected in a series of pipes.

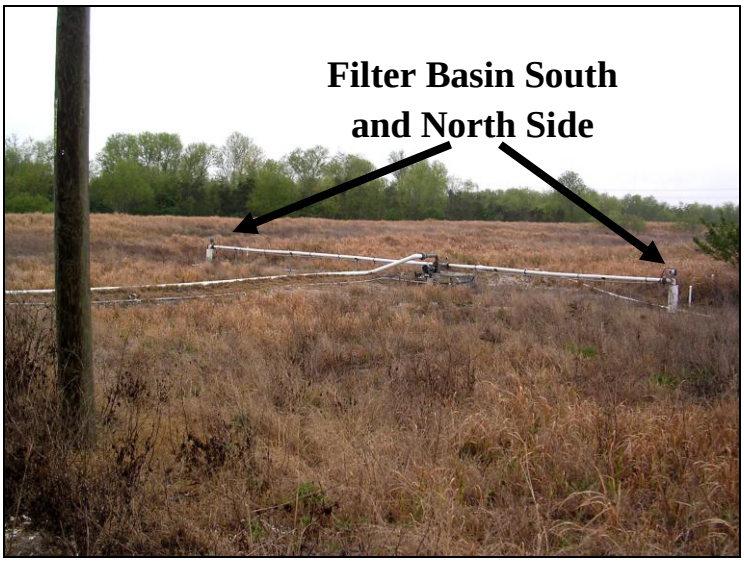

Figure 5. Photographs of the filter basin system.

Note: Highlighted in blue- treated wetland water discharged onto the filter basin surface forming a biofilm “schmutzdecke” (in red).

1.5. Geology

The research area is located in Polk County, a part of the Southwest Florida Water Management District (SWFWMD) (Figure 2). Here the hydrogeological framework can be subdivided into three discrete units from the bottom upward: the Floridan Aquifer System (FAS), the Intermediate Aquifer System (IAS) or Intermediate Confining Unit, and the Surficial Aquifer System (SAS) (Figure 6) (Miller, 1986).

The FAS underlies a region of approximately 259 000 km^2 throughout southern Alabama, southeastern Georgia, southern South Carolina, and the entire Florida peninsula; it is one of the most prolific and extensive aquifers in the world (Budd and Vacher, 2004; Scott, 1992). The Paleocene to Lower Miocene FAS consists of the following stratigraphic units (from oldest to youngest): The Oldsmar/Cedar Keys, and Avon Park Formations, the Ocala and Suwannee Limestones (Figure 7). In some areas, the Tampa Member and the lower part of the Arcadia Formation of the Hawthorn Group are included in the upper part of the FAS where it comprises permeable carbonate lenses (Scott, 1991). The FAS is a vertically continuous sequence of carbonate rocks with typically high porosity and permeability which is subdivided into the Lower Floridan Aquifer (LFA), the Middle confining unit, and the Upper Floridan Aquifer (UFA) based on the hydrologic properties of the lithologic units (Miller, 1986). The LFA system is comprised of the Oldsmar Formation and the upper the Cedar Keys Formation (Randazzo and Jones, 1997). The confining unit separating the Upper and Lower Floridan Aquifers consists of a very fine-grained (micritic) limestone, clay or dolomite filled with anhydrite in the pore space (USGS, 1999). Typically, the base of the UFA is identified by the presence of anhydrite beds, which are considered to be the top of the Cedar Keys

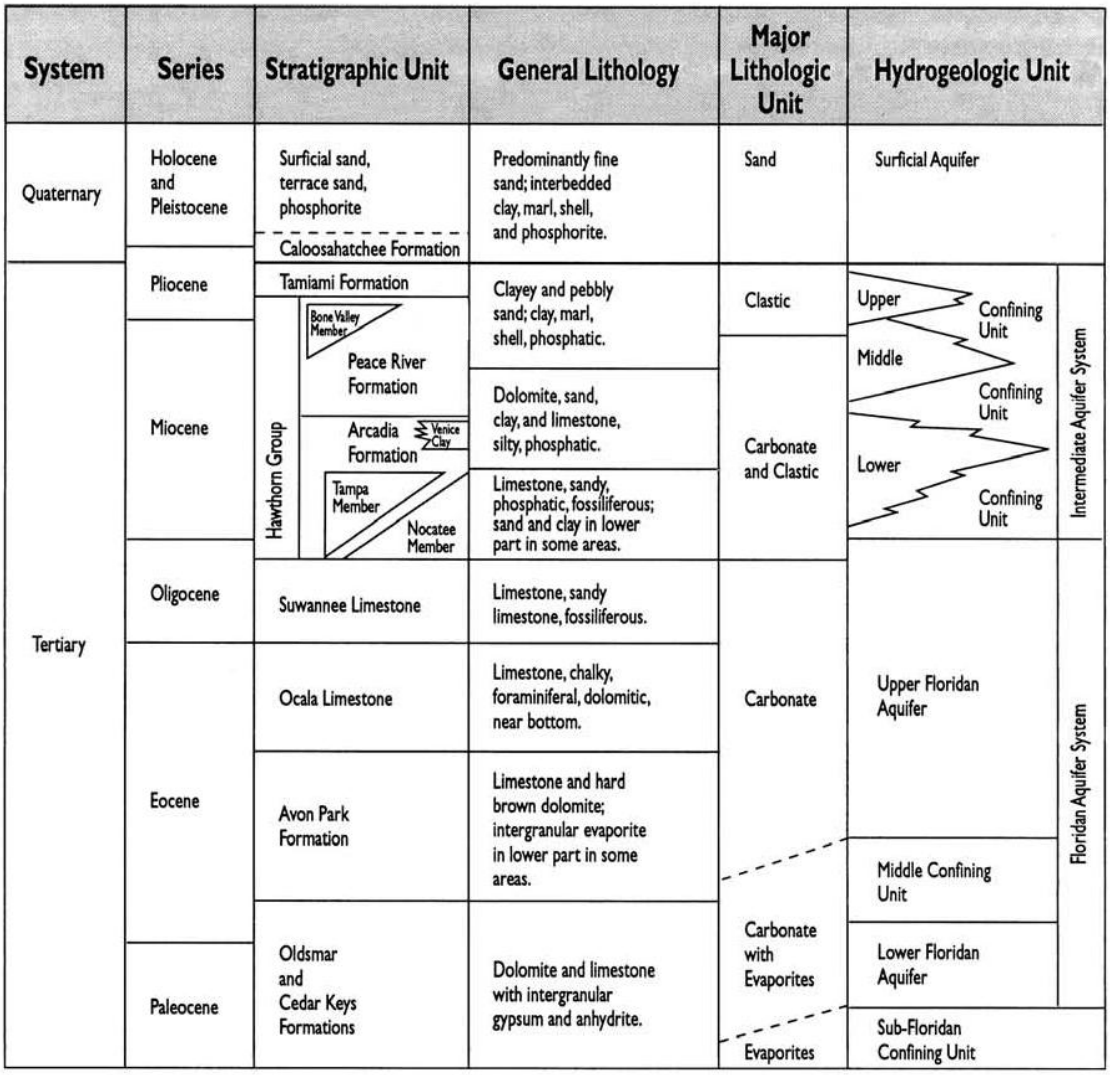

Figure 6. Lithostratigraphic and hydrogeologic units of the study area

(Modified from SWFWMD Report, 2000; Scott, 1989).

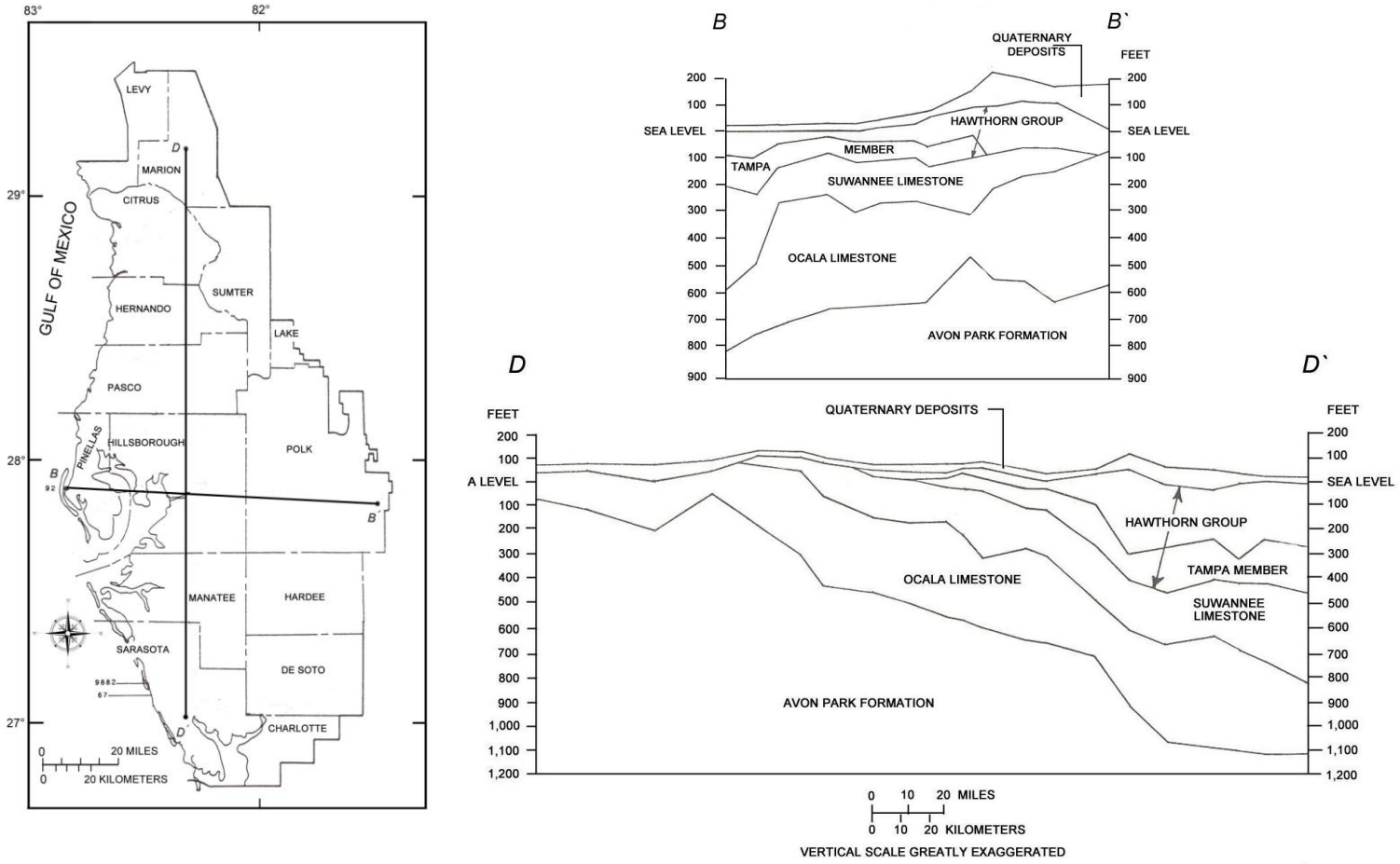

Figure 7. Geological cross sections of southwestern Florida (*Modified from Swancar and Hutchinson, 1995*).

Formation. The upper sections of the Ocala Limestone and the Avon Park Formation have the highest transmissivity throughout the UFA due to secondary porosity and permeability caused by fracturing and dissolution processes (Randazzo and Jones, 1997; Miller, 1986; Gilboy, 1985; Stringfield, 1966). Generally, the porosity levels throughout the FAS range from 10 to 50 % (Budd and Vacher, 2004).

The Middle Eocene Avon Park Formation is principally composed of interbedded fossiliferous limestone and dolostone with the distinctive dark brown fine crystalline dolomite unit containing a gypsiferous wackestone-mudstone towards the base of Formation (Arthur, 2008; Miller, 1986; Gilboy, 1985; Randazzo and Jones, 1997; Cander, 1991; Chen, 1965). The thickness of the Avon Park Formation varies from 305 m to 488 m (1000 ft to 1600 ft) (Miller, 1986). It is unconformably underlied by the Paleocene to Lower Eocene Oldsmar Formation (Randazzo and Jones, 1997). The limestone contains a variable amount of organic-rich laminations and marine grass fossil beds (Dippold, 2009; Budd and Vacher, 2004). In addition, minor pyrite, chert, and quartz were identified (Dippold, 2009; Arthur et al., 2008). The amount of gypsum and anhydrite interbedded in the dolomite increases with depth. The dolomite can occur highly fractured and sucrosic in texture (Arthur et al., 2008). Generally, the Avon Park Formation has interparticle porosity as well as dissolution channels with conduit-type permeability zones (Cander, 1991).

The Upper Eocene Ocala Limestone overlies the Avon Park Formation and varies in thickness from 30 m to 152 m (100 ft to 500 ft) (Gilboy, 1985). It can be subdivided into lower and upper sections based on the lithological composition (Miller, 1986). The lower part consists of a white, poorly to moderately indurated and partially dolomitized

fossiliferous grainstone and packestone (Miller, 1986). The upper portion is composed of a white, poorly to well indurated, fossiliferous grainstone, packestone and wackestone. Minor amounts of quartz and pyrite were also observed. The present fossils are foraminifers, echinoids, bryozoans, mollusks and rare vertebrates (Scott, 1991). As noted above, the Ocala Limestone has very high transmissivity which is an important unit for the UFA and potentially for ASR procedure (Miller, 1986).

The Oligocene Suwannee Limestone reaches a thickness between 50 m and 100 m (164 ft to 328 ft) and is principally composed of wackestone to pelletal and foraminiferal grainstone with minor phosphate quartz sand and clays (Williams et al., 2002; Green et al., 1995; Miller, 1986; Gilboy, 1985). In addition, minor amounts of pyrite, organic material, and chert nodules are present (Green et al., 1995; Miller, 1986). Generally, the limestone has intergranular and high moldic porosity zones, which are particularly important for ASR procedure (Price and Pichler, 2006; Miller, 1986).

The Upper Oligocene to Lower Pliocene IAS is the predominantly composed of the Hawthorn Group, which is subdivided into a lower section comprising the undifferentiated Arcadia Formation, Tampa and Nocatee Members of the Arcadia Formation and the upper section of the Peace River Formation (Scott, 1988). The Arcadia Formation unconformably overlies the Oligocene Suwannee Limestone and achieves its maximum thickness of about 183 m (600 ft) in the Okeechobee Basin (Scott, 1988). It was initially interpreted to be primarily Lower Miocene (Scott, 1988), but is now recognized to be Lower Oligocene to Middle Miocene (Brewster-Wingard et al., 1997; Missimer, 1997). The undifferentiated Arcadia Formation is principally composed of variable amount of siliciclastics within carbonate matrix. Typically, the carbonates are

fossiliferous, yellowish gray to light greenish gray to light brown, micro- to finely crystalline limestones and dolostones with variable amount of quartz sands, gray to greenish gray clays, chert, phosphate material, and pyrite (Lazareva and Pichler, 2007; Scott, 1988). The clays are palygorskite, sepiolite, illite/smectite mixed layer, and insignificant amounts of kaolinite (Compton et al., 1993). Thin beds of sand and clay are widespread and molds and casts of mollusks are commonly found in the dolostones. The lithology of the Upper Oligocene to Lower Miocene Tampa Member of the Arcadia Formation varies from a white to yellow-gray marine wackestone to packestone containing variable amounts of dolostone, clay, quartz sand, and minor phosphate material (Wingard et al., 1993; Scott, 1988). Thin carbonate, quartz sand and clay beds are commonly observed throughout the Tampa Member. The Tampa Member is typically a poor to well indurated limestone with intergranular or moldic porosity containing variable amounts of fossils such as mollusks, corals, and foraminifera (Scott, 1988). The contact between the undifferentiated Arcadia Formation and Tampa Member in central Florida is sporadically marked by a chert layer at the top of the Tampa Member (Gilboy, 1985). The Upper Oligocene to Lower Miocene Nocatee Member forms the base of the Arcadia Formation in the southern area of SWFWMD. It contains the highest amount of siliciclastic material compared to the entire Arcadia Formation (Scott, 1988). The Middle Miocene to Lower Pliocene Peace River Formation, currently being exploited for the phosphate ore, unconformably overlies the Arcadia Formation and reaches a maximum thickness of 46 m to 61 m (150 ft to 200 ft) in the Okeechobee Basin (Scott, 1990). It is composed of gray to greenish gray clays (palygorskite, sepiolite, illite/smectite mixed layer), sandy clays, and carbonates with variable amount of phosphate sand and gravel,

iron oxides, and pyrite (Lazareva and Pichler, 2007; Green at al., 1995). The carbonates are comprised of interbedded limestones, dolostones, and a siliciclastic component dominates the Peace River Formation (Scott, 1988). The water-yielding beds of carbonate lenses in the IAS lie between clayey confining units. As a result, the water in the IAS is under principally confined conditions excluding local areas, where the upper confining unit is missing and the system is in direct hydraulic contact with the overlying SAS. The IAS is the major source of water supply in Charlotte and Sarasota Counties, where the underlying FAS is deeply buried and holds only brackish water (SWFWMD, 2000).

The Upper Pliocene to Pleistocene SAS is generally comprised of unconsolidated to poorly indurated clastic deposits such as sands, sandy clays, phosphorite and some well- indurated carbonate rocks. It is primarily unconfined with some semi- confined or locally confined sections (Gilboy, 1985). Generally, water moves downward from the SAS through the upper confining unit of the IAS subsequently following short flow paths and discharging to surface drainage area. On the other hand, some water penetrates downward through the lower confining unit of the IAS to recharge the underlying FAS (USGS, 1999).

1.6. Objectives

This dissertation was part of a 2-year project entitled “Pilot project to test if water from a natural treatment system will cause dissolution of pyrite in the Floridan Aquifer matrix during Recharge operations” (03-03-153R). The project was funded through a grant from the Florida Institute of Phosphate Research (FIPR) and the Southwest Florida Water Management District (SWFWMD) with assistance of Progress Energy Florida to

Mr. Peter Schreuder (Schreuder Inc.) and Dr. Thomas Pichler (University of South Florida). The purpose of the project was to improve the operation of the sand filtration system and to examine the hypothesis that anoxic water from the wetland and sand filter system would cause less dissolution of pyrite (and release of As) in the Floridan Aquifer limestone matrix, compared to highly oxygenated surface waters, when injected into recharge wells.

Of the overall research project, my part was:

1) To evaluate the performance of the wetland for 18 month in complex hydrogeological settings using a combined isotope/chemical mass-balance approach;

2) To consider the possible injection of the treated wetland water into the Upper Floridan Aquifer as the alternative source water for ASR;

3) To simulate the ASR process with a series of bench-scale leaching experiments;

4) To incorporate the experimental data into coupled reactive transport models using the Geochemist's Workbench, React, X1t code.

1.7. Arrangement of Dissertation

The dissertation is composed of five chapters. The first chapter introduces the reader to the sustainability of water resources around the world and importance of constructed wetlands for water reclamation and reuse with a possible injection into the Floridan Aquifer. In addition, the occurrence and toxicity of arsenic are reviewed, and a detailed description of geology and hydrogeology of site area is given. In order to avoid redundancy, the information given in the first chapter was omitted from all subsequent

chapters. The second chapter, “Long-term performance of a constructed wetland/filter basin system treating wastewater in complex hydrogeological settings” was published in a special issue of *Chemical Geology* (Lazareva and Pichler, 2010) and submitted to *Ecological Engineering* (Lazareva and Pichler, 2010). The third chapter, “Bench – scale leaching experiments to investigate geogenic arsenic contamination in Floridan Aquifer”, accounts for the bench-scale leaching experiments to simulate water-rock interaction between different types of water and Floridan Aquifer matrices and examine the pyrite dissolution potential and mobilization of geogenic As under a range of redox conditions. Publication of this chapter in *Environmental Science and Technology* is planned for later this year. The fourth chapter “Geochemical reactive transport modeling” summarizes the results of reactive transport modeling using the Geochemist’s Workbench. The results from this part will be published together with results from the previous chapter. The fifth chapter summarizes and synthesizes the scientific contributions of the previous chapters.

CHAPTER TWO

LONG-TERM PERFORMANCE OF A CONSTRUCTED WETLAND/FILTER FASIN SYSTEM TREATING WASTEWATER IN COMPLEX HYDROGEOLOGICAL SETTINGS

2.1. Introduction

Phosphate mining in central Florida is widely distributed and annually disturbs about 15-25 km^2 of land through generation of clay settling areas, open mine pits, and tailing sand deposits (FIPR). Florida law requires reclamation of previously mined phosphate lands as wildlife habitat and watershed enhancement. The reclamation of wastewater and phosphate mining lands using constructed wetland technology is very important in Florida, providing an excellent opportunity for environmental improvement and restoration (EPA, 1993). Studies showed that increased groundwater pumping from the Floridan Aquifer causes saltwater intrusion along the coast, and lowering of groundwater levels, thus affecting spring flows and lake levels (Peck et al., 2005). Therefore, a significant purpose of constructed wetland in Florida metropolitan areas could be the generation of water that meets drinking water standards to supplement rivers and streams and to satisfy public, industrial, and agricultural water demands.

Investigation of the performance and water balance of a constructed wetland in complex hydrogeological conditions can be very challenging. At the same time, isotopic composition of oxygen and hydrogen can provide important information about the source of water, i.e., the actual H_2O molecules rather than dissolved constituents. Applications range across the whole spectrum of hydrogeological and hydrological studies, including hydrothermal systems (e.g., McCarthy et al., 2005; Pichler, 2005a), aquifer recharge (e.g., Gonfiantini et al., 1998), groundwater - surface water interaction (e.g., Baskaran et al., 2009), contamination studies (e.g., Pichler, 2005b) and the water cycle (e.g., Craig, 1961). Delineating the source of water is particularly important for evaluating and managing this resource in areas with limited supply. The quantification of groundwater inflow into wetlands and lakes in Florida, for example, is an important component in the water balance equation (Sacks, 2002). Groundwater input can differ significantly depending on the topographic settings, type of soil, depth to bedrock, vegetation, fractures, climate, and the anthropogenic activity, affecting water levels and quality (Kendall and Coplen, 2001). Estimating this term can be very complicated, but quantification is possible using a chemical and isotope mass-balance method (Sacks, 2002; Winter, 1995; Krabbenhoft et al., 1990; Stauffer, 1985). The isotope mass-balance method for estimating the water balance of lakes and wetlands has been used extensively (e.g., Hunt et al., 1998, Yehdegho et al., 1997; Michaels, 1995; Krabbenhoft at al., 1994; Dincer, 1968) and successfully applied in central Florida (Sacks, 2002).

2.2. Methods and sampling procedure

The description of the study area was comprehensively described in first chapter and therefore excluded from this chapter. In order to evaluate the performance of a constructed wetland/filter basin treatment system under a variety of climatic conditions, the monitoring was carried out for 18 months. Water sampling began in April 2006 and finished in October 2007. Bi-monthly water samples were obtained from the effluent discharge (EF), cooling pond (CP), wetland pumping station (WP) and wetland surface (WS), tailing sand filter basin north (FBN) and south (FBS) pumping stations, and water bodies to the north and south of the wetland, N-15 and SA-8 (surface water) (Figure 2). The WP sample was collected from a submerged sump located at depth of 2 m and the WS sample - surface water from the same location (Figure 8). Overall, 244 samples were collected and analyzed. In addition, water samples from the CP, WP, FBS, and FBN were collected for primary, secondary drinking water standards (PDWS/SDWS), volatile organic compounds (VOC), synthetic organic compounds (SOC), radionuclides (RAD), total and fecal coliform bacteria with assistance of Schreuder Inc. PDWS and SDWS were collected monthly, and VOC, SOC and RAD were collected quarterly. In total, 98 samples were collected for the PDWS/SDWS, and 48 samples - for VOC, SOC, and RAD. A total of 88 samples were collected bi-monthly for fecal and total coliform.

To evaluate possible groundwater input into and water leaking out of the wetland, 6 monitor wells were installed along the flow path and sampled monthly. This was necessary to separate wetland induced changes in water chemistry from those due to dilution by Floridan groundwater or seepage from the water bodies to the north and south, N-15 and SA-8 (Figure 2). In total, 121 samples from MWs were collected and analyzed (Figure 8).

Figure 8. Water sampling from the wetland pumping station and wetland surface (right), and monitor wells (left).

In order to investigate and evaluate the change of water chemistry along the wetland flow path, samples were collected within the surface water at depths of 0 and 0.5 m using a peristaltic pump. During the dry season (March 19-20, 2007), water samples were collected at 17 stations and during the rainy season (September 24-25, 2007) - at 11 stations along the flow path of the wetland (Figures 9, 10).

2.2.1. Field and laboratory analysis

The water samples were analyzed immediately in the field for pH, temperature (T), oxidation-reduction potential (ORP) and conductivity using a Myron-L UltrameterTM. The meter was calibrated in the field with known buffer solutions. The dissolved oxygen (DO) concentration was determined using a HACH HQ40d Meter with a LDO (luminescent dissolved oxygen) probe. The LDO sensor was calibrated following the manufacturer's specifications. The concentration of ferrous iron (Fe(II)) was determined with a CHEMets Colorimetric field kit with a color chart, and sulfide (H_2S) was analyzed using a Methylene Blue Method on a HACH DR 2400 portable photospectrometer. The water samples were filtered through a 0.45 μm membrane and separated into two 30 mL HDPE bottles. One aliquot was used for the determination of major anion concentrations and stable isotopes. The other sample was acidified to 1% HNO_3 for the analysis of major cations and arsenic. In addition, the set of unfiltered and unacidified samples from the CP, WP and FBS/FBN was collected and analyzed for fecal and total coliform bacteria from September, 2006 to September, 2007.

The samples were stored in a cooler, transported and analyzed at the Center for Water and Environmental Analysis, University of South Florida, Tampa. Calcium (Ca),

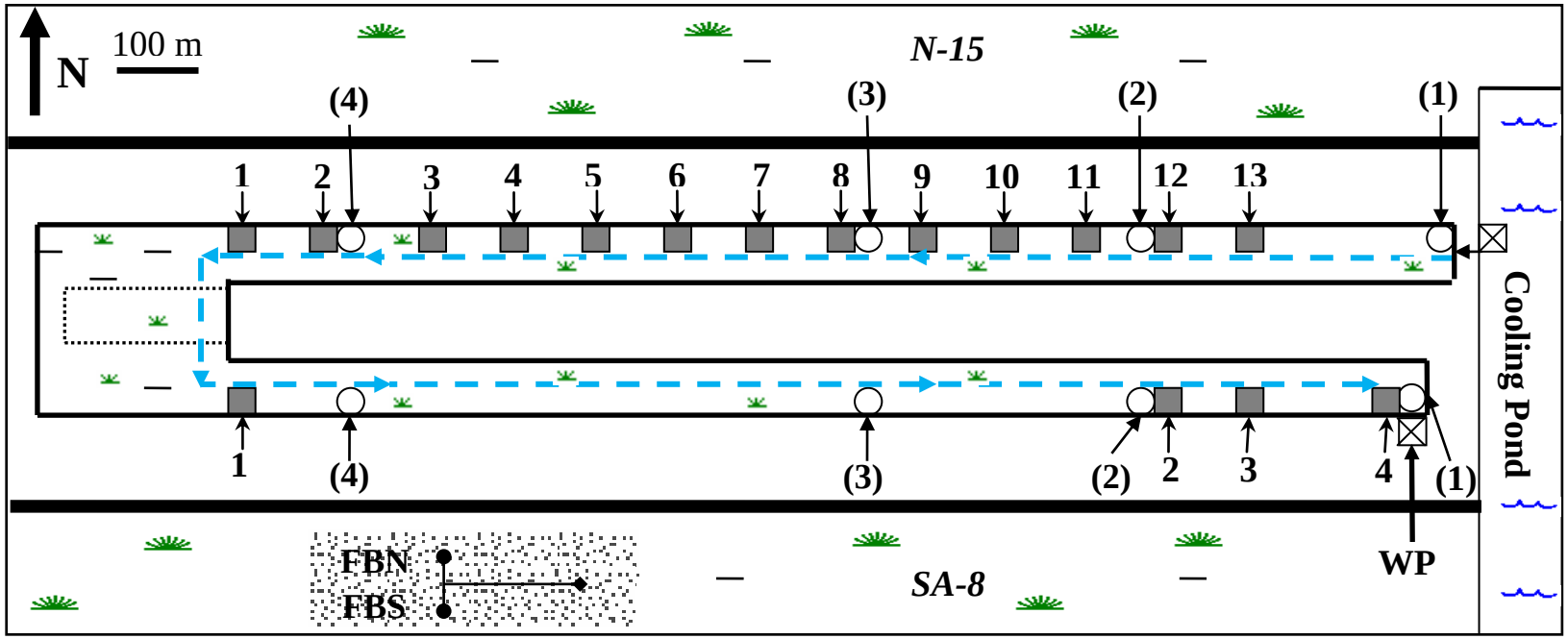

Figure 9. Evaluation of water quality along the wetland flow path.

Note: WP – wetland pump; FBN and FBS – filter basin north and south pumps; Dashed arrow - wetland flow path; Solid squares and empty circles – wetland water samples taken on March 2007 and September 2007, respectively.

Figure 10. Water sampling and analysis along the wetland flow path.

iron (Fe), magnesium (Mg), manganese (Mn), silica (Si), sodium (Na), potassium (K), and strontium (Sr) were measured on a Perkin Elmer Optima 2000 DV inductively coupled plasma - optical emission spectrometer (ICP-OES). Fluoride (F), chloride (Cl), sulfate (SO_4), nitrate (NO_3), nitrite (NO_2), bromide (Br), and phosphate (PO_4) were determined by ion chromatography (IC) using a Dionex ICS 2000 system. Total arsenic (As) concentrations were measured on a PSA 10.055 Millenium Excalibur hydride generation-atomic fluorescence spectrometer (HG-AFS). In preparation for HG-AFS analysis, 10 mL of the sample solution was treated with 30% concentrated HCl, 2% saturated potassium iodide (KI) solution, and deionised water (DI) with a final dilution volume of 50 mL (5:1). This special treatment of the samples causes the reduction of As (V) to As (III) prior to the formation of the arsenic hydride (AsH_3) via addition of sodium tetraborohydride ($NaBH_4$). The AsH_3 generator is based on the reaction of sodium borohydride, hydrochloric acid and the sample.

Formation of hydrogen free radical:

$NaBH_4 + 3H_2O + HCl = H_3BO_3 + 8H^- + NaCl$

Formation of the volatile arsenic hydride (gas)

$8H^- + As^{3+} = AsH_3 + H_2$ excess

In a consequence, the AsH_3 is atomized in a hydrogen flame and concentrations are determined by fluorescence spectrometry. The accuracy and precision of the measurements were verified through the use of internal and external standards, indicating a precision and accuracy better than 5%.

Stable isotopes of oxygen and hydrogen were determined at the University of South Florida stable isotope laboratory using a Finnegan Delta V 3 keV Isotope Ratio

Mass Spectrometer and a Gasbench II preparation device. For oxygen isotope determination, 200 µL of sample was equilibrated with 0.3 % CO_2 in He mixture for 24 hours at 25 °C. Prior to hydrogen isotope analysis, 20 mL of sample were reacted for 24 hours with 1 g of Cu wire to remove dissolved sulfides and to reduce the effects of H_2S gas on the Pt catalyst during the H_2 equilibration. Following this treatment, 200 µL of sample was equilibrated with a 1 % H_2 and He mixture for 10 min. Both oxygen and hydrogen isotope measurements were compared to the Vienna Standard Mean Ocean Water (VSMOW) standard and reported as $\delta^{18}O$ and δD. The average standard deviations for $\delta^{18}O$ and δD were 0.1 and 1.0 ‰, respectively.

Precipitation measurements (amount of rainfall) were performed by the staff from the Hines Energy Complex weather station. Surface water-level measurements were done by Schreuder Inc. and meteorological data was available from the nearby Frostproof Station of the Florida Automated Weather Network (FAWN). Measurements of fecal and total coliform bacteria, PDWS, SDWS, VOC, SOC and RAD were carried out at the Southern Analytical Laboratory of Florida using the Standard Operation Procedures outlined by Ch. 62-160, F.A.C (DEP, 2008).

2.3. Results

2.3.1. Monitor wells

The lithology of monitor well (MW) cores along the wetland was uniform and sediments were composed of light-tan to brown poorly to well-sorted fine sands or silts with occasional grey clay nodules. The brown color was due to the presence of organic

material. After installation, each MW was developed using a small submersible pump to recharge debris free water and sampled monthly for the duration of the study.

The chemical composition of water collected from the MWs was different from the cooling pond (CP), wetland pump (WP), and the wetland surface (WS), with values in the MWs either higher or lower (Appendix A, Tables 1 and 2). The chemical composition of the MWs was much closer in composition to sites SA-8 and N-15, and groundwater from the Intermediate Aquifer System (GW) (Sacks and Tihansky, 1996). In Figure 11A the average concentrations of SO_4, F, As, and Fe in monitor wells (MW-1 to MW-6) are compared. MWs were arranged according to the wetland flow path. MW-6 had the highest As (up to 9 µg/L) and Fe (up to 50 mg/L) concentrations among all MWs. The analyses of water samples from the MWs showed that there was little to no leakage from the sites N-15 and SA-8 into the wetland treatment system. The analysis of variance (ANOVA) of the conservative tracer Na was applied to examine the difference in water chemistry between MWs, SA-8 and N-15. For the first group of samples (MW-4 to MW-6 and SA-8), the F ratio (30.0) was significantly larger than the F critical value (2.7) indicating a statistically significant difference within the data set. For the second group of samples (MW-1 to MW-3 and N-15), the F ratio and F critical value were 7.5 and 2.7, respectively. The variance for MW-3 had the highest value (361.0) potentially demonstrating the highest influence from N-15 (Figure 11B).

2.3.2. Precipitation measurements

Due to periodic variations in precipitation and temperature in the study area two different seasons can be distinguished: the dry season from November to April, and the

Table 1. Maximum, minimum, arithmetic mean and standard deviation of analyzed parameters in the cooling pond, wetland pump and surface, filter basin south and north pumps.

			Max	Min	Med	AM	STD	N		Max	Min	Med	AM	STD	N		Max	Min	Med	AM	STD	N
Cooling Pond (CP)	T	°C	38.3	19.4	30.3	30.0	5.4	38	Wetland Pump (WP)	30.3	13.9	24.0	23.2	4.3	36	Wetland Surface (WS)	31.1	16.0	25.2	24.0	4.3	24
	pH		9.1	8.1	8.6	8.6	0.3	38		7.4	6.4	7.0	6.9	0.2	36		7.3	6.1	6.9	6.9	0.3	24
	ORP	mV	200	-122	23	18	85	38		-4	-176	-85	-80	39	36		101	-166	-38	-31	69	24
	Cond	µS/cm	1122	766	850	878	84	24		1000	273	704	638	214	22		1002	248	771	690	254	16
	H_2S	µg/L	51.0	0.0	3.5	10.2	13.9	37		1060.0	0.0	752.5	619.3	323.3	35		900.0	0.0	17.0	247.8	373.0	24
	As	µg/L	5.1	1.3	2.5	2.7	0.9	37		6.6	0.1	0.5	0.7	1.1	36		13.1	0.2	0.9	1.8	3.2	24
	DO		15.0	3.6	9.3	9.3	2.3	38		7.4	1.6	5.4	4.9	1.4	36		5.4	0.1	1.5	1.9	1.4	24
	F		4.5	1.5	3.4	3.4	0.6	38		4.4	0.7	2.5	2.4	0.9	36		4.3	0.2	2.9	2.6	1.1	24
	Cl		150.8	107.6	128.1	128.9	9.1	38		145.7	26.5	110.0	96.7	35.8	36		157.1	5.6	116.6	100.4	49.2	24
	NO_2		0.7	0.0	0.0	0.0	0.1	38		0.1	0.0	0.0	0.0	0.0	36		0.0	0.0	0.0	0.0	0.0	24
	Br		2.5	0.7	1.6	1.6	0.3	38		2.2	0.0	1.2	1.0	0.6	36		2.0	0.0	1.3	1.2	0.6	24
	NO_3		3.5	0.0	0.0	0.1	0.6	38		2.1	0.0	0.0	0.1	0.4	36		0.1	0.0	0.0	0.0	0.0	24
	PO_4		8.4	0.6	2.3	2.9	1.7	38		8.5	0.0	3.9	4.1	2.1	36		8.2	0.0	3.6	3.8	2.3	24
	SO_4		115.7	69.5	83.5	86.6	9.9	38		81.5	1.3	44.7	40.5	26.1	36		79.8	0.6	44.8	40.8	27.4	24
	K	mg/L	15.3	8.8	10.9	11.0	1.5	38		16.3	0.8	9.5	8.8	3.9	36		14.6	3.0	11.1	10.4	3.4	24
	Na		87.4	56.4	75.3	76.3	7.5	38		95.4	17.3	67.6	59.4	23.1	36		79.2	17.0	55.0	54.1	15.7	24
	Ca		74.9	45.2	54.7	53.9	5.4	38		62.1	17.2	47.2	44.1	11.7	36		63.3	17.0	44.6	44.9	12.9	24
	Mg		39.6	28.7	33.5	33.6	3.2	38		39.5	8.5	28.7	25.3	9.6	36		39.5	8.9	28.6	27.4	8.7	24
	Fe(II)		0.1	0.0	0.0	0.0	0.0	38		1.0	0.0	0.2	0.3	0.2	34		0.8	0.0	0.2	0.3	0.2	24
	Fe		0.3	0.0	0.0	0.0	0.0	38		0.6	0.0	0.1	0.2	0.1	36		0.5	0.0	0.0	0.1	0.1	24
	Mn		0.0	0.0	0.0	0.0	0.0	38		0.1	0.0	0.0	0.0	0.0	36		0.1	0.0	0.0	0.0	0.0	24
	Si		1.2	0.1	0.2	0.3	0.2	38		2.0	0.0	1.2	1.2	0.5	36		0.5	0.1	0.4	0.4	0.1	24
	Sr		0.6	0.5	0.5	0.5	0.0	38		0.5	0.1	0.4	0.3	0.1	36		3.8	0.0	1.1	1.2	0.8	24

Table 1. Continued

			Max	Min	Med	AM	STD	N		Max	Min	Med	AM	STD	N
Filter Basin South Pump (FBS)	T	°C	28.2	15.9	24.7	23.7	3.7	30	**Filter Basin North Pump (FBN)**	30.1	16.8	24.5	23.8	3.8	25
	pH		7.3	6.3	6.8	6.8	0.3	30		7.5	6.3	6.9	6.8	0.3	25
	ORP	mV	2	-100	-55	-53	33	30		87	-108	-9	-16	51	25
	Cond	µS/cm	932	250	732	688	199	19		925	275	741	730	163	16
	H_2S	µg/L	160.0	0.0	15.5	23.8	32.5	30		40.0	0.0	6.0	8.8	11.4	25
	As	µg/L	2.7	0.5	1.0	1.2	0.6	29		2.2	0.5	0.9	1.3	0.6	25
	DO		6.2	0.9	2.3	2.6	1.3	30		6.5	1.2	5.0	4.6	1.7	25
	F		3.4	1.0	2.1	2.2	0.6	29		3.4	0.3	2.2	2.3	0.8	25
	Cl		158.6	10.1	104.4	92.5	39.3	29		158.4	23.5	111.1	103.1	38.8	25
	NO_2		0.2	0.0	0.0	0.0	0.1	29		0.2	0.0	0.0	0.0	0.1	25
	Br		2.0	0.0	1.2	1.0	0.5	29		2.7	0.3	1.3	1.3	0.6	25
	NO_3		4.0	0.0	0.2	0.4	0.7	29		5.8	0.1	0.4	0.8	1.2	25
	PO_4		4.3	0.0	1.7	1.6	1.0	29		5.1	0.0	2.6	2.4	1.1	25
	SO_4		81.8	0.6	36.9	37.2	21.6	29		76.6	5.6	46.1	43.9	21.1	25
	K	mg/L	13.8	3.9	9.7	9.7	3.0	29		13.9	4.1	10.5	10.3	2.6	25
	Na		75.5	28.5	52.2	52.5	12.4	29		74.8	30.4	54.4	55.0	9.9	25
	Ca		57.4	25.6	43.0	42.5	8.8	29		56.5	22.0	43.9	43.5	8.1	25
	Mg		35.1	10.5	26.0	25.3	7.3	29		35.7	8.9	27.6	26.9	6.8	25
	Fe(II)		3.0	0.3	1.5	1.4	0.7	30		1.5	0.1	0.4	0.5	0.4	25
	Fe		2.3	0.1	0.7	0.9	0.7	29		1.3	0.0	0.2	0.3	0.3	25
	Mn		0.1	0.0	0.0	0.0	0.0	29		0.1	0.0	0.0	0.0	0.0	25
	Si		0.4	0.2	0.3	0.3	0.1	29		0.4	0.2	0.3	0.3	0.1	25
	Sr		2.5	0.5	1.4	1.4	0.5	29		2.0	0.0	1.3	1.3	0.5	25

Table 2. Maximum, minimum, arithmetic mean and standard deviation of analyzed parameters in monitor wells MW-1 to MW-6 and water. Note: MWs arranged according to the wetland flow path.

			Max	Min	Med	AM	STD	N		Max	Min	Med	AM	STD	N		Max	Min	Med	AM	STD	N
MW-1	T	°C	28.7	19.8	25.8	25.3	2.5	21	MW-2	28.2	19.2	26.5	25.3	2.7	21	MW-3	27.8	20.8	26.2	25.1	2.2	21
	pH		6.6	5.5	5.9	5.9	0.3	21		6.2	5.6	6.0	6.0	0.2	21		6.5	5.6	6.0	6.0	0.2	21
	ORP	mV	152	-39	20	47	58	21		164	-45	1	19	54	21		233	-32	90	81	67	21
	Cond	µS/cm	725	186	281	350	170	15		768	330	578	567	125	15		744	213	305	405	190	14
	H_2S	µg/L	76.0	0.0	10.0	19.3	21.7	20		58.0	0.0	4.0	8.6	13.6	19		28.0	0.0	4.0	7.2	7.4	20
	As	µg/L	3.7	0.4	2.8	2.5	1.0	21		7.6	0.4	4.1	4.1	2.4	21		5.0	0.5	1.7	2.1	1.2	21
	DO		5.6	0.9	3.2	2.9	1.3	21		4.6	0.8	2.4	2.6	1.1	21		6.3	1.2	3.6	3.5	1.5	21
	F		3.5	0.5	0.9	1.0	0.6	21		1.4	0.4	1.0	1.0	0.2	21		1.9	0.3	0.6	0.7	0.3	20
	Cl		147.4	4.8	10.8	21.6	31.6	21		61.5	10.2	23.1	26.6	23.7	21		136.6	12.9	25.5	48.4	40.7	20
	NO_2		1.0	0.0	0.0	0.1	0.3	21		1.1	0.0	0.0	0.1	13.4	21		0.2	0.0	0.0	0.0	0.1	20
	Br		5.3	0.0	0.2	0.6	1.2	21		1.2	0.2	0.5	0.6	0.3	21		1.9	0.0	0.2	0.4	0.6	20
	NO_3		149.8	0.0	0.4	22.1	44.4	21		341.0	0.0	0.2	44.8	100.0	21		58.2	0.0	2.1	8.2	13.7	20
	PO_4		3.0	0.0	0.0	0.3	0.7	21		0.1	0.0	0.0	0.0	0.0	21		1.0	0.0	0.0	0.2	0.3	20
	SO_4		97.4	3.4	18.0	21.6	21.0	21		32.3	5.4	15.4	16.3	7.1	21		38.2	0.5	18.3	18.5	8.9	20
	K	mg/L	8.0	1.3	3.2	3.3	1.4	21		20.4	0.9	1.7	2.7	4.1	21		10.6	1.0	3.4	4.0	2.4	20
	Na		63.7	3.1	4.4	9.1	13.6	21		17.1	5.3	7.9	9.3	3.5	21		58.5	5.8	10.6	20.5	19.0	20
	Ca		71.8	21.2	33.7	35.8	12.7	21		81.1	39.8	58.2	58.5	11.9	21		47.2	23.0	31.0	33.3	7.1	20
	Mg		34.5	6.9	10.9	12.9	7.0	21		40.6	16.6	26.5	27.7	6.5	21		16.8	6.0	10.4	10.8	3.3	20
	Fe(II)		9.0	0.1	1.5	2.9	3.2	21		10.0	0.3	2.0	4.3	4.2	21		8.0	0.2	0.9	1.5	1.8	21
	Fe		18.1	0.0	2.5	4.8	5.1	21		21.2	0.3	8.7	8.0	6.4	21		6.5	0.1	0.3	1.0	1.7	20
	Mn		0.2	0.0	0.1	0.1	0.0	21		0.2	0.1	0.1	0.1	0.0	21		0.2	0.1	0.1	0.1	0.0	20
	Si		0.2	0.0	0.1	0.1	0.1	21		0.2	0.1	0.1	0.1	0.0	21		0.2	0.0	0.1	0.1	0.0	20
	Sr		9.8	3.7	5.0	5.3	1.6	21		17.7	5.3	7.6	8.0	3.4	21		5.4	3.3	4.1	4.2	0.7	20

Table 2. Continued.

			MW-6						MW-5						MW-4					
			Max	Min	Med	AM	STD	N	Max	Min	Med	AM	STD	N	Max	Min	Med	AM	STD	N
	T	°C	30.1	20.2	24.9	24.6	2.5	19	33.2	20.0	26.6	26.2	3.3	19	28.6	20.5	25.8	25.0	2.3	20
	pH		6.3	5.9	6.0	6.0	0.1	20	6.4	5.7	6.1	6.1	0.2	19	6.0	5.3	5.6	5.6	0.2	20
	ORP	mV	-5	-109	-58	-58	24	20	47	-71	3	-4	31	19	72	-61	37	33	36	20
	Cond	µS/cm	916	413	736	746	125	13	493	240	331	358	83	12	714	119	269	305	158	13
	H_2S	µg/L	166.0	0.0	39.5	47.7	43.6	19	119.0	0.0	8.0	17.9	27.8	19	184.0	0.0	37.0	71.5	66.7	19
	As	µg/L	17.9	2.1	8.7	8.8	4.2	20	5.8	0.5	1.9	2.3	1.5	19	5.8	0.1	1.9	2.2	1.5	20
	DO		3.8	0.5	1.8	1.9	0.7	20	7.5	1.2	5.4	5.1	1.5	19	7.0	0.9	3.5	3.2	1.4	20
	F		1.4	0.5	1.0	1.0	0.2	20	3.1	0.4	0.9	1.0	0.6	19	3.1	0.5	0.7	0.9	0.6	20
	Cl		51.2	9.3	28.1	26.3	8.7	20	139.7	8.7	17.0	27.3	29.2	19	123.9	3.6	31.5	37.7	28.9	20
	NO_2		0.0	0.0	0.0	0.0	0.0	20	0.1	0.0	0.0	0.0	0.0	19	0.1	0.0	0.0	0.0	0.0	20
	Br		2.0	0.4	1.3	1.2	0.4	20	3.4	0.4	1.0	1.4	0.9	19	3.0	0.1	0.7	0.9	0.6	20
	NO_3		1.1	0.0	0.0	0.1	0.3	20	5.9	0.0	0.1	0.5	1.4	19	0.7	0.0	0.0	0.1	0.1	20
	PO_4		0.2	0.0	0.0	0.0	0.0	20	1.9	0.0	0.0	0.2	0.6	19	5.4	0.0	0.0	0.8	1.6	20
	SO_4	mg/L	17.3	0.0	0.9	3.5	5.2	20	69.9	0.8	8.0	11.7	15.6	19	56.8	0.0	1.8	5.6	12.5	20
	K		4.9	0.5	1.2	1.4	1.1	20	4.0	0.8	1.5	1.7	0.8	19	3.3	0.7	1.3	1.4	0.6	19
	Na		22.6	7.8	18.9	18.1	3.5	20	12.5	3.2	6.9	7.4	2.6	19	22.6	1.8	7.8	9.0	5.8	19
	Ca		93.6	38.7	73.2	70.9	13.2	20	47.2	19.1	29.6	31.2	7.6	19	88.8	14.5	24.6	28.0	16.7	19
	Mg		39.2	16.3	32.3	31.4	6.1	20	25.3	8.1	14.7	16.0	4.5	19	18.2	2.6	6.2	7.4	3.8	19
	Fe(II)		>10	0.0	10.0	9.5	2.2	20	>10	2.5	10.0	9.2	2.3	19	>10	3.5	10.0	9.1	2.0	20
	Fe		68.0	13.8	55.2	47.9	16.9	20	45.2	0.7	11.3	13.7	10.7	19	37.3	0.8	5.7	8.7	9.2	19
	Mn		0.3	0.1	0.2	0.2	0.0	20	0.3	0.0	0.1	0.1	0.1	19	0.5	0.0	0.0	0.1	0.1	19
	Si		0.2	0.0	0.1	0.1	0.0	20	0.1	0.0	0.1	0.1	0.0	19	0.2	0.0	0.1	0.1	0.0	19
	Sr		8.1	2.7	3.4	3.7	1.2	20	5.3	2.3	3.2	3.4	0.7	19	7.8	2.3	4.1	4.5	1.5	19

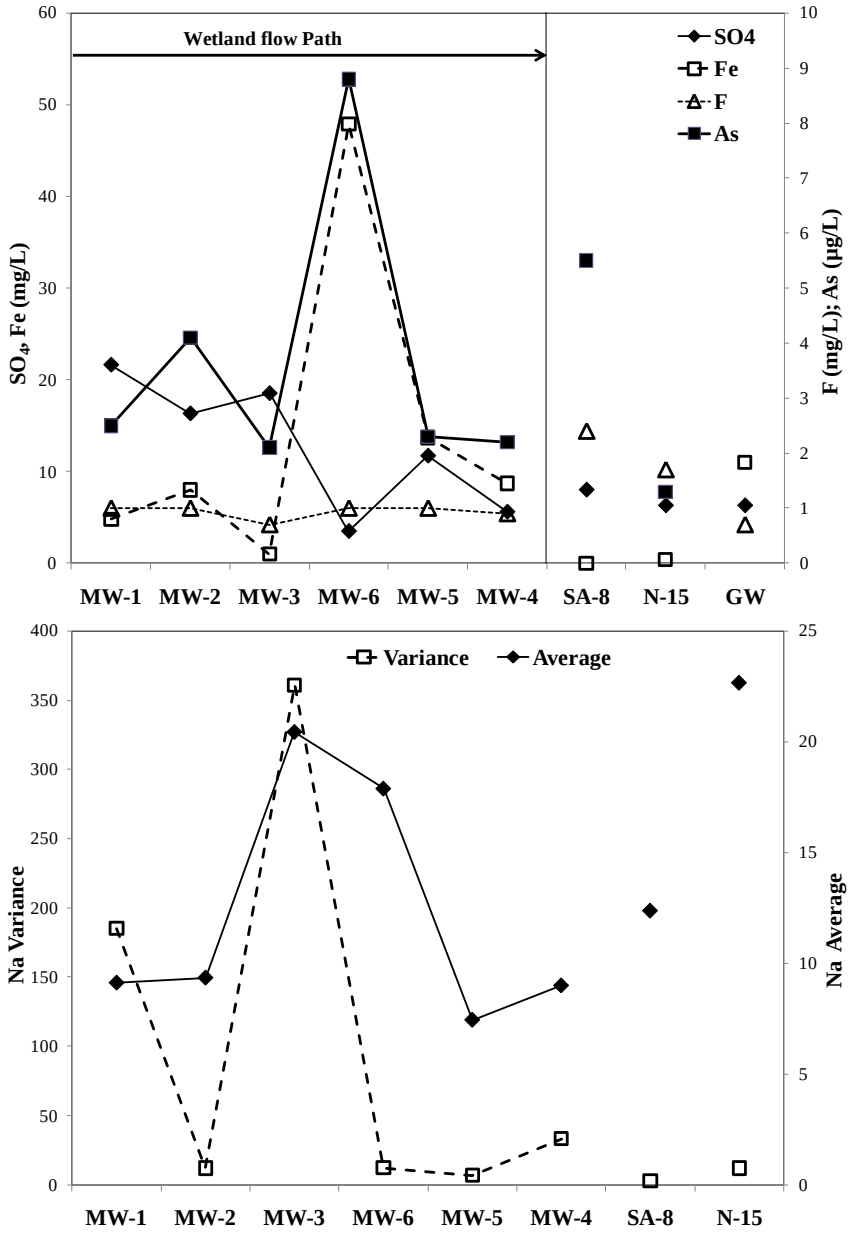

Figure 11. (A) Average values of SO_4, Fe, F, and As and (B) Average and variance of Na estimated by ANOVA at MW-1 to MW-6, N-15 and SA-8.

Note: MW-1, 2, 3, 6, 5 to MW-4 – monitor wells arranged according to the wetland flow path; GW* - Floridan groundwater from the Intermediate Aquifer System (well ROMP 45 from Sacks and Tihansky, 1996).

rainy or wet season from May to October. Daily precipitation was recorded at the Hines Energy Complex weather station from May 1, 2006 to October 31, 2007, covering one dry and two rainy seasons (Figure 12). The highest levels of rainfall (up to 123 mm) were detected during the major hurricane events (Ernesto and Alberto) in June and August 2006. The mean monthly rainfall ranged from 0 to 11 mm. Total seasonal precipitation during the dry season of 2006 was 324 mm, while the rainy seasons of 2006 and 2007 had between 917 and 782 mm, respectively.

2.3.3. Surface water-level measurements

The monitoring of surface water-level elevations above National Geodetic Vertical Datum (NGVD) showed that the SA-8 had a higher level (51.6 - 52.5 m) compared to the N-15 (49.9 - 50.7 m) and the cooling pond (CP) (49.0 - 49.3 m) (Figure 13). The elevation of wetland water surface (WS) ranged from 49.7 to 50.8 m with the lower levels in April – May 2007. Records showed that at the end of April the CP pump was turned off and the WS was lowered approximately 1 m for maintenance purposes. After one month the CP pump was turned back on and the wetland treatment system became again operational.

2.3.4. Evaluation of water quality along the wetland flow path

Evaluation of the wetland during the dry (March 19-20, 2007) and rainy (September 24-25, 2007) seasons was important to understand the consistency and reliability of the treatment system in time and space (Figure 9). The wetland transect showed a distinct pattern of change in water chemistry along the flow path from the input

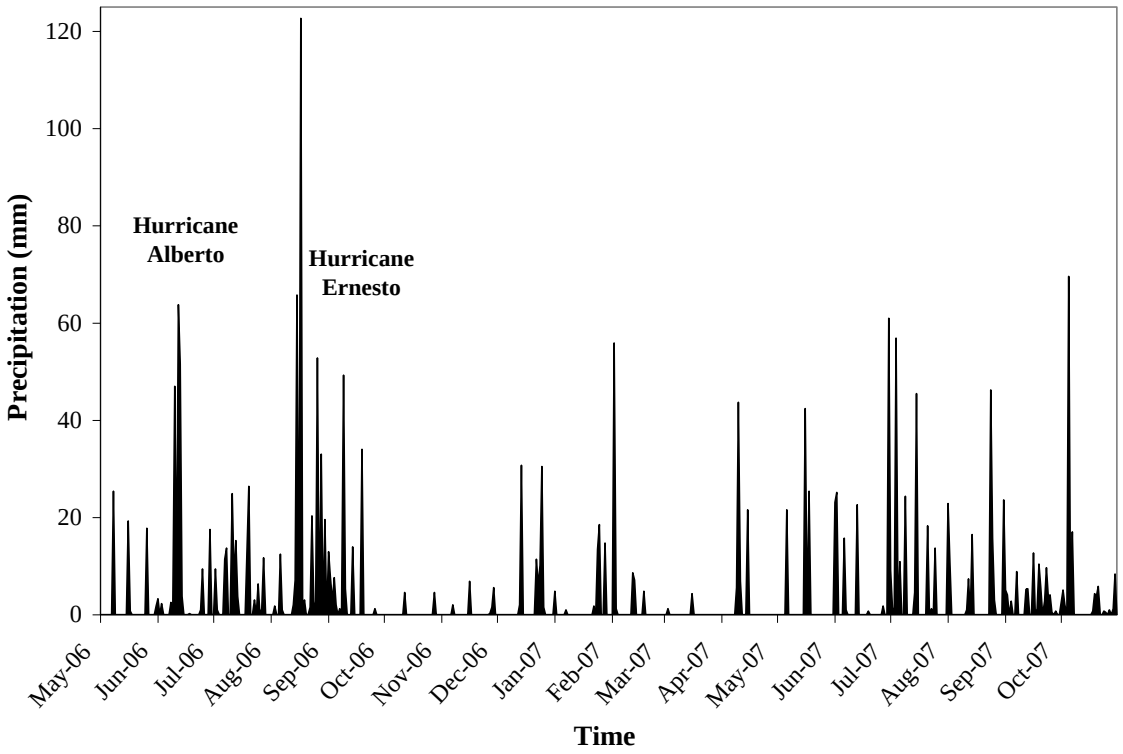

Figure 12. Precipitation hydrograph recorded at the study area from May 1, 2006 to October 31, 2007, covering one dry and two rainy seasons.

Note: major hurricane events (Ernesto and Alberto) in June and August 2006.

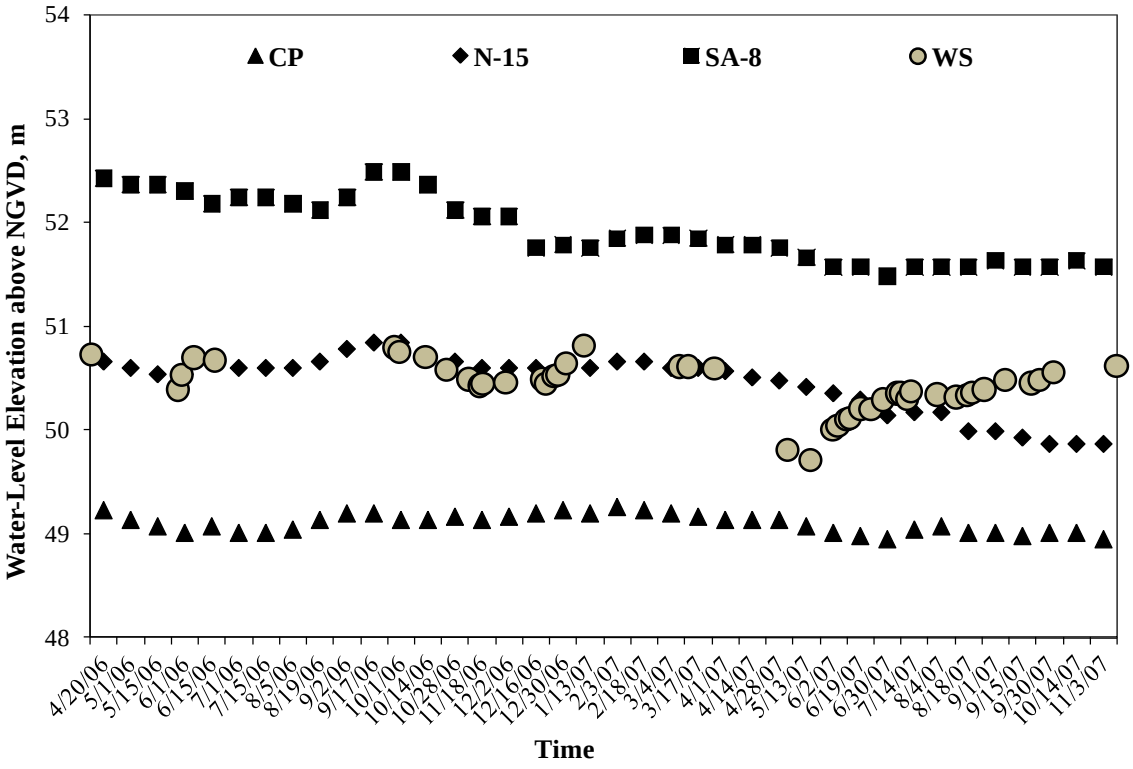

Figure 13. Water-level elevations at the CP, WS, N-15 and SA-8 above National Geodetic Vertical Datum (NGVD).

Note: CP- cooling pond; N-15 and SA-8 - water bodies to the north and south of the wetland; WS – wetland water surface.

-cooling pond (CP) to the output – wetland water from pump (WP) (Table 3, Figure 14).

2.3.4.1. Field measurements

Temperature (T). Generally, during the dry and rainy seasons temperature in the wetland was < 20 and 25°C, respectively. However during the dry season, it reached up to 24.8 °C (500-800 m) on the wetland surface.

pH. The pH values were reduced along the wetland flow path from 8.9 to about 7.0, but reached up to 8.7 on the wetland surface (500-700 m and 1400 m) during the dry season. The formation of organic acids in the wetland was likely responsible for this drastic change in pH.

Oxidation-Reduction Potential (ORP). Generally, ORP was negative in the wetland indicating more reducing conditions. At the same time during the dry season algal blooms, the ORP level at 300-700 m on the wetland surface and at a depth of 0.5 m reached +254 and +217 mV, respectively.

Sulfide (H_2S). During the dry season the concentration of H_2S was up to 900 µg/L and did not show the trend along the wetland. In contrast, during the rainy season H_2S reached up to 2545 µg/L increasing along the wetland flow path.

Dissolved Oxygen (DO). After entering the wetland, DO along the wetland flow path was generally reduced to < 0.5 mg/L. During the dry season it reached up to 8.7 mg/L on wetland surface (200-700 m of the wetland flow path). The concentration of DO at the WP during the dry and rainy seasons was up to 6.0 and 3.3 mg/L, respectively. This was likely due to trapping of oxygen during the pumping procedure.

Ferrous Iron (Fe(II)). Concentration of Fe(II) at the WP was up to 0.2 mg/L but was not

Table 3. Change in water composition from the cooling pond (CP) to the wetland from pump (WP) during the dry (March 2007) and rainy (September 2007) seasons.

		Dry Season		***Rainy Season***	
		CP -Input	**WP - Output**	**CP -Input**	**WP-Output**
DO	**mg/L**	9.4	6.0	9.4	3.3
T	**° C**	23.1	16.5	32.1	25.0
pH		8.7	7.0	8.9	7.0
ORP	**mV**	63	-84	-116	-171
Cond	**µS/cm**	865	767	958	1056
H_2S	**µg/L**	30	731	10	1175
As		2.0	0.2	2.3	0.2
Fe2+		n/d	0.1	n/d	0.2
F		3.8	3.1	3.9	2.8
Cl		129.8	118.5	137.6	107.3
NO2		n/d	n/d	n/d	n/d
Br		1.5	1.3	2.2	1.5
NO3		n/d	n/d	1.5	n/d
PO4		3.9	3.9	1.7	3.0
SO4	**mg/L**	89.1	58.1	92.1	25.0
Na		56.2	56.6	71.6	52.3
Mg		30.1	29.0	40.4	27.1
K		10.3	10.8	14.4	9.3
Ca		47.5	45.9	60.8	40.6
Sr		0.4	0.4	0.5	0.3
Mn		0.0	0.0	0.0	0.0
Fe		0.0	0.1	0.0	0.0
Si		0.0	0.5	0.1	2.0

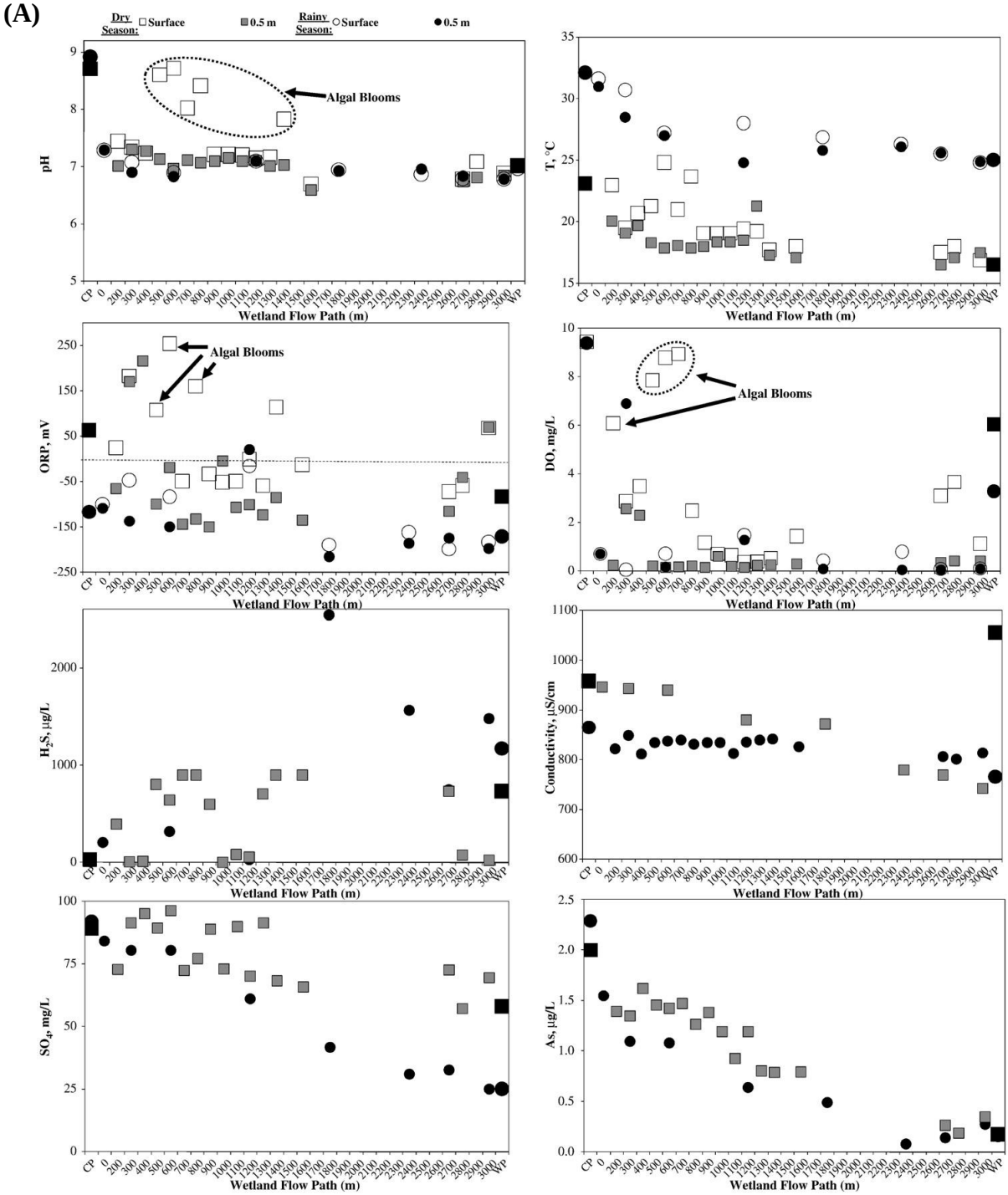

Figure 14. Continued.

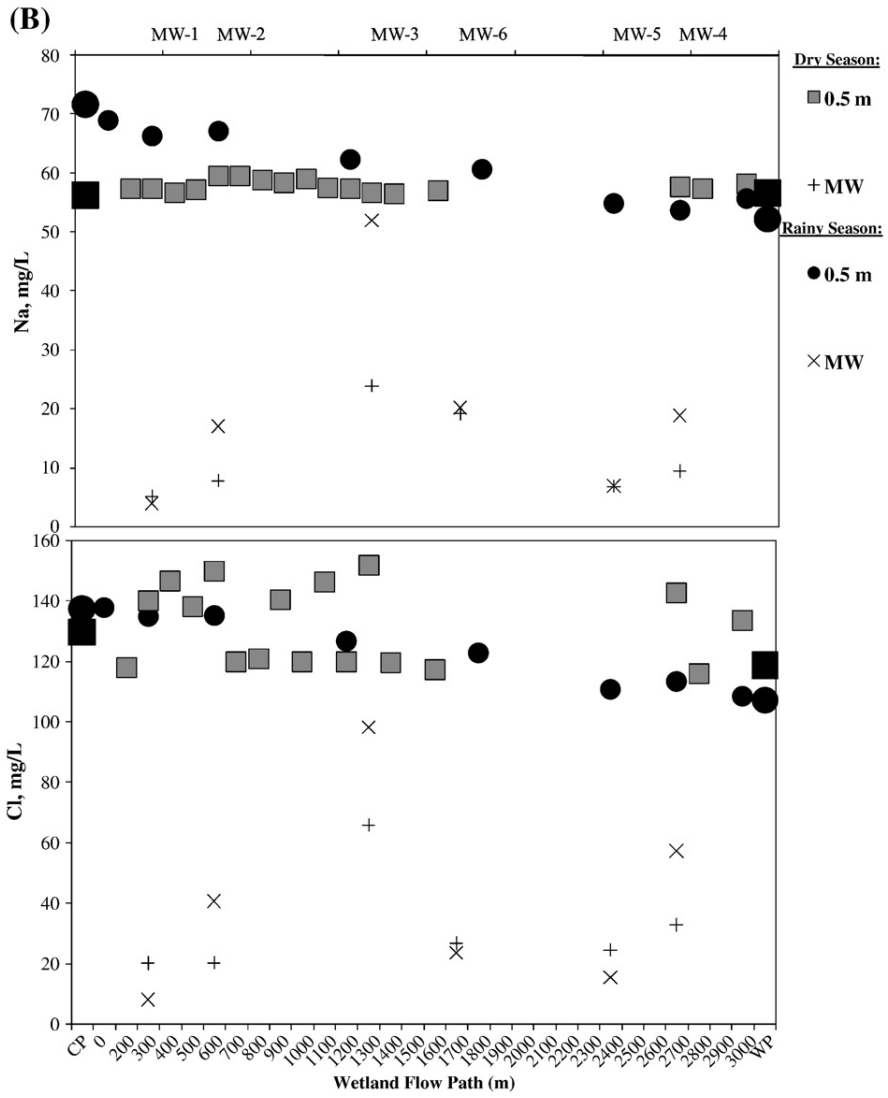

Figure 14. (A). Evaluation of T, pH, ORP, DO, H_2S, SO4, conductivity, and As along the wetland flow path during the dry (March 2007) and rainy (September 2007) seasons; (B): Distribution of Na and Cl along the wetland flow path and at the MWs during the dry (March 2007) and rainy (September 2007) seasons.

Note: CP - cooling pond pump; WP - wetland pump; MW - monitor wells arranged according to the wetland flow path; Elevated pH, DO, T, positive ORP, and low H_2S during the dry season were caused by algal blooms.

present in the CP, which was likely due to high DO levels.

2.3.4.2. Laboratory analysis

Anions. During the dry and rainy seasons the concentrations of most anions decreased along the wetland flow path (Table 3). The F, Cl, and SO_4 levels gradually decreased from 3.1 to 2.8 mg/L, 118 to 107 mg/L, and 58 to 25 mg/L, respectively. The concentration of NO_2 and NO_3 was mostly below detection at the WP and the CP. During the dry season, the concentration of Br and PO_4 at the WP was similar to the concentration at the CP. In the contrast, during the rainy season the level of Br was 1.5 times lower but PO_4 was 1.7 times higher in the wetland.

Cations. Generally, the behaviour of most cations had a comparable pattern. During the dry season, the concentration of Na, Mg, K, Ca, and Sr in the wetland was close to the CP. In contrast, during the rainy season the concentration of these cations in the wetland was around 1.5 times less than in the CP. This behaviour could be caused by a dilution effect or due to minor groundwater inflow. The concentration of Mn and Fe (total) was mostly below detection. The CP water was virtually Si-free. At the same time, during the dry and rainy seasons Si at the WP was 0.5 and 2 mg/L, respectively.

Arsenic (As). During both seasons the concentration of As significantly decreased along the wetland flow path from 2.3 to < 0.2 µg/L.

The concentration of conservative tracer elements Na and Cl at the monitor wells (MWs), sampled on April 3 and October 3, 2007, was considerably lower than in the wetland water and CP (Figure 14 B).

2.3.5. Wetland/filter basin water quality monitoring

The major purpose of this study was to investigate the possibility of using a constructed wetland for the wastewater treatment in an area used during phosphate mining for clay settling. The results derived from the field and laboratory analyses are summarized in Table 1. The distribution of pH, ORP, and T in the cooling pond (CP) as the input and wetland (WP) as the output waters is demonstrated in Figure 15. The 18-month monitoring showed a significant change in pH from about 9 to 6.5–7, negative ORP confirming the reducing conditions of the wetland treatment system and a substantial decrease of water temperature (up to 10 °C during rainy seasons). Generally, the wetland water T plotted closely to the reported average air T obtained from the Frostproof Station in Polk County (FAWN) (Appendix A).

The performance of the wetland was evaluated by mass flux of analytes removed from or contributed to the wetland water (Table 4). The mass fluxes were calculated as concentration * flow rate = mass/time. The flow rates used for calculation varied depending on the season between 5012, 6757 (rainy seasons 2006 and 2007, respectively) and 9255 L/day (dry season 2006). The percent removal of each parameter was calculated as ((mass flux CP – mass flux WP)/mass flux CP)*100 with and without the rainfall dilution factor over the study area (Table 4). The average amount of rainfall over the wetland area varied from 1995, 1697 (rainy seasons 2006 and 2007,respectively) to 745 L/day (dry season 2006).The corrected concentration with the rainfall dilution factor was calculated as concentration *(flow rate/(flow rate –rainfall)) and subsequently used for the mass fluxes and percent removal.

Along the wetland flow path most of the monitored constituents were removed

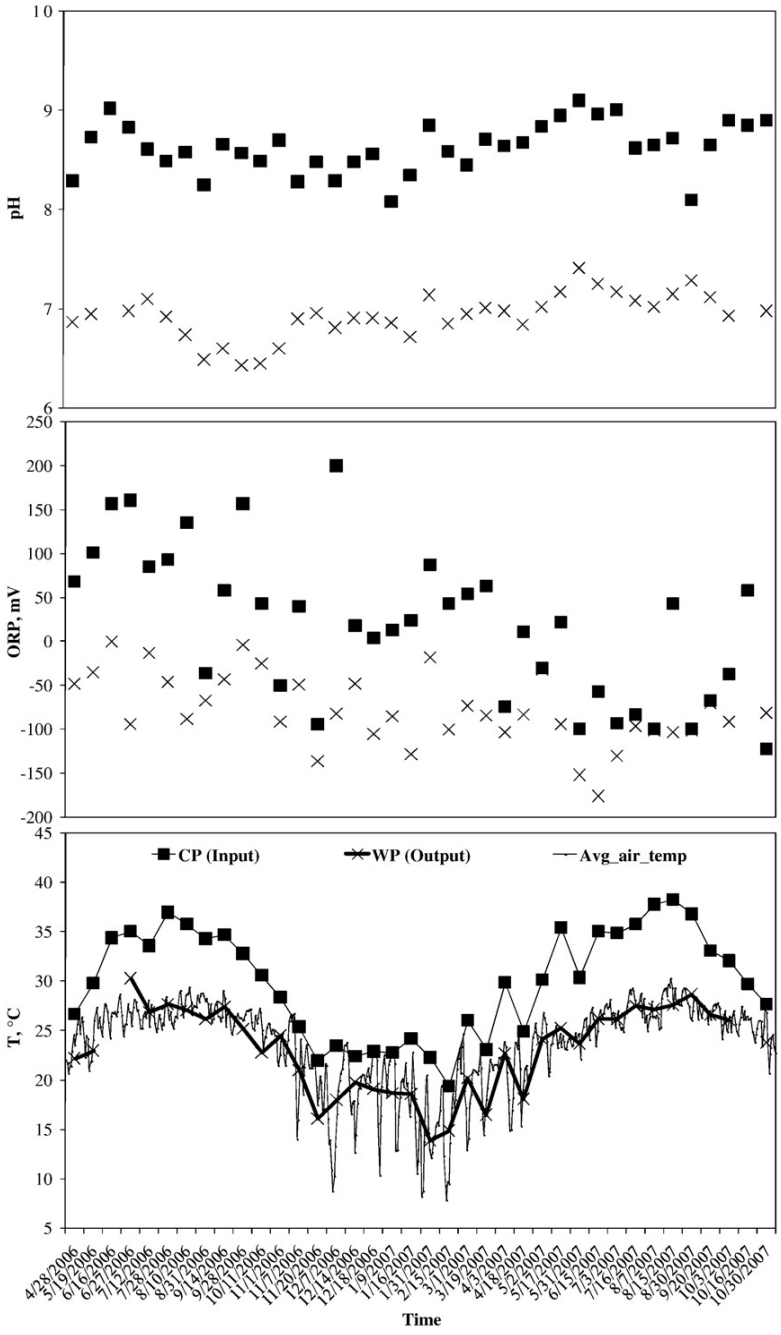

Figure 15. Distribution of pH, ORP, and temperature (T) in the CP - input and WP - output waters.

Note: CP - cooling pond pump; WP - wetland pump; Average air T measured at elevation of 0.6 m was obtained from the Frostproof Station in Polk County (FAWN).

from the CP with the exception of Si, PO_4, and Fe. During the rainy season 2007 (May-July), however, the wetland contributed mass to the water due to technical difficulties. In addition, during the dry season, the wetland contributed mass in form of K (up to 40 %), likely from plant stem and root systems (Fisher, 1971).

2.3.5.1. Primary, secondary drinking water standards, volatile organic compounds, synthetic organic compounds, and radionuclides.

The results for primary, secondary drinking water standards (PDWS/SDWS), volatile organic compounds (VOC), synthetic organic compounds (SOC), and radionuclides (RAD) are demonstrated in Tables 5-8. The analysis showed no exceedances of the PDWS, VOC, SOC or RAD compounds. At the same time, there were several exceedances for the SDWS for the following chemical constituents: were aluminum (7/49), fluoride (55/74), iron (22/74), manganese (10/74), color (56/74), odor (57/74), total dissolved solids (13/49) and foaming agents (1/49).

2.3.5.2. Fecal and total coliform

Previous studies demonstrated the capability of constructed wetlands to reduce pathogenic microorganisms in wastewater (e.g., Hill and Sobsey, 2001; Neralla and Weaver, 2000). Removal efficiency was > 90% for total coliform and > 80% for fecal streptococcus (Kadlec and Knight 1996).

Fecal and total coliform in the CP ranged between <1 - 370 count/100mL and <1 - 2000 count/100mL, respectively (Figures 16 A-B). The maximum contaminant level (MCL) for total coliform (including fecal coliform) is that no more than 5.0 % of the

Table 4. The wetland performance evaluated with the percent removal of each analyzed parameter.

	Date	As	As*	K	K*	Na	Na*	Ca	Ca*	Mg	Mg*	Sr	Sr*	S^T	S^T*	SO_4	SO_4*	F	F*	Cl	Cl*	Br	Br*	Si	Si*	PO_4	PO_4*
Rainy Season 2006	4/28			70	50	74	58	14	-42	68	47	70	50	97	96	98	97	56	26	78	63	100	100	-536	-957	-323	-602
	5/19	69	48	56	26	70	51	-5	-74	64	39	54	23	96	94	98	97	58	29	73	55	100	100	-610	-1080	-229	-446
	6/27	71	52	45	9	63	39	51	18	60	33	64	41	91	86	92	87	51	19	64	40	83	72	-593	-1052	-221	-434
	7/12	79	65	50	17	63	39	27	-22	58	30	58	31	94	89	94	90	49	15	64	40	72	53	-619	-1094	-275	-523
	7/28	89	82	44	7	55	26	36	-6	57	28	60	34	94	91	94	91	51	18	54	24	75	58	-808	-1408	-268	-512
	8/10	94	90	29	-17	46	10	21	-32	46	10	51	18	91	85	94	90	42	3	46	10	66	44	-1015	-1753	-169	-347
	8/31	53	22	59	32	65	42	57	28	67	45	80	67	90	83	92	86	42	3	66	43	60	34	-1162	-1996	-103	-237
	9/14	74	57	68	47	70	49	62	37	70	51	74	56	95	91	95	92	60	34	69	49	87	78	-348	-645	-650	-1146
	9/28	79	65	72	53	73	55	61	35	71	52	85	75	95	92	96	93	69	48	74	57	90	83	-374	-687	-68	-179
	10/11	96	94	66	44	61	35	48	13	61	36	68	46	91	86	92	87	48	14	61	36	73	55	-920	-1594	-99	-231
Dry Season 2006-2007	11/1	85	84	3	-5	11	3	4	-4	16	9	34	28	39	34	43	38	100	100	11	3	100	100	-358	-398	7	-2
	11/7	88	87	4	-4	10	2	3	-5	15	7	21	15	23	16	26	19	-10	-19	8	0	11	3	-107	-125	-110	-128
	11/20	65	62	-8	-17	2	-7	-17	-27	2	-7	13	5	29	22	32	26	-3	-12	7	-2	7	-1	-12	-22	-125	-145
	12/7	83	82	93	93	8	0	6	-2	11	3	30	24	24	17	26	20	25	18	6	-2	19	12	113	114	-23	-34
	12/14	79	78	-14	-25	2	-6	2	-6	8	0	17	10	15	8	18	11	-5	-14	0	-9	-2	-11	-60	-75	-61	-75
	12/18	82	81	-25	-36	1	-7	-10	-19	-5	-14	6	-2	24	17	27	21	29	23	0	-8	26	19	-234	-263	-9	-18
	1/9	89	88	-29	-40	5	-3	20	12	11	3	20	12	43	38	47	42	-5	-14	10	2	-10	-20	-125	-144	-103	-121
	1/16	55	51	-39	-51	6	-2	10	3	11	4	24	17	36	30	39	34	28	22	11	3	26	20	-595	-656	-53	-67
	1/31	55	51	-4	-14	6	-2	13	6	13	5	17	10	19	12	19	12	-8	-17	10	2	-12	-22	-96	-113	-93	-110
	2/15	67	64	-5	-14	11	3	13	6	14	6	25	18	25	19	28	21	14	6	13	6	-32	-43	-419	-464	-24	-35
	3/1	73	71	-3	-12	9	1	6	-3	11	4	24	17	33	27	36	30	29	22	9	1	30	23	-3	-12	27	21
	3/19	92	91	2	-6	3	-5	7	-1	8	0	13	5	28	22	30	24	18	10	4	-4	12	4	-247	-277	-1	-9
	4/3	87	86	9	1	9	1	-1	-10	0	-8	-4	-13	29	22	31	25	-10	-19	8	0	-18	-28	92	92	-52	-66
	4/18	88	87	-5	-14	5	-4	11	3	10	2	12	4	32	26	34	28	0	-8	5	-3	-24	-35	-1545	-1689	-43	-55

Table 4 Continued.

	Date	As	As*	K	K*	Na	Na*	Ca	Ca*	Mg	Mg*	Sr	Sr*	S^T	S^T*	SO_4	SO_4*	F	F*	Cl	Cl*	Br	Br*	Si	Si*	PO_4	PO_4*
Rainy Season 2007	5/2	80	74	-8	-45	0	-34	4	-29	3	-29	4	-29	28	4	28	5	8	-23	4	-28	9	-21	-1168	-1593	-53	-104
	5/17	76	68	-16	-54	-9	-46	-3	-37	-4	-40	0	-34	18	-10	20	-7	38	18	-7	-42	4	-28	-1620	-2197	100	100
	5/31	77	69	-11	-48	-14	-52	-5	-41	-9	-46	-2	-36	16	-12	18	-10	82	76	-9	-45	46	28	-496	-696	100	100
	6/15	62	49	-4	-39	0	-34	6	-25	3	-29	11	-19	25	0	28	3	-26	-68	3	-29	83	77	-1000	-1369	55	40
	7/3	-30	-74	7	-24	10	-20	6	-26	3	-30	9	-22	32	10	35	14	-14	-53	10	-20	8	-23	-665	-921	-394	-559
	7/16	67	55	33	10	24	-1	31	8	30	7	37	15	52	36	54	38	23	-3	25	0	31	8	-816	-1124	-96	-162
	8/7	79	72	44	26	25	0	29	5	28	4	35	13	65	54	68	58	48	30	27	3	55	40	-947	-1298	76	69
	8/15	84	78	44	25	26	1	29	5	30	6	35	13	68	57	71	61	37	16	26	1	45	27	-647	-898	53	37
	8/30	88	84	33	10	22	-4	25	-1	25	0	32	10	60	47	63	50	24	-2	23	-3	31	8	-466	-656	-46	-95
	9/20	95	93	39	19	28	4	34	12	34	11	42	22	66	55	69	58	33	10	28	4	43	24	-925	-1269	58	44
	10/3	92	90	23	-3	17	-10	25	0	25	-1	31	8	59	45	62	49	26	1	21	-5	29	5	-1065	-1456	-83	-144
	10/30	90	86	10	-20	17	-11	17	-11	20	-7	26	1	58	45	61	49	28	4	19	-8	25	-1	-2074	-2804	40	20

Note: * - percentage included the rainfall dilution factor over the site area; Positive values – wetland removes mass and negative - wetland contributes mass to the water that flows through it; percent removal of total S was calculated from a sum of S(VI) and S(-II); Most of NO_2 and NO_3 was not detected in input and output waters; Fe was not detected in the CP.

Table 5. Analysis of Primary Drinking Water Standards (PDWS).

Parameter	PDWS	# of Samples	# of Exceedences
Antimony	0.006 mg/L	49	0
Arsenic	0.01 mg/L	49	0
Barium	2 mg/L	49	0
Beryllium	0004 mg/L	49	0
Cadmium	0.005 mg/L	49	0
Chromium	0.1 mg/L	49	0
Cyanide	0.2 mg/L	49	0
Fluoride	4.0 mg/L	74	0
Lead	0.015 mg/L	49	0
Mercury	0.002 mg/L	49	0
Nickle	0.1 mg/L	49	0
Nitrate	10 mg/L as N	49	0
Nitrite	1 mg/L as N	49	0
Selenium	0.05 mg/L	49	0
Soidum	160 mg/L	49	0
Thallium	0.002 mg/L	49	0

Table 6. Analysis of Secondary Drinking Water Standards (SDWS).

Parameter	SDWS	# of Samples	# of Exceedences
Aluminum	0.2 mg/L	49	7 *
Chloride	250 mg/L	49	0
Copper	1.0 mg/L	49	0
Fluoride	2.0 mg/L	74	55
Iron	0.3 mg/L	74	22
Manganese	0.05 mg/L	74	10
Silver	0.1 mg/L	49	0
Sulfate	250 mg/L	49	0
Zinc	5.0 mg/L	49	0
Color	15 CU	74	56
Odor	3 TON	74	57
pH	6.5 - 8.5	74	0
Total Dissolved Solids	500 mg/L	49	13
Foaming Agents	0.5 mg/L	49	1

* - These exceedences were found in the cooling pond only.

Table 7. Analysis of synthetic organic compounds (SOC).

Parameter	SOC	# of Samples	# of Exceedences
2,3,7,8-TCDD (Dioxin) (ug/L)	3 * 10-8 mg/L	16	0
2,4-D (ug/l)	0.07 mg/l	16	0
2,4,5-TP (Silvex)(ug/l)	0.05 mg/l	16	0
Alachor (ug/l)	0.002 mg/l	16	0
Atrazine (ug/l)	0.003 mg/l	16	0
Benzo(a)pyrene (ug/l)	0.0002 mg/l	16	0
Carbofuran (ug/L)	0.04 mg/l	16	0
Chlorodane (ug/l)	0.002 mg/l	16	0
Dalapon (ug/l)	0.2 mg/l	16	0
Di(2-ethylhexyl)adipate (ug/l)	0.4 mg/l	16	0
Di(2-ethylhexyl)pthalate (ug/l)	0.006 mg/l	16	0
Dibromochloropropane (ug/l)	0.0002 mg/l	16	0
Dinoseb (ug/l)	0.007 mg/l	16	0
Diquat (ug/l)	0.02 mg/l	16	0
Endothall (ug/l)	0.1 mg/l	16	0
Endrin (ug/l)	0.002 mg/l	16	0
Ethylene dibromide (ug/l)	0.00002 mg/l	16	0
Glyphosate (ug/l)	0.7 mg/l	16	0
Heptachlor (ug/l)	0.0004 mg/l	16	0
Heptachlor Epoxide (ug/l)	0.002 mg/l	16	0
Hexachlorobenzene (ug/l)	0.001 mg/l	16	0
Hexachlorocyclopentadiene (ug/l)	0.05 mg/l	16	0
gamma-BHC (Lindane) (ug/l)	0.0002 mg/l	16	0
Methoxychlor (ug/l)	0.04 mg/l	16	0
Oxamyl (Vydate) (ug/l)	0.2 mg/l	16	0
Pentachlorophenol (ug/l)	0.001 mg/l	16	0
Picloram (ug/l)	0.5 mg/l	16	0
Polychlorinated byphenal (PCB) (ug/l)	0.0005 mg/l	16	0
Simazine (ug/l)	0.004 mg/l	16	0
Toxaphene (ug/l)	0.003 mg/l	16	0

Table 8. Analysis of Volatile Organic Compounds (VOC) and Radionuclides

Parameter	VOC	# of Samples	# of Exceedences
1,1-Dichloroethene	0.007 mg/L	16	0
1,1,1-Trichloroethane	0.2 mg/L	16	0
1,1,2-Trichloroethane	0.005 mg/L	16	0
1,2-Dichloroethane	0.003 mg/L	16	0
1,2-Dichloropropane	0.005 mg/L	16	0
1,2,4-Trichlorobenzene	0.07 mg/L	16	0
Benzene	0.001 mg/L	16	0
Carbon Tetrachloride	0.003 mg/L	16	0
cis-1,2-Dichloroethene	0.07 mg/L	16	0
Dichloromethane	0.005 mg/L	16	0
Ethylbenzene	0.7 mg/L	16	0
Monochlorobenzene	0.1 mg/L	16	0
o-Dichlorobenzene	0.6 mg/L	16	0
p-Dichlorobenzene	0.075 mg/L	16	0
Styrene	0.1 mg/L	16	0
Tetrachloroethene	0.003 mg/L	16	0
Toluene	1 mg/L	16	0
trans-1,2-Dichloroethylene	0.1 mg/L	16	0
Trichloroethylene	0.003 mg/L	16	0
Vinyl Chloride	0.001 mg/L	16	0
Xylenes	10 mg/L	16	0
m/p-xylenes	0.5 µg/L (DL)	16	0
o-xylene	0.5 µg/L (DL)	16	0

Radionuclide Contaminants			
Parameter	DWS	# of Samples	# of Exceedences
Gross Alpha	15 pCi/L	16	0
Radium 226	5 pCi/L	16	0
Radium 228	5 pCi/L	16	0

samples should detect total coliform in one month (US EPA Drinking Water Standards). Therefore, in this study, coliform bacteria must be < 1 count/100mL. The highest fecal and total coliform levels were detected in those samples collected at the end of the wetland flow path (WP). Levels were 30-730 count/100mL fecal and 1000-7000 count/100mL for total coliform bacteria. This maybe caused by feces from fish, reptiles, amphibians, insects, and birds which were abundant in the wetland. In contrast, fecal and total coliform at the FBS/FBN were generally < 2 count/100mL (except one sample of 29 count/100mL) and <100 count/100mL, respectively. These results clearly demonstrate the crucial role of the biofilm "schmutzdecke". It formed on the tailing sand surface providing mechanical filtration, degradation of soluble organics and elimination of pathogens, color and odor contaminants (Muhammad et al., 1997; Huisman and Wood, 1974).

2.3.6. Isotopic composition

The monitoring of δD and δ18O was used (1) to evaluate possible groundwater input into 6 monitor wells installed along the wetland flow path; (2) to differentiate potential sources of water in the wetland, and (3) to understand the possible factors controlling the fluid mixing in the wetland and monitor wells. The values of δ18O and δD were used in combination with Na data. This approach proved necessary due to the complex hydrogeological framework at the site, which resulted in six possible sources of water to the wetland: (1) groundwater, (2) municipal effluent, (3) industrial waste water, (4) seepage from a water body to the north, (5) seepage from a water body to the south and (6) surface runoff/rain.

2.3.6.1. Wetland water

During the 18-month period of the study, the δD and $\delta^{18}O$ composition of wastewater in the cooling pond (CP) was relatively constant and ranged from 20.2 to 29.0 ‰ and 4.4 to 6.0 ‰, respectively (Table 9, Appendix B). The isotopic composition of treated effluent (EF) discharging into the CP ranged from -8.3 to -9.2 ‰ for δD and -1.67 to -1.74 ‰ for $\delta^{18}O$. These values were close to the Upper Floridan groundwater line reported by Swancar and Hutchinson (1995). In contrast to the CP, the isotopic composition of wetland water collected from a pump (WP) at the end of the flow path showed seasonal variations. The δD and $\delta^{18}O$ values at the WP ranged from -10.6 to 29.3 ‰ and -2.31 to 5.62 ‰, respectively. The δD and $\delta^{18}O$ of the wetland water from surface (WS) were very similar to the WP and ranged from -10.7 to 28.5 ‰ and -2.31 to 5.69 ‰, respectively. The most depleted isotope values at the WP corresponded to hurricanes Ernesto and Alberto, in June and September 2006.

Figure 17 shows a high correlation between δD and $\delta^{18}O$ at the WP with the trendline equation of $\delta D = 5.1\ \delta^{18}O - 0.6$ ($R^2 = 0.98$). Kendall and Coplen (2001) reported that the local meteoric water line for Florida was δD = 5.4 δ18O + 1.3 (R^2 = 0.96). The regression equation for the Upper Floridan groundwater line published by Swancar and Hutchinson (1995) was $\delta D = 5.4\ \delta^{18}O + 1.5$ ($R^2 = 0.97$). The distribution of δD and $\delta^{18}O$ for the WP is very similar to the reported water lines but slightly lower in slope and intercept. The lower slope and intercept was caused by the pumping of the CP water into the wetland due to evaporative enrichment. The trendline for CP is $\delta D = 4.9\ \delta^{18}O - 0.97$ ($R^2 = 0.68$). As expected, the correlation between δD and $\delta^{18}O$ at the FBS and

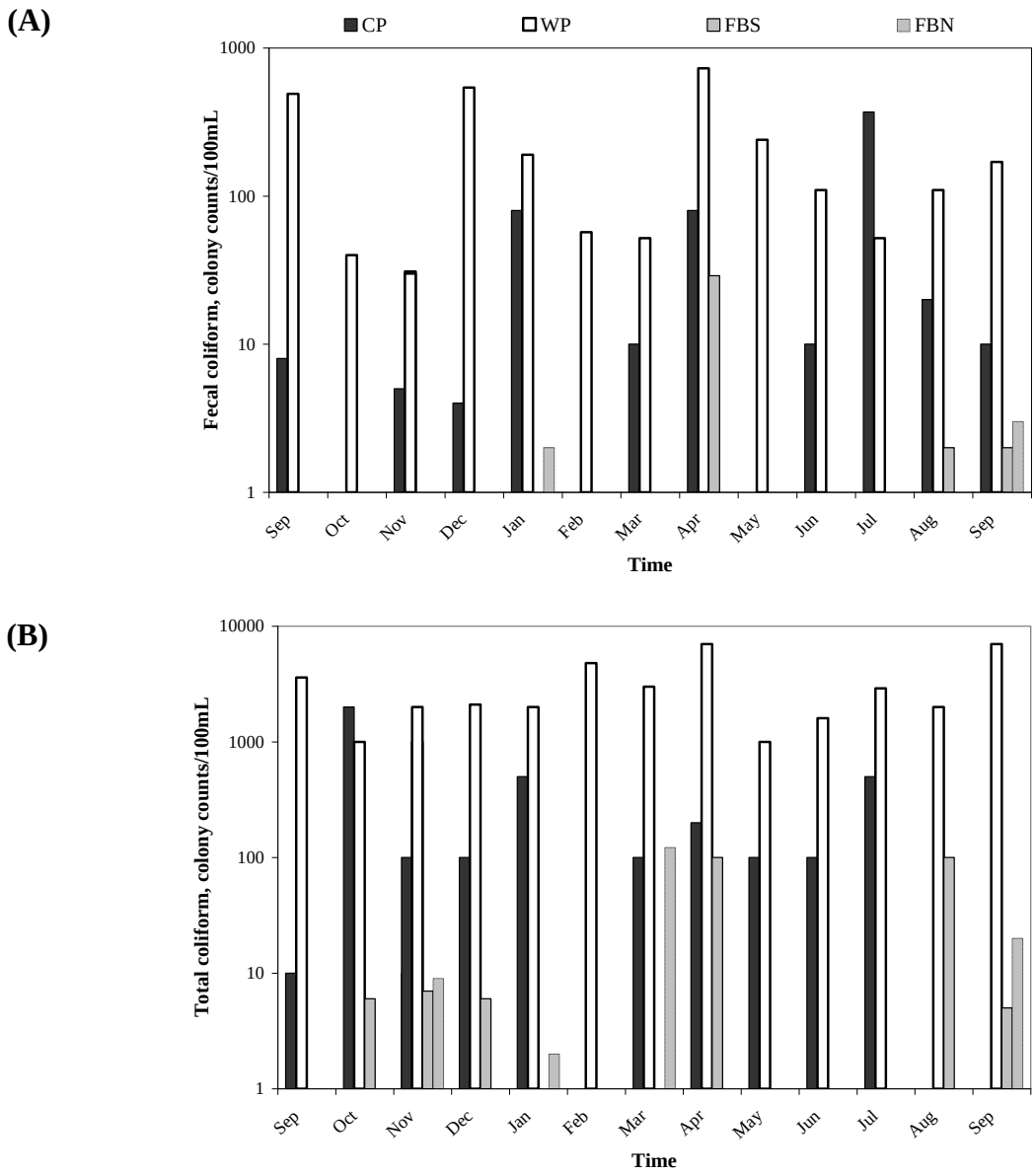

Figure 16. Fecal and total coliform bacteria detected at the CP, WP, FBS and at the FBN.

FBS/FBN had the lowest fecal and total coliform confirming the crucial role of the

biofilm “schmutzdecke”.

Note: CP- cooling pond pump; WP – wetland pump; FBS and FBN – filter basin south and north pumps; Concentrations displayed in logarithmic scale; Time ranged from Sept., 2006 to Sept., 2007.

FBN was compatible with the WP. The trendline equations for the FBS and FBN were $\delta D = 4.95\ \delta^{18}O - 0.04$ ($R^2 = 0.97$) and $\delta D = 4.89\ \delta^{18}O - 0.23$ ($R^2 = 0.96$), respectively (Figure 18). Generally, the offset to the right from the local meteoric water line reflects the influence of evaporation (Gat, 1996; Craig and Gordon, 1965). Evaporation from an open surface reservoir causes nonequilibrium enrichment of $\delta^{18}O$ in the remaining water due to the differences in gaseous diffusion rates for $\delta^{18}O$ and δD, particularly under low humidity conditions (Kendall and McDonnell, 2006; Craig and Gordon, 1965). As a result the slope of the meteoric water line drops below 8. In addition to humidity, the slope of evaporation loss depends on a number of environmental factors such as solar radiation, temperature and wind speed (e.g., Clark and Fritz, 1997). The average relative humidity of the study area from April 2006 to October 2007 was 74.6 % (FAWN). At this the slope of a local meteoric water line should be close to 5 (Kendall and Coplen, 2001).

2.3.6.2. Monitor wells, SA-8 and N-15

To evaluate possible seepage of water from N-15 and SA-8 into the wetland, 6 monitor wells (MWs) installed along the flow path were analyzed (Figure 2). The δD and $\delta^{18}O$ in MW-1, MW-2 and MW-3 ranged from -24.9 to 24.2 ‰ and from -4.19 to 4.95 ‰, respectively (Figure 19, Tables 9, Appendix B). For MW-1, the δD and $\delta^{18}O$ values had a highly defined peak in June - August 2007 as a result of pumping operation. The CP pump was turned off in April and May for maintenance purposes and restarted in June, which caused the change of isotopic signature in MW-1 due to its proximity to the CP. The δD and $\delta^{18}O$ values in MW-4, MW-5 and MW-6 showed less variation and ranged from -27.8 to -1.4 ‰ and -4.63 to -0.53 ‰, respectively, and plotted closely to -

Table 9. Minimum, maximum, mean, median and standard deviation values of $\delta^{18}O$ and δD in all sampling locations.

	$\delta^{18}O$					δD					
Location	Min	Max	Mean	Med	STD	Min	Max	Mean	Med	STD	N
CP	4.42	5.98	5.18	5.02	0.46	20.2	29.0	24.4	24.1	2.7	18
EF	-1.74	-1.67	-1.71	-1.73	0.04	-9.2	-8.3	-8.8	-8.7	0.5	3
WP	-2.31	5.62	2.47	2.54	2.16	-10.6	29.3	12.0	12.4	11.2	19
WS	-2.31	5.69	2.59	3.10	2.45	-10.7	28.5	13.0	15.4	11.9	14
FBN	-1.09	4.93	2.90	3.40	1.67	-4.5	23.8	14.0	14.3	8.3	12
FBS	-1.40	5.41	2.72	3.05	2.03	-6.7	28.8	13.4	13.1	10.2	14
MW-1	-4.18	4.95	-2.51	-2.93	2.08	-24.9	24.2	-12.9	-14.7	11.0	19
MW-2	-2.93	1.03	-1.85	-2.27	1.07	-15.6	4.6	-9.6	-10.8	5.5	20
MW-3	-3.66	4.15	-0.50	-0.93	2.39	-19.2	20.6	-3.0	-3.1	12.3	17
MW-6	-4.15	-2.51	-3.12	-3.13	0.31	-23.8	-12.5	-16.1	-15.6	2.5	18
MW-5	-4.12	-2.19	-3.01	-2.90	0.57	-23.8	-2.5	-14.5	-15.8	5.4	17
MW-4	-4.63	-0.53	-2.82	-2.76	1.00	-27.8	-1.4	-14.0	-14.2	7.2	18
SA-8	1.97	3.94	2.92	3.19	0.71	10.4	19.9	14.6	14.3	3.4	11
N-15	0.03	2.84	1.51	1.46	0.76	-1.9	12.9	7.3	6.9	4.0	18

Note: CP- cooling pond; EF – effluent; WP – wetland water from pump; WS – wetland water from surface; MW-1 to MW-6 – monitor wells arranged according to the wetland flow path; SA-8 and N-15 - water bodies to the north and south of the wetland; FBS and FBN – filter basin south and north pumping stations, respectively.

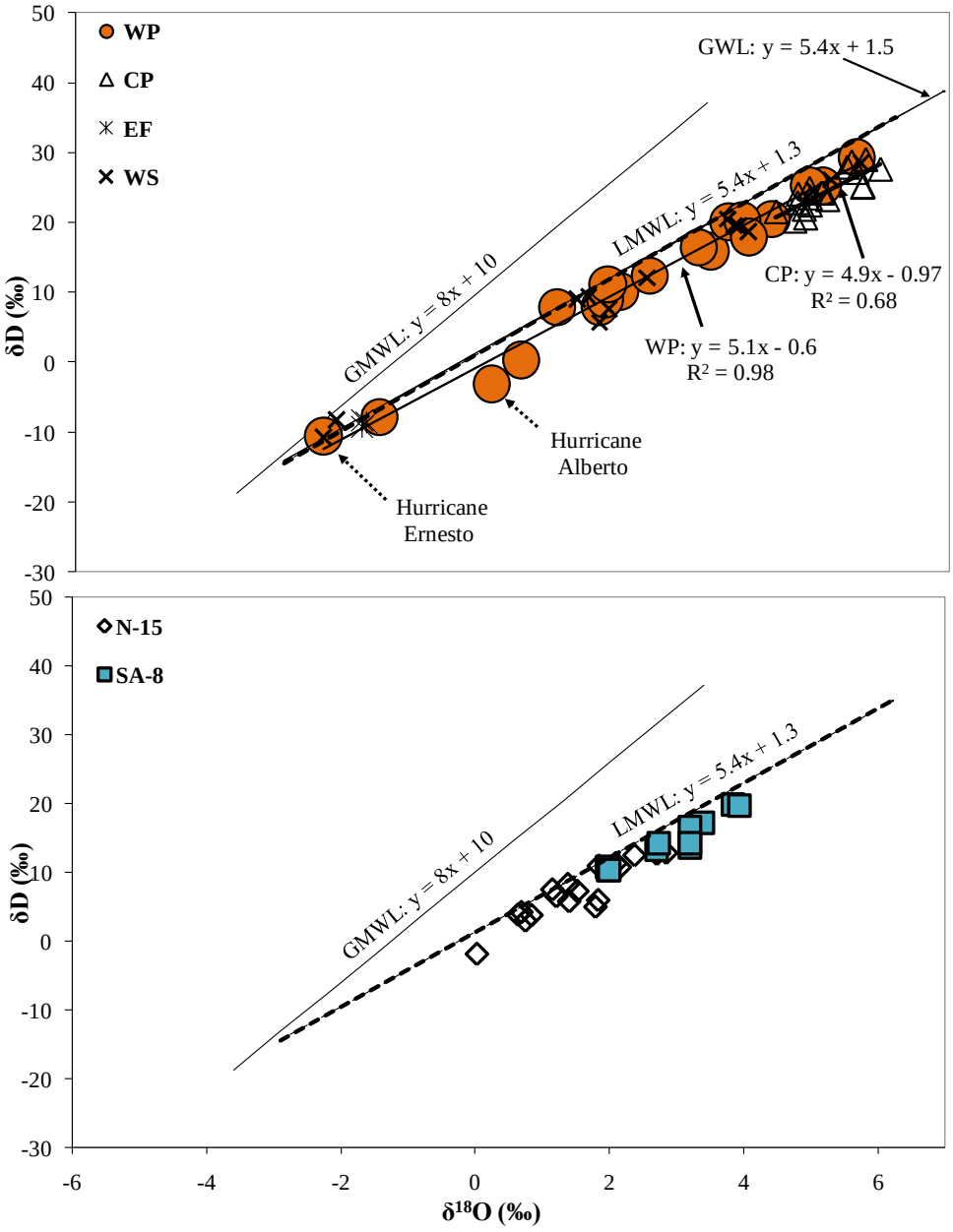

Figure 17. δD vs δ18O for the wetland (A) and, SA-8 and N-15 (B).

Note: WP – wetland water from pump; WS – wetland water from surface; CP - cooling pond; EF – effluent; N-15 and SA-8 - water bodies to the north and south of the wetland; Local meteoric water line (LMWL) is from Kendall and Coplen (2001). Global meteoric water line (GMWL) is from Craig (1961). Upper Floridan Aquifer groundwater line (GWL) is from Swancar and Hutchinson (1995).

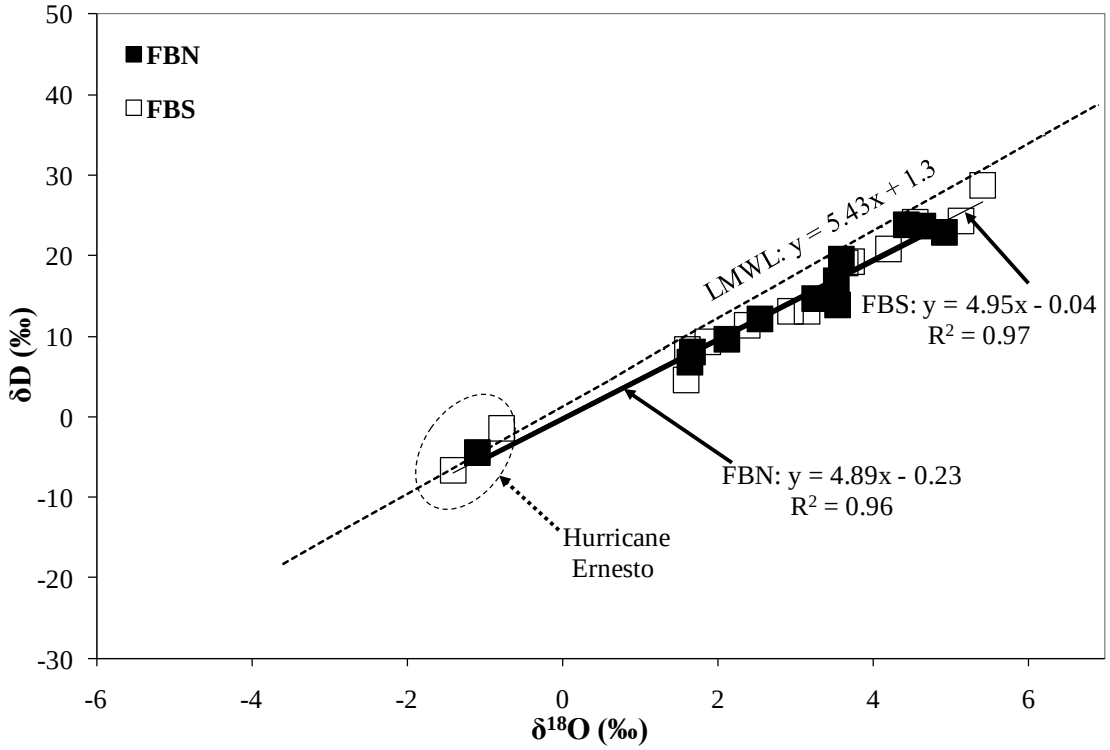

Figure 18. δD vs δ18O for the filter basin north and south pumps (FBN and FBS).

Note: Local meteoric water line (LMWL) is from Kendall and Coplen (2001).

18.0 ‰ for δD and -3.70 ‰ for reported $\delta^{18}O$ in the Intermediate Aquifer (Sacks and Tihansky, 1996) (Figure 19A). The δD and $\delta^{18}O$ values in N-15 varied between -1.9 to 12.9 ‰ and 0.03 to 2.84 ‰, respectively. The δD and $\delta^{18}O$ in SA-8 were from 10.4 to 19.9 ‰ and 1.97 to 3.94 ‰, respectively. Generally, of all wells MW-3 had the most distinctive isotopic composition compared to the groundwater value and was probably more influenced by the seepage from N-15 or WP (Figure 19).

2.4. Discussion

During the 18-month period of monitoring, the constructed wetland (CW) demonstrated promising treatment efficiency for the remediation of wastewater. The study showed a significant wetland cooling effect on water temperature with up to a 10 °C difference between the input - cooling pond (CP) and output – wetland water from pump (WP) (Figure 15). Seasonal fluctuations of the wetland water temperature could influence the processes of microbial transformation (Kadlec, 1999). Kadlec (2006) studied the surface flow wetlands (Tres Rios, Arizona) for temperature and energy flows. The author reported that wetland water temperature had a tendency to approach the mean air temperature depending on humidity. In this study, temperature cycles for WP and air demonstrated comparable distribution with the correlation coefficient R^2 of 0.83 (Figure 15). Treatment surface flow CW can have one or two thermal regions depending on the water residence time (Kadlec, 2006). When the residence time is > 5 days, the wetland can be divided into 2 zones: accommodation and balance zones (Kadlec, 2006). In an accommodation region, the temperature and evapotranspiration profiles are initially steep due to adjustments to weather conditions. In a balance zone, temperature in the wetland

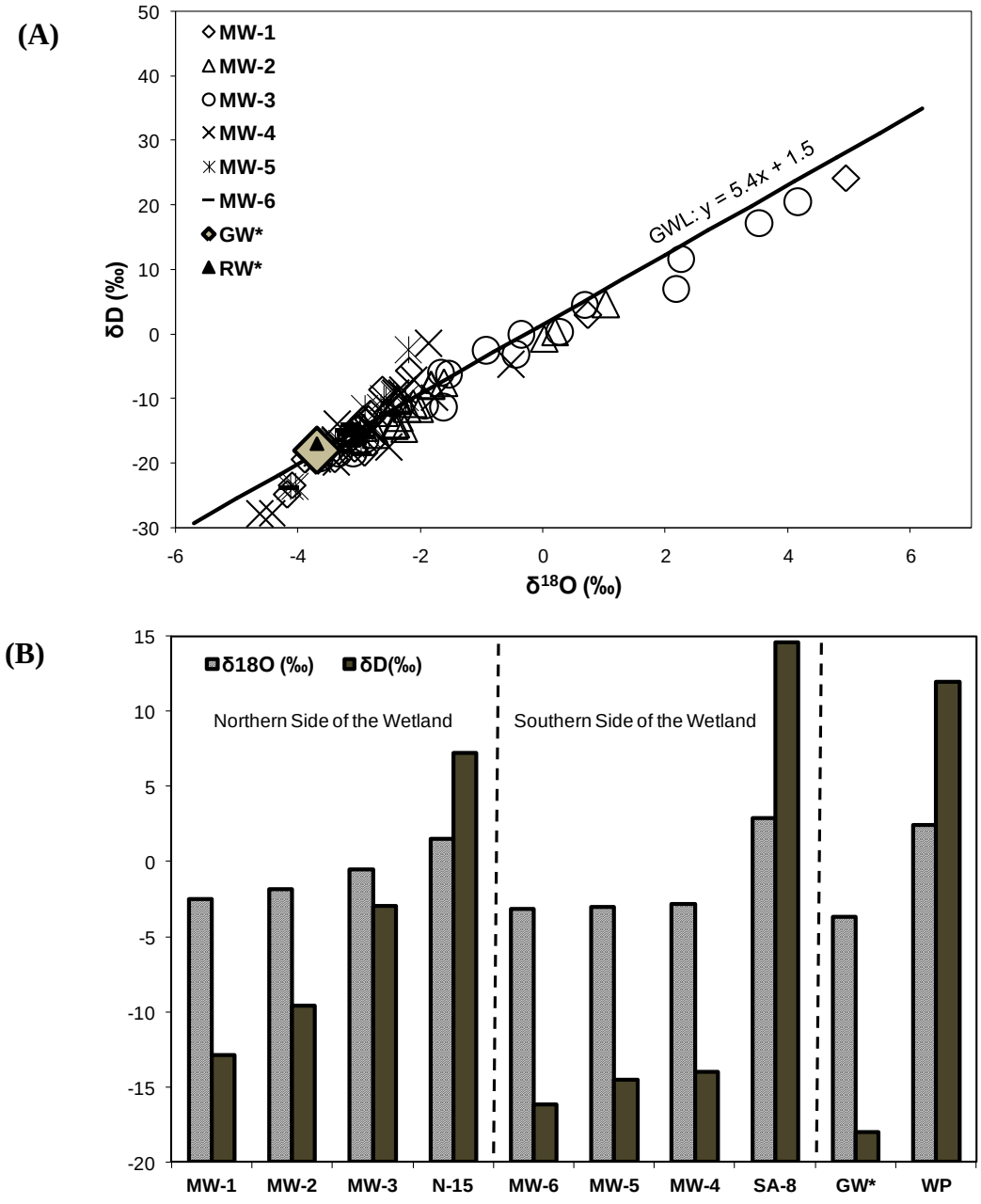

Figure 19. δD vs δ18O (A) and mean δD/δ18O histograms (B) for monitor wells.

Note: MW-1 to MW-6 – monitor wells arranged according to the wetland flow path, GW* - Floridan groundwater from the Intermediate Aquifer (well ROMP 45, Sacks and Tihansky, 1996), RW* - rain water (Kish et al., 2009); N-15 and SA-8 - water bodies to the north and south of the wetland; WP - wetland water from pump. Upper Floridan groundwater line (GWL) is from Swancar and Hutchinson (1995).

approaches to the balance level, i.e. adjusts to the existing meteorological conditions (Kadlec, 2006). This finding was very useful for evaluating temperature along the CW flow path. Generally, the water temperature was gradually reduced along the wetland and could be divided into 2 zones with the boundary line around 1300 m (Figure 14A). The cooling effect of the wetland could probably reduce evaporation losses.

Meteorological monitoring, conducted during the study, demonstrated the dominance of 3 tropical seasons: one dry and two rainy seasons (Figure 12). Therefore, it is very important to evaluate the performance of the treatment system in response to seasonal changes such as heavy rainfall and drought events. Generally, the behavior of most cations had a comparable pattern. During the dry season, the concentration of Na, Mg, K, Ca, and Sr in the wetland was close to the CP. In contrast, during the rainy season the concentration of these cations in the wetland was around 1.5 times less than in the CP. This behavior could be caused by dilution of the wetland water by rainfall. Elevated pH, DO, T, positive ORP of the wetland surface and low H_2S during the dry season were generally associated with algal blooms during spring time (Figure 14A). Sawyer and McCarthy (1978) reported that in shallow ponds during daylight algae use CO_2 for photosynthesis and release O_2 increasing the pH and DO levels as the carbonate-bicarbonate equilibrium is destabilized. During night time hours this process is generally reversed when algae and plants stop producing O_2 but start using the available oxygen.

In order to quantitatively establish the efficiency and the possible groundwater input into the wetland, the Na and Cl mass fluxes in the CP and WP were examined (Table 4, Figure 20). Both curves showed a comparable distribution as well as a significant change throughout the duration of the study. During the first rainy season

(April-October 2006), the mass fluxes of Na and Cl at the WP were around 60 % less than in the CP. These reduced mass fluxes were due to heavy rainfall during two hurricanes, which added low conductivity water directly and triggered enhanced groundwater input into the wetland (Criss and Winston, 2003). During the dry season (November 2006 – April 2007), the percentage removal of Na and Cl from the wetland was close to 0 % indicating the normal operation of the wetland treatment system, i.e. the balance between input and output. This allowed to estimate the residence time of water in the wetland to about 120 days. During the second rainy season (April – October 2007), the percent removal of Na and Cl from the wetland varied significantly from -52 to 4 %. At the end of April, the CP pump was turned off and the wetland surface was lowered approximately 1 m for maintenance purposes (Figure 20). From May 2007, the wetland treatment system became again operational. Therefore, during this time a considerable mass flux of Na and Cl accumulated in the wetland could be caused by mechanical issues as well as high evaporation. As soon as the maintenance problems were fixed, the percentage removal of Na and Cl from the wetland was close to 0 %.

Figure 21 was plotted to assess the variation of a weight concentration SO_4/Cl in the CP and WP as a function of time. The concentration of SO_4 changed through microbiological reduction which is greatly influenced by seasonal temperature (Urban et al., 1994). High temperatures during summer and fall accelerate microbial activity in decomposing organic material, thus producing higher levels of H_2S (Armannsson, 1999). The plot demonstrated a variability of SO_4/Cl ratio in the wetland throughout the period the study with the lower levels during the rainy seasons 2006 and 2007 (< 0.15 and < 0.3, respectively) and the highest (up to 0.6) - during the dry season 2006 (Figure 21). The

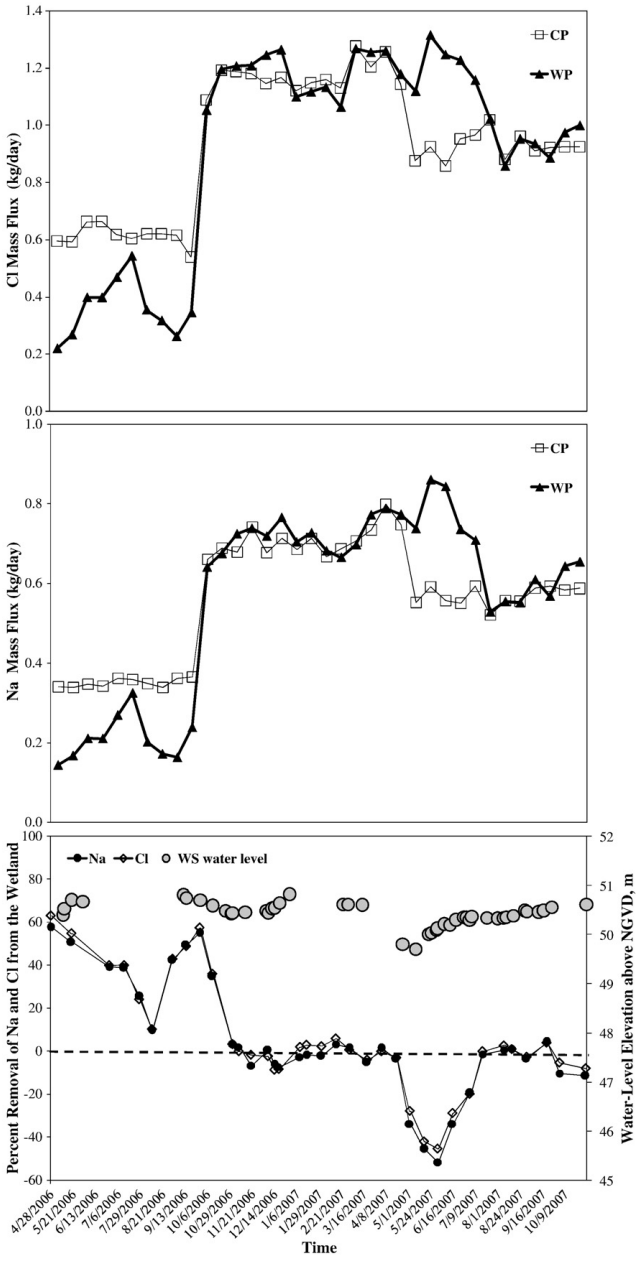

Figure 20. Mass fluxes of Na and Cl in the CP and WP, and the calculated percent removal of Na and Cl from the wetland.

Note: CP- cooling pond pump; WP – wetland pump; WS water level – wetland surface water level; NGVD – National Geodetic Vertical Datum; Calculation included the rainfall dilution factor over the site area; Positive values – wetland removes mass and negative - wetland contributes mass to the water that flows through it.

monitoring of the treatment system frequently showed higher concentrations of total Fe at the filter basin south (FBS) and north (FBN) pumps compared to the WP (Figure 22). During the dry season the average Fe level at the FBS was 0.34 mg/L, while at the WP and FBN it was 0.26 and 0.14 mg/L, respectively. In contrast, during the rainy seasons of 2006 and 2007, the average Fe at the FBS was up to 1.20 mg/L, while at the WP and FBN it was 0.20 and 0.42 mg/L, respectively. The distribution of Fe concentration at the WP, FBS and FBN with time demonstrated lower Fe at the WP and FBN compared to the FBS. At the same time, concentrations of Fe at the WP, which was being applied to the surface of the filter basin (FB), remained relatively constant, while Fe at the FBS fluctuated quite significantly. Moreover, substantially higher Fe levels at the FBS were detected particularly during the rainy seasons potentially indicating an outside source of water to the FB containing high Fe. This is possible due to the migration of the surficial groundwater into the FB from the surrounding area. Previous studies reported that the concentration of Fe in the surficial groundwater of the study area could be about 12 mg/L (ROMP 57A; Sacks and Tihansky, 1996). Field observations confirmed that the levels of the surficial groundwater outside the FB increased during heavy rainfall therefore increasing the hydraulic gradient around the FB. This fact was supported by visual observation of iron mud build-up clogging flow meters and pipes of the FB, especially at the FBS.

2.4.1. Behavior of arsenic

Arsenic (As) is an element of great interest in Florida principally to aquifer storage and recovery (ASR) (Arthur et al., 2005). Studies showed that geogenic As was

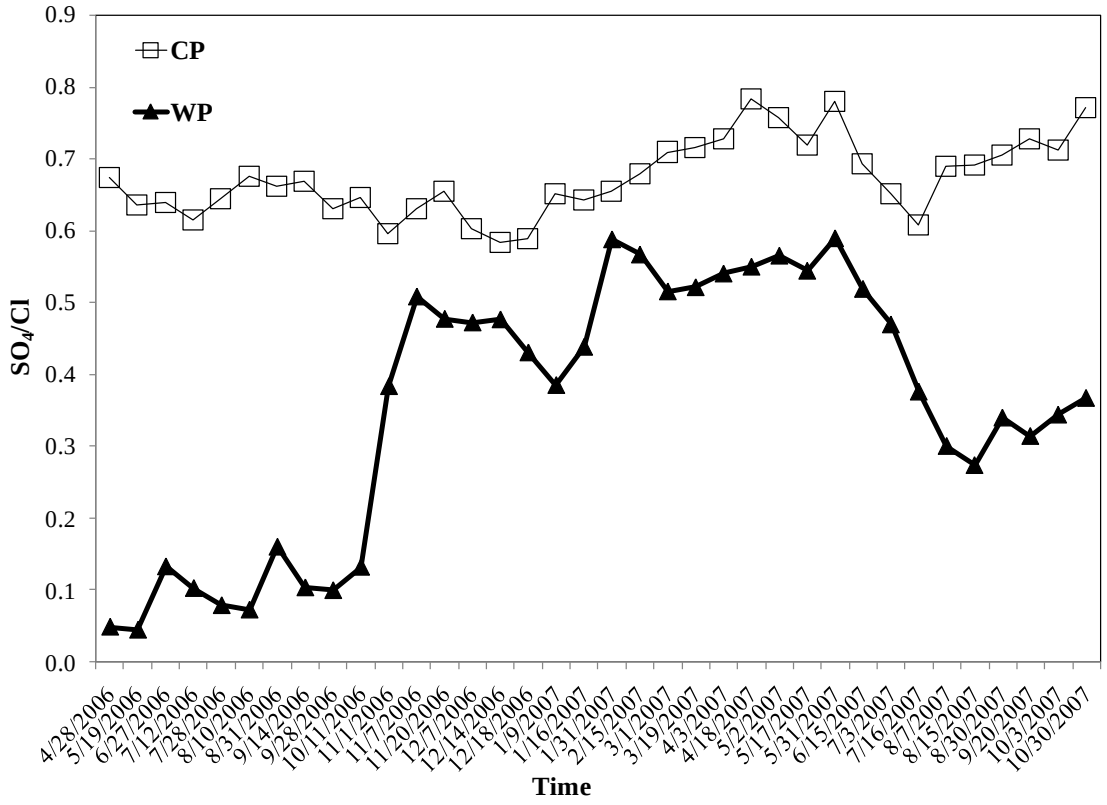

Figure 21. Variation of SO4/Cl in the cooling pond pump (CP) and the wetland pump (WP) as a function of time. Note: Values are in mg/L.

found in the carbonate Floridan Aquifer mostly associated with pyrite (Lazareva and Pichler, 2007; Price and Pichler, 2006). Pyrite is thought to dissolve and release As during ASR due to the injection of ozone-treated oxidizing surface waters into reducing native groundwater. As a result, concentrations of As in recovered water were up to 130 µg/L (Arthur et al., 2005), far above the 10 µg/L drinking water standard (DWS) for As (EPA). The type of constructed wetland/filter basin treatment system studied here could become a new alternative to treat wastewater in Florida and beyond. Water treatment processes in the wetland may consist of metal accumulation into vegetation, adsorption on soil particles, precipitation or co-precipitation caused by microbial activity (Stottmeister et al., 2006; Jacob and Otte, 2003; Stoltz and Greger, 2002; Dushenko et al., 1995). Following treatment through a CW, the water would be in reducing conditions with high sulfide and low oxygen levels which are favorable for the stability of pyrite (e.g., Jones and Pichler, 2007). Water of this composition would be physically and chemically similar to native groundwater and should not cause the dissolution of pyrite and leaching of As during ASR.

The pH, DO and temperature gradient from the CP to the wetland could be important for the behaviour of heavy metals such the redox-sensitive element As (Stottmeister et al., 2006). Concentrations of As in the CP (up to 5 µg/L) were considerably reduced at the WP and the FBS/FBN (< 2 µg/L) (Table 1). The mass loading of As in the CP and the wetland was calculated to understand the removal effectiveness of the wetland over time (Figure 23). The calculation was done with the rainfall dilution factor over the wetland study area. Generally, As in the wetland was reduced to 40-95 % of the original except on 07/03/08 it was 2 times higher than in the

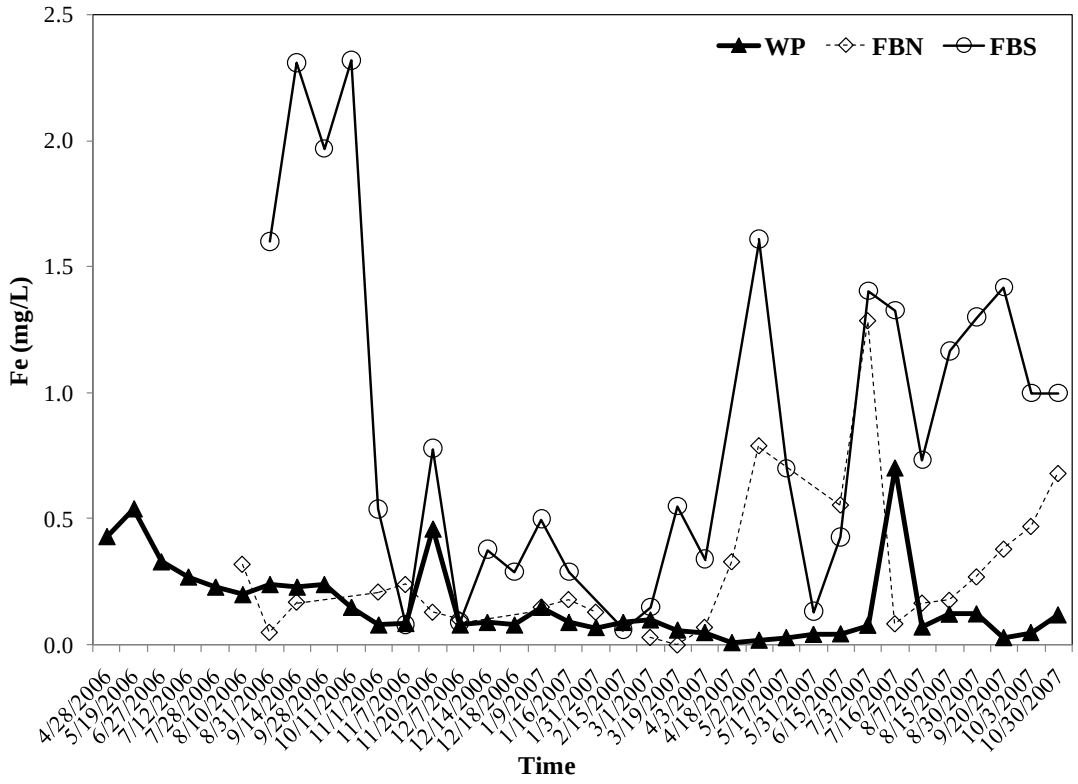

Figure 22. Distribution of Fe at the WP, FBS and FBN with time

Note: WP – wetland pump; FBS and FBN – filter basin south and north pumps.

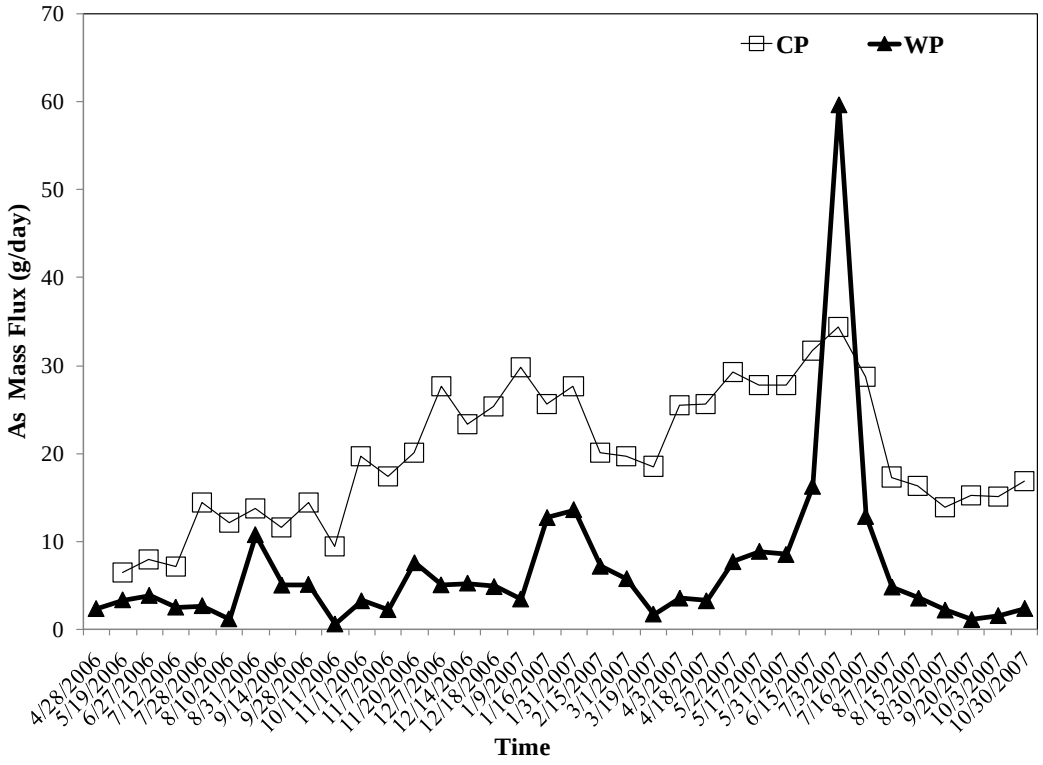

Figure 23. Mass fluxes of As in the CP and WP.

Note: CP – cooling pond pump; WP – wetland pump; Calculation included the rainfall dilution factor over the site area.

CP, which could be due to As-containing herbicides and insecticides used at the Hines Energy Complex. Seasonal variations of As in the treatment system showed lower concentrations during summer and fall and higher during winter and early spring. In the summer - fall seasons, when plants and algae grow they uptake and immobilize nutrients such as phosphorous and nitrogen into their biomass. Because of the high affinity between arsenate [As (V)] and phosphate, plants easily incorporate As (V) into their cells (Catarecha et al., 2007). In contrast, the reduced photosynthesis and decay of plants during winter - early spring facilitates the decrease of DO in water and releases nutrients back to the water column such as P and As. During certain seasons, plants and other wetland species could convert inorganic nutrients to organic compounds resulting in a net export of nutrients from the wetland (Devito and Dillon, 1993).

In addition to plant accumulation, the sandy clay – based sediment rich in organic material could be an important sink for As retention. Buddhawong et al. (2005) constructed a bench-scale experimental wetland in Grosskaya-Beuna area (Germany) to simulate the treatment of acid mine drainage. The authors reported that the highest efficiency of water treatment was achieved in the constructed wetland with the combined planted gravel/soil system. This type of wetland maintained the essential conditions (i.e., pH, redox, surface area) for As binding rather than those wetlands which were constructed exclusively using vegetation or soil matrix (Stottmeister et al., 2006). At the same time, As can be co-precipitated with iron oxides caused by root oxygen transport into rhizosphere. This transfer stimulates a significant metal buildup at the sediment-root boundary forming iron plaques on the plants roots (Colmer, 2003). In addition, elevated concentrations of HS^-/H_2S in the constructed wetland could develop favorable conditions

for coagulation or coprecipitation of As with S^{2-}. Langner et al. (1999) suggested that the formation of As(III)- S^{2-} phases could be an important sink of As (III) under reduced conditions such as wetlands. Also, the authors reported rapid reduction of As (V) and SO_4^{2-} to As (III) and S^{2-} using controlled wetland chambers. Additional contributions of As (V) and SO_4^{2-} could cause the formation of an amorphous As_2S_3 or Fe-AsS phases.

2.4.2. Evaluation of wetland performance using isotopic mass balance approach

The concentrations of Na in conjunction with $\delta^{18}O$ values were used in the isotope/chemical mass-balance approach to differentiate potential sources of water in the wetland and monitor wells and to understand factors controlling the flow of seepage water into the wetland. The concentration of Cl, which can also be used as a tracer, was not used due to the possible non-conservative behavior of Cl in wetland waters. Varner et al. (1999) reported that wetland can be a substantial source of methyl chloride (CH_3Cl) emission to the atmosphere. The flux of this compound is biologically mediated and greatly depends on temperature and vegetation density. Also, Cl can be incorporated into plant tissues (Alloway, 1992) or adsorbed onto soil or mineral surface through a non-specific adsorption (Katou et al., 1996; Altman, 1994).

2.4.2.1. Water composition in the wetland

The composition of wetland water can be described by a mixture of four possible sources such as: (1) Floridan groundwater from the Intermediate Aquifer System (ROMP 45 from Sacks and Tihansky, 1996), (2) cooling pond water, (3) water body to the north (N-15), and (4) to the south (SA-8) of the wetland (Figure 24). The groundwater and

rainwater sources were combined in one as "GW" because the local meteoric water line had a tendency to approach the Upper Floridan groundwater line (Figure 19 A) (Kish et al., 2009; Kendall and Coplen, 2001; Swancar and Hutchinson, 1995).

When these water sources are considered as end-members to the wetland water (i.e., have unique chemical composition compared to the mixture), it is possible to estimate mixing proportions between them waters using a mass-balance approach (e.g., Doctor et al., 2006; Christophersen and Hooper, 1992; Clark and Fritz, 1997). For this study, the following linear mass-balance equations were applied to describe the wetland water:

(A) Northern side of the wetland

This three-component mass-balance approach used two parameters ($\delta^{18}O$ and Na) and three equations to determine each variable. Assuming that the wetland water was a result of mixing groundwater (GW), cooling pond water (CP) and N- 15, the following equation could be used to assess the individual contributions from each source:

$$m_{WP} = m_{GW} + m_{CP} + m_{N-15} = 1 \quad (1)$$

Making a substitution of equation (1) into the isotopic mass-balance equation for $\delta^{18}O$,

$$m_{WP} * \delta^{18}O_{WP} = m_{GW} * \delta^{18}O_{GW} + m_{CP} * \delta^{18}O_{CP} + m_{N-15} * \delta^{18}O_{N-15} \quad (2)$$

and substitution of equation (1) into the chemical mass-balance equation for Na

$$m_{WP} * Na_{WP} = m_{GW} * Na_{GW} + m_{CP} * Na_{CP} + m_{N-15} * Na_{N-15} \quad (3)$$

followed by a combination of the equations 1, 2, and 3 to determine the proportion or mass of each water source in the wetland water:

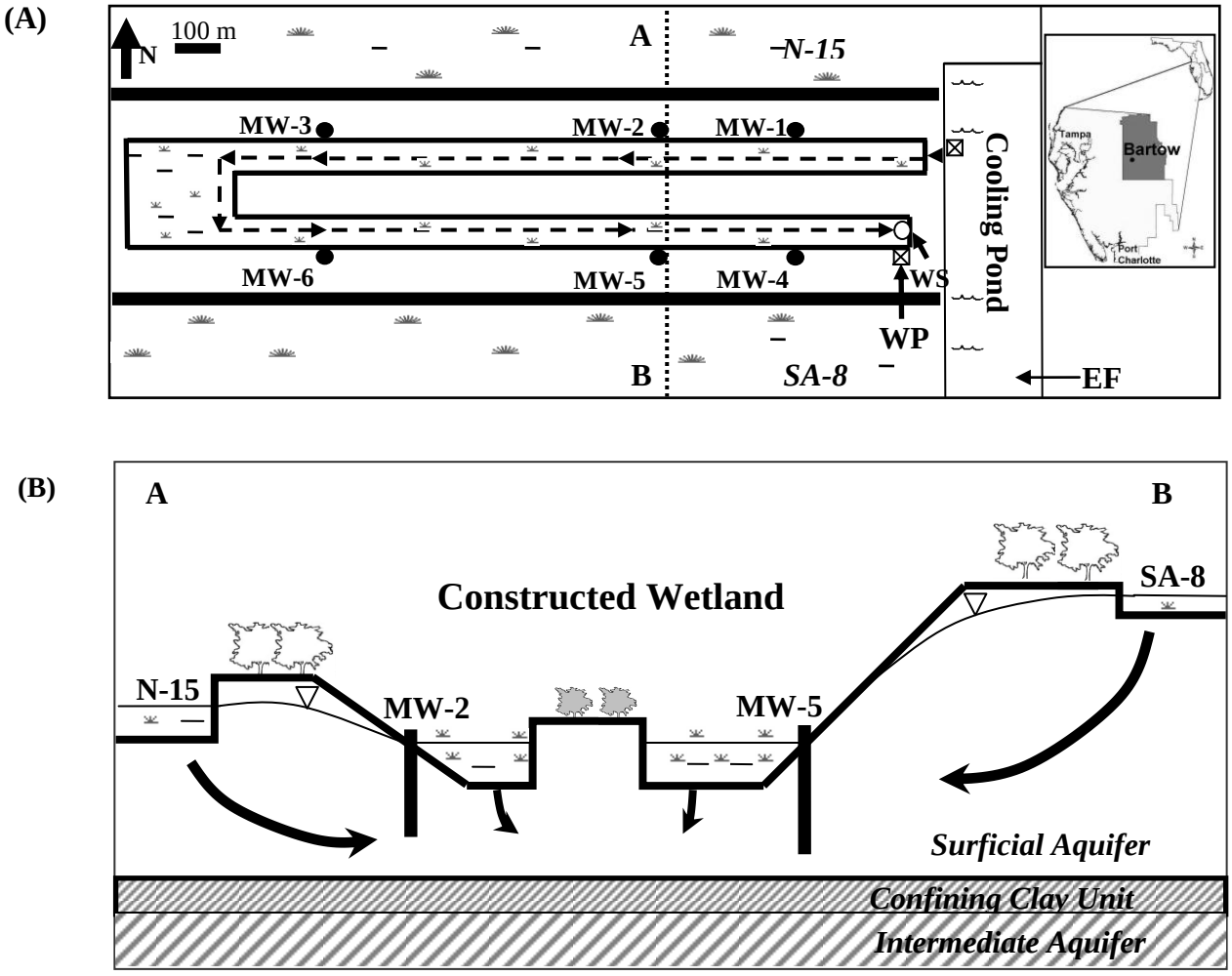

Figure 24. (A) Map of the study area including water transfer system from the cooling pond to the U-shaped constructed wetland; (B) Cross-section along transect 1 - 1′.

Note water sampling locations: MW-1 to MW-6 – monitor wells; WP – wetland water from pump; WS – wetland water from surface; N-15 and SA-8 - water bodies to the north and south of the wetland. Arrows represent possible groundwater flow paths.

$$m_{CP} = \frac{Na_{N-15} * (\delta^{18}O_{WP} - \delta^{18}O_{GW}) + Na_{GW} * (\delta^{18}O_{N-15} - \delta^{18}O_{WP}) + Na_{WP} * (\delta^{18}O_{GW} - \delta^{18}O_{N-15})}{Na_{N-15} * (\delta^{18}O_{CP} - \delta^{18}O_{GW}) + Na_{GW} * (\delta^{18}O_{N-15} - \delta^{18}O_{CP}) + Na_{CP} * (\delta^{18}O_{GW} - \delta^{18}O_{N-15})}$$

$$m_{N-15} = \frac{\delta^{18}O_{WP} - \delta^{18}O_{GW} + (\delta^{18}O_{GW} * m_{CP}) - (m_{CP} * \delta^{18}O_{CP})}{\delta^{18}O_{N-15} - \delta^{18}O_{GW}}$$

$$m_{GW} = 1 - m_{WP} - m_{N-15}.$$

(A) <u>Southern side of the wetland</u>

The mass-balance equations for the southern side of the wetland were analogous to the equations above with the substitution of N-15 for SA-8:

$$m_{WP} = m_{GW} + m_{CP} + m_{SA-8} = 1$$

$$m_{WP} * \delta^{18}O_{WP} = m_{GW} * \delta^{18}O_{GW} + m_{CP} * \delta^{18}O_{CP} + m_{SA-8} * \delta^{18}O_{SA-8}$$

$$m_{WP} * Na_{WP} = m_{GW} * Na_{GW} + m_{CP} * Na_{CP} + m_{SA-8} * Na_{SA-8}$$

$$m_{CP} = \frac{Na_{SA-8} * (\delta^{18}O_{WP} - \delta^{18}O_{GW}) + Na_{GW} * (\delta^{18}O_{SA-8} - \delta^{18}O_{WP}) + Na_{WP} * (\delta^{18}O_{GW} - \delta^{18}O_{SA-8})}{Na_{SA-8} * (\delta^{18}O_{CP} - \delta^{18}O_{GW}) + Na_{GW} * (\delta^{18}O_{SA-8} - \delta^{18}O_{CP}) + Na_{CP} * (\delta^{18}O_{GW} - \delta^{18}O_{SA-8})}$$

$$m_{N-15} = \frac{\delta^{18}O_{WP} - \delta^{18}O_{GW} + (\delta^{18}O_{GW} * m_{CP}) - (m_{CP} * \delta^{18}O_{CP})}{\delta^{18}O_{SA-8} - \delta^{18}O_{GW}}$$

$$m_{GW} = 1 - m_{WP} - m_{SA-8}$$

Subscripts for the m_{CPn}, m_{CPs}, m_{GWn}, m_{GWs}, m_{N-15s}, and m_{SA-8n} indicate the mass or percentage of each end-member in the wetland water calculated for the northern (*n*) and southern (*s*) sides. The wetland mass-balance was calculated using average values of $\delta^{18}O$ and Na from the CP, N-15 and SA-8.

Evaluation of the final percentage of four water sources (GW, CP, N-15, and SA-8) present in the wetland was calculated as an average value of waters from the northern and southern sides and was based on the following (Figure 25):

$$V_{CPn} = V_{CPs} = 1L$$
$$V_{CPn} * m_{CPn} + V_{CPs} * m_{CPs} = V_{CP} * m_{CP} = (V_{CPn} + V_{CPs}) * m_{CP}$$
$$m_{CP} = \frac{V_{CPn} * m_{CPn} + V_{CPs} * m_{CPs}}{(V_{CPn} + V_{CPs})}$$

Therefore, $m_{CP} = \frac{m_{CPn} + m_{CPs}}{2}$;

Similarly to the equation above,

$$m_{GW} = \frac{m_{GWn} + m_{GWs}}{2};\ m_{N-15} = \frac{m_{N-15n} + 0}{2}, \text{ and } m_{SA-8} = \frac{0 + m_{SA-8s}}{2}$$

2.4.2.2. Water composition in monitor wells

Similarly to the wetland water described above, the water composition in the monitor wells (MWs) was a mixture of three possible sources (Figures 24, 26 Table 11):

MW-1, 2 and 3: (1) groundwater (GW), (2) wetland water (WP), and (3) N-15.

MW-4, 5 and 6: (1) groundwater (GW), (2) wetland water (WP), and (3) SA-8.

Based on these assumptions the following linear mass-balance equations were applied to evaluate the proportions of different waters present in the monitoring wells:

MW-1 to MW-3:

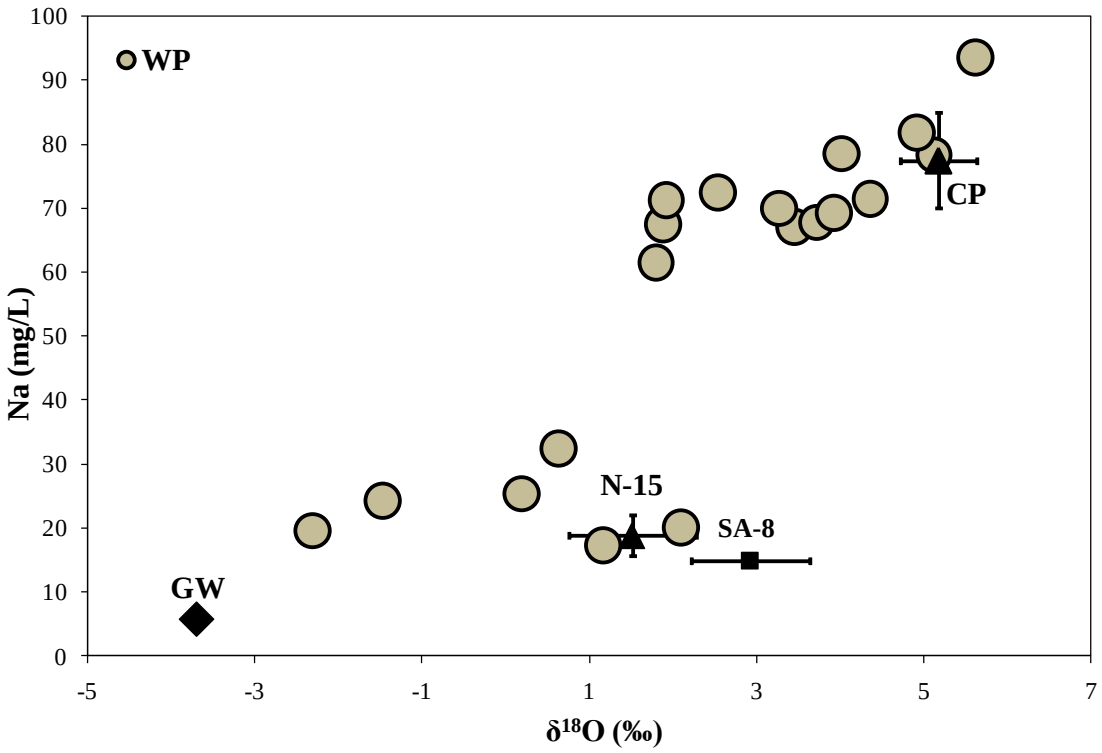

Figure 25. Four end-members for the WP used for the mass-balance approach.

Note: WP – wetland water from pump; CP – cooling pond; GW - Floridan groundwater from the Intermediate Aquifer System (well ROMP 45 from Sacks and Tihansky, 1996); N-15 and SA-8 - water bodies to the north and south of the wetland; Error bars – standard deviation.

Table 10. Chemical and isotopic data of waters used for the mass-balance approach.

Sample	Date	$\delta^{18}O$*	δD*	Na'	Sample	Date	$\delta^{18}O$*	δD*	Na'	Sample	Date	$\delta^{18}O$*	δD*	Na'
CP	4/28/06	4.42	21.5	67.9	N-15	4/28/2006	2.09	11.4	28.2	SA-8	12/14/2006	1.97	10.8	13.3
	5/19/06	4.75	24.0	67.7		5/19/2006	2.70	12.7	31.3		1/31/2007	1.98	10.4	13.7
	6/27/06	4.86	20.6	69.3		6/27/2006	1.79	5.0	25.7		3/1/2007	1.99	10.4	14.0
	7/28/06	5.11	24.2	72.3		7/28/2006	1.83	6.0	27.0		4/3/2007	2.70	13.3	14.5
	8/31/06	4.70	20.2	69.8		8/31/2006	0.03	-1.9	18.8		5/2/2007	3.39	17.3	15.3
	9/28/06	4.74	22.8	72.2		9/28/2006	0.75	3.0	22.0		5/31/2007	3.84	19.9	15.0
	11/7/06	no sample				11/7/2006	1.21	6.5	26.9		7/3/2007	3.94	19.7	15.6
	12/14/06	4.84	21.8	73.1		12/14/2006	1.52	7.3	27.7		8/7/2007	3.20	16.6	15.8
	1/9/07	4.93	23.5	74.0		1/31/2007	1.15	7.5	27.1		8/30/2007	3.19	13.6	15.3
	1/31/07	4.92	24.8	72.0		3/1/2007	1.38	8.3	28.7		10/3/2007	3.20	14.3	15.5
	3/1/07	4.93	22.5	76.3		4/3/2007	1.84	11.0	30.0		10/30/2007	2.74	14.3	15.6
	4/3/07	5.19	23.2	86.3		5/2/2007	2.37	12.5	29.6					
	5/2/07	5.48	27.9	81.6		5/31/2007	2.84	12.9	29.8					
	5/31/07	5.55	28.6	82.3		7/3/2007	2.15	10.8	28.6					
	7/3/07	5.76	29.0	87.7		8/7/2007	1.40	5.8	25.1					
	8/7/07	5.72	25.1	82.4		8/30/2007	0.84	3.8	24.1					
	8/30/07	5.98	27.6	87.1		10/3/2007	0.69	4.2	23.2					
	10/3/07	5.71	25.0	86.2		10/30/2007	0.64	3.9	24.7					
	10/30/07	5.63	27.1	86.9										

Sample	Date	$\delta^{18}O$*	δD*	Na'	*mCP*	*mGW*	*mN-15*	*mSA-8*
WP	4/28/06	1.17	7.8	17.3	4	18	47	31
	5/19/06	2.10	10.1	20.1	5	8	50	37
	6/27/06	0.19	-3.1	25.4	18	41	28	13
	7/28/06	0.63	0.3	32.4	30	41	20	9
	8/31/06	-1.47	-7.9	24.3	26	74	0	0
	9/28/06	-2.31	-10.6	19.6	22	78	0	0
	11/7/06	3.45	15.9	67.1	88	12	0	0
	12/14/06	4.36	20.5	71.4	92	8	0	0
	1/9/07	3.27	16.4	70.0	96	4	0	0
	1/31/07	3.72	20.1	67.8	88	12	0	0
	3/1/07	3.92	20.2	69.3	90	10	0	0
	4/3/07	5.12	25.2	78.3	100	0	0	0
	5/2/07	4.92	25.3	81.8	100	0	0	0
	5/31/07	5.62	29.3	93.5	100	0	0	0
	7/3/07	4.02	17.9	78.5	100	0	0	0
	8/7/07	1.80	8.0	61.5	87	13	0	0
	8/30/07	1.88	8.9	67.5	95	5	0	0
	10/3/07	1.92	11.1	71.3	99	1	0	0
	10/30/07	2.54	12.4	72.5	99	1	0	0

Note: CP- cooling pond; SA-8 and N-15 - water bodies to the north and south of the wetland; WP – wetland water from pump; GW - groundwater from the Intermediate Aquifer System (well ROMP 45 from Sacks and Tihansky, 1996); (*) - values in ‰; (´) – values in mg/L; *m* - mass or percentage of each end-member in the WP.

$$m_{Well} = 1$$

$$m_{Well} = m_{GW} + m_{WP} + m_{N-15}$$

$$1 = m_{GW} + m_{WP} + m_{N-15}$$

$$m_{well} * \delta^{18}O_{Well} = m_{GW} * \delta^{18}O_{GW} + m_{WP} * \delta^{18}O_{WP} + m_{N-15} * \delta^{18}O_{N-15}$$

$$m_{well} * Na_{Well} = m_{GW} * Na_{GW} + m_{WP} * Na_{WP} + m_{N-15} * Na_{N-15}$$

$$m_{WP} = \frac{Na_{N-15} * (\delta^{18}O_{Well} - \delta^{18}O_{GW}) + Na_{GW} * (\delta^{18}O_{N-15} - \delta^{18}O_{Well}) + Na_{Well} * (\delta^{18}O_{GW} - \delta^{18}O_{N-15})}{Na_{N-15} * (\delta^{18}O_{WP} - \delta^{18}O_{GW}) + Na_{GW} * (\delta^{18}O_{N-15} - \delta^{18}O_{WP}) + Na_{WP} * (\delta^{18}O_{GW} - \delta^{18}O_{N-15})}$$

$$m_{N-15} = \frac{\delta^{18}O_{Well} - \delta^{18}O_{GW} + (\delta^{18}O_{GW} * m_{WP}) - (m_{WP} * \delta^{18}O_{WP})}{\delta^{18}O_{N-15} - \delta^{18}O_{GW}}$$

$$m_{GW} = 1 - m_{WP} - m_{N-15}$$

MW-4 to MW-6:

The mass-balance equations for MW-4 to MW-6 were similar to the above with the substitution of N-15 for SA-8.

$$m_{Well} = 1$$

$$m_{Well} = m_{GW} + m_{WP} + m_{SA-8}$$

$$1 = m_{GW} + m_{WP} + m_{SA-8}$$

$$m_{well} * \delta^{18}O_{Well} = m_{GW} * \delta^{18}O_{GW} + m_{WP} * \delta^{18}O_{WP} + m_{SA-8} * \delta^{18}O_{SA-8}$$

$$m_{well} * Na_{Well} = m_{GW} * Na_{GW} + m_{WP} * Na_{WP} + m_{SA-8} * Na_{SA-8}$$

$$m_{WP} = \frac{Na_{SA-8} * (\delta^{18}O_{Well} - \delta^{18}O_{GW}) + Na_{GW} * (\delta^{18}O_{SA-8} - \delta^{18}O_{Well}) + Na_{Well} * (\delta^{18}O_{GW} - \delta^{18}O_{SA-8})}{Na_{SA-8} * (\delta^{18}O_{WP} - \delta^{18}O_{GW}) + Na_{GW} * (\delta^{18}O_{SA-8} - \delta^{18}O_{WP}) + Na_{WP} * (\delta^{18}O_{GW} - \delta^{18}O_{SA-8})}$$

$$m_{SA-8} = \frac{\delta^{18}O_{Well} - \delta^{18}O_{GW} + (\delta^{18}O_{GW} * m_{WP}) - (m_{WP} * \delta^{18}O_{WP})}{\delta^{18}O_{SA-8} - \delta^{18}O_{GW}}$$

$$m_{GW} = 1 - m_{WW} - m_{SA-8}$$

The final calculated composition of the wetland water from pumping station (WP) is shown in Figure 27. It clearly demonstrates the changes in the WP quality throughout the duration of the study reflecting the influence of dry/rainy seasons and pumping operations. At the beginning of the monitoring, the wetland consisted of a mix of waters from the SA-8, N-15, GW, and CP. During the period of April – July 2006 the composition of water at the northern side of the wetland had the following changes: input of N-15 decreased from 100 to 39 %, GW increased from 7 to 35 %, and the CP increased up to 26 %. At the same time, the composition of water at the southern side of the wetland showed that the contribution from SA-8 dropped from 63 to 19 %, GW increased from 16 to 46 %, and the CP increased to 35 %. However, between August and September 2006 the CP inflow dropped to 22 % but the GW input increased up to 78 %. According to the operational data, before the end of September 2006 the pumping of the CP water into the wetland had maintenance and power issues and was periodically turned off. In addition, the considerable GW inflow was impacted by heavy rainfall during two hurricanes in June-early September 2006, which added low conductivity water directly and triggered enhanced groundwater input into the wetland (Criss and Winston, 2003). Later, during the dry season (November – April 2006) the WP contained mostly the CP water (88 – 100 %) and minor inflows of GW (< 12 %) that were caused by short

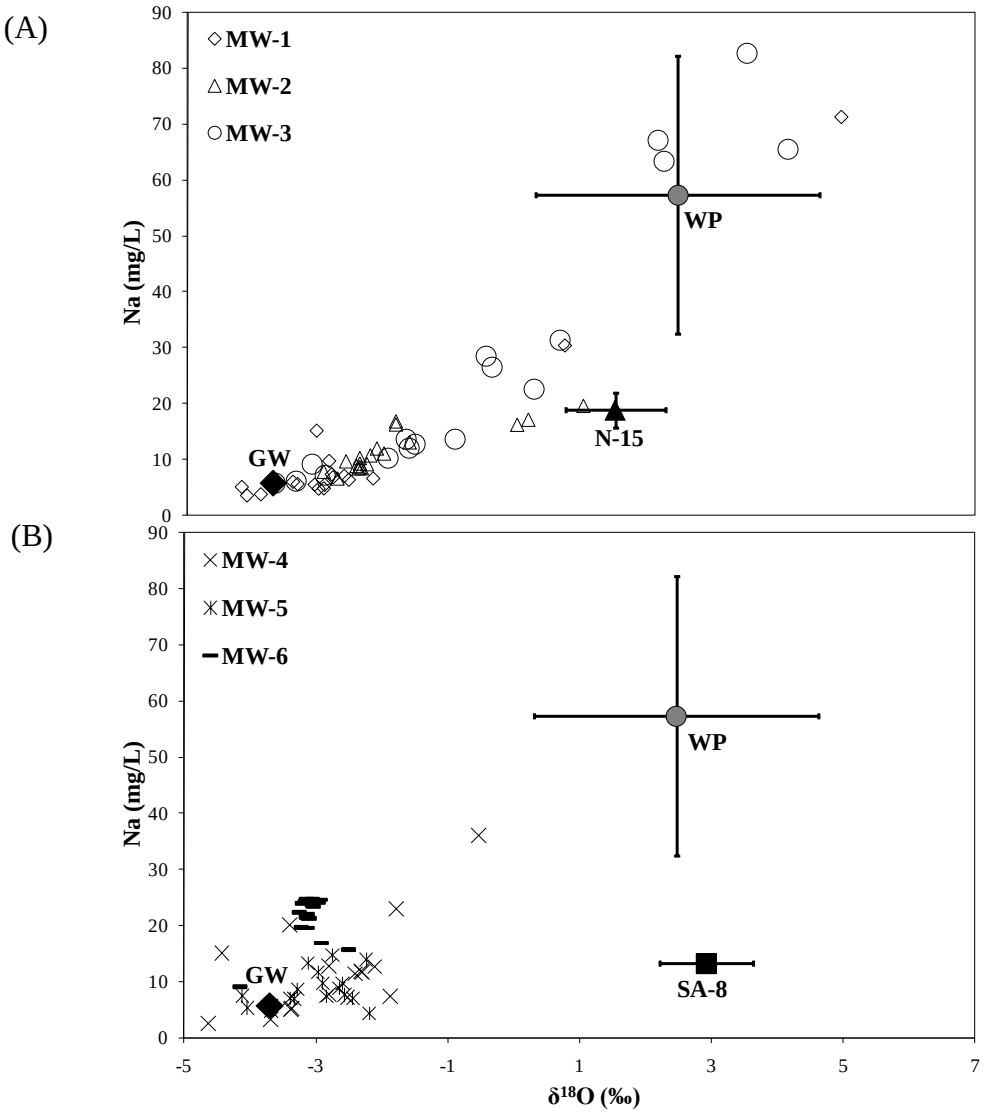

Figure 26. Three end-members for the monitor wells MW-1 to MW-3 (A), and MW-4 to MW-6 (B) used for the mass-balance approach.

Note: WP – wetland water from pump; CP – cooling pond; GW - Floridan groundwater from the Intermediate Aquifer System (well ROMP 45 from Sacks and Tihansky, 1996); N-15 and SA-8 - water bodies to the north and south of the wetland; Error bars – standard deviation.

Table 11. Chemical and isotopic data of the monitor wells (MW-1 to MW-6) used for the mass-balance approach.

Sample	Date	$\delta^{18}O$*	δD*	Na'	*mWP*	*mN-15*	*mGW*	Sample	Date	$\delta^{18}O$*	δD*	Na'	*mWP*	*mSA-8*	*mGW*
MW-1	4/28/06	-3.04	-14.7	15.2	24	0	76	MW-4	4/28/06	no sample					
	5/19/06	-2.85	-13.3	9.7	2	14	84		5/19/06	-2.71	-11.5	15.4	19	0	81
	6/27/06	-2.92	-18.4	5.5	0	15	85		6/27/06	-2.52	-17.5	7.2	0	18	82
	7/28/06	-2.79	-16.9	6.8	0	17	83		7/28/06	-2.80	-14.6	7.8	2	12	86
	8/31/06	-4.10	-23.4	3.6	0	0	100		8/31/06	-4.63	-27.8	2.5	0	0	100
	9/28/06	-3.89	-19.4	3.8	0	0	100		9/28/06	-3.69	-18.5	3.2	0	0	100
	11/7/06	-3.69	-19.7	5.9	0	0	100		11/7/06	-3.68	-19.3	4.9	0	0	100
	12/14/06	-3.33	-18.2	5.6	0	7	93		12/14/06	-3.37	-13.9	5.3	0	5	95
	1/9/07	-3.07	-17.8	5.5	0	12	88		1/9/07	-2.80	-15.0	12.8	13	1	85
	1/31/07	-2.62	-8.6	7.1	0	21	79		1/31/07	-1.87	-1.4	7.4	0	28	72
	3/1/07	-2.18	-5.7	6.6	0	29	71		3/1/07	-2.11	-7.1	12.7	11	14	75
	4/3/07	-2.55	-12.1	6.4	0	22	78		4/3/07	-2.32	-9.1	11.9	10	12	78
	5/2/07	-2.81	-12.3	7.4	0	17	83		5/2/07	-2.30	-8.6	11.8	10	12	78
	5/31/07	0.74	2.9	30.4	25	56	19		5/31/07	-2.41	-9.1	11.5	9	11	80
	7/3/07	4.95	24.2	71.4	100	0	0		7/3/07	-3.40	-16.3	20.1	32	0	68
	8/7/07	-3.01	-14.0	4.8	0	13	87		8/7/07	-3.38	-19.8	5.0	0	5	95
	8/30/07	-2.93	-13.3	4.8	0	15	85		8/30/07	-4.43	-27.8	15.1	24	0	76
	10/3/07	-4.18	-24.9	5.1	5	0	95		10/3/07	-1.78	-9.8	22.9	34	0	66
	10/30/07	-3.40	-19.4	6.0	0	6	94		10/30/07	-0.53	-4.7	36.1	60	0	40
MW-2	4/28/06	-1.83	-7.9	16.7	12	21	66	MW-5	4/28/06	no sample					
	5/19/06	-1.83	-8.0	16.1	10	24	66		5/19/06	-2.24	-9.9	14.0	14	9	77
	6/27/06	-2.27	-14.7	9.0	0	27	73		6/27/06	-2.97	-17.0	11.7	12	0	88
	7/28/06	-2.43	-14.2	8.7	0	24	76		7/28/06	no sample					
	8/31/06	-2.72	-15.6	6.5	0	19	81		8/31/06	-4.04	-23.8	5.3	0	0	100
	9/28/06	-2.93	-14.5	7.7	0	15	85		9/28/06	-3.68	-18.5	5.7	0	0	100
	11/7/06	-2.59	-12.2	9.5	0	21	79		11/7/06	-3.12	-17.2	13.3	16	0	84
	12/14/06	-2.35	-12.9	8.3	0	26	74		12/14/06	-2.75	-14.8	14.8	18	0	82
	1/9/07	-2.40	-14.0	8.3	0	25	75		1/9/07	-2.84	-15.8	7.4	1	12	87
	1/31/07	-2.38	-9.9	8.5	0	25	75		1/31/07	-2.19	-2.5	4.3	0	23	77
	3/1/07	-2.38	-10.4	9.2	0	25	75		3/1/07	-2.44	-9.5	7.1	0	19	81
	4/3/07	-2.38	-10.2	10.1	0	25	75		4/3/07	-2.65	-11.5	8.9	4	12	84
	5/2/07	-2.12	-10.8	11.9	0	30	70		5/2/07	-2.57	-10.4	7.7	1	16	83
	5/31/07	-2.22	-11.6	10.6	0	28	72		5/31/07	-2.60	-9.9	9.7	6	11	83
	7/3/07	-1.62	-7.6	12.9	0	40	60		7/3/07	-2.90	-11.7	9.8	7	6	87
	8/7/07	-2.01	-11.6	11.0	0	32	68		8/7/07	-3.39	-16.8	7.0	2	3	95
	8/30/07	0.02	-0.7	16.1	0	71	29		8/30/07	-4.12	-23.7	7.5	5	0	95
	10/3/07	1.03	4.6	19.5	0	91	9		10/3/07	-3.28	-16.8	8.6	5	1	93
	10/30/07	0.19	0.3	17.0	0	75	25		10/30/07	-3.33	-17.4	7.0	2	4	94
MW-3	4/28/06	-3.66	-19.2	5.7	0	1	99	MW-6	4/28/06	-3.14	-14.0	24.8	42	0	58
	5/19/06	-3.35	-18.4	6.0	0	7	93		5/19/06	-2.51	-12.5	15.7	19	0	81
	6/27/06	-1.94	-11.1	10.1	0	34	66		6/27/06	-3.11	-14.9	21.2	34	0	66
	7/28/06	-0.93	-2.5	13.6	0	53	47		7/28/06	no sample					
	8/31/06	-3.11	-18.4	9.2	4	7	89		8/31/06	-4.15	-23.8	9.0	9	0	91
	9/28/06	-1.54	-6.1	12.7	0	41	59		9/28/06	-3.22	-14.9	19.7	31	0	69
	11/7/06	-1.67	-5.9	13.5	0	39	61		11/7/06	-3.16	-17.2	24.3	41	0	59
	12/14/06	0.27	0.4	22.6	3	72	24		12/14/06	-2.93	-16.0	24.6	41	0	59
	1/9/07	-0.45	-3.1	28.4	34	22	44		1/9/07	-2.96	-18.5	24.1	40	0	60
	1/31/07	-0.36	0.1	26.4	26	33	41		1/31/07	-3.14	-14.0	19.6	30	0	70
	3/1/07	no sample							3/1/07	-3.06	-14.8	23.5	39	0	61
	4/3/07	0.68	4.6	31.4	29	50	21		4/3/07	-3.04	-16.8	23.4	39	0	61
	5/2/07	-1.63	-11.2	12.0	0	40	60		5/2/07	-3.06	-14.8	24.6	42	0	58
	5/31/07	-2.91	-16.3	7.1	0	15	85		5/31/07	-3.06	-15.6	24.8	42	0	58
	7/3/07	no sample							7/3/07	-3.14	-17.1	22.0	36	0	64
	8/7/07	4.15	20.6	65.6	100	0	0		8/7/07	-3.14	-16.8	21.4	35	0	65
	8/30/07	2.17	7.1	67.1	100	0	0		8/30/07	-3.25	-18.3	22.3	37	0	63
	10/3/07	2.25	11.7	63.3	100	0	0		10/3/07	-3.20	-15.7	23.9	41	0	59
	10/30/07	3.52	17.3	82.7	100	0	0		10/30/07	-2.92	-15.0	16.9	23	0	77

Note: (*) - values in ‰; (′) – values in mg/L; m - mass or of each end-member in MW.

mechanical problems. During the second rainy season (May – October 2007) the CP water inflow remained high (87 - 100 %). However, the maintenance/power issues and a significant rainfall in August - October caused the GW seepage to increase up to 13 %. Sacks (2002) used the isotope mass-balance method for estimating the water balance of lakes in central Florida. The author reported that the majority of lakes in upland areas of Polk and Highlands Counties had from medium to high groundwater inflows with 25 – 50 % and > 50 % of total inflow, respectively. The inflows depended on topography, humidity, air and lake-surface temperatures, lake depth, distance downward to the Upper Floridan Aquifer (thickness of the Surficial Aquifer and Intermediate Confining Unit) and fraction of wetlands.

Evaluation of the wetland surface water (WS) along the flow path showed a distinct pattern of change in isotopic signature from the input - CP to the output – WP (Figure 28). The wetland transect was done three times with the interval of about three weeks. First transect was performed at the beginning of the study on April 24, 2006. The $\delta^{18}O$ and δD values along the wetland were relatively heavy, ranging from 0.33 to 3.16 % and from 3.6 to 17.1 ‰, respectively. It was noticeable that at the beginning of the wetland $\delta^{18}O$ and δD were depleted by 3.88 ‰ and 17.3 ‰ compared to the CP. The second transect on May 15, 2006 showed a slow isotopic depletion along the wetland flow path where $\delta^{18}O$ and δD ranged from 0.60 to 4.09 ‰ and from 10.1 to 19.0 ‰, respectively. According to the mass-balance calculation explained above, the wetland water was composed of 50 % of N-15, 37 % of SA-8, 8 % GW, and 5 % of the CP waters (Figure 27). The third transect, performed after the hurricane Alberto (June 27, 2006), demonstrated even higher depletion of $\delta^{18}O$ and δD ranging between -0.02 to 3.25 ‰ and

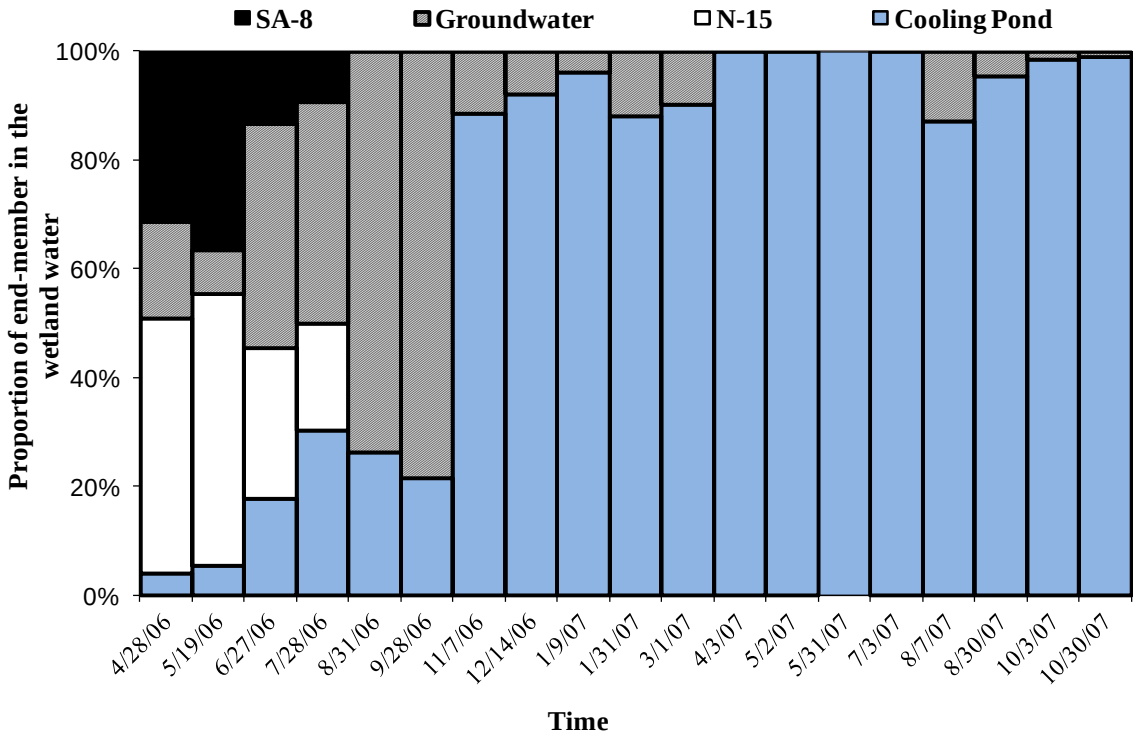

Figure 27. The calculated mass of each end-member in the wetland using an isotope/chemical mass-balance approach.

Note: WP – wetland water from pump; CP – cooling pond; GW - Floridan groundwater from the Intermediate Aquifer System (well ROMP 45 from Sacks and Tihansky, 1996); N-15 and SA-8 - water bodies to the north and south of the wetland; Error bars – standard deviation.

-3.1 to 14.5 ‰, respectively. The mass-balance estimation showed that the wetland water consisted of 41 % of GW, 28 % of N-15, 18 % of CP, and 13 % the SA-8 waters. Therefore, the decrease in isotopic fractionation of 1.91 ‰ for $\delta^{18}O$ and 13.2 ‰ for δD coincides with the drastic GW input into the wetland after a strong hurricane. At the same time, it is interesting to note that distinctive depletion of $\delta^{18}O$ and δD from 4/28 to 6/27 was evident between 1300 and 2700 m but reverse between 0 and 1300 m of the wetland flow path.

The calculated proportions of three end-members in MW-1 to MW-6 estimated by the isotope/chemical mass-balance approach are shown in Table 11. The composition of MW-1 to MW-3 was substantially induced by the seepage from the N-15 with the highest levels at MW-2 and MW-3 (up to 91 %). The estimated GW inflow varied from 0 to 100 % decreasing from MW-1 to MW-3. The highest input from the WP (up to 100 %) was to MW-3 in August - October 2007. The composition of MW-4 to MW-6 was mostly controlled by the GW inflow (40 - 100%). The estimated seepage from the SA-8 was < 28 % with increasing inflow from MW-5 to MW-4. The highest inflow from the WP (< 42 %) was to MW-6 (except one MW-4 sample from 10/30/08).

The influence of each end-member on the composition of MWs could be caused by several factors such as (1) lithologic settings of the study area causing a variability in porosity and permeability; (2) total depth of MWs; (4) hydrologic gradient; (5) proximity of N-15 and SA-8 to the wetland; and (6) periodic variations in precipitation(dry/rainy season). The lithology of MWs cores along the wetland was relatively uniform and sediments were composed of light-tan to brown poorly to well-sorted fine sands or silts with occasional grey clay nodules. The brown color was due to the presence of organic

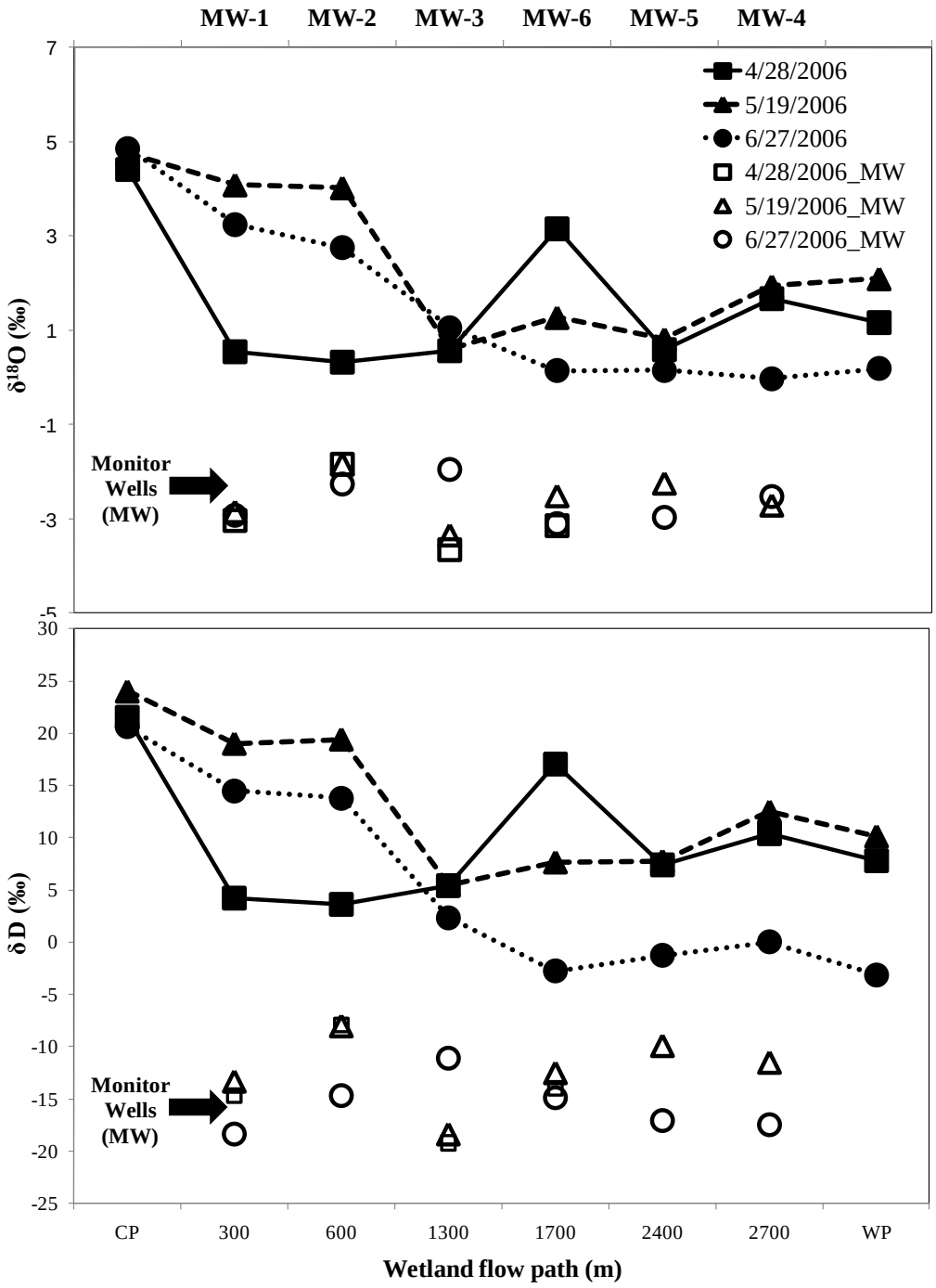

Figure 28. Evaluation of wetland surface water isotopic composition along the flow path.

Note: CP – cooling pond; WP – wetland water from pump.

material. Generally, clay content was higher at MW-4 to MW-6 compared to MW-1 to MW-3. At the same time, of all wells MW-3 had more medium-fine sands at the top 1.5 m. The monitoring of water-level elevations showed that the SA-8 had a higher level compared to N-15, CP, and the wetland (Figure 13). However, the isotope/chemical mass-balance method showed that the seepage from SA-8 was substantially lower than from N-15. The higher inflow of N-15 into MWs could be due to a closer location to the wetland compared to SA-8. In addition, MW-1 to MW-3 were shallower than MW-4 to MW-6 and were less affected by the GW inflow but more affected by the N-15 dilution. The total depths of MW-1 to MW-3, and MW-4 to MW-6 were 3 and 4 m, respectively. As a result, the deeper wells could generally have a higher input of GW. Despite the fact that the inputs from N-15 and SA-8 were detected in MWs, they were not identified in the wetland once the treatment system became fully operational potentially indicating a water loss from the wetland.

2.5. Conclusions

1) Evaluation of the wetland performance during dry and rainy seasons was important to assess the reliability of the treatment system in time and space. The wetland transect showed a distinct pattern of change in water chemistry along the flow path from the input cooling pond (CP) to output – wetland water from pump (WP).

2) The study showed the following changes in water quality from the cooling pond (CP) to the constructed wetland/filter basin treatment system (CW/FB):

1. Substantial decrease of water temperature (up to 10 °C);
2. Significant change in pH from about 9 to 6.5–7;

3. Negative ORP confirming the reducing conditions of the treatment system;

4. Substantial increase of H_2S (up to 1060 μg/L).

5. Reduction of As from up to 5 μg/L to < 2 μg/L (mostly < 0.5 μg/L). Seasonal variations of As in the wetland showed lower concentrations during summer–fall and higher during winter-early spring.

6. Substantial reduction of SO_4, F, Cl, NO_3, NO_2, Br, Na, K, Ca, and Mg.

7. No exceedances of the primary drinking water standards, volatile organic compounds, synthetic organic compounds, and radionuclides. Several exceedances for the secondary drinking water standards, such as Al, F, Fe, Mn, color, odor, total dissolved solids, and foaming agents.

8. Reduction of fecal and total coliform at the FBS/FBN from 30 - 730 and 1000 – 7000 count/100 mL to < 2 and < 100 count/ 100 mL, respectively. These results clearly demonstrate a crucial role of a biofilm "schmutzdecke".

3) Stable isotopes of hydrogen (δD) and oxygen ($\delta^{18}O$) in combination with geochemical data were useful tools to discriminate major sources of water in the constructed wetland and monitor wells (MWs).

4) The composition of water in MWs was determined to be groundwater dominated. However, water in MW-1 to MW-3 was substantially induced by the seepage from N-15.

5) The possible factors controlling the fluid mixing in the monitoring wells (MWs) can be: (1) lithologic settings of the study area causing a variability in porosity and permeability; (2) total depth of MWs; (4) hydrologic gradient; (5) proximity of the

water bodies to the north and south (N-15 and SA-8) of the wetland; and (6) periodic variations in precipitation (dry/rainy season).

6) The composition of water in the wetland varied throughout the period of the study. During the first 6 months of monitoring, the wetland water was composed of a mix of waters from SA-8, N-15, GW, and CP. The water quality was impacted by major hurricanes in June-early September 2006 and inconsistent pumping operation due to maintenance/power issues. Once pumping operations stabilized and without the influence of hurricanes, the wetland water was mostly composed of the CP water (88 - 100 %) and minor inflow from GW caused by occasional rainfall and short mechanical problems.

The performance of the wetland/filter basin treatment system showed a great potential to improve the water quality of industrial and municipal wastewater. Despite significant seasonal variations with respect to temperature, rainfall and humidity, the chemical/microbiological composition of treated water remained relatively constant.

CHAPTER THREE

BENCH-SCALE LEACHING EXPERIMENTS TO INVESTIGATE GEOGENIC ARSENIC CONTAMINATION IN THE FLORIDAN AQUIFER

3.1. Introduction

During the past 20 to 30 years numerous occurrences of elevated arsenic (As) concentrations in groundwater were reported. With a few exceptions the source of As was geogenic, i.e., naturally occurring in the aquifer matrix. The release of As from the aquifer, however, was generally caused by anthropogenic perturbations of the physicochemical conditions, especially a redox change. There are a multitude of scientific publications addressing this issue, including several excellent reviews (e.g., Amini et al., 2008; Ferguson and Gavis, 1972; Korte and Fernando, 1991; McNeill et al., 2002; Smedley and Kinniburgh, 2002). This type of As contamination is a public health issue world-wide. In particular the catastrophic problems in Bangladesh and West Bengal have been front-page stories in newspapers and scientific journals (e.g., Ahmed et al., 2006). Despite more than 20 years of ongoing research into the As problem in Bangladesh there is no consensus about the geochemical mechanisms of As mobilization. The dissolution of hydrous ferric oxide (HFO) is called upon, as well as the oxidation of pyrite (e.g., Polizzotto et al., 2005; Swartz et al., 2004; van Geen et al., 2008). Nevertheless, it is becoming clear that the problem of As release is a complex problem of

agriculture, hydrogeology, microbiology and inorganic geochemical processes, which reaches far beyond the simple approach of oxic vs. anoxic conditions (Dhar et al., 2008; Stute et al., 2007; Zheng et al., 2005).

Similar to the problem outlined for Bangladesh, there are many other locations where similar geogenic As contamination exists; independent of the aquifer matrix, whether fluvial sediments, marine shale or carbonate rocks. Surprisingly little is known about geogenic As contamination in limestone/carbonate aquifers. A thorough literature search provided only 5 references (Armienta and Segovia, 2008; Gbadebo, 2005; Romero et al., 2004; Simsek et al., 2008; Vesper and White, 2003). Limestones, although excellent aquifers, are problematic because due to karstification, contaminants can be easily transported over large distances, posing a threat to public and private water supplies (e.g., Ducci et al., 2008; Katz, 2004; Kovacova and Malik, 2007; McMahon et al., 2008; Obeidat et al., 2008; Zhou and Beck, 2008). Groundwater can flow through conduits so that there is little opportunity for filtration or sorption of contaminants onto aquifer material. Thus it is important to assess and understand geogenic As contamination in limestone aquifers, where anthropogenic perturbations could cause the release of As from the limestone matrix at a large distance from the area where eventually elevated As values occur.

Arsenic in the Floridan Aquifer, an extensive carbonate aquifer, is mostly associated with pyrite as a substitute for sulfur in the FeS_2 structure (Lazareva and Pichler, 2007; Price and Pichler, 2006). Thus, a change in the redox conditions from anoxic to oxic could cause the dissolution of pyrite and the mobilization of As (Figure29). This scenario is the current working hypothesis to explain elevated As

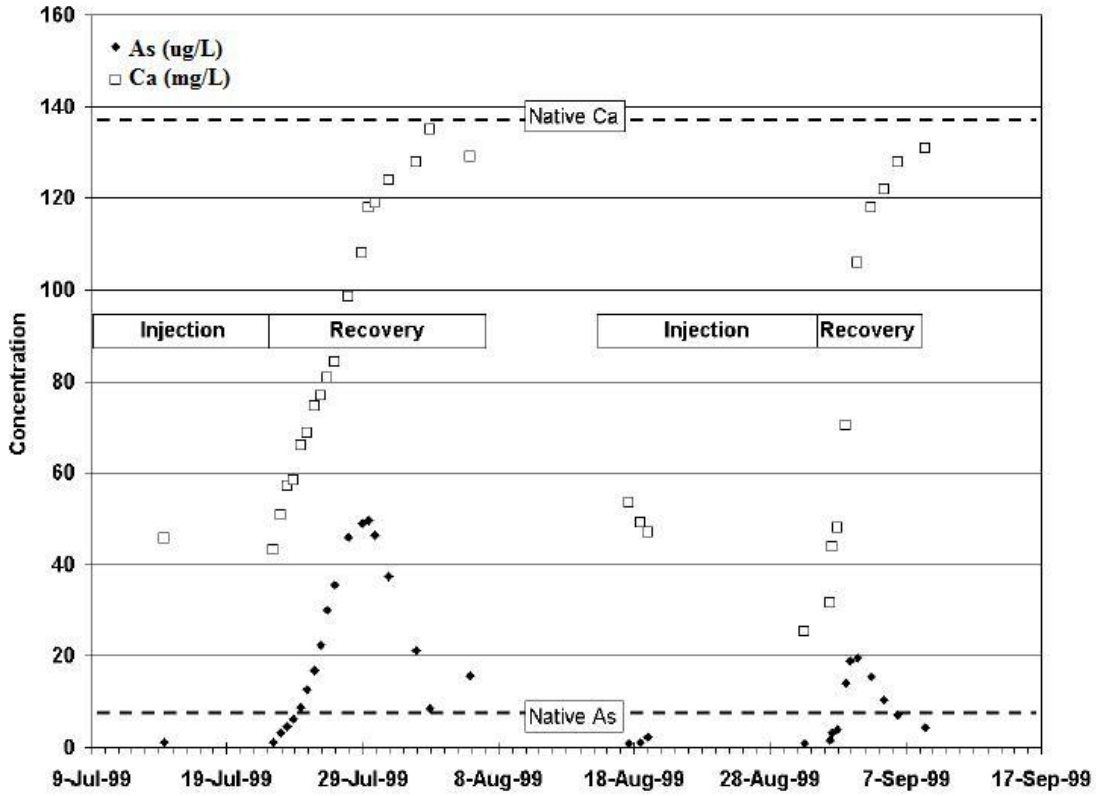

Figure 29. Concentrations of As and Ca through time for the ASR Punta Gorda cycle during aquifer storage and recovery (ASR) operation in Charlotte County, southern Florida (from Arthur et al., 2002).

concentration observed during aquifer storage and recovery (ASR) operations in Florida. The principle behind ASR is the storage of treated surplus surface water in a confined aquifer during rainy seasons followed by its recovery during times of need. During ASR cycle tests, the injection of oxygenated surface water into reducing native groundwater causes a transformation of the redox environment, oxidative dissolution of pyrite, and the release of As with values in recovered water of up to 130 µg/L (Arthur et al., 2005; Arthur et al., 2002; Williams et al., 2002; Arthur et al., 2001).

The objective of this investigation was to carry out a series of bench-scale leaching experiments to study the mobilization of geogenic As under a range of redox conditions.

3.2. Methods

3.2.1. Rock preparation and analysis

Rock cuttings were collected during well installation in central Florida (Polk County). Stratigraphically, the cuttings represent the Suwannee Limestone, Ocala Limestone and the Avon Park Formation. Until time of analysis they were stored under a nitrogen atmosphere at the Center for Water and Environmental Analysis, University of South Florida (USF). Later, the cuttings were dried and carefully examined with a 10·x hand lens as well as a stereo microscope for the possibility of post-drilling oxidation of redox sensitive minerals, such as pyrite. Generally 2 random samples and 2 samples of special interest were taken per interval. Samples of special interest represented single chips of rocks that were deemed to have higher As concentrations, such as, clays, pyrite, etc. Several samples were selected for a more focused mineralogical analysis using a

Hitachi S-3500N scanning electron microscope (SEM) with energy dispersive spectrometry (EDS) at the College of Marine Science, USF. To determine bulk chemical composition the samples were powdered and homogenized in an agate mortar. To avoid cross-contamination, the mortar and pestle were cleaned with pure silica sand and de-ionized water (DI) water between samples. Approximately 0.5 ± 0.01 g of powdered sample was weighed into a digestion vessel and 10 mL of a 3:1 mixture of hydrochloric (HCl) and nitric acid (HNO_3) was added. The digestion vessel was immediately capped with a reflux cup to trap any arsine gas. The sample was heated in a HotBlock™ to a temperature of 95°C for 30 min. After digestion, the solution was cooled, diluted to 50 mL (5:1) with DI, centrifuged for 15 min, filtered out with FilterMate™ to remove any suspended solids (silicates), and stored until analysis.

Calcium, Fe, Mg, Mn, S, P, Si and Al were determined using a Perkin Elmer Optima 2000 DV inductively coupled plasma - optical emission spectrometer (ICP-OES). Sample preparation consisted of the dilution of 2 mL of the stored sample solution with DI into a 10 mL centrifuge tube. The sample dilution (5:1) was needed due to the high acid concentration. Bulk As concentration was measured on a PSA 10.055 Millennium Excalibur hydride generation-atomic fluorescence spectrometer (HG-AFS). The accuracy and precision of the measurements were better than 5% verified through the use of internal and external standards. Acid blanks for digestion and HG-AFS did not reveal any detectable As. Background signal drift monitor was less than 2%. In total 206 rock samples were dissolved and subsequently analyzed (Appendix C, D, and E).

After the chemical analysis, rock cuttings from the following sampling intervals were chosen for the bench-scale column experiments based on results explained below in

section 3.3.1.: Suwannee Limestone (136 m to 139 m, and 171 m to 174 m), Ocala Limestone (195 m to 199 m), and the Avon Park Formation (255 m to 257 m; and 260 m to 261 m) (Table 13).

3.2.2. Water collection and analysis

During the experiments 7 different types of water were used: (1) Tampa drinking water; (2) Native Floridan groundwater; (3) Native Floridan groundwater saturated with air; (4) Wetland water; (5) Wetland water exposed to UV; (6) Water from the filter basin, and (7) Water from the filter basin treated with UV. A complete chemical analysis is provided in Appendix F.

Drinking water was directly collected from a tap in the laboratory after extensive flushing. That water was used as an analogue for ASR water (injectate), because ASR injectate has to be treated to meet all drinking water standards and requirements. Thus, tap water and ASR injectate are chemically and physically similar, i.e., pH, T, high dissolved oxygen and high oxidation-potential level.

Groundwater was collected from a well located on the USF Tampa campus and used as a baseline for comparison with the other waters. The production zone of that well was from 103.9 m to 184.4 m. Groundwater was sampled carefully into 9.5 L amber carboys filled with N_2 to avoid contact with atmospheric oxygen and the resulting change in redox. The carboys were equipped with quick disconnect closures, which have internal valves that automatically close when a fitting was removed. Immediately after collection, the water was transported to the laboratory for the leaching tests. To evaluate As mobilization in

the presence of O_2 the same groundwater was saturated with air prior to injection into the columns.

Wetland water was obtained from the wetland/filter basin treatment system discussed in the second chapter. It was collected directly from the wetland from a depth of 0.5 m using a peristaltic pump to ensure uniform water flow (Figure 30). Similarly to groundwater sampling, wetland water was stored in 9.5 L amber carboys treated with N_2 prior to collection. After collection, carboys were immediately transported to the laboratory for the leaching tests. The experiments were divided into a series of tests with wetland water, as collected and treated with ultra violet light (UV) prior to injection (Figure 30). The application of UV is of importance in commercial water treatment to kill bacteria. Thus it was deemed important to investigate how UV treatment would affect the dissolution of pyrite and the associated mobilization of As.

Filter basin water was collected from the filter basin pump at the same location as the wetland water. The experiment was divided into a series of tests with the untreated and the UV treated filter basin water. In contrast to the wetland water, water from the filter basin was exposed to UV directly in the field.

Following the sampling procedure, the water samples were analyzed as described in the second chapter. The accuracy and precision of the measurements were verified through the use of internal and external standards, indicating a precision and accuracy better than 5%. In addition, the concentration of dissolved organic carbon (DOC) and total N were measured by Dr. Thorsten Dittmar at the Department of Oceanography, Florida State University.

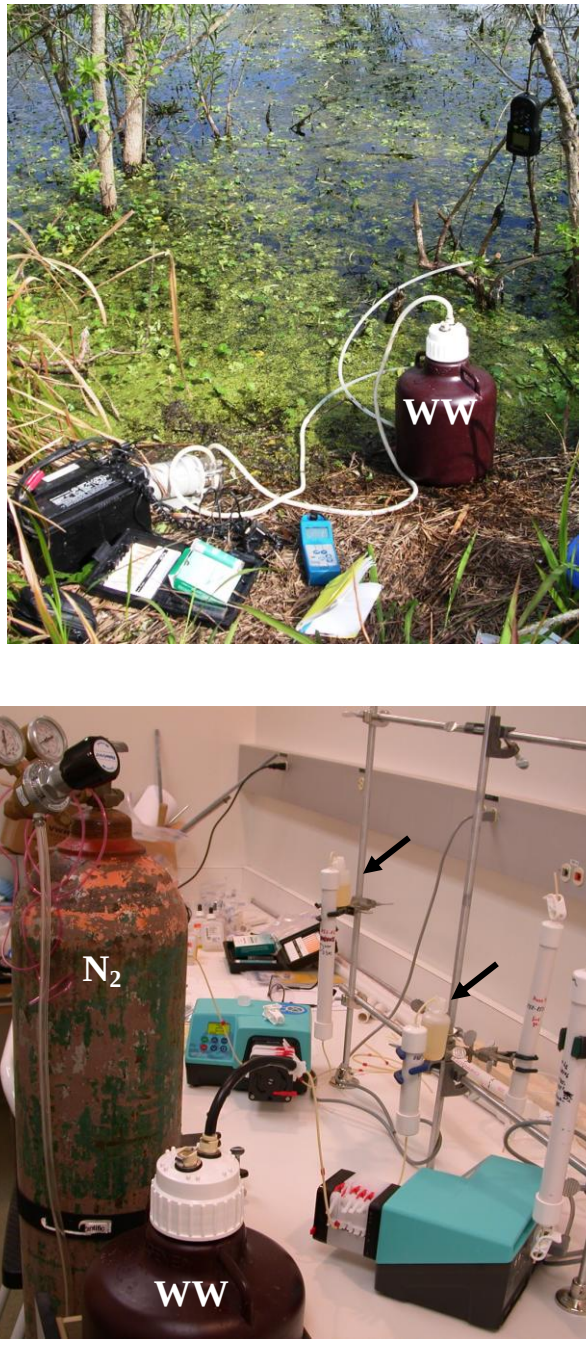

Figure 30. Collection of the wetland water (WW) from a depth of 0.5 m using a peristaltic pump (top).Bench-scale column leaching experiments using WW (bottom). Note: leachate samples on the bottom are indicated by arrows.

3.2.3. Experimental setup

The leaching experiments were performed in standing PVC columns of 0.019 m in diameter, 0.3 m and 1 m in length using the different water compositions and aquifer matrices described above. Prior to each experiment, rock cuttings were dried (to prevent oxidation of pyrite), ground and homogenized in agate grinder to a size of coarse sand to increase the surface area, but at the same time to avoid clogging of tubing lines. After packing, the columns were flushed with nitrogen for about 24 hours to eliminate any oxygen present in the pore space. The source water was percolated into the columns against gravity entering from the bottom, thus allowing for a more uniform flow through the column and a complete saturation of the rock. To achieve a flow rate of 2 mL/min and to avoid any contact with atmospheric oxygen Watson-Marlow multichannel peristaltic pumps were used (Figures 30 and 31). A membrane filter was not used to ensure an undisturbed water flow through the columns. The leachate samples were collected from the top of the columns at certain intervals (every 60 mL) and subsequently analyzed for physical and chemical parameters described in second chapter. The column porosity was determined as the ratio of the weight of water filled the column to the total weight of water and sediment in the column, subtracting the weight of the column as $n = mass\ (water)/\ (mass\ (water + sediment)) * 100$ %.

3.3. Results

3.3.1. Rock chemical composition

Geochemical and mineralogical analysis of core material for this study corresponded to the reported studies of the Suwannee and Ocala Limestones, and the

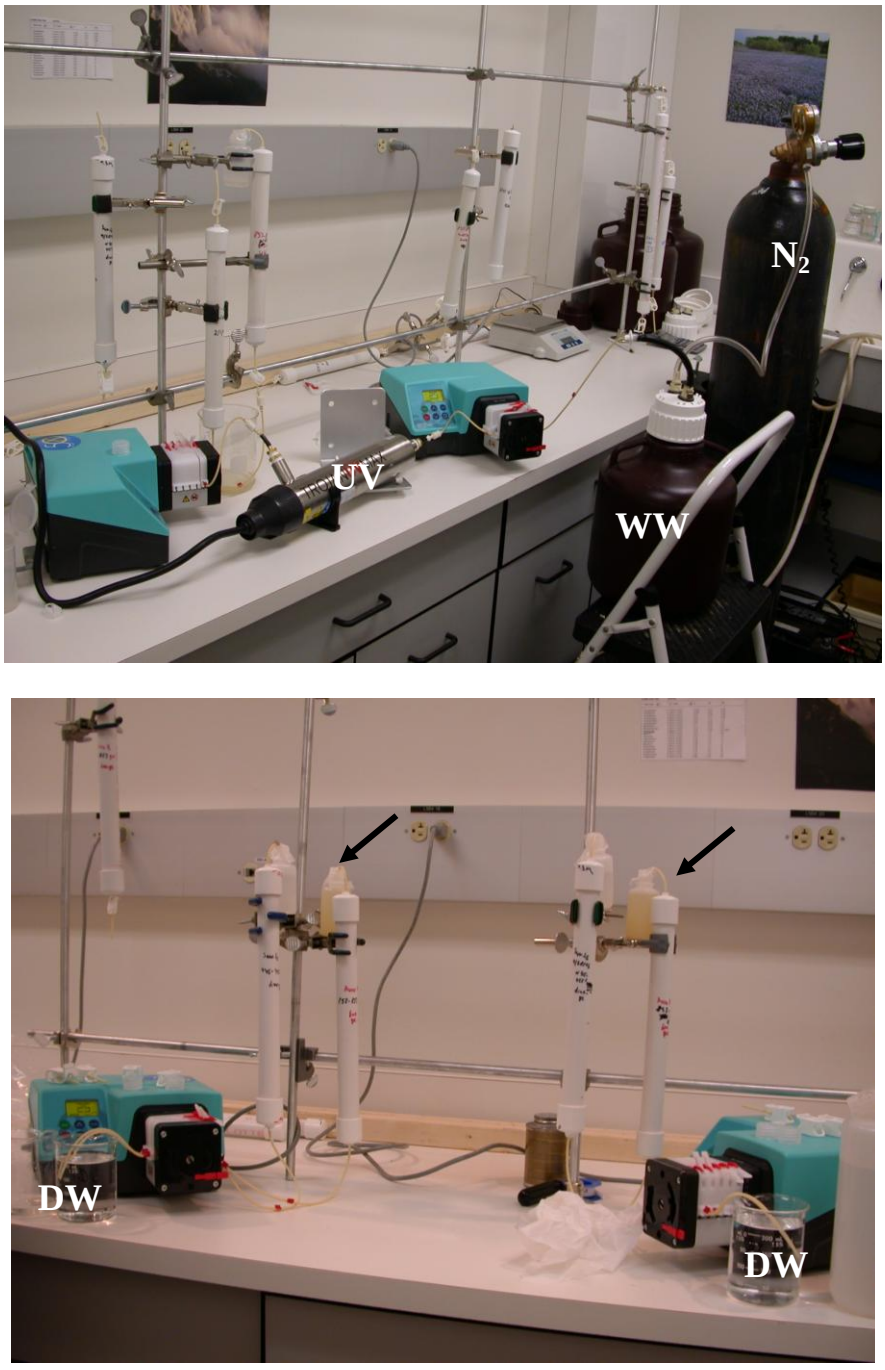

Figure 31. Bench-scale leaching experiments using wetland water (WW) treated with UV (top) and drinking water (DW) (bottom).

Note: yellow color in leachates was due to pyrite oxidation (indicated by arrows).

Avon Park Formation (Dippold, 2009; Price and Pichler, 2006; Scott, 1990; Scott 1988; Miller, 1986). Complete lithologic descriptions of all core samples were listed in Appendix C, D, and E. The majority of the analyzed samples from the Suwannee Limestone were composed of pure white limestone with a minor percentage of dolomite, clay, chert, quartz, iron oxides, phosphate grains, and pyrite. Generally, the limestone had intergranular and high moldic porosity zones. The mineralogical composition of the Ocala Limestone consisted of white dolomitized fossiliferous limestone, poorly to moderately indurated with minor quartz, iron oxides, phosphate, clays and pyrite. Porosity was moldic and intergranular. The majority of samples from the Avon Park Formation were dolostone dominated with a variable percentage of limestone, minor quartz, pyrite, phosphate, iron oxides, dark brown clays, and gypsum. Commonly, the dark brown dolostone was highly fractured and sucrosic in texture. The SEM analysis of the samples selected for the column leaching experiments confirmed the presence of euhedral and framboidal pyrite crystals with unoxidized surfaces (Figures 32 - 34).

Bulk rock chemical composition conducted on the ICP-OES and HG-AFS for Ca, Fe, Mg, Si, S, P, Al, Na, K, and As of all samples were presented in Appendix C, D, and E. Minimum, maximum, mean, and standard deviation of As concentrations were listed in Table 12. The mean included both interval samples and samples of the special interest and, therefore, should be used with caution. Based on those data it seemed that the Ocala Limestone may be the preferred aquifer storage and recovery (ASR) storage zone (not considering any hydraulics) with the lowest potential to contaminate groundwater with As. The injection of oxygen-rich surface water would mobilize As from all three units, but the amount released from the Ocala should be comparatively less. However, the

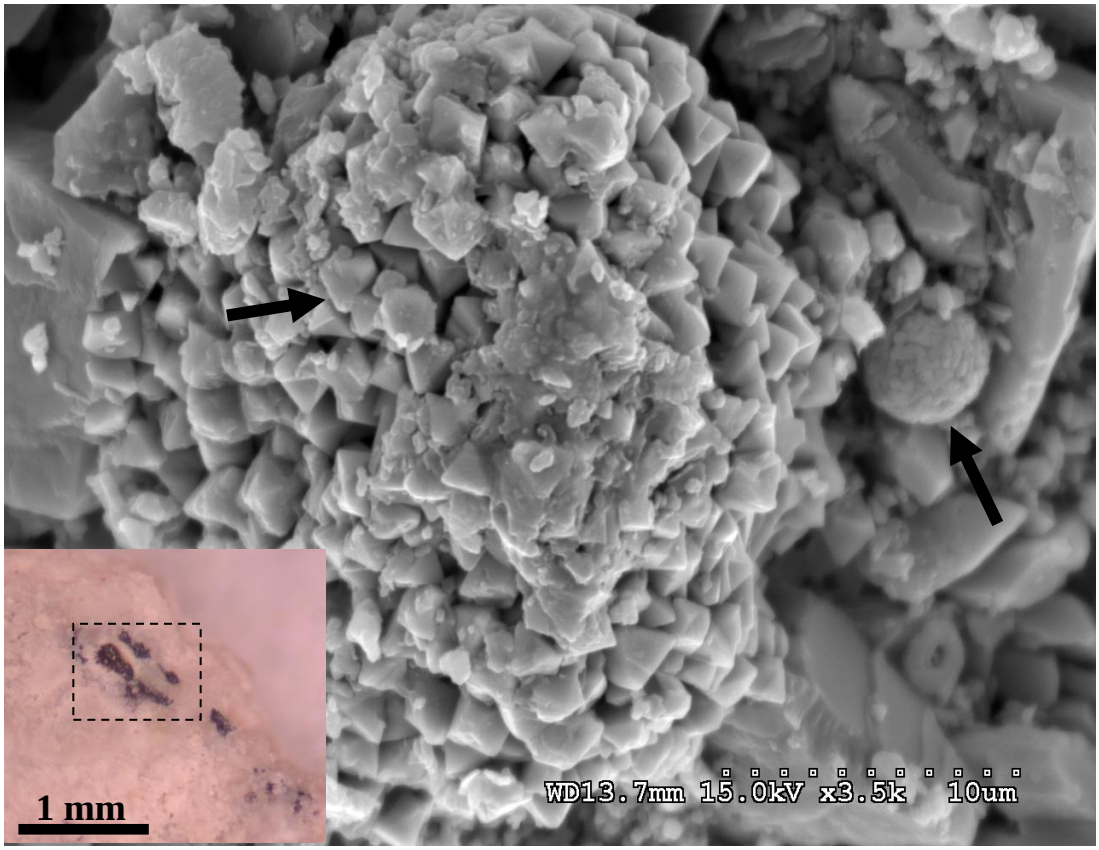

Figure 32. Photomicrograph and the scanning electron micrograph of framboidal and euhedral pyrites (shown by arrows) found in the Suwannee Limestone (136 m to 139 m).

Note: Bar scale in lower right is 10 µm.

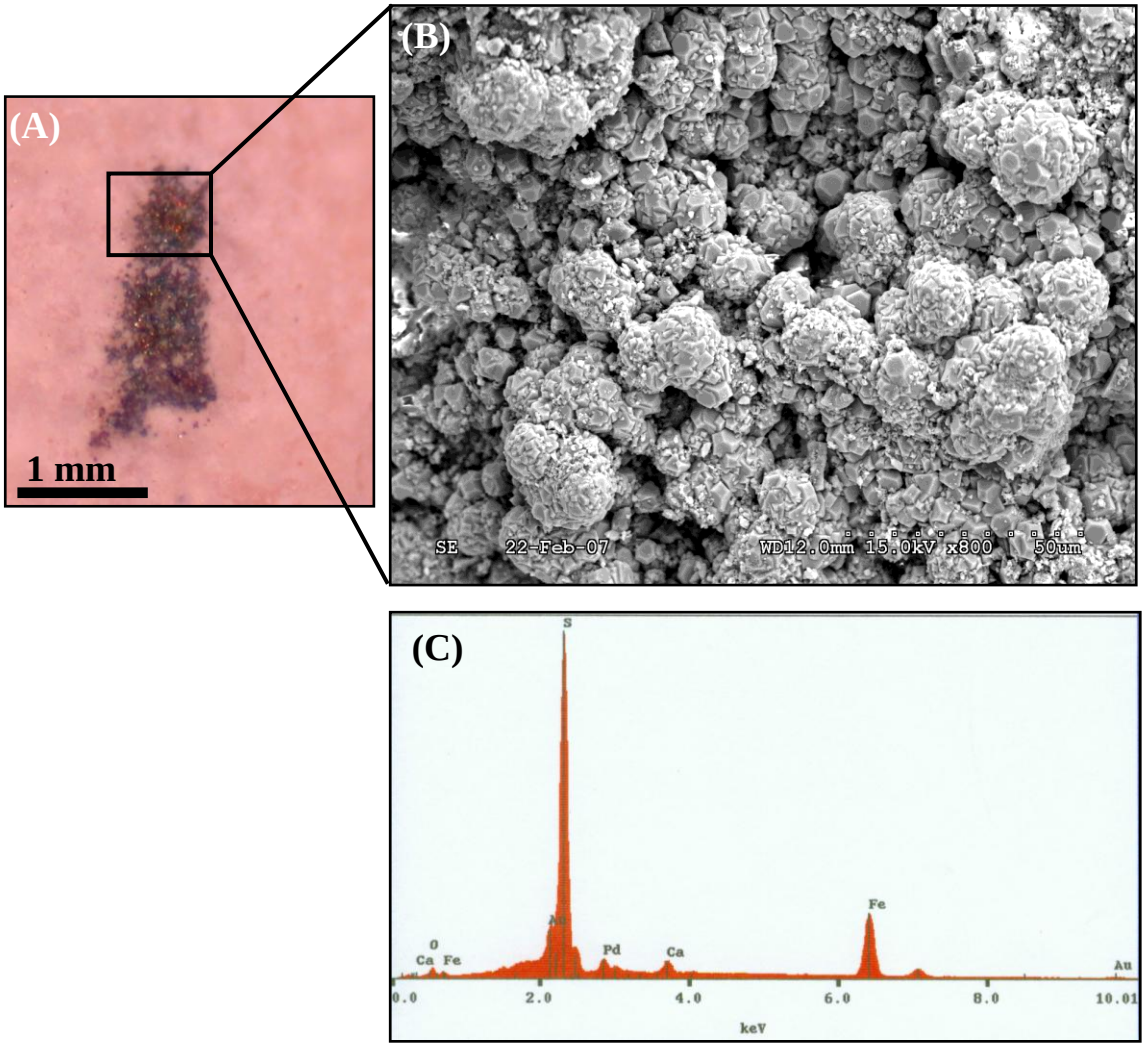

Figure 33. (A) Photomicrograph and (B) the scanning electron micrograph of framboidal pyrites found in the Ocala Limestone (195 m to199 m); (C) EDS spectra confirming the presence of pyrite.

Note: Bar scale for the SEM image in lower right is 50 µm.

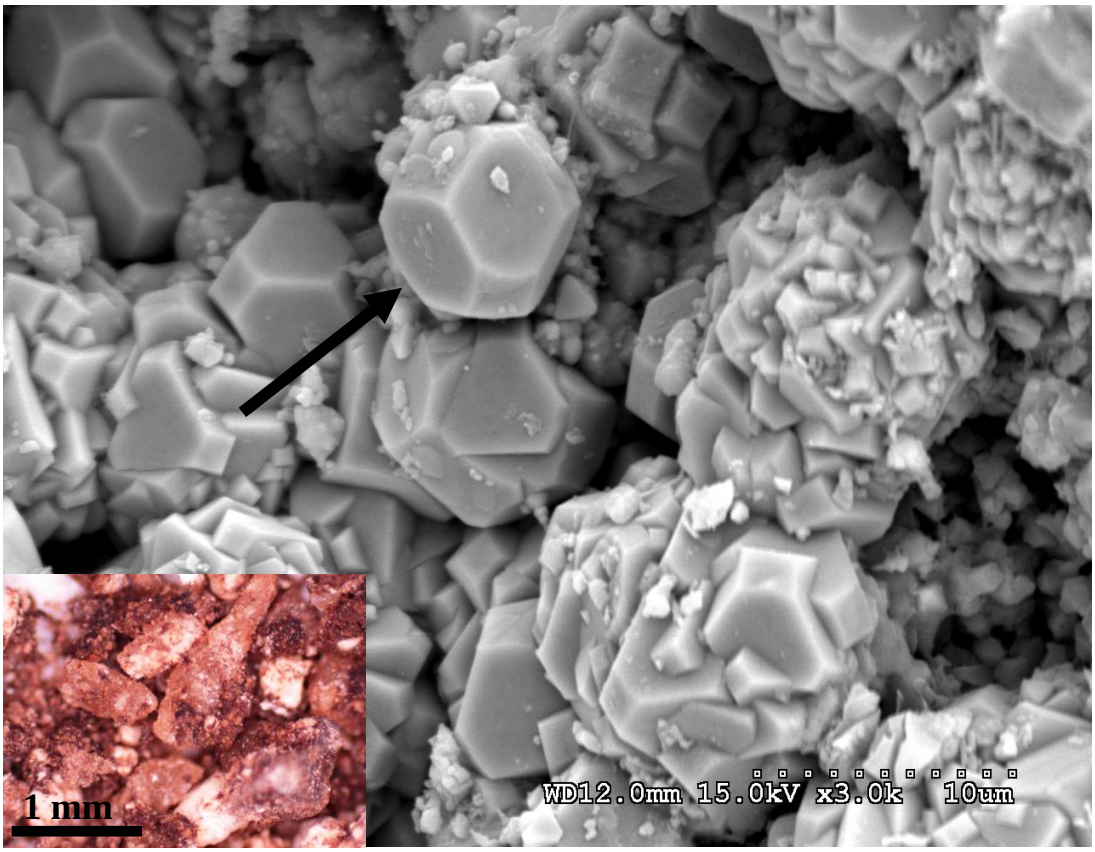

Figure 34. Photomicrograph and the scanning electron micrograph of framboidal and euhedral pyrites found in the Avon Park Formation (255 m to 257 m).

Note: Bar scale in lower right is 10 µm.

Table 12. Maximum, minimum, mean and standard deviation of As concentrations in mg/kg for the Suwannee Limestone, Ocala Limestone and Avon Park Formation

	Suwannee Limestone	Ocala Limestone	Avon Park Fm.
Minimum	0.02	0.02	0.64
Maximum	16.15	14.74	14.19
Mean	**2.96**	**1.49**	**2.87**
Standard Deviation	4.18	2.93	2.98
(N)	104	67	35

average concentration may be a meaningless measure of As availability if its location/association within the aquifer matrix was not known. For example, if As was bound by hydrous ferric oxide (ferrihydrite) then only reducing conditions would cause its release into the groundwater. Alternatively if As would be present as impurities in pyrite, only oxidizing conditions could cause its release. Since pyrite in these rocks was generally of very small size a statistical technique was applied to determine whether pyrite was present in appreciable amounts and if that pyrite had the potential to be a source of As. The only elements that showed an appreciable degree of correlation with As were Fe, S and Al. Furthermore those elements also showed a good correlation to each other indicating that they occur together in the aquifer matrix. Since there was no known mineral that contains both Al and S the correlation of the two can only be explained by the coexistence of two discrete minerals. The correlation of Fe and S can be attributed to the presence of pyrite and the correlation of Fe and As to the presence of glauconite, a Fe-bearing clay mineral. All of those minerals were previously described in the Suwannee Limestone, Ocala Limestone and Avon Park Formation. This indicated that As was almost exclusively associated with pyrite and clay minerals in all three rock units which in turn allowed to compare their averages.

After the bulk rock chemical and mineralogical analysis of all samples, the following sampling intervals were chosen for the bench-scale column experiments based on a variable amount of pyrite, clays and concentration of As: Suwannee Limestone (136 m to 139 m, and 171 m to 174 m), Ocala Limestone (195 m to 199 m), and the Avon Park Formation (255 m to 257 m; and 260 m to 261 m) (Table 13). Figure 35 demonstrated the distribution of bulk rock As concentration and the calculated amount of pyrite for each

selected interval. Based on a strong linear correlation between S and Fe in those samples, it was conceivable that Fe and S was controlled largely by the presence of pyrite. The weight percent of pyrite can be determined based on molar ratio of Fe to S:

Fe (mg/kg) = S (mg/kg) * 55.85/ (32.07 *2)

FeS_2 (wt %) = (Fe (mg/kg) + S (mg/kg))/1000*(100/1000)

All S was assumed to be associated with pyrite. At the same time, the amount of pyrite in the Avon Park samples was calculated from the bulk Fe data due to the presence of gypsum (Table 13). The distribution of bulk rock As concentration demonstrated a strong correlation with the calculated amount of pyrite (R^2 = 0.92) except the 260 m – 261 m interval from the Avon Park Formation (Figure 36). This result can be explained by the overestimation of pyrite constituent or existence of additional potential source of As such as dark brown clays (Table 12) (Lazareva and Pichler, 2007).

3.3.2. Leaching experiments

All data from the bench-scale leaching experiments, including the composition of original waters and recovered leachates were presented in Appendix F.

3.3.2.1. Suwannee Limestone

(136 m to 139 m)

The lithological composition of the Suwannee Limestone from the 136 m to 139 m interval consisted of limestone with minor percentage of quartz, pyrite, clays, and phosphate grains (Table 13). During the leaching experiments, drinking water (DW), wetland water (WW), untreated and air-saturated groundwater (GW), as well as untreated (BW) and UV-treated filter basin waters (BW-UV) were injected into 0.3 m columns

Table 13. List of rock samples selected for the leaching experiments.

Stratigraphic Unit	Interval m	Sample	Bulk Rock Composition, mg/kg										FeS_2 wt.%	Average FeS_2 wt. %	Aver. As mg/kg	As/FeS_2 molar	Mineralogy	SEM
			Ca	Mg	Si	P	Al	Na	K	Fe	S	As						
	136-139	136-139(1)	390803	2779	247	210	<5	328	6	305	763	0.9	0.14	0.13	5.9	0.007	ls+Q-ph-c mtrx.(99/1)	
		136-139(2)	406554	2733	253	207	<5	297	<5	355	744	16.1	0.14				ls+Q-ph-c mtrx.(99/1)	p
		136-139(a)	413063	3111	300	235	<5	232	13	105	598	0.8	0.11				ls	
Suwannee Limestone	171-174	171-174(1)	411173	3701	474	204	<5	138	1	528	731	5.5	0.14	0.58	5.0	0.001	ls+Q-ph-c mtrx.(95/5)	
		171-174(2)	390803	3586	603	189	<5	134	<5	407	699	0.9	0.13				ls+Q-ph-c mtrx.(95/5)	
		171-174(a)	452979	3472	209	211	<5	117	20	229	564	1.2	0.11				dolom.ls,p, Q	p
		171-174(b)	396081	3365	2037	317	19609	679	510	22326	10293	12.5	1.93				Q-ph-c mtrx, c, p	
	195-199	195-199(1)	400345	3290	326	292	<5	275	24	112	734	1.3	0.02	0.02	0.9	0.009	ls+ds (99/1)	
Ocala Limestone		195-199(2)	396391	4136	87	141	<5	131	<5	80	796	0.8	0.02				ls+ds (99/1)	p
		195-199(a)	403269	3735	65	82	<5	112	<5	33	647	0.6	0.01				ls, p	
	255-257	255-257(1)	260225	103345	613	336	83	690	65	515	1548	4.8	0.11	0.08	4.7	0.01	ls+ds(75/25), gy	
		255-257(2)	262277	92004	617	251	<5	621	67	432	1590	5.2	0.09				ls+ds(75/25)	p
		255-257(a)	233087	112509	389	237	<5	604	52	193	1432	3.7	0.04				l.b ds	
Avon Park Formation		255-257(b)	275500	139000	446	246	<5	720	82	285	1760	5.2	0.06				d.b ds sucrosic	
	260-161	260-161(1)	307825	87736	801	300	569	498	191	789	1610	4.8	0.17	0.18	3.9	0.004	ds+ls(90/10)	
		260-161(2)	301630	97259	1175	259	706	539	199	854	1692	3.7	0.18				ds+ls(90/10), c	p
		260-161(a)	269138	142548	888	286	1016	765	247	821	1869	3.2	0.18				d.b ds sucrosic,p, gy, c	

Note: ls –limestone; ds- dolostone; p-pyrite; c-clay; Q-quartz; gy – gypsum; ph – phosphate; l.b - light brown; d.b - dark brown; Sample(1), (2) - interval (bulk rock) analysis; Sample(a), (b) - sample of special interest

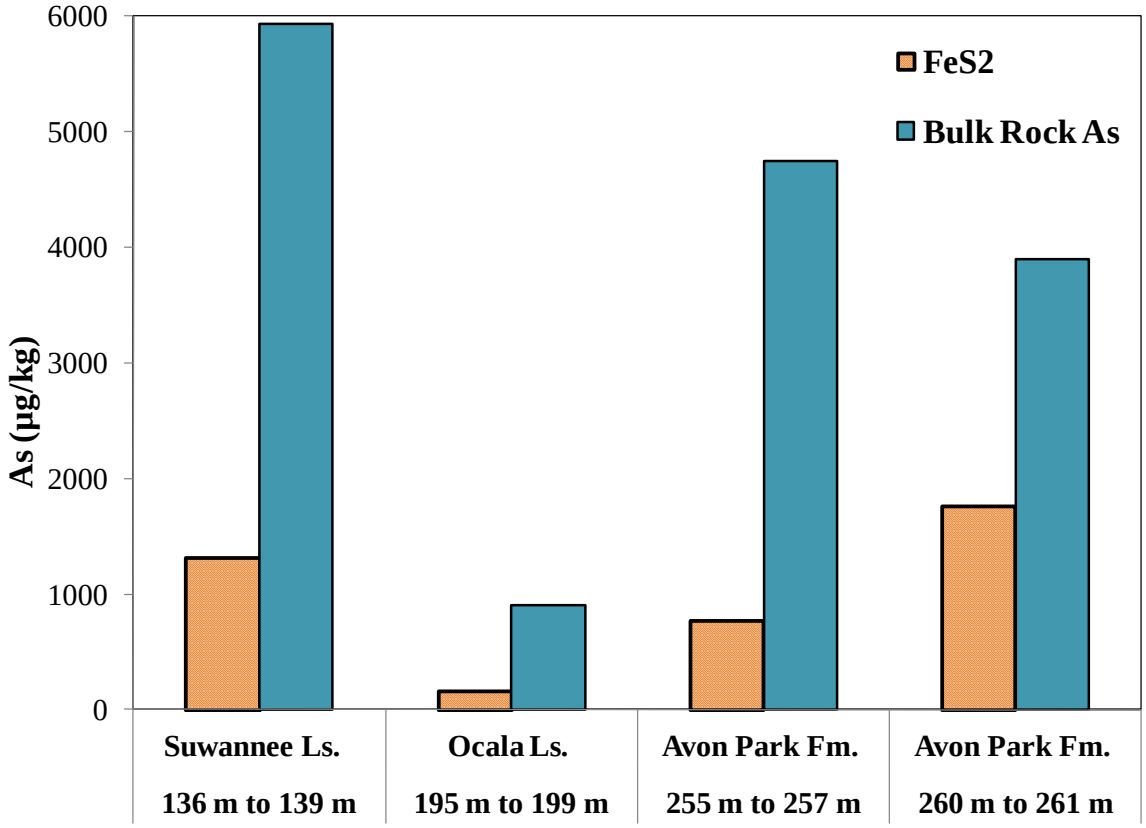

Figure 35. The calculated amount of pyrite and measured bulk rock As concentration in the Suwannee and Ocala Limestones, and the Avon Park Formation.

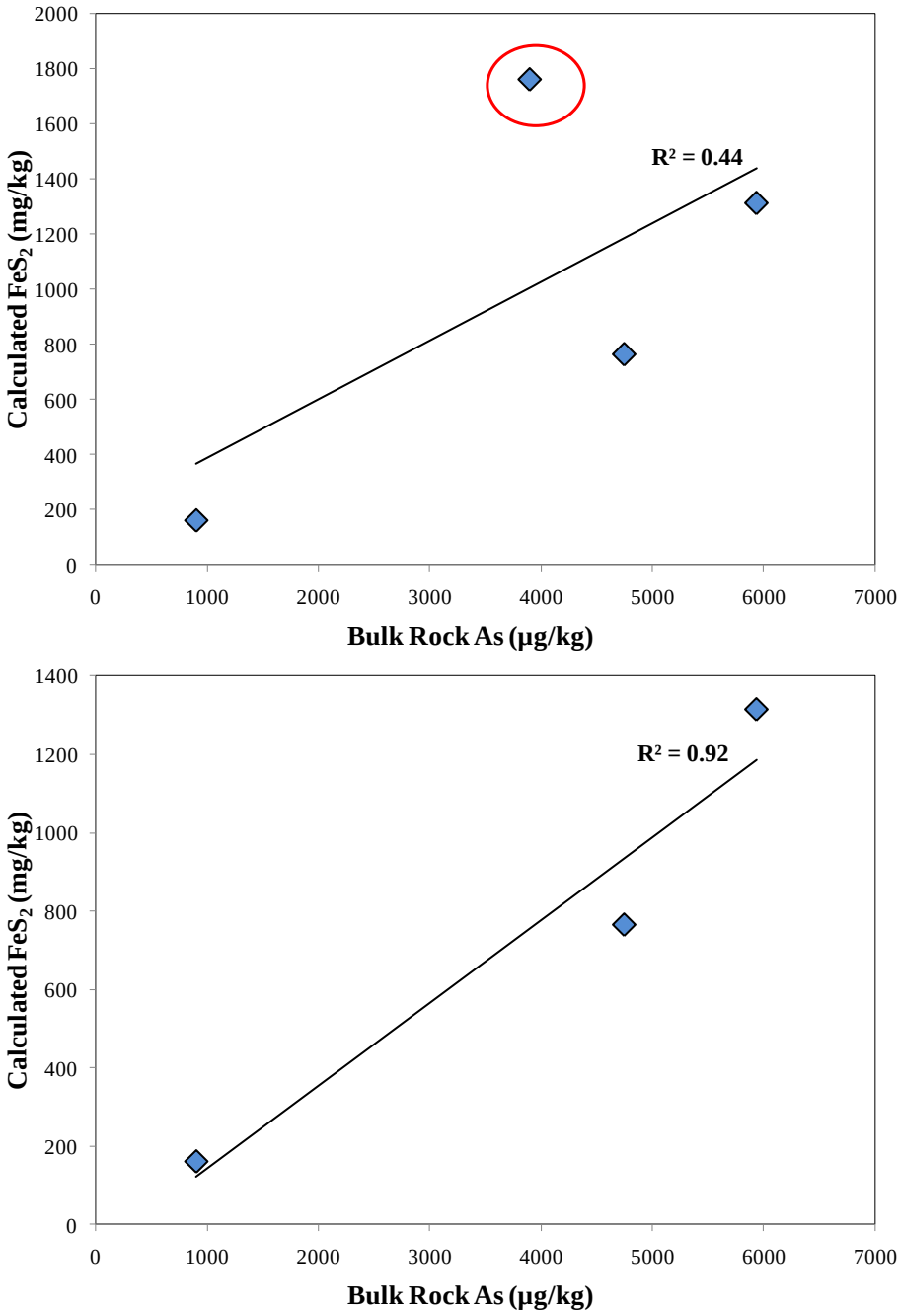

Figure 36. Correlation between calculated amount of pyrite and measured bulk rock As concentration for the analyzed rock intervals with (top) and without the outlier (bottom). Note: the outlier (in circle) – data from the Avon Formation (260 m to 261 m).

(Appendix F, Table 14, Figure 37). The leaching columns contained from 113 g to 150 g of limestone with an average porosity of 24.5 %. The study showed that the injection of BW-UV and BW caused the highest release of As from the aquifer matrix with concentrations of up to 6.1 µg/L and 4.6 µg/L, respectively. The UV treatment changed the redox potential of the BW from reducing to oxidizing indicated by the increase of dissolved oxygen (DO), positive oxidation-reduction potential (ORP), and reduction of Fe(II), which in turn facilitated the oxidation of pyrite (Table 14). In total, about 32 µg of As were recovered from a column using the BW and 24 µg of As - from the injection of BW-UV (Figure 37).

The WW was injected for 2 days and during the first 4 hours of experiment, the concentration of As was up to 4.6 µg/L. The pH values changed from 6.8 to 7.4 and the ORP varied from -143 mV to 38 mV. Generally, the ORP level was negative during the first day of the study confirming the reducing conditions of the system. At the end of first day, the leaching column was closed overnight and the experiment was restarted next morning. On the second day of experiment, the concentration of As was up to 5.3 µg/L and the ORP was up to 108 mV. Overall, 60 µg of As were recovered using the WW.

The injection of native GW from the Floridan Aquifer caused minor to no release of As from the limestone matrix. The concentration of As in first leachate was 1.5 µg/L and decreased to < 0.4 µg/L thereafter. After the injection, pH and OPR values in first leachate decreased from 7 to 6.8 and from -120 mV to -156 mV, respectively. The first peak of As could be due to a possible micro-oxidation of pyrite surface and formation of a ferrous sulfate phase, such as szomolnokite ($FeSO_4 \bullet H_2O$) prior to the experiment

(Costagliola et al., 1997). That phase containing As would dissolve during the injection of reducing

Table 14. Initial water (before injection) and leachate recovered from 0.3 m columns filled with the Suwannee Limestone (136 m to 139 m) using different types of water.

Date	Sample	DO	pH	ORP	T	As	SO_4	Fe(II)	H_2S	Leaching column details	n	m(s)	m(w)	s/w
		mg/L		mV	°C	µg/L	mg/L	mg/L	mg/L		%	g	g	
10/24/2006	DW	2.9	6.7	320	21.2	0.0	39.0	0.0	0.0		21.3	152.1	41.1	3.7
10/24/2006	1 leachate		7.4	122	21.1	2.0	345.9	0.0	0.0					
3/11/2008	WW	0.4	6.8	-143	18.0	1.2	43.4	0.1	3.0		24.9	121.9	40.4	3.0
3/11/2008	1 leachate		7.3	-88	21.2	3.9	298.1	0.0	0.3					
2/11/2008	GW	1.2	7.0	-120	26.1	0.4	556.4	0.6	0.2		24.0	124.0	39.2	3.2
2/11/2008	1 leachate		6.8	156	18.4	1.5	665.9	0.0	0.0					
2/13/2008	GW/air	7.6	7.5	161	20.3	0.4	556.4	0.0	0.0		25.6	119.2	41.1	2.9
2/13/2008	1 leachate		7.1	145	21.1	4.3	870.5	0.0	0.0					
1/29/2008	BW	1.7	6.7	-56	17.3	0.7	46.3	1.0	0.0		26.7	113.5	41.4	2.7
1/29/2008	1 leachate		7.0	94	19.6	4.6	251.0	0.0	0.0					
1/29/2008	BW before UV	1.7	6.7	-56	17.3	0.7	46.3	1.0	0.0		24.3	115.3	37.1	3.1
1/29/2008	BW-UV	3.4	6.9	11	19.3	0.8	45.7	0.4	0.0					
1/29/2008	1 leachate		7.1	175	20.1	6.1	292.5	0.0	0.0					

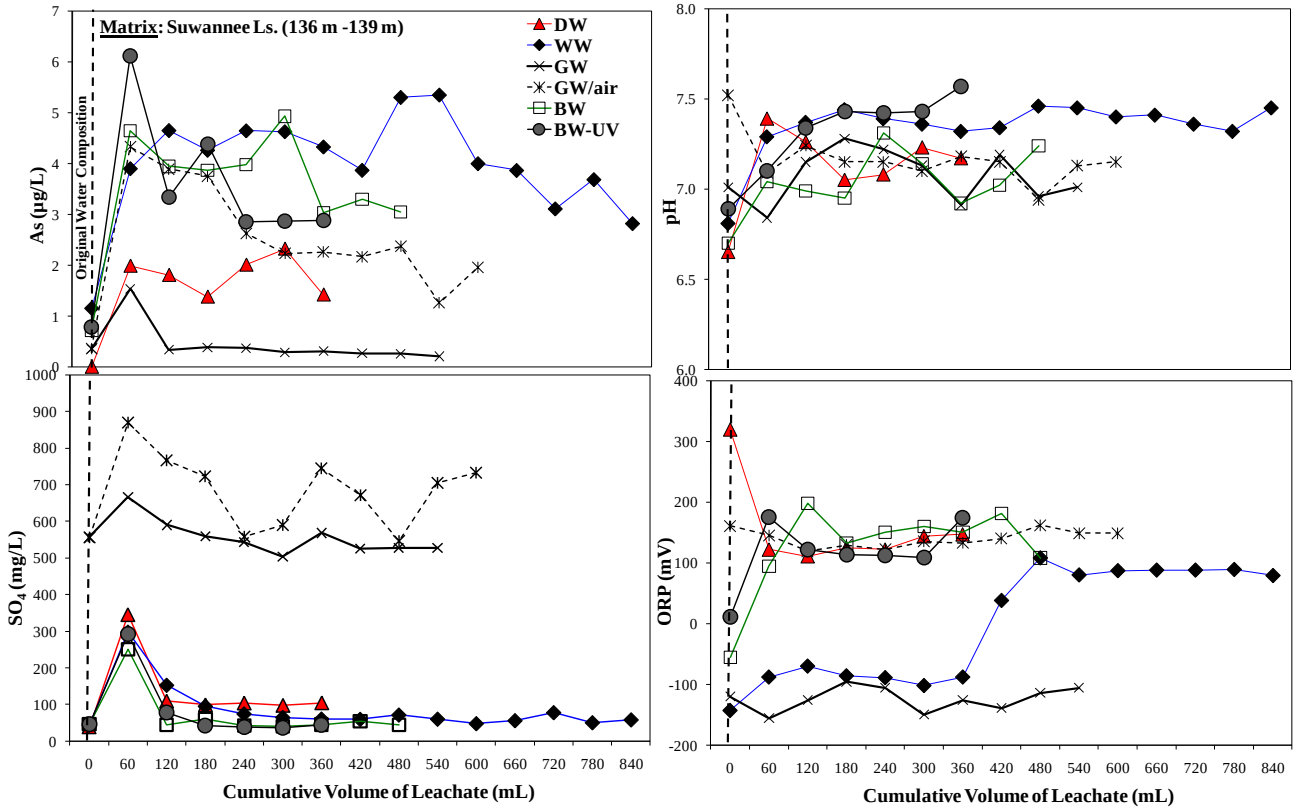

Figure 37. As, SO_4, pH, and ORP in leachates recovered from the Suwannee Limestone (136 m to 139 m) using 0.3 m columns.

Note: DW: drinking water; WW: wetland water; GW: groundwater; GW w/air: groundwater saturated with air; BW and BW-UV: untreated and UV treated filter basin water.

groundwater, resulting in a possible As mobilization. Generally during the experiment, the ORP was negative, confirming the reducing conditions of GW preserved in the amber carboy. The introduction of the same GW treated with air had a significant effect on the oxidation of pyrite with As values up to 3 times higher than the untreated GW, clearly indicating the important role of DO. Overall, 27 µg of As were recovered in leachates after the injection of aerated GW. The introduction of DW caused about 2 times less leaching of As (11 µg) than the GW saturated with air, which could be due to 5.5 times lower concentration of DO detected in the DW.

In a summary, the concentration of As in leachates arranged from highest to lowest was arranged as: ***BW-UV > BW > GW/air > WW >DW > GW***

(171 m to 174 m)

The lithological composition of the Suwannee Limestone from the 171 m to 174 m interval consisted of limestone and dolostone mixed with minor quartz, pyrite, clays, and phosphate grains (Table 13). During the leaching experiments, drinking (DW), wetland (WW), and groundwater (GW) were injected into 1 m columns (Appendix F, Table 15, Figure 38). These experiments were performed to compare the leaching of As from a different interval of the same stratigraphic unit using longer column. The columns contained from 440.4 g to 441.0 g of sediment with an average porosity of 22.6 %. The study confirmed that the injection of WW caused the highest release of As with concentrations of up to 19.4 µg/L exceeding the As drinking water standard (DWS) of 10 µg/L (EPA, 2009) (Figures 38 - 39). During the first 8 hours of experiment, the concentration of As was increasing with time to 14.8 µg/L. The pH level changed from

Table 15. Initial water (before injection) and leachate recovered from 1 m columns filled with the Suwannee Limestone (171 to 174 m) using different types of water.

Date	Sample	DO	pH	ORP	T	As	SO_4	Fe(II)	H_2S	Leaching column details	n	m(s)	m(w)	s/w
		mg/L		mV	°C	µg/L	mg/L	mg/L	µg/L		%	g	g	
2/12/2008	DW-1	5.0	7.0	223	22.9	0.1	58.1	0.0	0.0		19.7	440.4	108.2	4.1
2/12/2008	1 leachate		7.7	107	21.1	8.1	491.6	0.0	0.0					
3/11/2008	WW - 1	0.4	6.8	-143	18.0	1.2	43.4	0.1	3.0		25.6	441.0	151.5	2.9
3/11/2008	1 leachate		8.1	96	21.3	9.0	511.1	0.0	0.0					
6/6/2006	GW -1	1.6	7.2	-19	27.7	1.1	524.2	0.4	0.1		no data			
6/6/2006	1 leachate		10.8	-35	22.5	0.2	207.0	0.1	0.0					

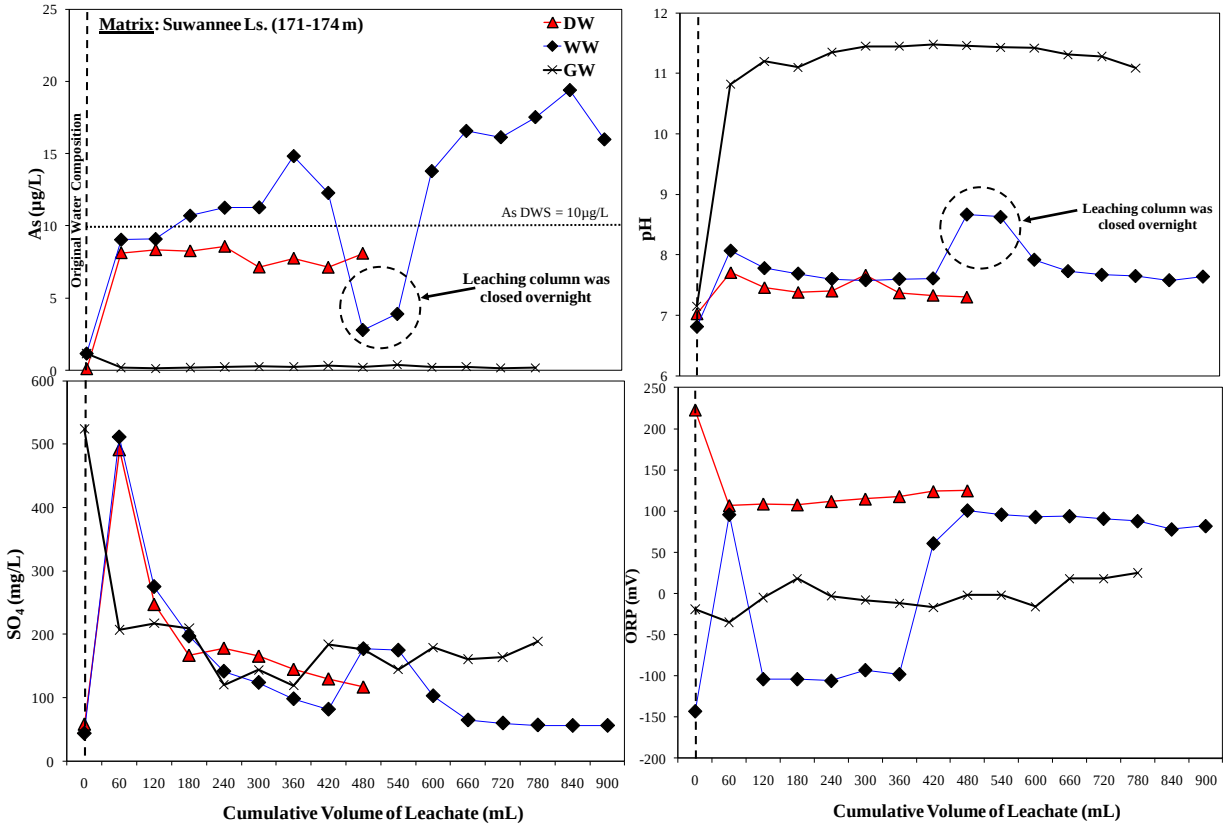

Figure 38. As, SO_4, pH, and ORP in leachates recovered from the Suwannee Limestone (171 m to 176 m) using 1 m columns.

Note: DW: drinking water; WW: wetland water; GW: groundwater; DWS: Drinking Water Standard..

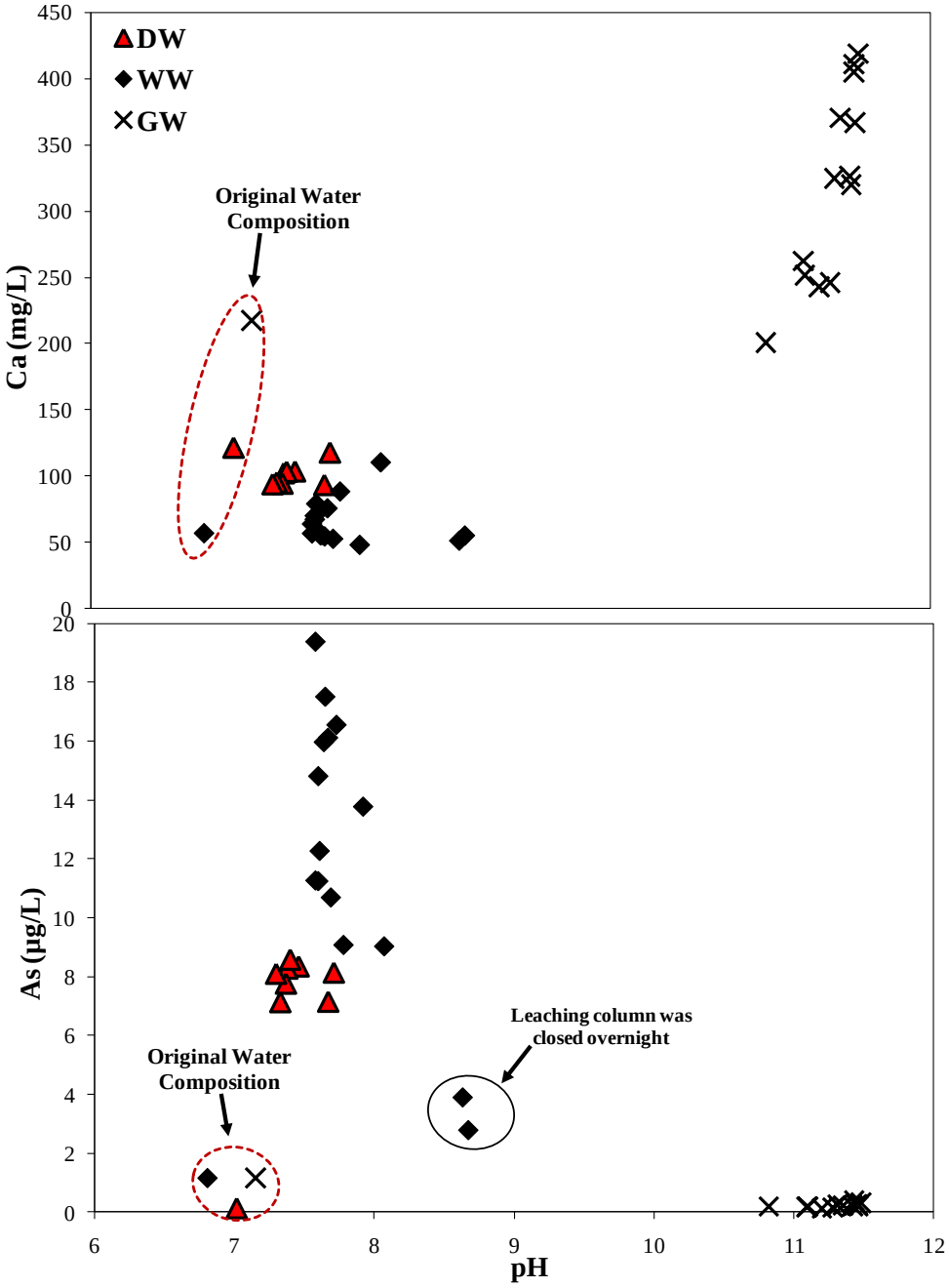

Figure 39. Distribution of Ca versus pH (top) and As versus pH (bottom) in leachates recovered from the Suwannee Limestone (171 m to 176 m) using 1 m columns.

Note: DW: drinking water; WW: wetland water; GW: groundwater.

6.8 to 8.1. The ORP in first leachate increased from -143 V to 96 mV and decreased back to -106 mV, confirming the reducing conditions of the WW preserved in the amber carboy. At the end of first day, the leaching column was closed overnight and the experiment was restarted next morning. On the second day of experiment, the first and second leachates had higher pH (up to 8.7), positive ORP and the As values < 4µg/L, possibly indicating As sorption to neo-formed HFO and co-deposition in limestone matrix. Subsequently, pH level dropped to 7.6 and As concentration in leachates increased to up to 20 µg/L. Previous studies showed that arsenite exhibits a strong affinity and great sorption capacity for ferrihydrite and goethite (Manning et al., 1998). This process is pH-dependent with an adsorption envelope at pH 8 to 9 (Manning et al., 1998) (Figure 39). In total, about 186 µg of As were recovered using the WW injectant.

The injection of DW demonstrated the leaching of As from the column with concentrations of up to 8.1 µg/L. The ORP in first leachate declined from 223 mV to 107 mV due to consumption of oxygen for pyrite oxidation. Overall, about 63 µg of As were recovered from a column using DW.

Native GW from the Floridan Aquifer was injected into a column for 2 days. The experiment was not interrupted overnight; however the injection rate was changed from 2 to 0.2 mL/min. Groundwater did not cause the oxidation of pyrite and leaching of As. Moreover, the concentration of As in leachates was 2.5 times less than the initial water (< 0.4 µg/L). After the injection, pH values in leachates increased from 7.2 to 11.5 due to the presence of dolomite (Figure 39). Generally, the ORP was negative, confirming the reducing conditions of GW preserved in the amber carboy.

In a summary, the concentration of As in leachates arranged from highest to lowest was arranged as: ***WW > DW > GW.***

3.3.2.2. Ocala Limestone

(195 m to 199 m)

The lithological composition of the Ocala Limestone from the 195 m to 199 m interval consisted of a white dolomitized fossiliferous limestone, poorly to moderately indurated with minor quartz, and pyrite (Table 13). During the leaching experiments, drinking water (DW), wetland water (WW), groundwater (GW), untreated (BW) and UV treated filter basin waters (BW-UV) were injected into 0.3 m columns (Appendix F, Table 16, Figure 40). The columns contained from 118.5 to 128.7 g of sediment with an average porosity of 25.9 %. The study demonstrated that the injection of BW and BW-UV caused the highest release of As with concentrations of up to 35.6 µg/L and 23.6 µg/L, respectively. In total, about 163 µg of As were recovered from the BW and 128 µg of As – from the BW-UV (Figure 40).

The leaching of As from the injection of WW was up to 23.6 µg/L behaving similarly to the BW-UV injectant. Even though the oxidation-reduction potential of the system remained under reducing conditions, the mobilization of As from the aquifer matrix was higher than from the DW. Overall, 134 µg of As was leached during the injection of WW. The concentration of As in leachates from the injection of DW was up to 17.1 µg/L. Overall, about 50 µg of As were recovered using the DW.

The injection of GW from the Floridan Aquifer showed that As was up to 2.8 µg/L in the first leachate and dropped to < 0.1 µg/L at the end of experiment. Similarly to

Table 16. Initial water (before injection) and leachate quality recovered from 0.3 m columns filled with the Ocala Limestone (195 to 199 m) using different types of water.

Date	Sample	DO	pH	ORP	T	As	SO_4	Fe(II)	H_2S	Leaching column details	n	m(s)	m(w)	s/w
		mg/L		mV	°C	µg/L	mg/L	mg/L	mg/L		%	g	g	
1/25/2007	DW	5.0	7.0	268	22.5	0.3	11.9	0.0	0.0		27.1	121.1	45.1	2.7
1/25/2007	1 leachate		7.4	182	21.2	17.1	275.2	0.0	0.0					
3/11/2008	WW	0.4	6.8	-143	18.0	1.2	43.4	0.1	3.0		25.4	123.4	42.1	2.9
3/11/2008	1 leachate		7.4	-95	20.8	23.6	124.6	0.0	0.5					
2/11/2008	GW		7.0	-120	26.1	0.4	556.4	0.6	0.2		27.2	118.5	44.3	2.7
2/11/2008	1 leachate	1.2	7.2	138	18.5	2.8	688.9	0.0	0.0					
1/29/2008	BW	1.7	6.7	-56	17.3	0.7	46.3	1.0	1.0		25.2	128.7	43.4	3.0
1/29/2008	1 leachate		7.2	82	19.6	35.6	153.3	0.0	7.0					
1/29/2008	BW before UV	1.7	6.7	-56	17.3	0.7	46.3	1.0	0.0		24.7	127.6	41.9	3.0
1/29/2008	BW-UV	3.4	6.9	11	19.3	0.8	45.7	0.4	0.0					
1/29/2008	1 leachate		6.6	102	19.6	23.6	153.7	0.0	2.0					

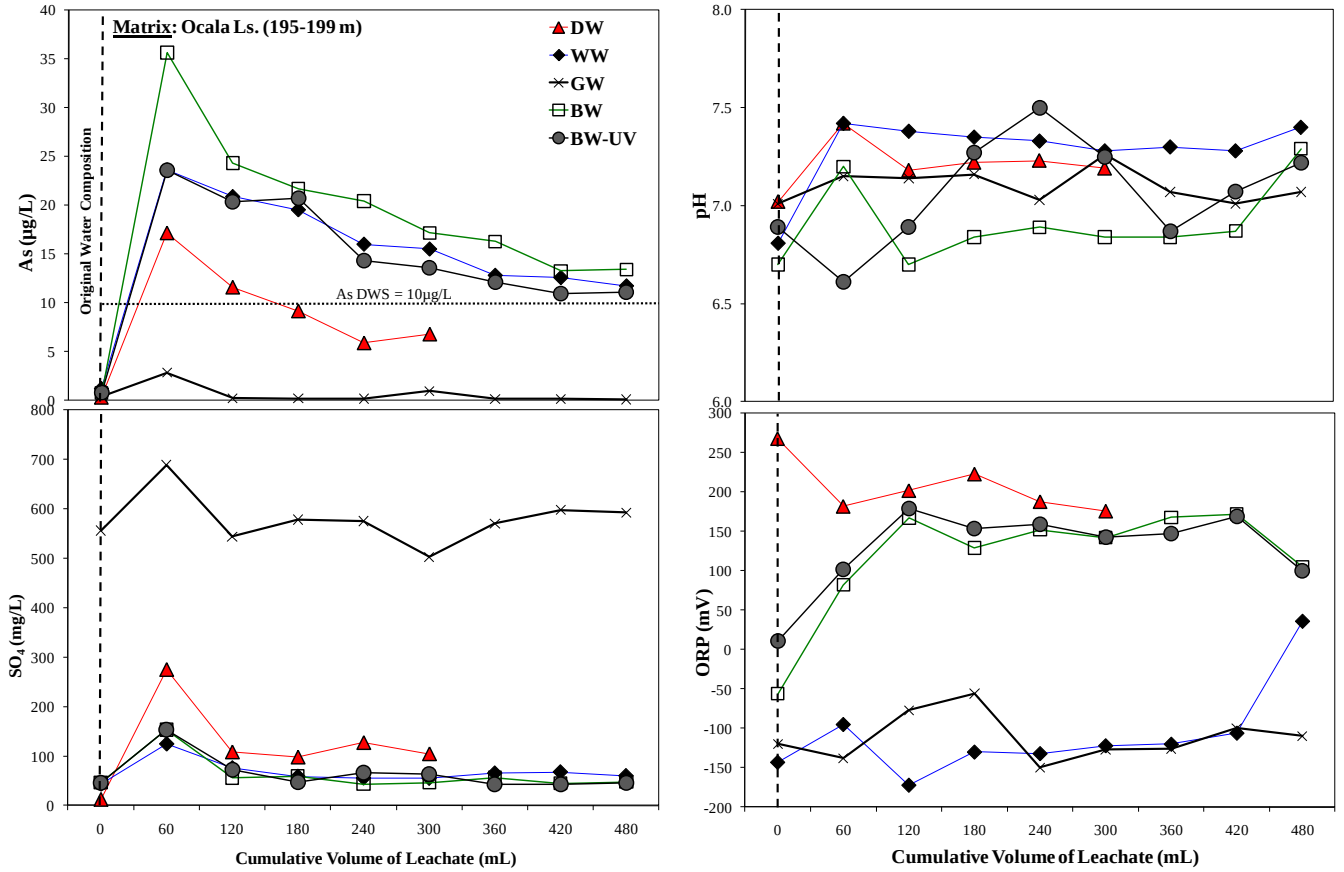

Figure 40. As, SO_4, pH, and ORP in leachates recovered from the Ocala Limestone (195 to 199 m) using 0.3 m columns.

Note: DW: drinking water; WW: wetland water; GW: groundwater; BW and BW-UV: untreated and UV treated filter basin waters

the column filled with the Suwannee Limestone (136 m to 139 m), the first peak of As could be due to a possible micro-oxidation of pyrite surface and formation of a ferrous sulfate phase, such as szomolnokite ($FeSO_4 \bullet H_2O$) prior to the experiment (Costagliola et al., 1997) resulting in a potential release of As. The pH values in all leachates ranged from 6.9 to 7.5. Generally during the experiment, the ORP was negative, confirming the reducing conditions of GW preserved in the amber carboy.

In a summary, the concentration of As in leachates arranged from highest to lowest was arranged as: ***BW > BW-UV = WW > DW > GW.***

3.3.2.3. Avon Park Formation

(255 m to 257 m)

The lithological composition of the Avon Park Formation from the 255 m to 257 m interval consisted of limestone – sucrosic dolostone matrix with minor mineral phases, such as pyrite, gypsum and quartz (Table 13). During the leaching experiments, drinking water (DW), untreated (WW) and UV treated wetland water (WW-UV), untreated (GW) and aerated groundwater (GW/air), untreated (BW) and UV treated filter basin waters (BW-UV) were injected into 0.3 m columns (Appendix F, Table 17, Figure 41). The columns contained from 157.3 g to 186.4 g of sediment with average porosity of 16.8 %. Similarly to the Ocala and Suwannee Limestones (136 m to 139 m interval), the injection of BW and BW-UV caused the highest release of As with concentrations of up to 65.5 µg/L and 56.2 µg/L, respectively (Figure 41). Those values were 6.5 and 5.6 times higher than the As maximum contaminant level for DW (EPA, 2009). In total, about 246 µg and 174 µg of As were recovered using the BW and BW-UV, respectively.

The injection of WW caused the mobilization of As to up to 47.1 µg/L. At the same time, the introduction of WW-UV resulted in As leaching to up to 35.3 µg/L. Overall, about 198 µg and 131 µg of As were leached out from the columns during the injection of WW and WW-UV. The pH values in all leachates ranged from 6.4 to 7.5. During both experiments, the ORP of the system changed from reducing to oxidizing. Figures 42 - 44 demonstrated the effect of the UV radiation on the concentration of As, DO, ORP, dissolved organic carbon (DOC), total nitrogen (N) and total/fecal coliform. Generally, total and fecal coliform were present in the WW and BW. After UV treatment, however, fecal coliform was absent, but total coliform was 1 ct/100 mL in both types of water. The DO and ORP significantly increased after UV treatment due to formation of oxygen radicals and other by-products such as trace ozone (Masschelein, 2002) changing the redox state of water from reducing to oxidizing. As a result, the level of As in leachate increased after UV treatment. The concentration of DOC did not change.

In addition, the injection of DW into two columns of 0.3 m and 0.5 m was performed for a period of 4 months at a 3-week sampling interval. The water was injected in the columns on July 18, 2006 for about 5 hours. Analyses showed that As in first leachates was up to 26.2 µg/L (DW-0.3) and 35.3 µg/L (DW-0.5), respectively (Figure 45). Distribution of As in both columns revealed a similar pattern. The concentration of SO_4 increased dramatically from 58 mg/L to 679 mg/L (DW-0.3) and 1051 mg/L (DW-0.5), respectively. The pH levels increased from 6.9 to 7.7 (DW-0.3) and 7.9 (DW-0.5), while ORP declined from 223 mV to 175 mV (DW-0.3) and 148 mV (DW-0.5) due to consumption of oxygen for pyrite oxidation. At the end of the day, the experiments were stopped and the columns saturated with the DW were sealed. Subsequently, the tests were

Table 17 . Initial water (before injection) and leachate recovered from 0.3 m columns filled with the Avon Park Formation (255 m to 257 m) using different types of water.

Date	Sample	DO	pH	ORP	T	As	SO_4	Fe(II)	H_2S	Leaching column details	n	m(s)	m(w)	s/w
		mg/L		mV	°C	µg/L	mg/L	mg/L	mg/L		%	g	g	
7/18/2006	DW	5.0	6.9	223	22.3	0.1	58.1	0.0	0.0		12.9	186.4	27.6	6.8
7/18/2006	1 leachate		7.7	175	22.3	26.2	678.5	0.0	0.0					
4/4/2006	WW	0.1	6.9	-82	20.5	0.6	69.6	0.1	0.3		17.8	167.7	36.3	4.6
4/4/2006	1 leachate		7.0	141	21.1	47.1	439.8	0.0	0.0					
5/1/2007	WW before UV	0.2		-145	22.8	0.6	55.1	0.1	2.8		18.1	167.7	37.0	4.5
5/1/2007	WW-UV	4.6	6.9	-67	24.1	1.0	54.4	0.0	0.0					
5/1/2007	1 leachate			136	20.4	35.3	334.7	0.0	0.0					
2/11/2008	GW	1.2	7.0	-120	26.1	0.4	556.4	0.6	0.2		16.1	161.1	30.9	5.2
2/11/2008	1 leachate		6.8	131	19.2	4.2	776.4	0.0	0.0					
2/13/2008	GW air	7.6	7.5	161	20.3	0.4	556.4	0.0	0.0		16.7	159.8	32.0	5.0
2/13/2008	1 leachate		7.1	139	21.1	40.7	1246.9	0.0	0.0					
1/23/2007	BW	1.3	6.7	-38	20.3	0.8	62.0	0.9	0.1		18.7	157.3	36.2	4.3
1/23/2007	1 leachate		7.3	124	20.4	65.5	1144.8	0.0	0.0					
5/4/2007	BW before UV	1.3	6.4	-35	23.5	0.4	65.1	0.7	0.0		17.4	167.6	35.3	4.7
5/4/2007	BW-UV	4.7	6.6	7	25.1	0.3	70.5	0.4	0.0					
5/4/2007	1 leachate		7.5	64	22.9	56.2	537.0	0.0	0.0					

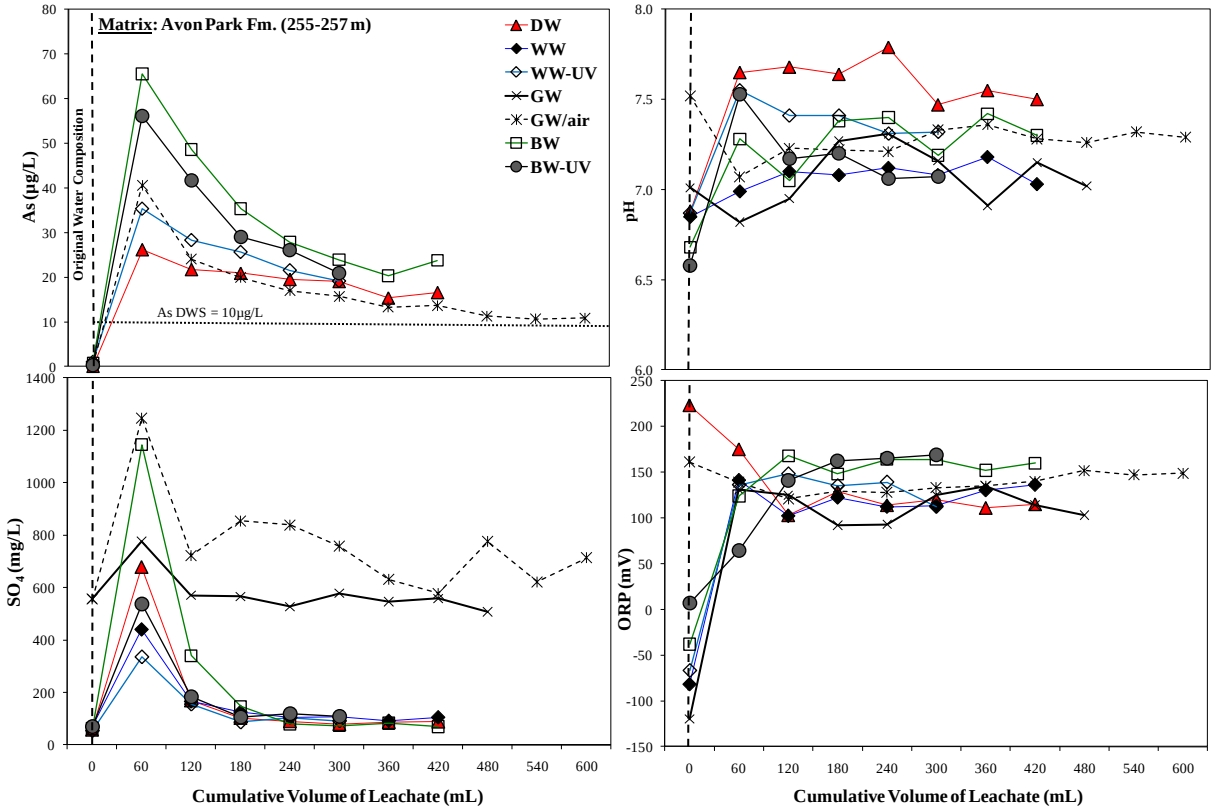

Figure 41. As, SO_4, pH, and ORP in leachates recovered from the Avon Park Formation (255 m to 257 m) using 0.3 m columns.

Note: DW: drinking water; WW and WW-UV: wetland water untreated and treated with UV; GW and GW/air: groundwater untreated and treated with air; BW and BW-UV: filter basin water untreated and treated with UV.

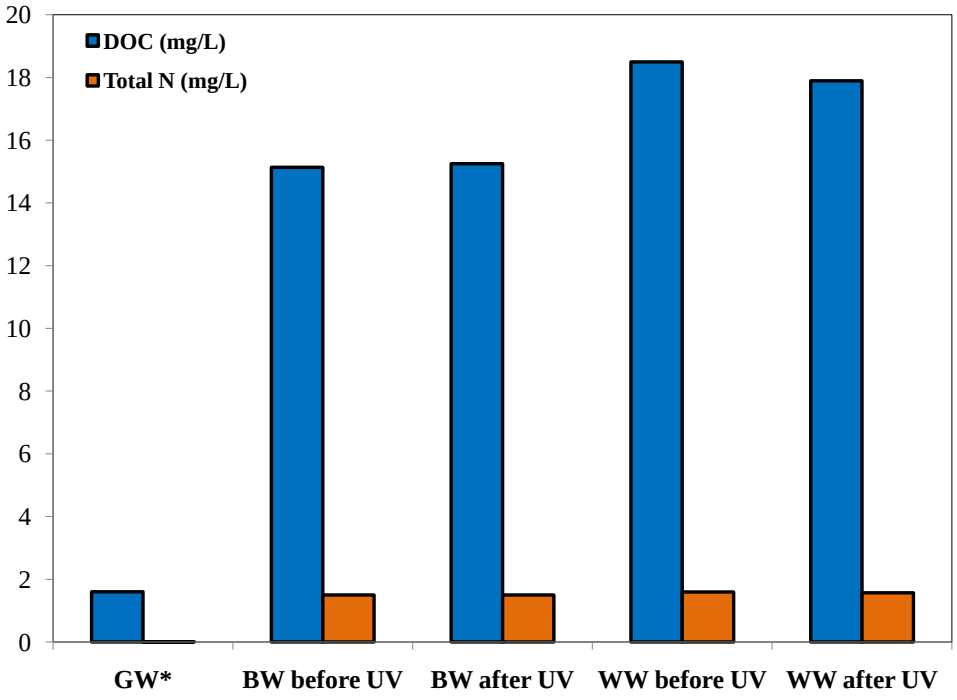

Figure 42. Dissolved organic carbon (DOC) and total nitrogen (TN) in the groundwater (GW), wetland (WW) and filter basin water (BW) before and after UV.

Note: GW* - data for the Upper Floridan Aquifer ROMP 45 from Sacks and Tihansky (1996).

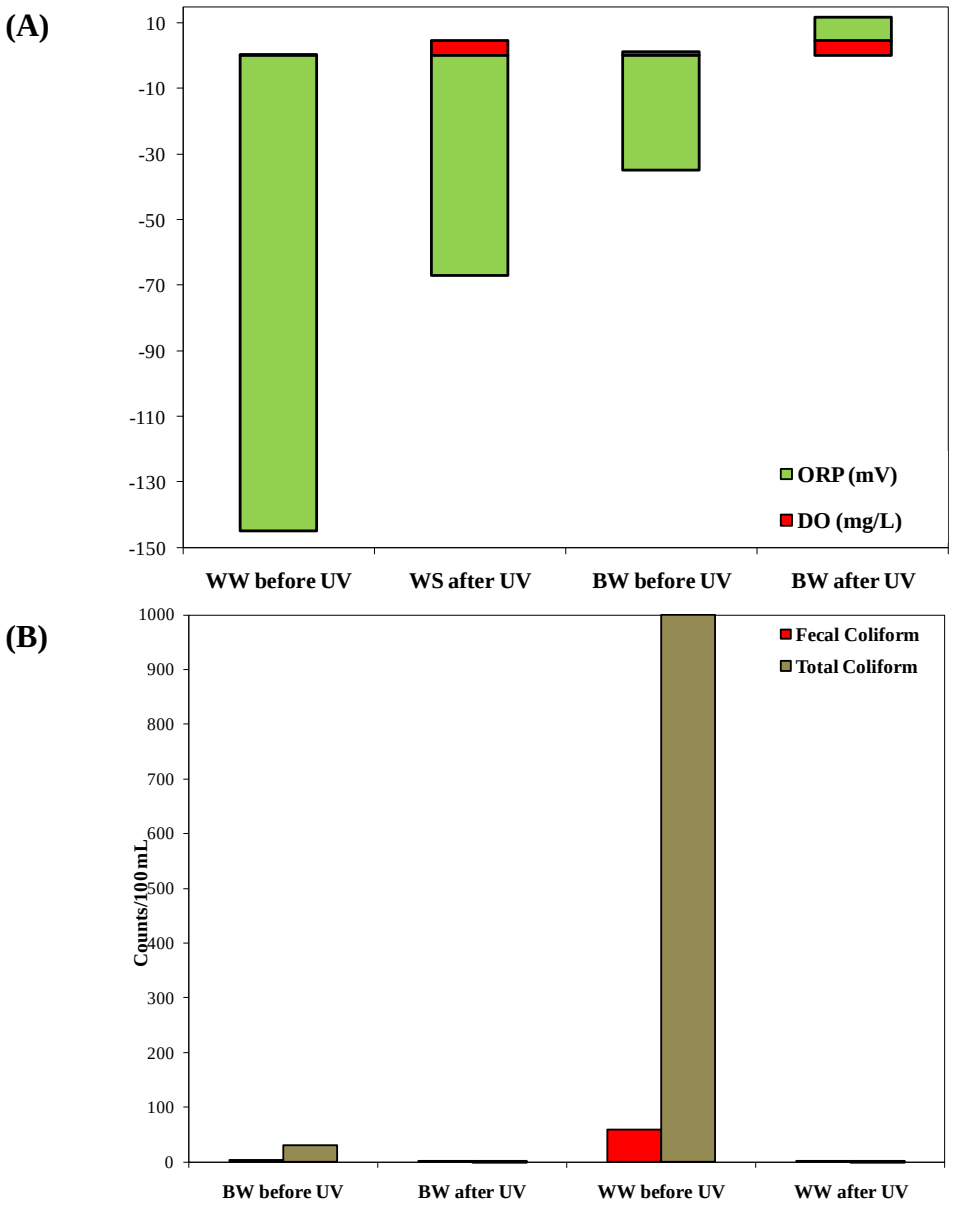

Figure 43. (A) Dissolved oxygen (DO) and oxidation-reduction potential (ORP); and (B) Fecal and total coliform of the wetland (WW) and filter basin water (BW) before and after UV.

Note: diagram (B) clearly represents a great value of the filter basin treatment.

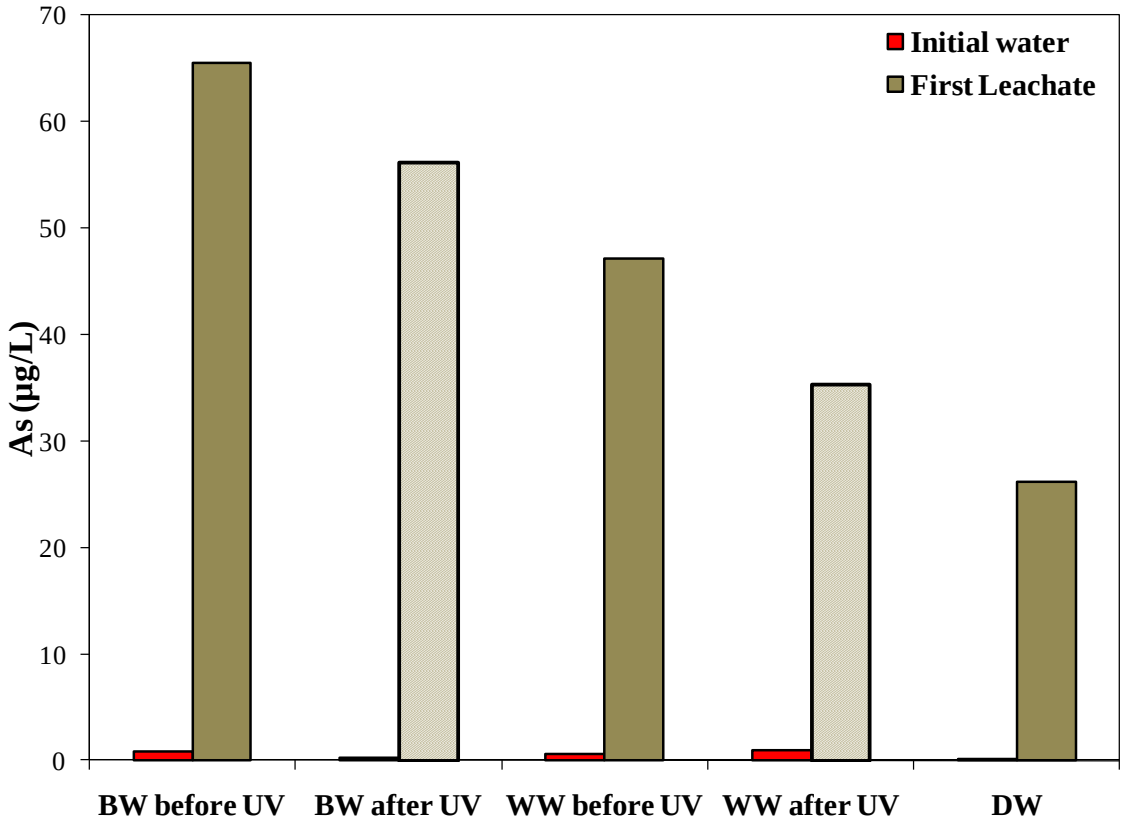

Figure 44. Arsenic (As) in the initial water and first leachate recovered from the Avon Park Formation (255 m to 257 m) using wetland (WW) and filter basin water (BW) before and after UV, and drinking water (DW).

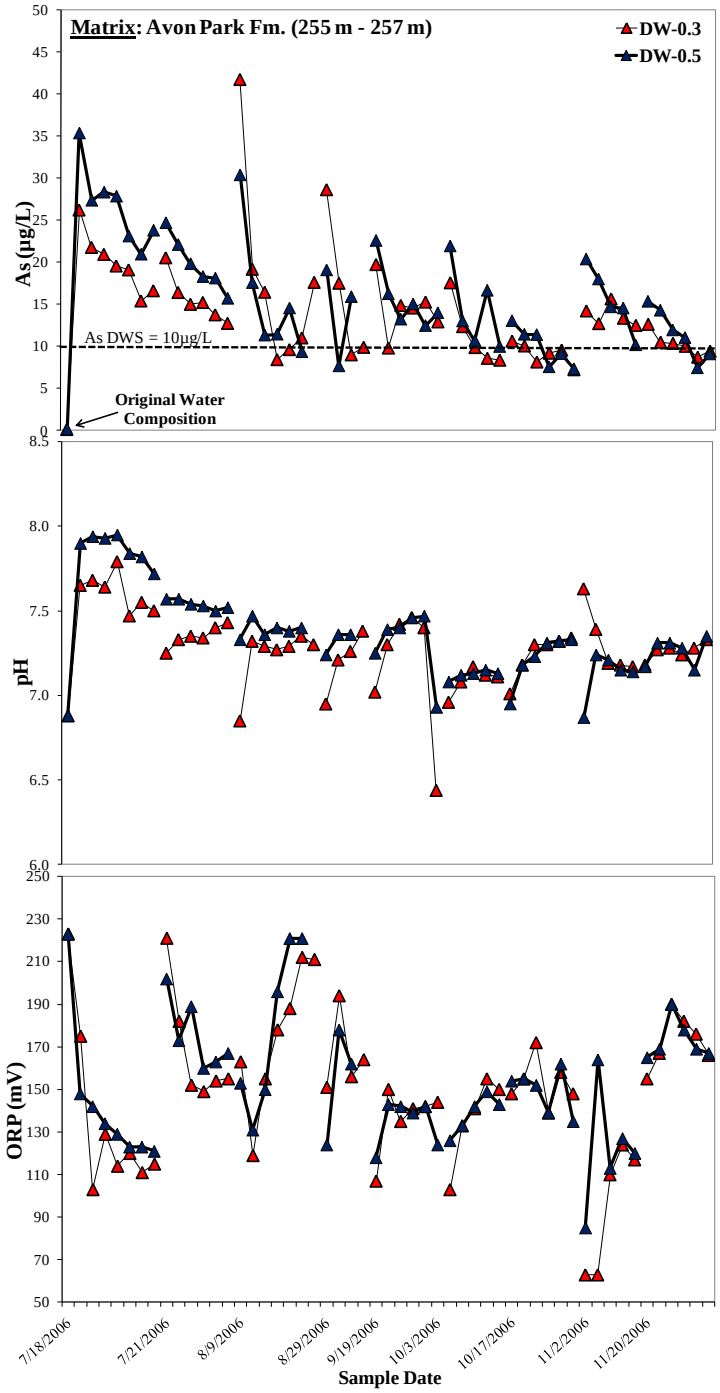

Figure 45. Arsenic, pH and ORP in leachates recovered from the Avon Park Formation (255 m to 257 m) using drinking water (0.3 m and 0.5 m columns) for a period of four months at three weeks interval.

restarted on July 21, August 9 and 29, September 19, October 3 and 17, November 2 and 20. Generally, the leachates taken at the beginning of each experiment had the highest peaks of As and lowest ORP due to the extended time of water-rock interaction in the columns. After 4 months of experiments, the concentration of As in both columns decreased to < 10 µg/L. In total, about 750 µg of As was recovered from a 0.3 column and 815 µg of As - from a 0.5 m column. Therefore, based on the calculated molar ratio As/FeS_2, the amount of FeS_2 dissolved from 0.3 and 0.5 m columns was 121.4 mg/kg and 131.8 mg/kg, respectively. These values are about 6 times less than total amount of pyrite present in the columns (Table 13). The significant difference could be due to As co-precipitation with HFO formed during the water-rock interaction, which were visually observed during the experiments.

In addition to the experiments above, the 4-day injection sequence of the BW and DW was performed in a 0.3 m column. This procedure was necessary to evaluate and compare the concentration of total As and arsenite/arsenate (As (III)/As (V)) species from the same column by two types of water. During the 1-day injection of BW, the concentration of As in varied from 59.3 µg/L to 23.8 µg/L (Figure 46). The concentration of SO_4 increased from 44 mg/L to 757 mg/L and subsequently dropped to 80 mg/L. Similar distribution of SO_4 and As confirmed the dissolution of pyrite. During the 2-day injection of DW, the concentration of As changed from 66.8 µg/L to 13.8 µg/L. During the 3-day injection of BW, As values ranged from 35.4 µg/L to 16.7 µg/L. During the 4-day injection of DW, the concentration of As changed from 28.9 µg/L to 7.7 µg/L. The speciation of As showed that it was predominantly present as As(V) which is common under oxidizing conditions. This experiment clearly showed that As concentration in

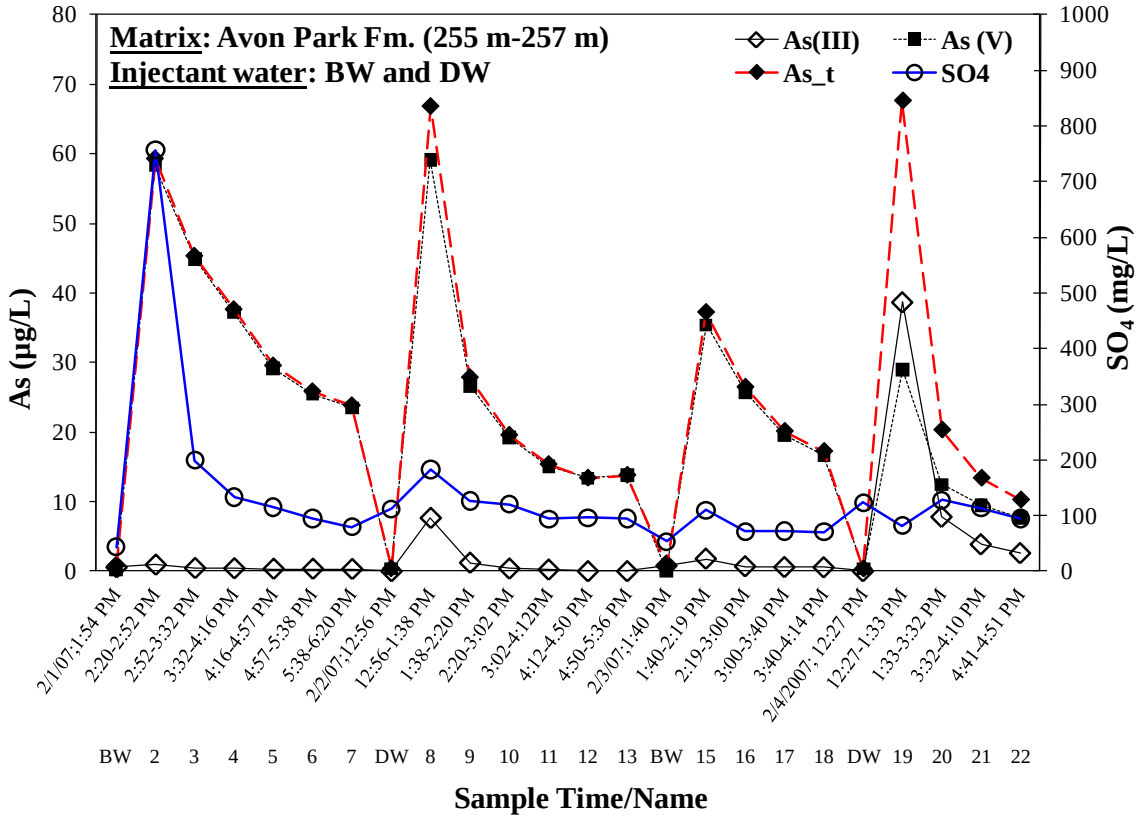

Figure 46. Distribution of SO_4, As species and As total concentrations in leachates recovered from the Avon Park Formation (255 m to 257 m) from the consecutive injection of filter basin (BW) and drinking (DW) waters into a 0.3 m column.

leachates from BW was generally higher than from DW even though it was initially more reducing. In total, about 593 µg of As were recovered from the column.

The injection of GW from the Floridan Aquifer demonstrated that As was up to 4.3 µg/L in the first leachate and dropped to 0.1 µg/L at the end of experiment (Figure 41). Similarly to the experiments above, the first peak could be due to a possible micro-oxidation of pyrite surface to a ferrous sulfate phase before the experiment resulting in release of As. The introduction of the same GW saturated with air had a tremendous effect on the oxidation of pyrite with As values 10 times higher than the untreated water clearly indication the important role of DO.

In a summary, the concentration of As in leachates arranged from highest to lowest was arranged as: ***BW > BW-UV > WW > GW air > WW-UV > DW > GW.***

(260 m to 261 m)

The lithological composition of the Avon Park Formation from the 260 m to 261 m interval was dolostone dominated with a presence of limestone, minor framboidal pyrite, and gypsum (Table 13). During the leaching experiments, drinking (DW), wetland (WW), filter basin (BW), and groundwaters (GW) were injected into 0.3 m columns (Appendix F, Table 18, Figure 47). The columns contained from 146.6 g to 183.1 g of sediment with average porosity of 18.2 %. Similarly to the Suwannee Limestone (interval 171 m to- 174 m), the highest concentration of As was detected after the injection of WW ranging between 28.8 µg/L to 66.9 µg/L after about 8 hours of experiment. The leaching of As from the column was progressive throughout the experiment (Figure 47 - 48). The pH changed from 6.6 to 7.5. The OPR ranged between -214 mV to -90 mV confirming

the reducing conditions of the system. Overall, 452 µg of As were recovered from the WW injectant. To evaluate the potential difference in mobilization of As, WW was filtered in-situ through a 0.2 µm membrane filter in order to eliminate particulate matter and reduce or remove present microorganisms. The experiment showed that in contrast to the unfiltered WW, filtration resulted in a reduction of As from 30.0 µg/L to 16.4 µg/L (Figure 47). These results clearly demonstrated the important role of microorganisms on the stability and surface reactivity of pyrite. Overall, about 91 µg of As were recovered from this experiment.

The injection of DW caused the mobilization of As of up to 9.0 µg/L, which was 7.5 - 9 times lower than from the WW. The concentration of SO_4 in leachates from DW increased to 1199 mg/L. The ORP in first leachates declined from 320 mV to 1 mV, likely due to the oxidation of pyrite and formation of HFO which were visually observed during the experiments. Overall, 55 µg of As were recovered from the DW.

The leaching of As from the BW showed a comparable behavior to the injection of DW. Generally, the concentration of As in leachates was < 8 µg/L, while the concentration of SO_4 was up to 1553 mg/L. However, after about 6 hours of the experiment the concentration of As reached up to 29.1 µg/L. This could be due to trapping of oxygen during the water pumping and the following oxidation of water in carboys. In total, about 124 µg of As were leached during the injection of BW. In a contrast to the WW, the injection of DW, BW, and GW caused the pH levels to increase from 6.5 to 10.8 due to the dissolution of dolomite (Figure 48).

As expected, the groundwater from the Floridan Aquifer caused minor to no mobilization of As from the aquifer matrix. The concentration of As in first leachate was

Table 18. Initial water (before injection) and leachate recovered from 0.3 m columns filled with the Avon Park Formation (260 m to 261 m) using different types of water.

Date	Sample	DO	pH	ORP	T	As	SO_4	Fe(II)	H_2S	Leaching column details	n	m(s)	m(w)	s/w
		mg/L		mV	°C	µg/L	mg/L	mg/L	mg/L		%	g	g	
10/24/2006	DW	2.9	6.7	320	21.2	0.0	39.0	0.0	0.0		16.6	183.1	36.5	5.0
10/24/2006	1 leachate		10.8	1	20.3	7.8	1199.1	0.2	0.0					
4/9/2006	WW	0.8	6.6	-214	22.9	0.0	21.7	0.1	8.3		18.3	146.6	32.8	4.5
4/9/2007	1 leachate		7.4	-125	23.1	28.8	917.1	0.0	0.5					
5/8/2008	WW_filt_0.2um	0.5	6.8	-200	24.1	0.0	27.6	0.2	3.8		16.4	147.3	28.9	5.1
5/8/2008	1 leachate		7.5	45	21.3	16.4	1402.9	0.0	0.1					
10/19/2006	GW	1.6	6.8	-108	26.5	0.1	522.4	2.0	0.1		16.1	183.0	35.7	5.1
10/19/2006	1 leachate		10.1	-25	23.4	1.4	2054.2	0.2	0.0					
11/15/2006	BW	1.0	6.5	-66	24.9	0.5	39.5	1.0	0.0		23.6	170.0	52.6	3.2
11/15/2006	1 leachate		9.4	-20	23.2	6.7	1553.2	0.2	0.0					

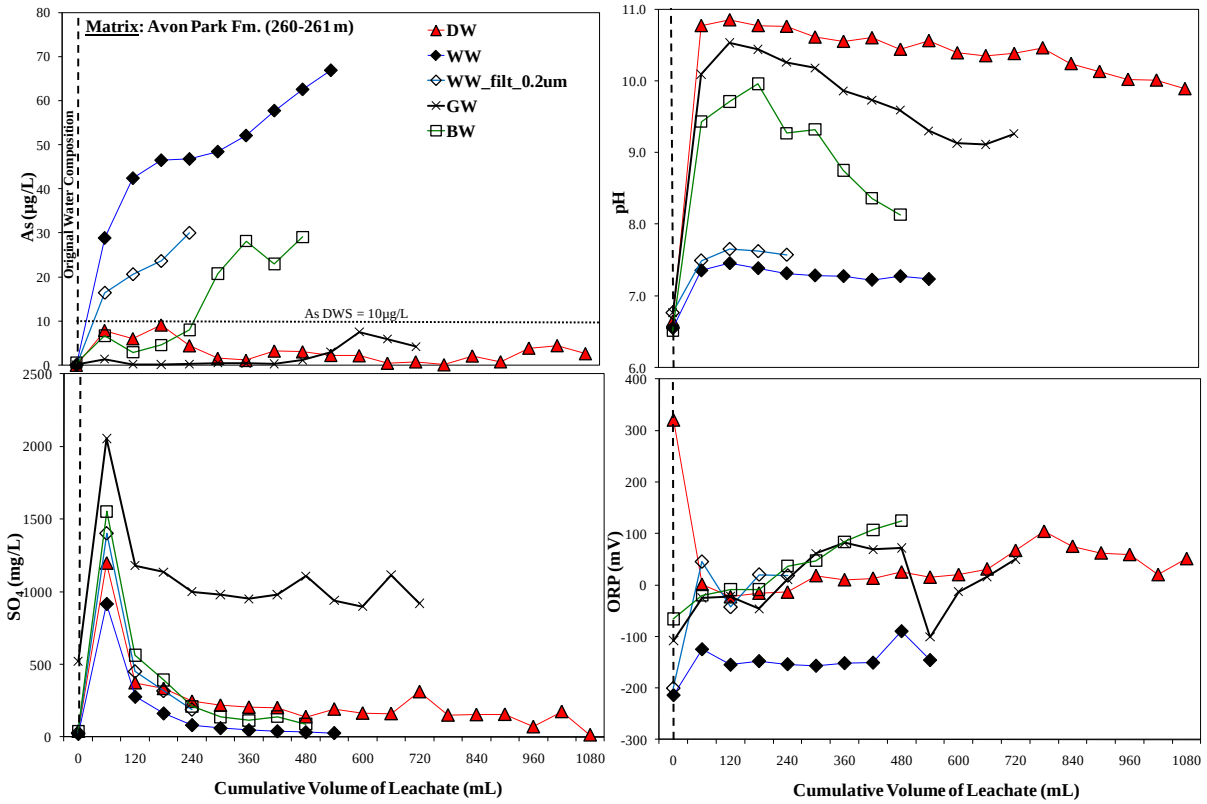

Figure 47. As, SO_4, pH, and ORP in leachates recovered from the Avon Park Formation (260 m to 261 m) using 0.3 m columns.

Note: DW: drinking water; WW: wetland water; WW_filt_0.2um: wetland water filtered in-situ through 0.2 um membrane; GW: groundwater; BW: filter basin water.

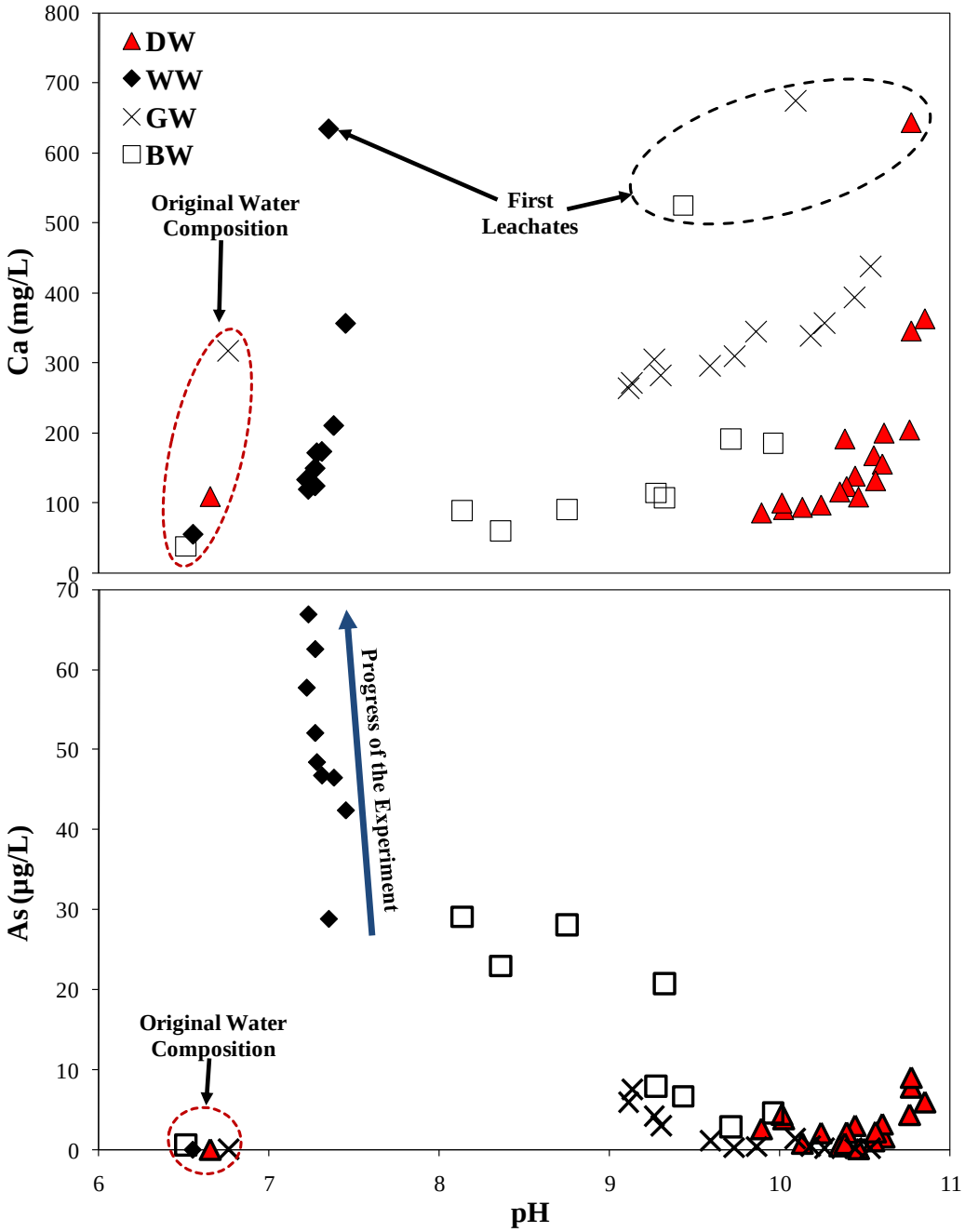

Figure 48. Distribution of Ca versus pH (top) and As versus pH (bottom) in leachates recovered from the Avon Park Formation (260 m to 261 m) using 0.3 m columns.

Note: DW: drinking water; WW: wetland water; GW: groundwater; BW: filter basin water; Original water composition and first recovered leachates were highlighted in red and black; respectively.

1.4 µg/L and dropped to < 0.5 µg/L within 5 hours of the experiment.

In a summary, the concentration of As in leachates arranged from highest to lowest was arranged as: ***WW > WW_filt_0.2um > DW > BW > GW.***

3.4. Discussion

A multitude of scientific publications reported that the oxidative dissolution of pyrite was a principal mechanism responsible for the release of arsenic (As) during aquifer storage and recovery (ASR) (Arthur et al., 2007; Arthur et al., 2005; Pichler et al., 2004; Arthur et al., 2002; Williams et al., 2002; Arthur et al., 2001; de Ruiter and Stuyfzand, 1998). The bench-scale leaching tests of this study were intended to simulate the ASR process in a laboratory and provide insights important to the future of ASR in Florida and potentially worldwide. The experiments showed that the amount of As released from the Upper Floridan Aquifer (UFA) was not perfectly correlated with the bulk rock As concentration (Figures 35 and 49). The highest level of As was leached out from the Avon Park Formation and the lowest – from the Suwannee Limestone, although the Ocala Limestone had the lowest bulk rock As. This conclusion corresponded to the work by Arthur et al. (2007) who performed bench-scale leaching experiments and the sequential extraction of As, Mo, and Sb from the lithostratigrafic units of the UFA. This study demonstrated that the highest fraction of As was extracted from the Hawthorn Group, following by the Suwannee Limestone, Avon Park Formation, and the Ocala Limestone. Most of the As in all units was associated with sulfides (i.e., pyrites), although, organic matter, hydrous ferric oxides (HFO), and carbonates could also contribute to the bulk rock As (Arthur et al., 2007). The trend of As leaching from the

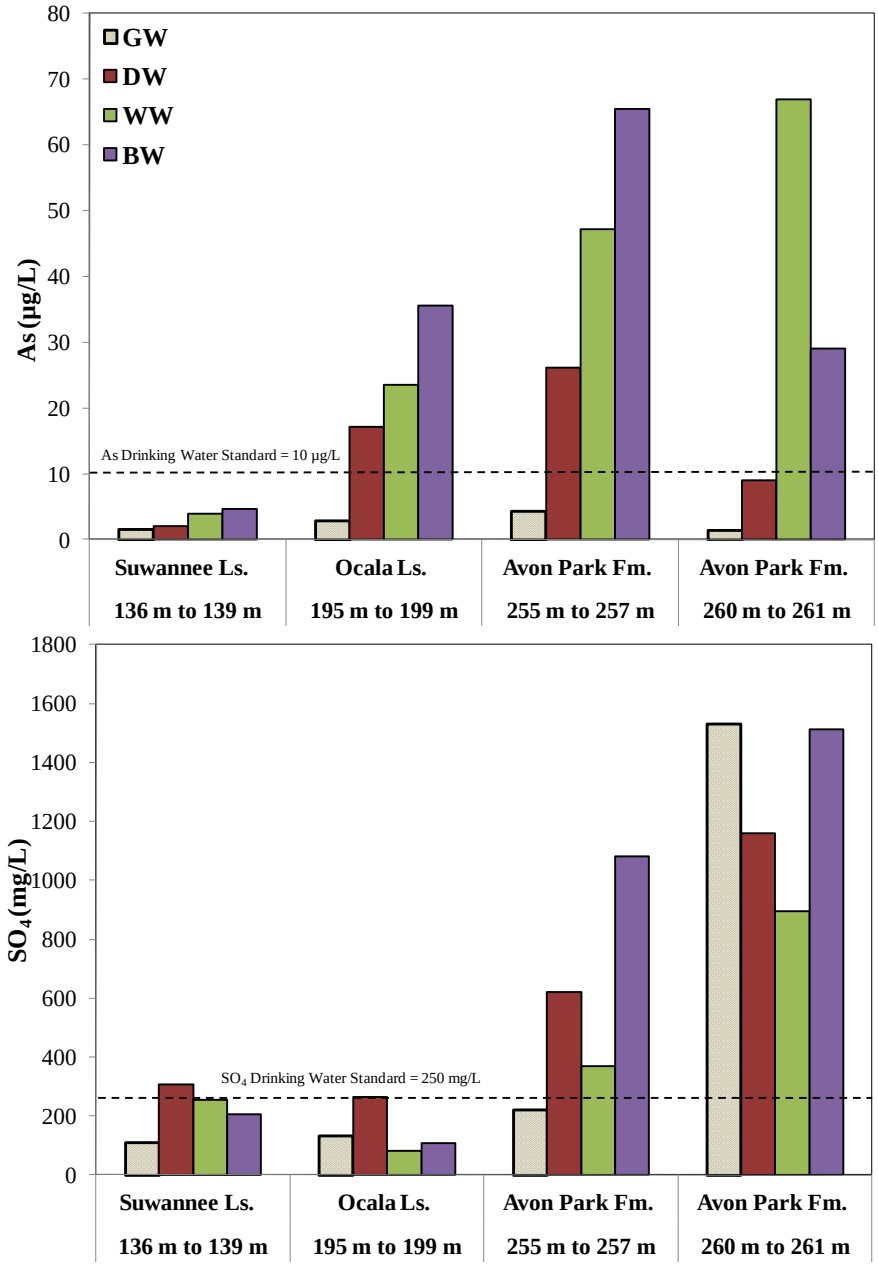

Figure 49. Distribution of maximum As (top) and SO_4 (bottom) concentrations in leachates recovered from each interval (with the subtraction of initial concentration)

Note: GW: groundwater; DW: drinking water; WW: wetland water: BW: basin water

aquifer matrix could be governed by combination of several factors, such as the porosity and permeability of the aquifer influencing the rate and degree of free water saturation, amount of pyrite to be exposed to the preferential flow paths during water-rock interactions, surface reactivity of pyrite, concentration of As and selective As leaching from individual pyrite crystals. The additional factors affecting the mobility of As during ASR may include the chemistry of input and native groundwater, aquifer matrix chemistry/mineralogy, site hydrogeology, injection water-rock contact time, and the amount of cycle tests (Arthur et al., 2005).

The Eh-pH diagram of the mineral stability in the Fe-S-O system shows that pyrite is not stable under oxidizing conditions whereas $Fe(OH)_3$ is not stable under reducing subsurface environment (Evangelou, 1995) (Figure 1). Generally, the oxidation of pyrite by O_2 acts as a source of acid, sulfate, iron and arsenic, and can be illustrated by three steps (Evangelou, 1995):

(1) $FeS_2 + 7/2O_2 + H_2O \rightarrow Fe^{2+} + 2SO_4^{2-} + 2H^+$

Fe^{2+} can be further oxidized to Fe^{3+}, which hydrolyzes into HFO (displayed as $Fe(OH)_3$) to discharge extra amount of acid into the environment:

(2) $Fe^{2+} + 1/4O_2 + H^+ \rightarrow Fe^{3+} + 1/2H_2O$ and

(3) $Fe^{3+} + 3H_2O \rightarrow Fe(OH)_3 + 3H^+$

Consequently, As can be re-sorbed onto HFO if the conditions remain sufficiently oxygenated to promote HFO stability, but released back to native groundwater under reducing conditions.

As demonstrated above, the dissolution of pyrite in the limestone matrix is influenced by the oxidants of the reacting water. Native Floridan groundwater from the

USF well was used as a baseline reference for comparison with other types of water and caused no to minor As mobilization during all leaching experiments. Generally, the concentration of As was slightly elevated in the first pore volume leachates and subsequently declined to < 1 µg/L. This could be due to micro-oxidation of pyrite surface and the possible formation of a thin film ferrous sulfate before the experiment (Pratesi and Cipriani, 2000). Costagliola et al. (1997) investigated the deterioration of pyrite surfaces based on specimens from the Mineralogical Museum of the University of Florence. The authors determined that the alteration mineral present along the pyrite surface fractures and crystal borders was mainly in a form of szomolnokite ($FeSO_4 \bullet H_2O$). Therefore, the injection of reducing groundwater could facilitate a minor release of As associated with a ferrous sulfate phase. At the same time, several studies showed that the exposure of pyrite/arsenopyrite surfaces to the atmosphere developed micro-oxidation products such as iron oxyhydroxide with minor polysulfide and thiosulfate products (Eggleston et al., 1996; Nesbitt et al., 1995; Nesbitt and Muir, 1994). SEM analysis of the samples selected for the leaching experiments showed that pyrite surfaces were not oxidized (Figures 32 - 34). The bench-scale leaching tests performed by Arthur et al. (2007) on more than 40 rock samples from the UFA revealed that the injection of low-dissolved oxygen (DO) native groundwater caused the decrease of ORP and mobilization of As (up to 34 µg/L), Sb, and Mo (Figure 50). During the injection of low-DO surface waters (SW), the concentration of As in leachates reached up to 25 µg/L. However, the introduction of high-DO SW facilitated a sharp decrease of As in leachates, possibly due to As sorption and co-precipitation with a solid or colloidal phase of HFO (Arthur et al., 2007; Lu et al., 2005). Tampa drinking water, which chemically and physically resembles

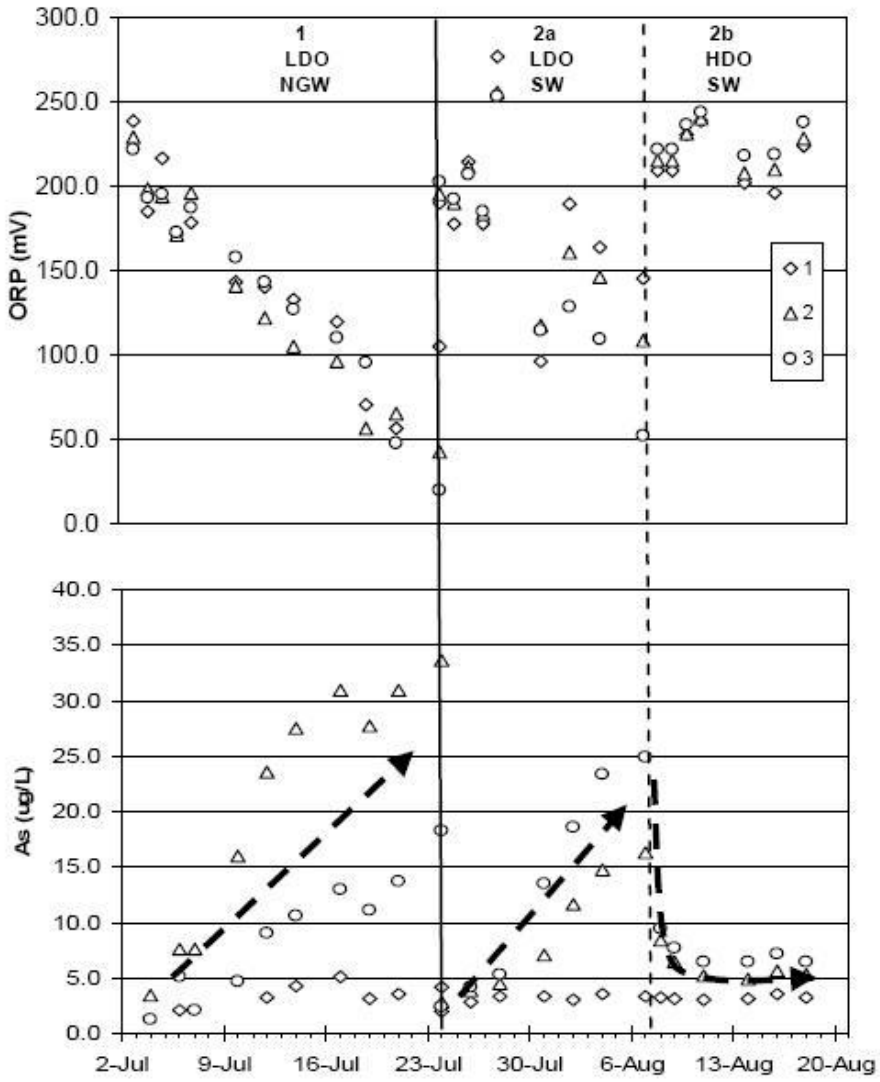

Figure 50. Distribution of ORP and As in leachates recovered during a different phases of the bench-scale leaching experiments (Modified from Arthur et al., 2007).

Note: LDO NGW: low dissolved oxygen native groundwater from cored interval; LDO SW and HDO SW: low and high dissolved oxygen treated surface water from nearby canal; 1 and 2: Hawthorn Group core samples (166 m and 194 m bls, respectively); 3: Suwannee Limestone (262 m bls).

the injection water used in ASR operation, caused the leaching of As of up to 27 µg/L which was higher than the current As drinking water standard of 10 µg/L (EPA, 2009) (Figure 49). One of the most important objectives of this study was to consider using the wetland water to recharge the UFA as the ASR water of choice. However, the leaching experiments using the filter basin and wetland waters demonstrated the highest degree of As mobilization (up to 68 µg/L) from the aquifer matrices (Figure 49). This was unexpected because those types of water were less oxygenated than Tampa drinking water and thus should be less aggressive. Also, the leaching of As using the wetland water was noticeably correlated with depth (R^2 = 0.99) (Figure 49). As expected, the highest concentration of SO_4 was observed in leachates recovered from the Avon Park Formation due to occurrence of gypsum. It was interesting to notice that the injection of Floridan groundwater saturated with air (high DO) caused as much As release as the filter basin and drinking waters. The breakthrough curves for As and SO_4 were compatible for the majority of leaching tests. The distribution of As and SO_4 in the leachates versus time demonstrated initially high levels followed by a considerably rapid decline before reaching relatively steady-state conditions of mineral dissolution after about 3 hours. Walker et al. (2006) reported that the sudden reduction of arsenopyrite oxidation within the first 15 hours of experiment was governed by limited surface oxidation and preferential reactions on fractured mineral surfaces (Borda et al., 2004). Taking into consideration a molar ratio of Fe to S associated with pyrite (1:2), the concentration of Fe in leachates was substantially lower or even undetectable compared to S (as sulfate) demonstrating that most of Fe was attenuated within a column and aquifer matrix (Appendix F). Most likely, the released Fe consequently oxidized to HFO and

precipitated either on the column walls or on the pyrite surface (Walker et al., 2006; Nesbitt, 1995; Richardson and Vaughan, 1989). Therefore, due to high sorption capacity the released As could be strongly attracted and subsequently adsorbed onto neo-formed HFO and co-deposited in the column (Arthur et al., 2007; Lu et al., 2005; Hongshao and Stanforth, 2001; Nickson et al., 2000; Pichler et al., 1999; Hinkle and Polette, 1999; Manning et al., 1998; Evangelou, 1995; Bowell, 1994; Chao and Theobald, 1976).

The ultraviolet (UV) had different effects on the leaching of As depending on the aquifer matrix. Originally, the UV treatment system was installed in the field and laboratory to reliably remove microorganisms present in the filter basin and wetland waters and to understand its influence on the ORP of water potentially causing the dissolution of pyrite and mobilization of As. It has been shown that UV can reduce the amount of odor-causing agents, which primarily targets and destroys compounds such as ammonia and hydrogen sulfide creating an oxic environment. At the same time, the UV effect may potentially create hydroxyl radicals and other by-products such as trace ozone, and change the redox state of water (Masschelein, 2002). Hydrogen peroxide (H_2O_2) in combination with UV light decomposes to hydroxyl radical (•OH) through a Haber–Weiss mechanism as $\bullet O^{2-} + H_2O_2 \rightarrow \bullet OH + OH^- + O_2$ (Druschel et al., 2004; Pettigara et al., 2002; Watts et al., 1999; Stumm and Morgan, 1996). According to Masschelein (2002), •OH resulted from UV radiation have both reducing and oxidizing properties. The reducing properties are due to the following dissociation: $\cdot OH = O^- + H^+$ which are attributed to the oxygen mono-ion. In addition, the reducing properties of ·OH can establish reactions in oxidation of, for example, ferrous iron (Fe(II)): Fe(II) + ·OH = (Fe(III) - OH^-). The author emphasizes that there are no precise standard methods for the

detection and determination of ·OH radicals under conditions applicable to the processes of drinking water treatment, concluding that the lifetime of hydroxyl radicals is in a range of nanoseconds. Previous study showed that H_2O_2 and •OH increase the rate of pyrite oxidation (McKibben and Barnes, 1986). It was reported that sulfite can be rapidly oxidized in the presence of H_2O_2 and ·OH with rate constants on the order of 10^5 M^{-1} sec^{-1} and $5x \times 10^9$ L mol^{-1} sec^{-1}, respectively (Ermakov et al., 1997; Huie and Neta, 1987). The current study showed that UV treatment significantly reduced both fecal and total coliform bacteria, but facilitated the increase of dissolved oxygen in initial waters, change in ORP from the reducing to oxidizing conditions, and subsequently, the increase of As concentration in leachates. However, the experiment with the Avon Park Formation (interval 255 m to 257 m) showed the opposite results, where As levels from the injection of the filter basin and wetland waters treated with UV were less than those from untreated waters (Figure 44).

3.4.1. Importance of dissolved organic carbon for arsenic mobilization

The concentration of dissolved organic carbon (DOC) in fresh waters usually ranges from 0.1 to 20 mg/L and reaches higher values in wetlands (Bauer and Blodau, 2006; Volk et al., 2002). The reported DOC in the Everglades varied between 23 and 136 mg/L (Aiken, 2002). The DOC in the wetland and filter basin waters of the study area were up to 18.5 and 15.3 mg/L, respectively. Those values were about 10 times higher than the Upper Floridan groundwater (from Sacks and Tihansky, 1996). The elevated DOC in the wetland is inferred to be the result of excretion and decomposition of organisms including fish, reptiles, amphibians, insects, birds, bacteria as well as vascular

plants and algae (Volk et al., 2002). The concentration of total nitrogen (TN) in the filter basin and wetland waters was up to 1.5 and 1.6 mg/L, respectively. In a contrast, the TN in the Upper Floridan groundwater, reported by Sacks and Tihansky (1996), was < 0.002 mg/L (Figure 42). The elevated TN in the wetland was governed by dissolved/particulate inorganic and organic nitrogen coming from phytoplankton, bacteria and aquatic life.

Several studies demonstrated that the DOC is very important in the mobilization, redox transformation and solubility of As in aquatic systems through the formation of strong complexes (Buschmann et al., 2006; Buschmann et al., 2005; Warwick et al., 2005; Saada et al., 2003; Redman et al., 2002; Kaiser et al., 1997). The DOC may induce As methylation and become a source of energy for Fe, SO_4^{2-} and humic-reducing microorganisms resulting in reduction of Fe-oxides and metal sulfide precipitation (Tufano and Fendorf, 2008; Huang and Matzner, 2006; Koretsky et al., 2003; Roden et al., 2000). Therefore, the elevated DOC in the wetland and filter basin waters could greatly influence on the release of As from the Floridan Aquifer matrix. Bauer and Blodau (2006) reported that DOC could influence desorption and redox transformations of As bound to soils, sediments, and Fe-oxides with the mobilization to up to 53.3 % of the total sorbed As. The authors emphasized that the principal mechanism for As mobilization from the solid phases was the competition for sorption sites between organic anions and As. The cycling of DOC and Fe in Bangladesh Aquifers was associated with elevated As concentrations (Mladenov et al., 2010; Anawar et al., 2003; Harvey and Swartz, 2002). In addition, Aguilar et al. (2007) demonstrated that the highest concentration of As extracted from soils was leached by oxalic-oxalate to up to 24 - 36 % of the total As. Lalvani et al. (1996) suggested that the dissolution of pyrite was enhanced

by the oxalic acid abundantly present in many plants. Leaching experiments with the Avon Park Formation aquifer matrix (interval 260 m to 261 m) evidently demonstrated the crucial role of microorganisms on the stability and surface reactivity of pyrite. The experiment showed that in contrast to the unfiltered wetland water, in-situ filtration through a 0.2 µm membrane filter resulted in a 2-fold reduction of As leaching ranging from 16 µg/L to 30 µg/L.

3.5. Conclusions

The bench-scale leaching experiments to investigate the mobilization of geogenic arsenic (As) in the Floridan Aquifer under a range of redox conditions showed that:

1) The amount of As released from the aquifer matrix was not perfectly correlated with the bulk rock As concentration. The highest level of As was leached out from the Avon Park Formation and the lowest – from the Suwannee Limestone, although the Ocala Limestone had the lowest bulk rock As.

2) Little to no As release using native Floridan groundwater.

3) Tampa drinking water, which chemically and physically resembles the ASR injection water, caused the leaching of As of up to 27 µg/L which was higher than the current As drinking water standard.

4) Wetland and filter basin waters showed the highest release of As (up to 68 µg/L), which was unexpected because the wetland water was much less oxygenated than Tampa drinking water and thus should be less aggressive.

5) UV treatment significantly reduced both fecal and total coliform bacteria, but facilitated change in oxidation-reduction potential (ORP) from the reducing to oxidizing conditions, and subsequently, the increase of As concentration in leachates.

6) Dissolved organic carbon (DOC) in the wetland and filter basin was 10 times higher than the native Floridan groundwater which was likely very important in the mobilization, redox transformation and solubility of As in aquatic systems;

7) The leaching of As from the aquifer matrix could be governed by combination of factors, such as the porosity and permeability of the aquifer influencing the rate and degree of free water saturation, amount of pyrite to be exposed to the preferential flow paths during water-rock interactions, limited surface reactivity of pyrite, favored reactions on fractured mineral surfaces, concentration of As and selective As leaching from individual pyrite crystals.

Overall, the results demonstrated above could be very important to forecast As behavior during anthropogenic physico-chemical changes such as the aquifer storage and recovery procedure. The bench-scale leaching experiments showed that perturbations of native aquifer conditions caused the release of As from the Floridan Aquifer matrix, although the reaction may not be as simple as the dissolution of pyrite by oxygen, but additionally governed by a complex set of factors including the oxidation-reduction potential of the system, SO_4^{2-}/S^{2-}, Fe^{3+}/Fe^{2+}, dissolved organic carbon and microbial activity. In addition, the oxidative dissolution of pyrite caused coprecipitation of released As with neo-formed hydrous ferric oxides which could become an additional source of As for the native groundwater under reducing conditions.

CHAPTER FOUR

GEOCHEMICAL REACTIVE TRANSPORT MODELING

4.1. Introduction

Aquifer storage and recovery (ASR) is the storage of treated surplus surface water in a confined aquifer during rainy seasons followed by its recovery during times of need (Arthur et al., 2001). The ASR procedure was widely supported around the world to meet increasing water demands and to provide more sustainable alternative to the extensive groundwater consumption (Alley et al., 1999). However, an impediment to ASR development in Florida, Australia, Denmark, and the Netherlands was due to the mobilization of arsenic (As) from the aquifer matrix (Jones and Pichler, 2007; Vanderzalm et al., 2007; Mirecki, 2006; Arthur et al., 2005; Mikecki 2004; Stuyfzand and Timmer, 1999; Stuyfzand, 1998). Particularly, the injection of oxygenated surface water into reducing native Floridan groundwater caused a transformation of the redox environment, oxidative dissolution of pyrite, and the release of As with values in recovered water of up to 130 µg/L (Arthur et al., 2005; Williams et al., 2002).

For the past several years, increasing efforts were devoted to gain a better understanding of As behavior in the subsurface environment implementing numerical modeling and 1D flow systems (Postma et al., 2007; Stollenwerk et al., 2007; Moldovan and Hendry, 2005; Appelo and de Vet, 2003; Appelo et al., 2002; Dzombak and Morel,

1990). In addition, Wallis et al. (2009) developed conceptual and reactive transport models to evaluate the impact of chemical, physical, and biochemical factors on the mobilization of As under field-scale conditions in South-West Netherlands.

The major objective of this investigation was incorporate the results of the bench-scale leaching experiments demonstrated in the third chapter into fully coupled reactive transport models using the Geochemist's Workbench software (Bethke, 2006; Bethke, 1998). The modeling of fluid-rock interactions was important to characterize the geochemical processes in the columns, to understand and to verify if the model could predict the results of simulated injections. Particularly, geochemical modeling was essential to examine the aquifer redox conditions, the stability of pyrite, and the behavior of As during injections of treated ASR water into the Floridan Aquifer.

4.2. Methods

The chemical reactions and chemical evolution of the liquid phase were modeled using the Geochemist's Workbench (GWB) Professional (version 6.0.5) including the React and X1t modules (Bethke, 2006a; Bethke, 2006b). The React program models the equilibrium states of aqueous species in a fluid, the state of fluid saturation with respect to minerals, as well as the fugacity of dissolved gases (Bethke, 2006a). It can consider a number of mineral interactions, kinetic constrains on reactions, and mixing scenarios. At the same time, X1t allows constructing a 1D reactive transport model composed of a groundwater flow and transport models coupled to the React chemical reaction model (Bethke, 2006b). The transport model takes in consideration the movement of groundwater and chemical species dissolved in it by hydrodynamic dispersion, molecular

diffusion, and advection (Bethke, 2006). The model can be constructed for open or closed environmental systems with a particular primary or secondary fluid and the initial reactant chemical composition (i.e., aquifer matrix). It can trace several types of reaction paths, such as the titration, flow-through model, flush model, and picking up the results of a run (Bethke, 2006a). During the titration the program adds a small amount of one or more reactants (i.e., minerals) to the system and recalculates the system's equilibrium states over the path of the simulation. At the same time, a flow-through model is useful to trace the fluid reaction as it migrates through an aquifer preventing the minerals from dissolution once they precipitated. In contrast to a previous model, during the flush model the fluid, added as a reactant, displaces or flushes existing fluid from the system. Finally, the React allows "picking up" the results of an entire system, fluid or the mineral fraction and implementing those results as a new equilibrium system for a new simulation (Bethke, 2006a). This type of the model was especially important for the present study to simulate the water-rock interaction between the native groundwater and aquifer matrix with the subsequent injection of surface water resembling the ASR scenarios.

The geochemical modeling was based on the composition of drinking water from the City of Tampa and the bulk rock chemical analysis of the Avon Park Formation (255 m to 257 m) described in the third chapter (Appendix F and G). City of Tampa drinking water was used as an analogue for ASR surface water (injectate), because ASR injectate has to be treated to meet all drinking water standards and requirements. Therefore, both the drinking water and ASR injectate were chemically and physically similar, i.e., pH, T, high concentration of dissolved oxygen (DO) and high oxidation-reduction potential level (ORP). Due to the complexity of the carbonate system in the leaching columns, such as

the progressive transformation of aquifer fluid and rock saturation states, the geochemical modeling was divided into several case studies. Particularly, it was important to develop the end-member models representing theoretical extremes of the column experiments in terms of an open or closed system, i.e. the available DO which was crucial to the stability of pyrite and the mobilization of As. Generally, the simulation was set for 5 hours. The volume of reacting fluid was 60 mL to reflect the conditions of leaching experiments described in the third chapter (Appendix G). During the geochemical modeling, the "precipitation option" was turned on to show the mineral precipitation during simulation. In a contrast, the "exclude sorbed species" option was turned off to evaluate all sorbed As species formed during the simulation.

Prior to the simulations, thermodynamic data for arsenopyrite (AsFeS) in the *thermo.dat* database (Wolery et al., 1986) was modified as "arsenopyrite2" to integrate the redox couple HS^-/SO_4^{2-} and constrain Eh of the system. This way the product of arsenopyrite dissolution was set to one $As(OH)_4^-$ species instead of the redox couple $AsH_3(aq)/As(OH)_4^-$. The arsenopyrite was added to the model as a source of As based on As/FeS_2 molar ratio calculated from the bulk rock analysis (Table 12). The dissolution reaction of arsenopyrite was modified from (1) to (2):

$$AsFeS + 2\ H_2O + 0.5\ H^- = Fe^{++} + 0.5\ As(OH)_4^- + 0.5\ AsH_3 + HS^- \quad (1)$$

$$AsFeS + 2.5\ H_2O + 0.375\ H^+ + 0.375\ SO_4^{--} = Fe^{++} + As(OH)_4^- + 1.375\ HS^- \quad (2)$$

In addition to the thermodynamic database *thermo.dat*, the *FeOH.dat* database, included in the GWB package was implemented to account for As sorption to hydrous ferric oxides (HFO) formed from the oxidation of pyrite. The "*FeOH.dat*" database

included the surface complexation constants, surface site density, and the specific surface area of the HFO species (Dzombak and Morel, 1990).

4.3. Results and Discussion

The geochemical modeling was divided into a set of case studies explained below. The groundwater, surface water, and rock composition for each scenario is given in Appendices F and G.

(1) Water-rock interaction between the aquifer matrix and surface water (Closed System).

The major hypothesis of this model was to describe the water-rock interaction between the aquifer matrix and drinking water where the water was reacted directly with rock (i.e., reactant) using the React code. These conditions were similar to the bench-scale leaching experiments. During this simulation, the system was considered to be closed, i.e. the source of O_2 was limited. Based on the bulk rock chemical analysis, the aquifer matrix was composed of 258 g of calcite ($CaCO_3$), 35 g of dolomite ($CaMgCO_3$), 10 g of gypsum ($CaSO_4$), 0.2 g of pyrite (FeS_2), and 0.002 g of arsenopyrite (AsFeS).

The geochemical modeling showed that about 0.6 mg of pyrite and 0.006 mg of arsenopyrite were dissolved over 5 hours. The pH of the system increased from 6.9 to 7.3 (Figure 51B). The redox changed from the oxidizing to reducing conditions by 4.5 hours indicated by Eh. It decreased from +800 mV to -150 mV (Figure 51A). The increasing concentration of Ca^{2+} indicated the dissolution of limestone during water-rock interactions. About 110 µg/L of As was sorbed onto HFO via weak bonding ($FeOHAsO_4^{2-}$) until 4.5 hours of the simulation, but released back to solution (70 ug/L) as $As(OH)_3$ through the reductive dissolution of HFO (Figure 52A). At the same time, the

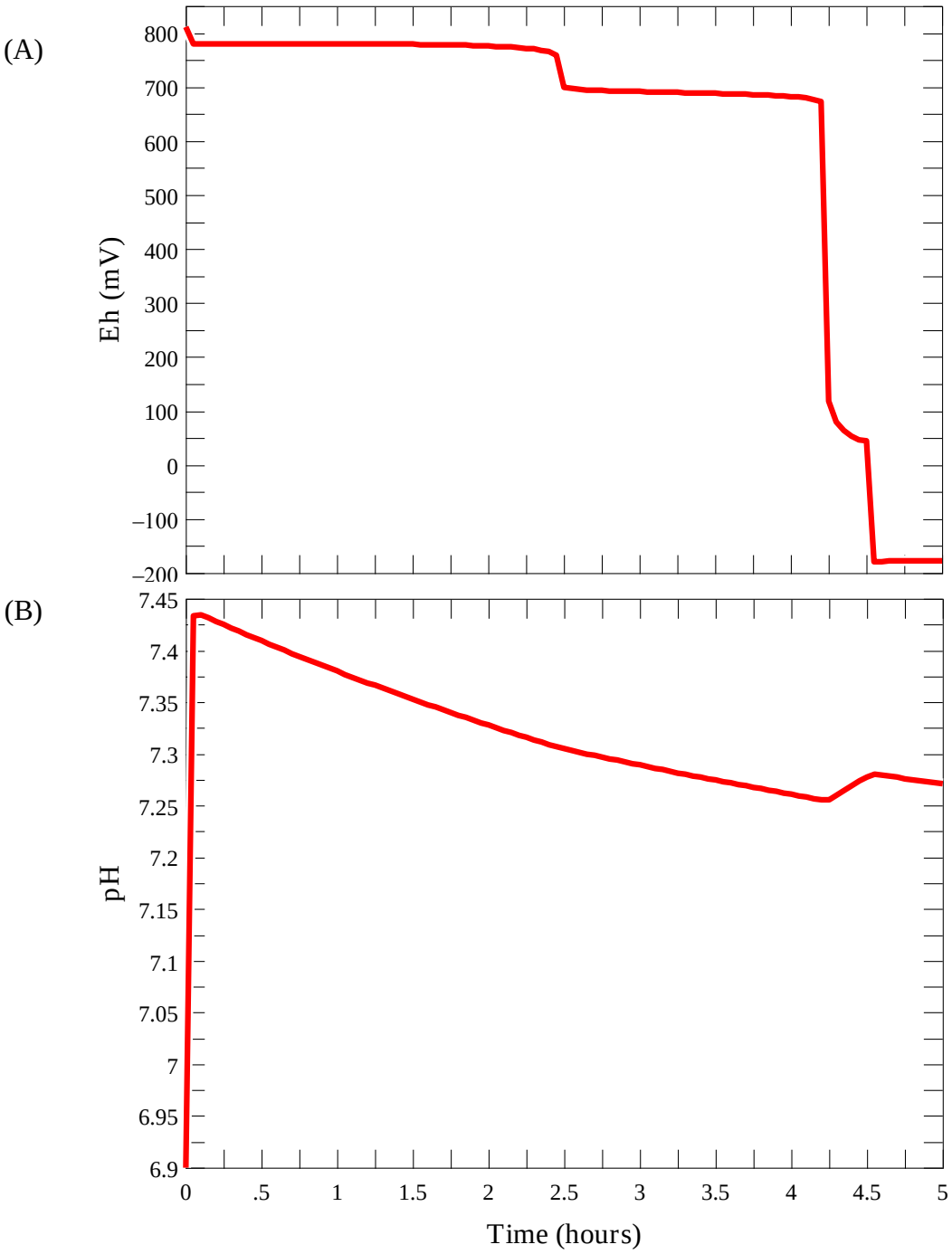

Figure 51. Distribution of Eh (A) and pH (B) during simulated injections of model (1).

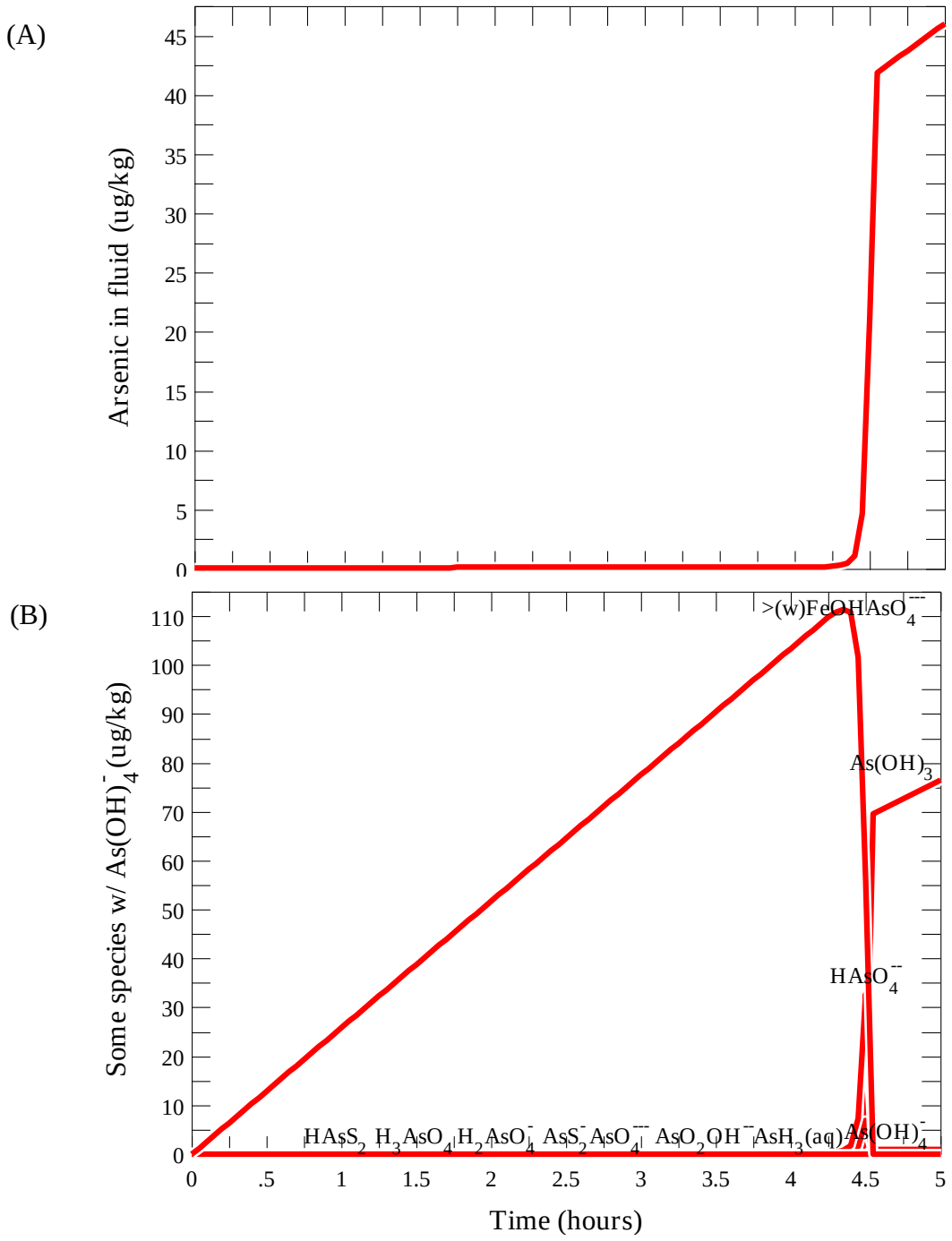

Figure 52. Distribution of As in fluid (A) and As species (B) during simulated injections of model (1).

concentration of total As in the fluid was up to 45 µg/L (Figure 52B). This type of the model was compatible to the results of the leaching experiments demonstrated in third chapter (Figure 45).

(2) Water-rock interaction between the aquifer matrix and surface water (Open System).

The main hypothesis of this model was to describe the water-rock interaction between the aquifer matrix and drinking water where the water was reacted directly with rock but it a contrast to model (1) the system was considered to be open, i.e. the source of O_2 was fixed and essentially infinite (i.e., did not decrease). This step was important to evaluate how much pyrite would react and the amount of As would be leached out from the aquifer matrix, if O_2 were not limited. The composition of the aquifer matrix was following: 258 g of calcite ($CaCO_3$), 35 g of dolomite ($CaMgCO_3$), 10 g of gypsum ($CaSO_4$), 0.2 g of pyrite (FeS_2), and 0.002 g of arsenopyrite (AsFeS) and was based on the bulk rock chemical analysis.

This geochemical modeling exercise demonstrated that similarly to model (1) about 0.6 mg of pyrite and 0.006 mg of arsenopyrite were dissolved over 5 hours. The pH of the system increased from 6.9 to 7.3 at the end of reaction progress (Figure 53B). In contrast to a model (1), Eh remained positive indicating oxidizing environment (Figure 53A). Although, the same amount of pyrite and arsenopyrite reacted during the simulations (0.6 mg and 0.006 mg, respectively), the concentration of As in the fluid was only 0.3 ug/L (Figure 54A). About 125 µg/L of As was sorbed onto HFO via weak bonding ($FeOHAsO_4^{2-}$ and $FeHAsO_4^{-}$) (Figure 54B). Therefore, the type of model did not reflect the results of leaching experiments demonstrated in third chapter.

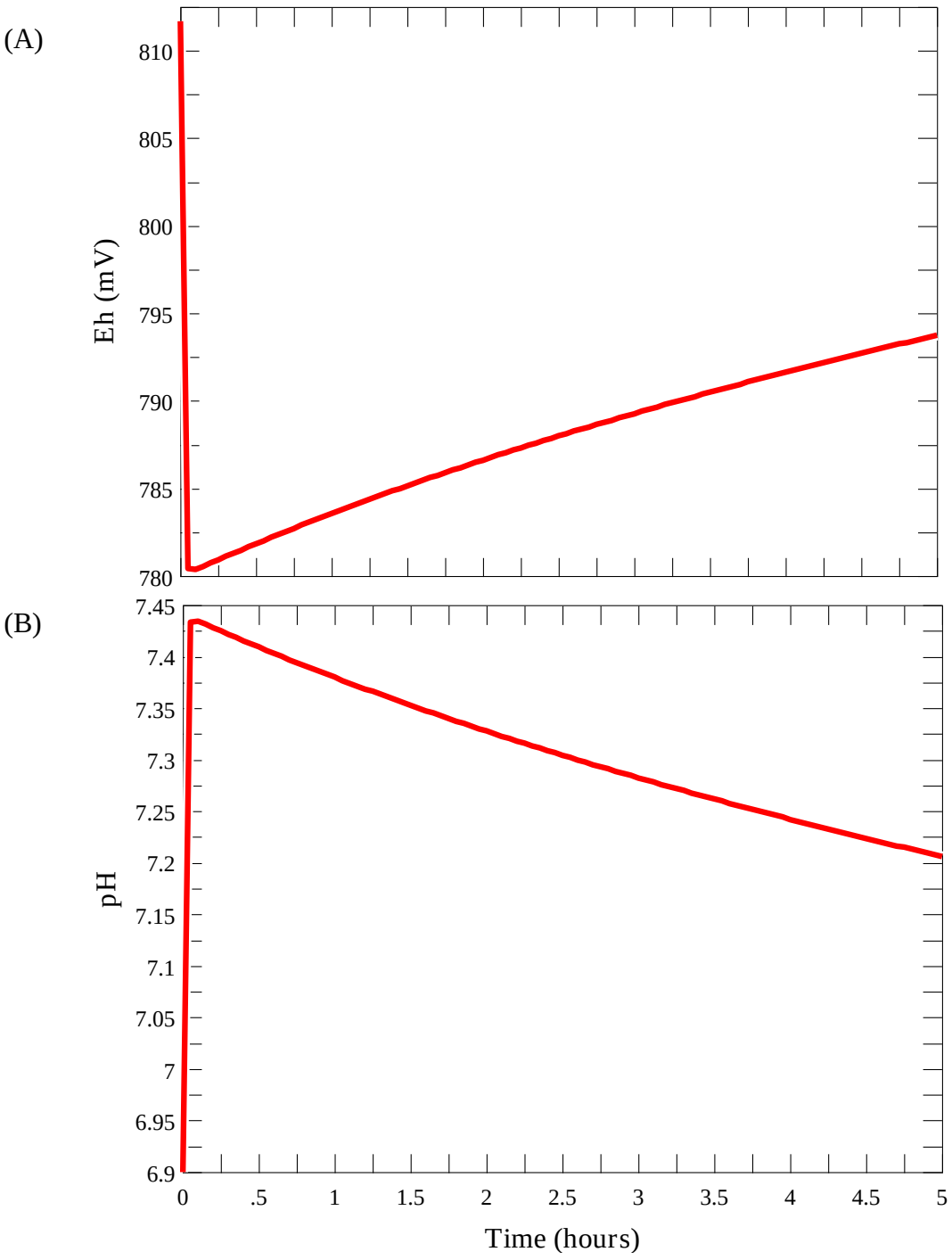

Figure 53. Distribution of Eh (A) and pH (B) during simulated injections of model (2).

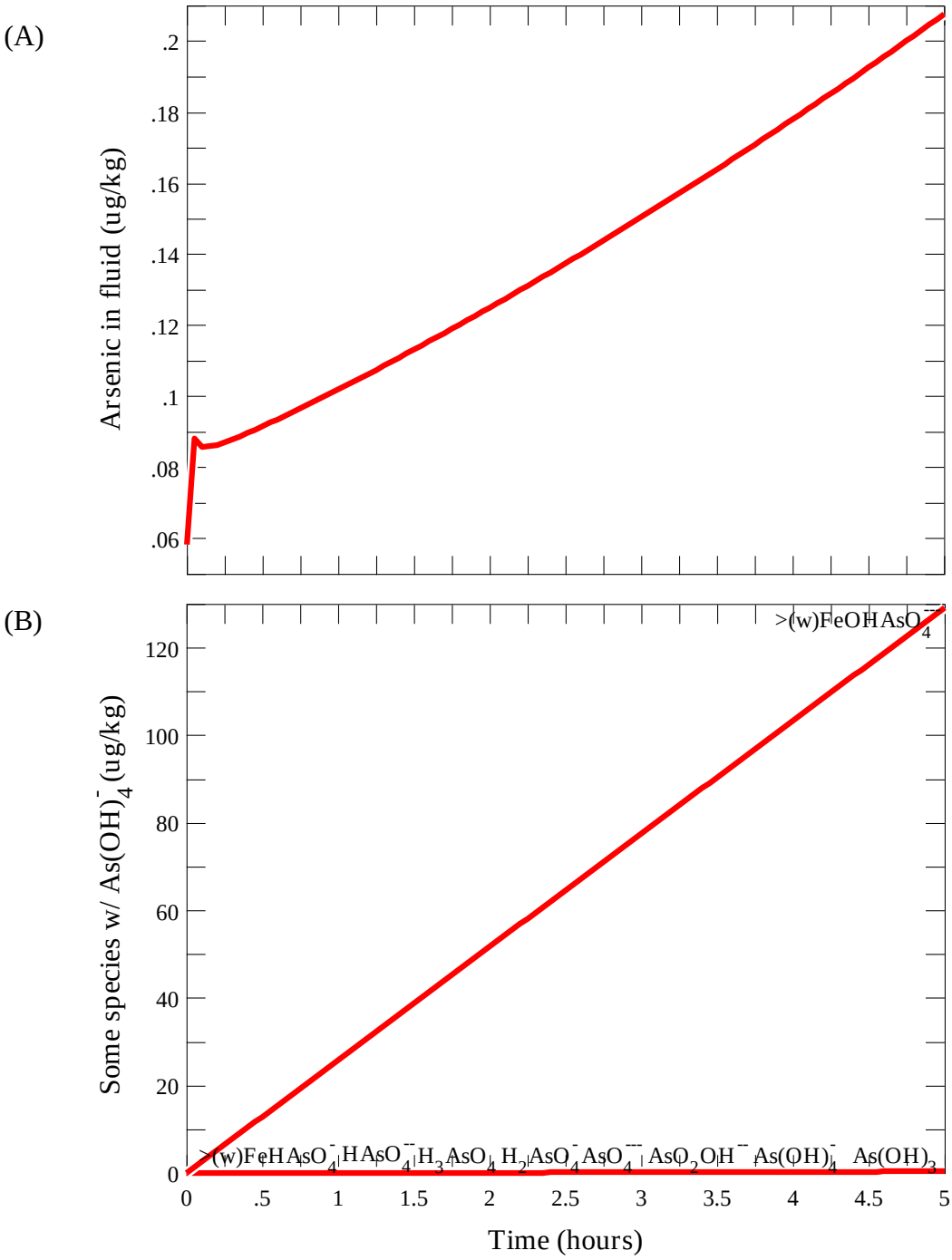

Figure 54. Distribution of As in fluid (A) and As species (B) during simulated injections of model (2).

(3) Water-rock interaction between the aquifer matrix and surface water (Open System; high amount of pyrite).

The major hypothesis of a model (3) was to describe the water-rock interaction of the system that would release the same amount of As as in a model (1) by increasing the amount of pyrite/arsenopyrite but remaining open (fixed source of O_2) as a model (2). Here, the aquifer matrix was composed of 258 g of calcite ($CaCO_3$), 35 g of dolomite ($CaMgCO_3$), 10 g of gypsum ($CaSO_4$), and the amount of pyrite (FeS_2) and arsenopyrite (AsFeS) was modified to 0.7 g and 0.007 g, respectively.

According to geochemical simulations, Eh of the system remained positive indicating oxidizing environment (Figure 55A). The pH of the system dropped from 6.9 to 5.5 contradicting with the experimental data (Figures 55B and 41). Similarly to the model (1), the concentration of total As in the fluid was up to 45 µg/L (Figure 56). In order to achieve this level of As concentration, approximately 700 mg of pyrite needed to be dissolved from the column. According to the bench-scale leaching tests, the Avon Park Formation (255 m to 257 m) contained about 800 mg/kg of pyrite (Table 13) or 200 mg in the column. Therefore, this type of model did not agree with the results of leaching experiments demonstrated in the third chapter and should be considered with caution.

(4) 1D reaction-transport model of water-rock interaction between the aquifer matrix and surface water (Closed System).

The X1t code was used to model reactive transport in one dimension (Bethke, 2006b). This model was important to closely simulate the results of bench-scale experiments in time and space and to evaluate the geochemical processes in the leaching

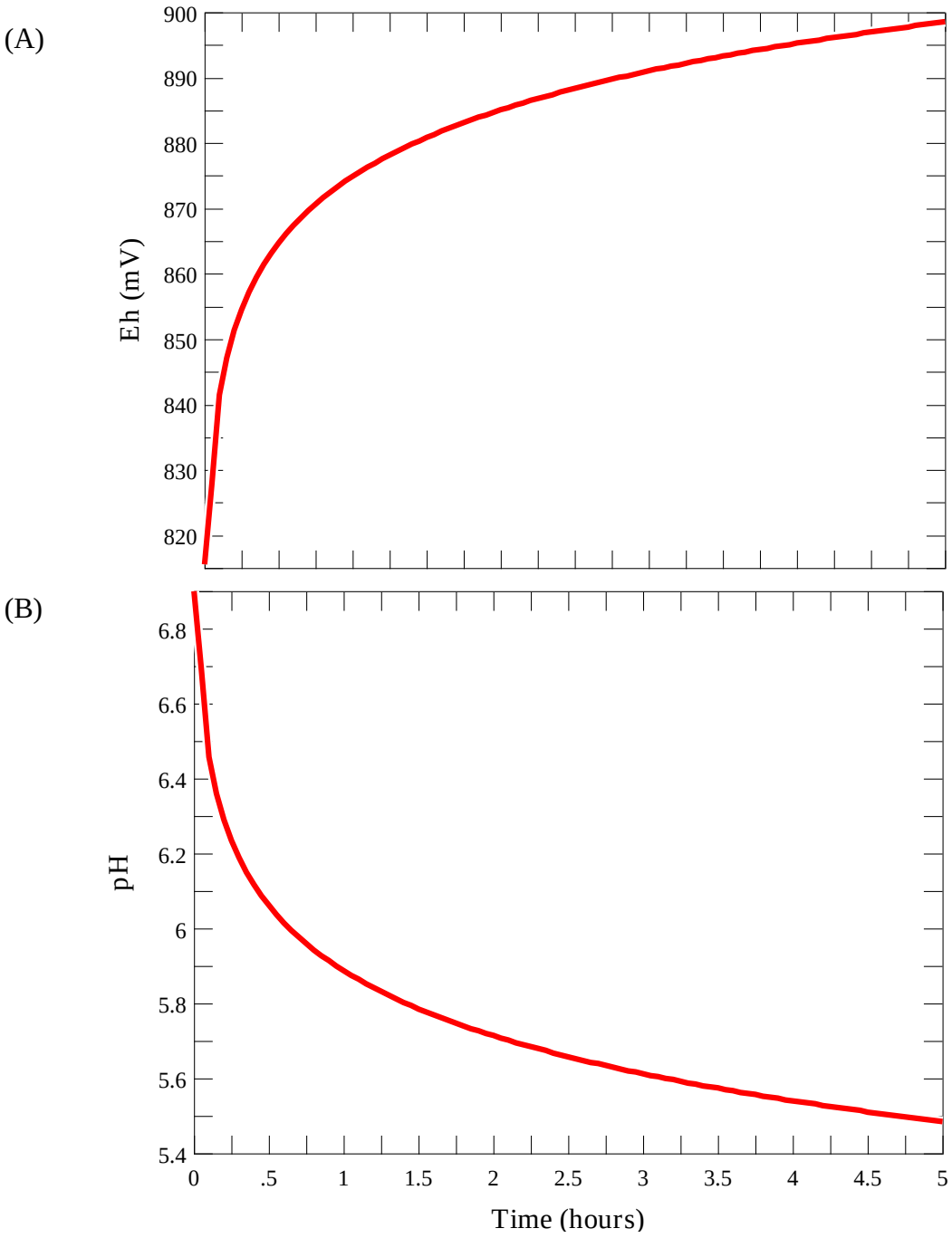

Figure 55. Distribution of Eh (A) and pH (B) during simulated injections of model (3).

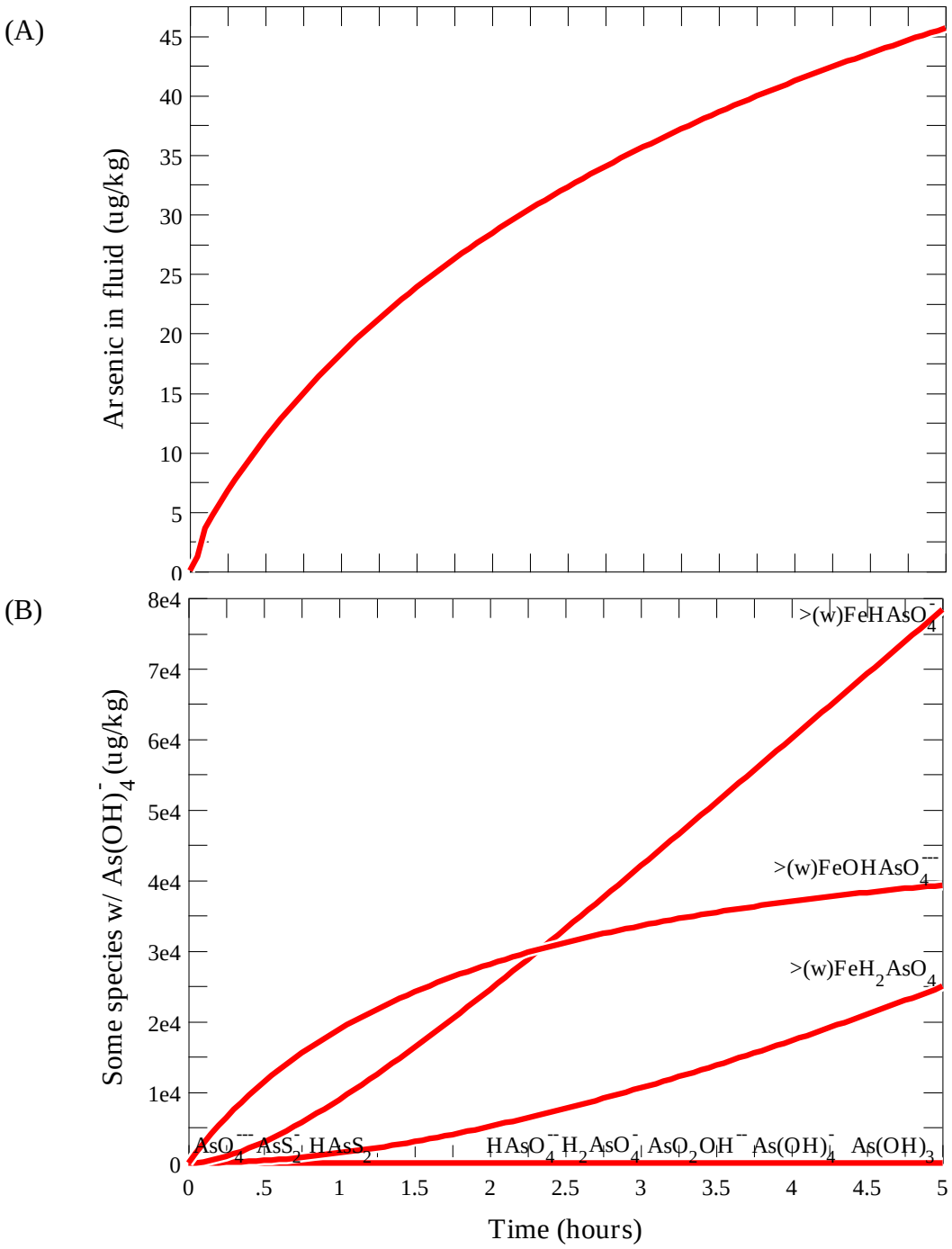

Figure 56. Distribution of As in fluid (A) and As species (B) during simulated injections of model (3)

column such as the stability of pyrite and HFO, and the mobility of As. The transport model was constructed for a closed system (i.e. the source of O_2 was limited), with the same composition of initial and inlet water (drinking water) and the following aquifer matrix composition: 258 g of calcite ($CaCO_3$), 35 g of dolomite ($CaMgCO_3$), 10 g of gypsum ($CaSO_4$), 0.2 g of pyrite (FeS_2), and 0.002 g of arsenopyrite (AsFeS) (the same as models (1) and (2)) (Appendix G). The simulation column dimensions were 50 cm (Length) by 2 cm (Width). Based on the leaching experiments, the discharge rate of fluid in the column was 0.01 cm^3/cm^2 sec, and the porosity was 15 %.

This geochemical modeling exercise showed that about 0.06 mg/cm^3 and 0.00006 $gm/cm^3$of pyrite and arsenopyrite were dissolved in the column over 5 hours. The pH of the system varied from 6.9 (initial fluid) to 7.4. At the same time, the highest pH was detected at 2.5 cm and gradually decreased to about 7.2 at 50 cm (Figure 57C). The concentration of As in the fluid reached up to 65 µg/L at the end of the column (Figure 58A). Figure 59 demonstrated interesting behavior of As species along the column. According to the model, the oxidative dissolution of pyrite/arsenopyrite, depletion of O_2, and As sorption onto newly-formed HFO via weak bonding ($FeOHAsO_4^{2-}$, $FeHAsO_4^-$, FeH_2AsO_4, and FeH_2AsO_3) was between 0 cm and 22 cm (Figure 59B). However, Eh of the system changed rapidly from the oxidizing to reducing (+700 to -150 mV) between 22 cm and 27 cm (Figure 57B). The model showed a sharp decrease of adsorbed As and steep increase of aqueous As concentration around 24 cm which was governed by the reductive dissolution of HFO. Ideally, the slope of absorbed and mobilized As should be the same but it was lower for the released As (Figure 59). The column interval between 27 cm and 50 cm showed that $As(OH)_3$ and $As(OH)^-_4$ species were dominant in the

(A)

(B)

(C)

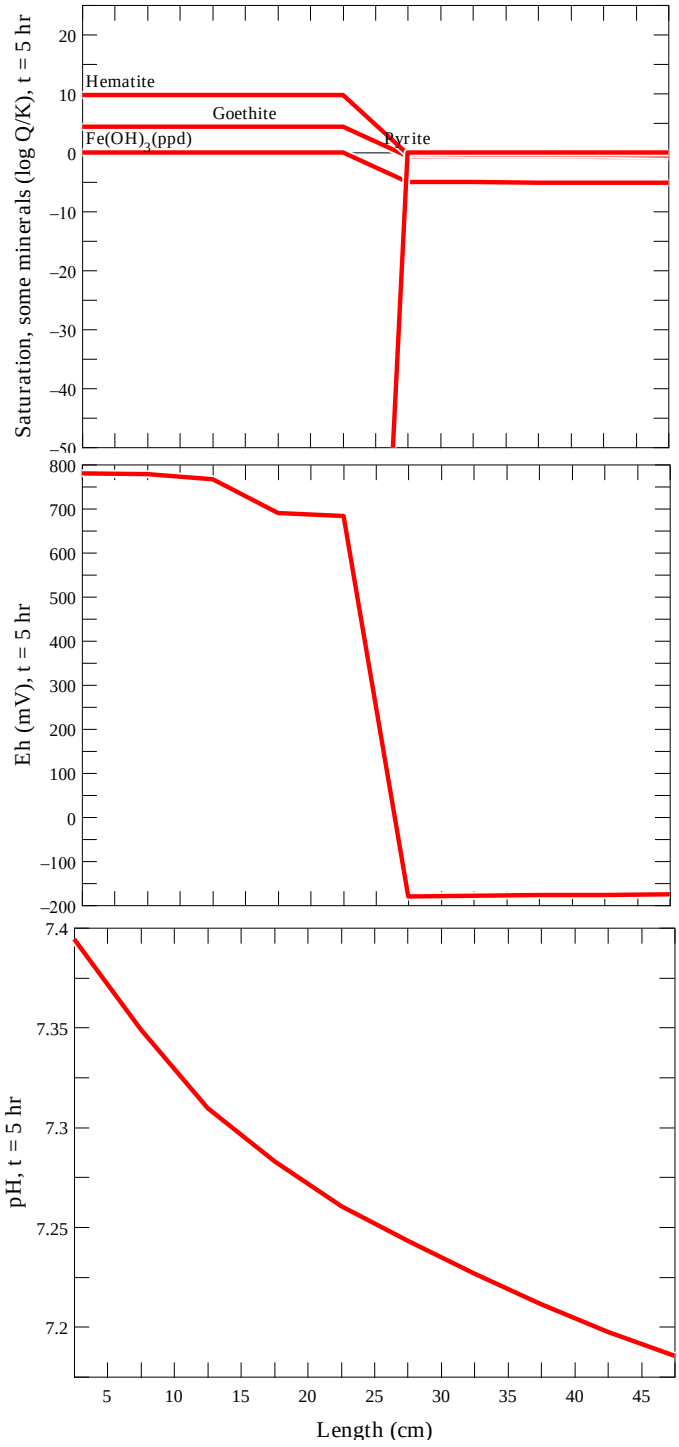

Figure 57. Distribution of mineral saturation states (A), Eh (B), and pH (C) along the column during 5 hours of simulated injections of model (4).

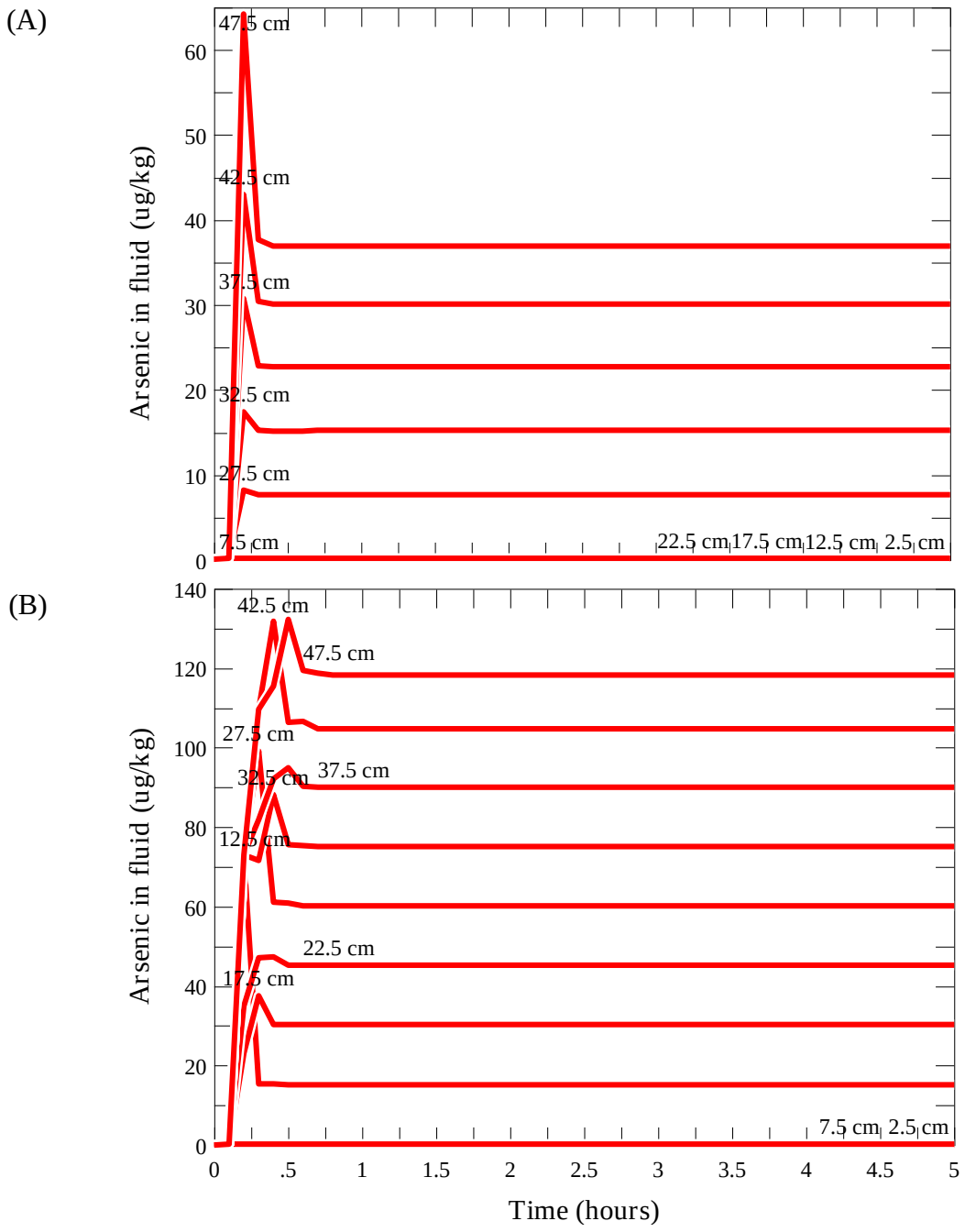

Figure 58. Distribution of As concentration in fluid along the column with discharge rate of 0.01cm/sec (top) and 0.005 cm/sec (bottom) during 5 hours of simulated injections of model (4).

(A)

(B)

(C)

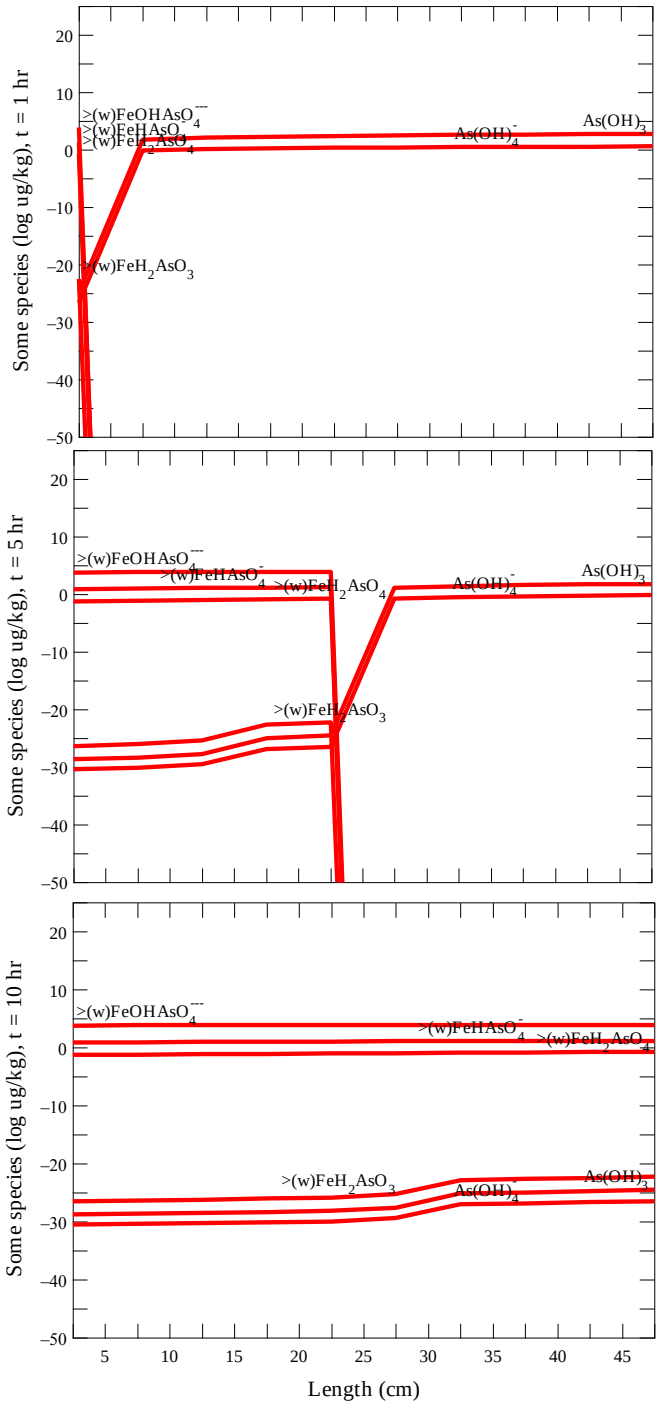

Figure 59. Distribution of As species along the column during 1 hour (A), 5 hours (B), and 10 hours (C) of simulated injections of model (4).

column and the system was saturated with respect to pyrite (Figures 57A and 59B). This pattern could be due to a possible non-oxidative dissolution of pyrite or arsenopyrite driven by pH. The decrease of discharge rate from 0.01 cm^3/cm^2 sec to 0.005 cm^3/cm^2 sec (or 1 mL/min) demonstrated the reduced size of the reaction front of sorbed As species between 0 cm and 7 cm. In contrast, the concentration of As in the fluid increased from 65 µg/L to 150 µg/L (Figure 58B).

In addition to 5 hours, injection times of 1 hour and 10 hours were investigated (Figures 59A and C). According to those simulations, the concentration of As in leachate varied from 350 µg/L (for 1 hour) to 0.2 µg/L (for 10 hours). Figure 59 clearly showed a broader distribution of sorbed As species during the 10 hour simulation compared to 1 hour. This tendency could be explained by a longer fluid flushing through aquifer matrix which supplied O_2 for oxidative dissolution of pyrite. As mentioned above, the elevated concentrations of As during 1 hour simulation could be governed by pH which drives nonoxidative dissolution of pyrite or arsenopyrite. Figure 60 showed the distribution of As species, negative Eh, and pH along the column supporting this hypothesis.

5) 1D reaction-transport model of water-rock interaction between the aquifer matrix, groundwater and surface water (Closed System).

The present geochemical model, based on the model (4), was significantly modified to potentially reflect the actual water-rock interactions occurring during the injection of treated ASR water into the Floridan Aquifer. The composition of the aquifer matrix was the same as in model (4). In contrast, during this simulation the groundwater was equilibrated initially with the aquifer matrix. The second simulation was set for 5

(A)

(B)

(C)

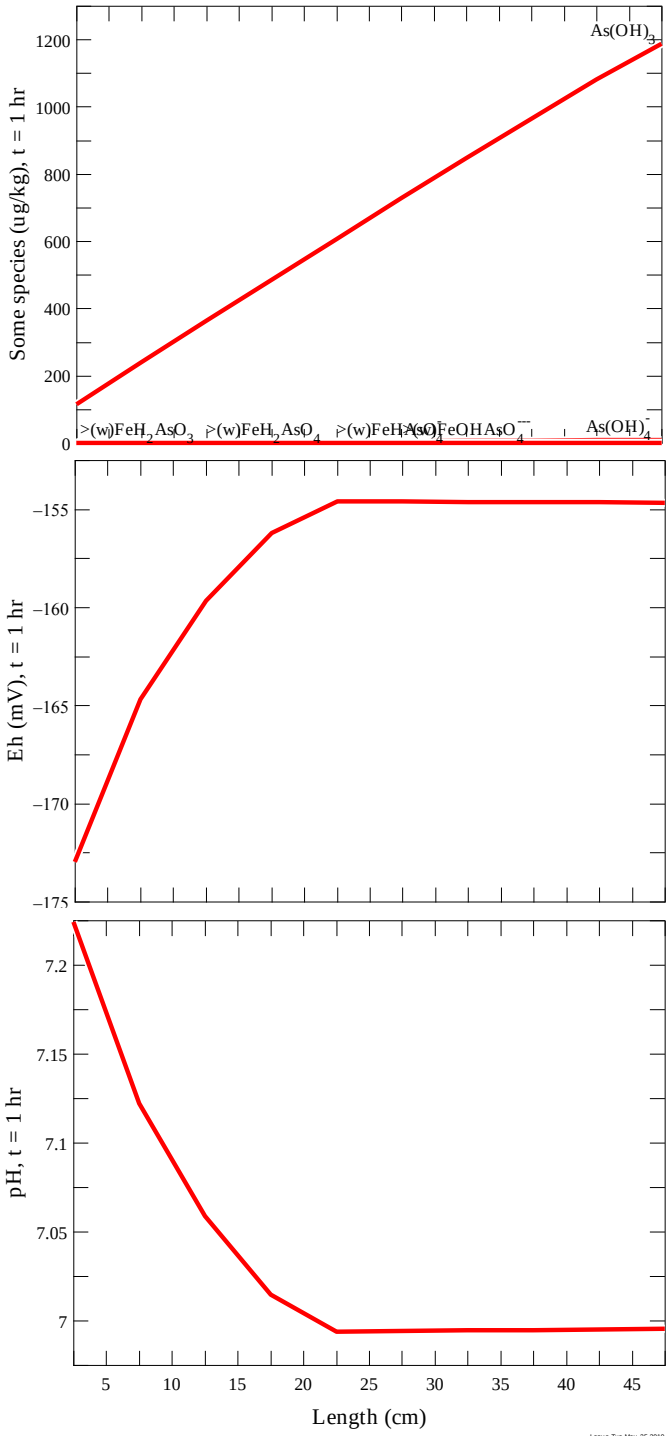

Figure 60. Distribution of As species (A), Eh (B), and pH (C) along the column during 1 hour of simulated injections of model (4).

hours as the “pickup” of the whole water-rock system used above as a new equilibrium system followed by a new simulation with the injection of drinking water. This way the simulation of ASR could be comparable to field tests.

According to geochemical simulations, the starting solution (groundwater + rock) was under reducing conditions and was favorable for pyrite stability preventing the release of As into solution. Subsequently, the starting fluid was displaced by the oxic fluid (drinking water) which was indicated by increase in Eh from -150 mV to +750 mV (Figure 61A). Particularly, during the first 20 minutes of the simulation, pyrite/arsenopyrite was oxidized releasing large amounts of As giving an initial As pulse (Figure 62A). Subsequently, HFO were newly-formed adsorbing most the dissolved As (Figure 62B). About 0.004 % of pyrite was dissolved during 5 hours of simulation resulting in the concentration of As of up to 135 µg/L (Figure 62A). The pH of the system increased from 7.1 to 7.4. The highest pH was detected at 2.5 cm and gradually decreased to about 7.3 at 50 cm (Figure 61B). The increasing concentration of Ca^{2+} indicated the dissolution of limestone during water-rock interactions. At the end of simulations, about 24 pore volumes were displaced which was equal to 1440 mL.

Overall, the geochemical models correlated well to the results from the column leaching experiments and clearly showed that the injection of oxidizing surface waters into reducing native groundwater caused a change in redox potential of the system and thus promoted the dissolution of pyrite and mobilization of As. Particularly, models (1) and (4) constructed for closed systems were probably the most reliable to characterize the geochemical processes in the columns. In contrast, the models (2) and (3) developed for open systems showed that most of the pyrite was dissolved and almost all As was sorbed

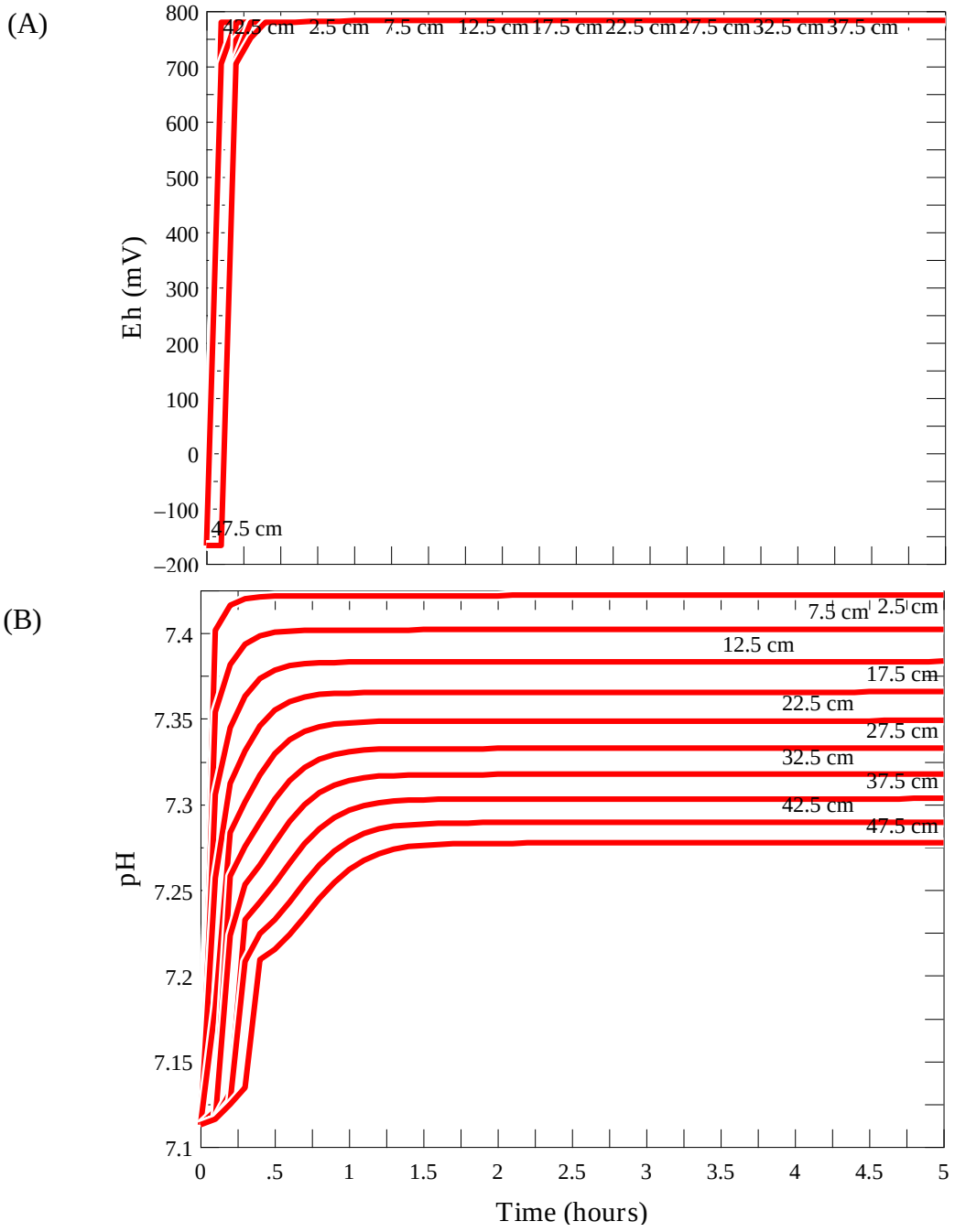

Figure 61. Distribution of pH (A) and Eh (B) during simulated injections of model (4).

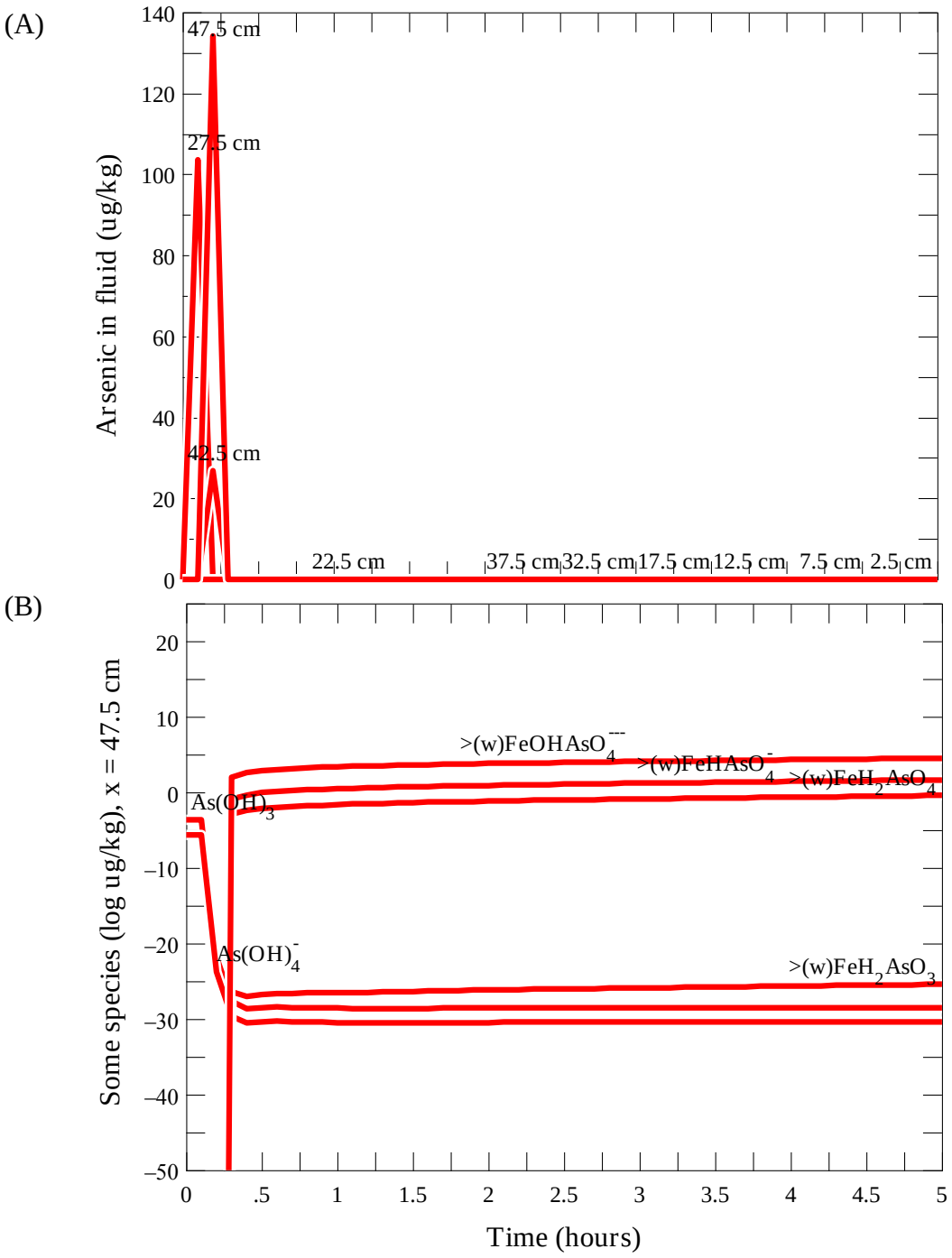

Figure 62. Distribution of As in fluid (A) and As species (B) during simulated injections of model (4).

onto HFO via weak bonding and only 0.3 ug/L was present in the fluid (for model 2). Model (3) showed that approximately 700 mg of pyrite needed to be dissolved from the column to achieve the level of As concentration compatible to the leaching experiments. Those results did not agree with the bulk rock chemical composition demonstrated in the third chapter.

This study confirmed the previous model of Jones and Pichler (2007), which predicted the instability of pyrite in the Suwannee Limestone that would result in the leaching of As into storage-zone water. Reactive transport modeling by Wallis et al. (2009) confirmed that the behavior of As from the aquifer matrix in the Netherlands was governed by dissolution of arsenopyrite, which was stoichiometrically connected to pyrite oxidation, transformation of As(III) to As(V), followed by As adsorption on neo-precipitated HFO via surface complexation.

4.4. Conclusions

The geochemical reactive transport modeling has shown to be a valuable tool for providing important information about water-rock interactions in the Floridan Aquifer. The combination of bench-scale leaching experiments and modeling could become essential to forecast redox conditions of the aquifer matrices during operation and development of aquifer storage and recovery systems in Florida and potentially worldwide. The results from the current models correlated well to those from the column experiments and clearly showed the following:

1) Fluid-rock reaction between the aquifer matrix and native groundwater was favorable for pyrite stability preventing the release of As into solution.

2) The injection of oxidizing surface water into reducing native groundwater caused a change in redox potential of the system thus promoting the dissolution of pyrite and precipitation of newly-formed HFO.

3) The evaluation of open vs. closed systems (fixed vs. limited O_2) illustrated the following results:

- Closed system: the model was compatible to the leaching experiments. The concentration of As in the leachate was to 45 µg/L.
- Open system: the model did not agree with the leaching experiments. The concentration of As in the leachate was only 0.3 ug/L and about 125 µg/L of As was sorbed onto HFO via weak bonding.

4) 1D geochemical model of water-rock reaction between the aquifer matrix and drinking water showed a remarkable behavior of As along the column, such as:

- Oxidative dissolution of pyrite, mobilization and sorption of As onto neo-formed HFO;
- Reductive dissolution of HFO and secondary release of adsorbed As;
- Potential non-oxidative dissolution of pyrite contributing to the additional source As in the solution.

CHAPTER FIVE

SUMMARY AND CONCLUSIONS

The reclamation of wastewater and phosphate mining lands using constructed wetland/filter basin (CW/FB) treatment technology could prove to be especially important as Florida law requires reclamation of previously mined phosphate lands into wildlife habitat and watershed enhancement. In addition, the CW/FB system may provide water that meets drinking water standards to supplement lakes and rivers, satisfy industrial, agricultural and domestic water supply demands, and to provide more sustainable alternative to extensive groundwater consumption.

This study investigated the efficiency of the CW/FB treatment system to improve the water quality of industrial and municipal wastewater. The system was constructed in closed phosphate mines used for clay settling and sand tailings in Polk County, Florida. An 18-month performance study of the CW/FB showed that despite of significant seasonal variations with respect to temperature, rainfall and humidity, the chemical/microbiological composition of treated water remained relatively constant. The study showed the following changes in water quality between the input and output: substantial decrease of water temperature (up to 10 °C), reduction of As, SO_4, F, Cl, NO_3, NO_2, Br, Na, K, Ca, and Mg, change in pH from about 9 to 6.5–7, increase of H_2S (up to 1060 μg/L), and negative oxidation-reduction potential confirming the reducing

conditions of the treatment system. There were no exceedances of the primary drinking water standards, volatile organic compounds, synthetic organic compounds, and radionuclides, but a number of exceedances for the secondary drinking water standards (Al, F, Fe, Mn, color, odor, total dissolved solids, and foaming agents). The concentration of fecal and total coliform bacteria at the filter basin was reduced from 30 - 730 and 1000 – 7000 count/100 mL to < 2 and < 100 count/ 100 mL, respectively. These results clearly demonstrated a crucial role of a biofilm "schmutzdecke".

A combined isotope/chemical mass-balance approach to evaluate the performance of the wetland in complex hydrogeological settings demonstrated the following: (1) composition of water in the wetland varied throughout the period of the study; (2) depletion of isotopic composition along the wetland flow path; (3) wetland was mostly composed of wastewater (88 - 100 %) during normal pumping operations; however, hurricanes and inconsistent pumping added low conductivity water directly and triggered enhanced groundwater inflow into the wetland of up to 78 %; (4) composition of water in monitor wells was mostly groundwater dominated; however it was periodically induced by the seepage from a water body to the north; and the (5) seepage from water bodies surrounding the wetland were not identified in the wetland water once the system became operational potentially indicating a water loss from the wetland.

Of particular interest in this study were the bench-scale leaching experiments to investigate the mobilization of geogenic arsenic (As) in the Floridan Aquifer under a range of redox conditions. They showed that the amount of As released from the aquifer matrix was not perfectly correlated with the bulk rock As concentration. The highest level of As was leached out from the Avon Park Formation and the lowest – from the

Suwannee Limestone, although the Ocala Limestone had the lowest bulk rock As. Minor to no As was released using native Floridan groundwater. Tampa drinking water, which chemically and physically resembled the ASR injection water, caused the leaching of As of up to 27 µg/L which was higher than the current As drinking water standard. Wetland and filter basin waters showed the highest release of As (up to 68 µg/L), which was unexpected because the wetland water was much less oxygenated than Tampa drinking water and thus should be less aggressive.

Overall, these results could be very important to forecast As behavior during anthropogenic physico-chemical changes such as the aquifer storage and recovery procedure. The experiments confirmed that perturbations of native aquifer conditions caused the release of As from the Floridan Aquifer matrix, although the reaction may not be as simple as the dissolution of pyrite by oxygen, but additionally governed by a complex set of factors including the oxidation-reduction potential of the system, SO_4^{2-}/S^2, Fe^{3+}/Fe^{2+}, dissolved organic carbon and microbial activity. The oxidative dissolution of pyrite caused coprecipitation of released As with neo-formed hydrous ferric oxides (HFO) which could become an additional source of As for the native groundwater under reducing conditions. Moreover, the following set of parameters could have a fundamental role in the mobilization of As, such as the porosity and permeability of the aquifer influencing the rate and degree of free water saturation, amount of pyrite to be exposed to the preferential flow paths during water-rock interactions, limited surface reactivity of pyrite, favored reactions on fractured mineral surfaces, concentration of As and selective As leaching from individual pyrite crystals.

The results of the geochemical reactive transport modeling using the Geochemist's Workbench (React and X1t) correlated well to those from the column experiments. The modeling clearly showed that fluid-rock interaction between the aquifer matrix and natural groundwater was favorable for pyrite stability preventing the release of As into solution. In contrast, the injection of oxidizing surface water into reducing native groundwater caused a change in redox potential of the system thus promoting the dissolution of pyrite. The 1D geochemical model simulating a water-rock reaction between the aquifer matrix and surface water demonstrated the following processes along the column: oxidative dissolution of pyrite, mobilization and simultaneous sorption of As onto neo-formed HFO, followed by the reductive dissolution of HFO and secondary release of adsorbed As, and a potential non-oxidative dissolution of pyrite contributing the additional source As into the solution.

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APPENDIX A.

AN 18-MONTH PERFORMANCE STUDY OF THE WETLAND/FILTER BASIN TREATMENT SYSTEM

Sample	Date	pH	Temp	ORP	Cond	TDS	DO	H_2S	Fe^{2+}	As	F	Cl	NO_2	NO_3	PO_4	SO_4	Br	K	Na	Ca	Mg	Fe	Mn	Sr	Si
			° C	mV	uS/cm	mg/L	mg/L	ug/L	mg/l	ug/L	mg/L														
Cooling Pond (CP)																									
CP-1	04/28/06	8.3	26.7	68	1122		10.3	23	0.1		3.1	118.6	0.0	0.0	2.0	80.0	1.1	12.9	67.9	49.3	28.9	0.0	0.0	0.5	0.2
CP-2	05/19/06	8.7	29.8	101	843		9.1	5	0.1	1.3	3.2	118.1	0.0	0.1	2.2	75.2	1.2	8.8	67.7	47.3	28.7	0.0	0.0	0.5	0.2
CP-3	06/16/06	9.0	34.4	157	943		12.8	0	0.0	1.6	2.9	117.3	0.0	0.1	2.0	76.1	1.7	10.0	64.5	54.8	32.6	0.0	0.0	0.5	0.3
CP-4	06/27/06	8.8	35.1	161	826		10.7	2	<0.1	1.6	4.0	132.2	0.0	0.0	2.2	84.6	1.7	9.3	69.3	50.6	29.4	0.0	0.0	0.5	0.2
CP-5	07/12/06	8.6	33.6	85	801		8.9	0	0.1	1.4	3.4	132.3	0.0	0.0	1.9	81.5	1.5	10.5	68.5	48.1	28.9	0.0	0.0	0.5	0.2
CP-6	07/28/06	8.5	37.0	93	833		7.0	0	<0.1	2.9	3.0	123.2	0.0	0.0	1.8	79.4	1.6	9.6	72.3	49.5	30.7	0.0	0.0	0.5	0.1
CP-7	08/10/06	8.6	35.8	135	857		7.2	2	0.1	2.4	3.4	120.5	0.0	3.5	2.0	81.5	1.6	9.7	71.8	48.7	30.5	0.0	0.0	0.5	0.2
CP-8	08/31/06	8.3	34.3	-36			3.6	3	<0.01	2.7	3.3	123.7	0.0	0.0	2.2	81.9	1.8	9.3	69.8	47.0	29.5	0.0	0.0	0.5	0.1
CP-9	09/14/06	8.7	34.7	58			9.7	0	0.0	2.3	3.7	123.8	0.0	0.1	0.8	82.9	1.7	9.2	67.8	45.2	28.7	0.0	0.0	0.5	0.3
CP-10	09/28/06	8.6	32.8	157	816	408	8.6	0	<0.1	2.9	3.5	122.6	0.0	0.0	3.0	77.4	2.0	9.5	72.2	47.0	30.6	0.0	0.0	0.5	0.2
CP-11	10/11/06	8.5	30.6	43	812	405	11.0	0	0.0	1.9	2.6	107.6	0.0	0.0	1.9	69.5	1.6	9.6	72.9	47.0	30.5	0.0	0.0	0.5	0.1
CP-12	11/01/06	8.7	28.4	-50			10.2	20	0.0	2.1	2.6	117.5	0.0	0.0	2.2	70.1	1.1	9.9	71.3	49.5	31.1	0.0	0.0	0.5	0.3
CP-13	11/07/06	8.3	25.4	40			9.0	0	0.0	1.9	2.9	128.9	0.0	0.0	2.0	81.3	1.4	9.9	74.3	50.8	32.2	0.0	0.0	0.5	0.6
CP-14	11/20/06	8.5	22.0	-94	807	404	8.6	25	0.0	2.2	3.5	128.2	0.1	0.0	3.3	84.0	1.7	10.1	73.3	49.9	31.5	0.3	0.0	0.5	1.2
CP-15	12/07/06	8.3	23.5	200	829	409	8.7	51	0.0	3.0	3.2	127.4	0.0	0.1	2.8	76.9	1.4	11.6	80.0	57.8	35.5	0.0	0.0	0.5	0.2
CP-16	12/14/06	8.5	22.4	18	766	363	9.6	0	0.0	2.5	2.7	123.9	0.7	0.4	2.3	72.4	1.2	10.1	73.1	52.2	32.2	0.1	0.0	0.5	0.7
CP-17	12/18/06	8.6	22.9	4			10.7	23	0.0	2.7	2.9	126.0	0.0	0.1	2.8	74.4	1.3	10.4	77.1	51.3	31.9	0.0	0.0	0.5	0.3
CP-18	01/09/07	8.1	22.8	13	785	393	3.8	40	0.0	3.2	2.6	121.1	0.0	0.1	2.7	78.9	1.2	10.7	74.0	57.3	33.2	0.1	0.0	0.5	0.4
CP-19	01/16/07	8.4	24.2	24	784	392	10.6	13	0.0	2.8	3.3	124.0	0.0	0.1	2.9	79.7	1.5	11.7	77.1	56.2	34.6	0.0	0.0	0.5	0.1
CP-20	01/31/07	8.9	22.3	87			15.0	1	0.0	3.0	3.3	125.4	0.0	0.5	2.9	82.1	1.6	10.2	72.0	54.4	33.5	0.0	0.0	0.5	0.2
CP-21	02/15/07	8.6	19.4	43			11.1	5	0.0	2.2	3.4	122.1	0.0	0.0	3.5	82.9	1.6	10.3	74.2	54.4	32.9	0.0	0.0	0.5	0.1
CP-22	03/01/07	8.5	26.1	54			8.3	2	0.1	2.1	3.9	146.9	0.0	0.1	5.4	98.0	1.9	10.3	76.3	51.9	33.5	0.0	0.0	0.5	0.3
CP-23	03/19/07	8.7	23.1	63			9.4	30	0.0	2.0	3.8	130.1	0.0	0.0	3.9	93.1	1.5	11.1	79.3	55.7	35.5	0.0	0.0	0.5	0.2
CP-24	04/03/07	8.6	29.9	-74			14.4	0	0.0	2.8	4.0	135.7	0.0	0.0	4.3	98.7	1.7	12.2	86.3	54.7	35.2	0.1	0.0	0.5	0.8
CP-25	04/18/07	8.7	24.9	11			7.8	0	0.1	2.8	2.8	123.5	0.0	0.0	2.2	96.7	1.3	11.1	80.7	56.0	35.0	0.0	0.0	0.5	0.1
CP-26	05/02/07	8.8	30.2	-30			12.2	15	0.0	4.3	4.3	129.5	0.0	0.0	2.4	98.2	1.9	11.2	81.6	54.8	35.4	0.0	0.0	0.5	0.1
CP-27	05/17/07	9.0	35.4	22			10.3	44	0.0	4.1	4.5	136.8	0.0	0.0	2.6	99.4	1.6	12.5	87.4	60.3	37.8	0.0	0.0	0.5	0.1
CP-28	05/31/07	9.1	30.4	-99	906		10.3	0	0.0	4.1	3.9	128.0	0.0	0.0	2.4	99.0	1.7	11.4	82.3	56.4	35.5	0.0	0.0	0.5	0.1
CP-29	06/15/07	9.0	35.1	-57	909		10.8	6	0.0	4.7	1.5	140.9	0.0	0.0	1.7	97.8	0.7	11.0	81.3	55.0	35.2	0.0	0.0	0.5	0.1

Sample	Date	pH	Temp	ORP	Cond	TDS	DO	H_2S	Fe^{2+}	As	F	Cl	NO_2	NO_3	PO_4	SO_4	Br	K	Na	Ca	Mg	Fe	Mn	Sr	Si
			° C	mV	uS/cm	mg/L	mg/L	ug/L	mg/l	ug/L	mg/L														
CP-30	07/03/07	9.0	34.9	-93	826		11.2	0	0.0	5.1	3.2	143.1	0.0	0.0	0.6	93.3	1.5	15.3	87.7	59.7	38.1	0.0	0.0	0.6	0.2
CP-31	07/16/07	8.6	35.8	-83	885	647	7.5	1	0.0	4.2	3.7	150.8	0.0	0.0	1.8	91.7	1.8	11.4	77.1	55.3	34.4	0.0	0.0	0.5	0.2
CP-32	08/07/07	8.7	37.8	-99	936	684	7.9	4	0.0	2.6	3.0	130.4	0.0	0.1	8.4	90.0	1.5	11.4	82.4	55.6	35.5	0.0	0.0	0.5	0.2
CP-33	08/15/07	8.7	38.3	43	936	688	9.1	1	0.0	2.4	3.9	142.1	0.0	0.0	5.4	98.2	1.9	11.6	82.1	55.7	35.5	0.0	0.0	0.5	0.2
CP-34	08/30/07	8.1	36.8	-99	946	691	7.6	8	0.0	2.1	3.9	134.7	0.0	0.0	1.9	95.1	2.1	12.5	87.1	57.6	37.2	0.0	0.0	0.6	0.3
CP-35	09/20/07	8.7	33.1	-67			5.5	22	0.0	2.3	3.9	136.3	0.0	0.0	6.8	99.3	2.1	13.1	87.8	59.8	38.8	0.0	0.0	0.6	0.2
CP-36	10/03/07	8.9	32.1	-37	972	716	8.7	8	0.1	2.2	4.0	136.8	0.0	0.0	1.3	97.4	2.0	12.2	86.2	59.1	38.4	0.0	0.0	0.6	0.2
CP-37	10/16/07	8.9	29.7	58	962	711	7.7	7	0.0	2.7	3.4	133.6	0.0	0.0	3.0	86.0	2.0	15.3	56.4	74.9	39.6	0.0	0.0	0.6	0.1
CP-38	10/30/07	8.9	27.7	-122	968	719	9.4	28	0.0	2.5	4.5	136.9	0.0	0.1	7.9	105.7	2.5	12.4	86.9	56.7	37.9	0.0	0.0	0.6	0.1
Wetland Pump (WP)																									
WP-1	04/28/06	6.9	22.2	-48	383		5.6	261	0.5	0.3	1.4	26.5	0.0	0.1	8.5	1.3	0.0	3.9	17.3	42.3	9.2	0.4	0.0	0.1	1.3
WP-2	05/19/06	7.0	23.0	-35	438		4.9	425	0.8	0.4	1.4	32.2	0.0	0.4	7.2	1.5	0.0	3.9	20.1	49.5	10.5	0.5	0.0	0.2	1.6
WP-3	06/27/06	7.0	30.3	-94	361		6.8	277	0.5	0.5	1.9	47.8	0.0	0.4	6.9	6.4	0.3	5.1	25.4	24.8	11.9	0.3	0.0	0.2	1.1
WP-4	07/12/06	7.1	26.9	-13	434		7.3	106		0.3	1.7	47.8	0.0	0.1	7.0	4.9	0.4	5.3	25.3	35.2	12.2	0.3	0.0	0.2	1.5
WP-5	07/28/06	6.9	27.7	-46	424		6.7	0	0.4	0.3	1.5	56.3	0.0	0.0	6.7	4.5	0.4	5.4	32.4	31.5	13.3	0.2	0.0	0.2	1.3
WP-6	08/10/06	6.7	27.1	-88	497		5.9	876	0.3	0.1	2.0	65.2	0.0	0.0	5.3	4.8	0.6	6.9	39.1	38.6	16.6	0.2	0.0	0.2	1.7
WP-7	08/31/06	6.5	26.2	-67			5.3	502	0.4	1.3	1.9	42.6	0.0	0.0	4.5	6.9	0.7	3.8	24.3	20.3	9.8	0.2	0.0	0.1	1.5
WP-8	09/14/06	6.6	27.4	-43	273	135	4.2	173	0.2	0.6	1.5	38.1	0.0	2.1	6.2	4.0	0.2	2.9	20.7	17.2	8.5	0.2	0.0	0.1	1.2
WP-9	09/28/06	6.4	25.2	-4			3.9	146	0.3	0.6	1.1	31.4	0.0	0.8	5.0	3.2	0.2	2.7	19.6	18.4	8.8	0.2	0.0	0.1	1.1
WP-10	10/11/06	6.5	22.8	-25	360	179	4.6	162	0.2	0.1	1.4	41.4	0.0	0.0	3.8	5.5	0.4	3.2	28.7	24.6	11.7	0.1	0.0	0.2	1.1
WP-11	11/01/06	6.6	24.5	-91	685	372	5.4	822	0.2	0.3	2.0	104.6	0.0	0.0	0.0	40.2	0.0	9.5	63.7	47.3	26.1	0.1	0.0	0.3	1.4
WP-12	11/07/06	6.9	21.0	-49			5.8	699		0.2	3.2	118.7	0.0	0.0	4.2	60.4	1.3	9.4	67.1	49.2	27.5	0.1	0.0	0.4	1.3
WP-13	11/20/06	7.0	16.1	-136	412	412	4.3	900	0.5	0.8	3.7	119.9	0.1	0.1	7.4	57.3	1.6	10.8	72.0	58.5	30.9	0.4	0.0	0.4	1.4
WP-14	12/07/06	6.8	18.0	-82	780	390	5.4	678	0.2	0.5	2.4	120.0	0.0	0.1	3.4	56.8	1.1	0.8	73.3	54.4	31.5	0.0	0.0	0.4	0.0
WP-15	12/14/06	6.9	19.8	-48	797	395	5.9	794	0.2	0.5	2.9	123.7	0.0	0.0	3.7	64.4	1.2	11.6	71.4	50.9	29.7	0.1	0.0	0.4	1.1
WP-16	12/18/06	6.9	19.1	-105			6.1	900	0.2	0.5	2.1	125.6	0.0	0.0	3.0	54.1	1.0	13.1	76.1	56.3	33.6	0.1	0.0	0.5	1.0
WP-17	01/09/07	6.9	18.7	-85	750	376	1.6	900	0.3	0.3	2.7	109.2	0.0	0.1	5.4	46.8	1.3	13.8	70.0	46.1	29.5	0.2	0.1	0.4	0.9
WP-18	01/16/07	6.7	18.6	-128	767	387	6.1	900	0.2	1.3	2.4	110.9	0.0	0.0	4.5	48.7	1.1	16.3	72.2	50.3	30.6	0.1	0.0	0.4	0.9
WP-19	01/31/07	7.1	13.9	-18			5.5	92	0.2	1.4	3.5	112.6	0.0	0.2	5.5	62.3	1.8	10.6	67.8	47.2	29.2	0.1	0.0	0.4	0.3
WP-20	02/15/07	6.9	14.9	-100			6.6	619	0.2	0.7	2.9	105.7	0.1	0.0	4.3	60.0	2.2	10.8	66.1	47.2	28.4	0.1	0.0	0.3	0.3
WP-21	03/01/07	7.0	20.2	-73			4.3	900	0.2	0.6	2.8	126.0	0.0	0.0	3.9	63.0	1.4	10.6	69.3	48.9	29.7	0.1	0.0	0.4	0.3
WP-22	03/19/07	7.0	16.5	-84			6.0	731	0.1	0.2	3.1	124.7	0.0	0.0	3.9	65.1	1.3	10.9	76.7	51.7	32.8	0.1	0.0	0.5	0.5

Sample	Date	pH	Temp	ORP	Cond	TDS	DO	H_2S	Fe^{2+}	As	F	Cl	NO_2	NO_3	PO_4	SO_4	Br	K	Na	Ca	Mg	Fe	Mn	Sr	Si
			° C	mV	uS/cm	mg/L	mg/L	ug/L	mg/l	ug/L															
WP-23	04/03/07	7.0	22.7	-103			7.4	900	0.1	0.4	4.4	125.1	0.0	0.0	6.6	67.7	2.0	11.2	78.3	55.4	35.1	0.0	0.0	0.5	0.1
WP-24	04/18/07	6.8	18.1	-83			5.5	794	0.1	0.3	2.8	117.2	0.0	0.0	3.1	64.5	1.6	11.6	76.9	49.8	31.6	0.0	0.0	0.5	1.2
WP-25	05/02/07	7.0	24.1	-32			4.8	28	<0.1	0.9	4.0	124.0	0.0	0.0	3.7	70.2	1.8	12.1	81.8	52.7	34.2	0.0	0.0	0.5	0.9
WP-26	05/17/07	7.2	25.3	-94			5.5	745	<0.1	1.0	2.8	145.7	0.0	0.0	0.0	79.4	1.5	14.5	95.4	62.1	39.5	0.0	0.0	0.5	1.9
WP-27	05/31/07	7.4	23.7	-152	1000		5.7	441	0.0	0.9	0.7	138.2	0.0	0.0	0.0	81.5	0.9	12.6	93.5	59.4	38.8	0.0	0.0	0.5	0.8
WP-28	06/15/07	7.3	26.2	-176	929		2.5	760	0.1	1.8	1.9	136.0	0.0	0.0	0.8	70.7	0.1	11.5	81.5	51.5	34.1	0.0	0.0	0.5	1.0
WP-29	07/03/07	7.2	26.2	-130	949		2.9	900	0.2	6.6	3.6	128.3	0.0	0.0	3.1	60.3	1.6	14.3	78.5	56.1	37.1	0.1	0.0	0.5	1.5
WP-30	07/16/07	7.1	27.5	-96	680	496	2.2	342	1.0	1.4	2.9	113.1	0.0	0.0	3.6	42.6	1.2	7.6	58.5	38.3	23.9	0.6	0.0	0.3	1.4
WP-31	08/07/07	7.0	27.2	-101	707	516	3.3	900	0.1	0.5	1.5	95.0	0.0	0.0	2.0	28.6	0.7	6.3	61.5	39.4	25.4	0.1	0.0	0.4	1.7
WP-32	08/15/07	7.2	27.6	-103	704	513	3.9	900	0.1	0.4	2.5	105.5	0.0	0.0	2.5	29.0	1.0	6.5	61.1	39.8	25.0	0.1	0.0	0.4	1.7
WP-33	08/30/07	7.3	28.7	-101	753	552	4.0	900	0.2	0.2	3.0	103.7	0.0	0.6	2.7	35.3	1.5	8.4	67.5	43.5	28.0	0.1	0.0	0.4	1.8
WP-34	09/20/07	7.1	26.6	-70			3.9	900	0.1	0.1	2.6	98.1	0.0	0.0	2.8	30.9	1.2	8.0	63.0	39.4	25.7	0.1	0.0	0.3	1.9
WP-35	10/03/07	6.9	26.1	-91	774	570	3.5	860	0.2	0.2	3.0	107.9	0.0	0.0	2.3	37.2	1.4	9.4	71.3	44.4	28.9	0.1	0.0	0.4	2.0
WP-36	10/30/07	7.0	23.8	-81	805	597	3.7	###	0.2	0.3	3.2	110.8	0.0	0.0	4.7	40.7	1.9	11.2	72.5	47.1	30.4	0.1	0.0	0.4	1.7
Wetland Surface(WS)																									
WS-1	04/28/06	6.3	24.2	38	330		0.9	11	0.6	0.3	1.4	42.5	0.0	0.0	8.2	1.5	0.0	4.6	17.0	25.6	10.5	0.5	0.1	0.2	0.6
WS-2	08/31/06	6.1	26.8	-63	269	135	0.7	171	0.7	0.8	1.6	34.6	0.0	0.1	5.8	4.6	0.5	4.1	29.4	18.4	8.9	0.4	0.1	0.2	2.0
WS-3	09/28/06	6.3	25.0	32	248	123	0.4	58	0.2	0.4	1.0	24.7	0.0	0.0	4.5	3.7	0.2	3.0	27.5	17.0	9.0	0.2	0.0	0.1	1.1
WS-4	12/07/06	6.6	17.5	-72	779	390	1.4	653	0.1	0.5	3.0	129.3	0.0	0.0	4.4	57.7	1.3	13.3	53.5	43.8	26.7	0.1	0.0	0.3	1.0
WS-5	12/14/06	6.8	21.8	-39	786	395	5.4	3	0.3	0.6	2.8	131.1	0.0	0.0	3.4	59.4	1.3	11.6	51.7	40.4	26.0	0.0	0.0	0.3	0.4
WS-6	01/31/07	6.9	16.2	68			2.7	2	0.2	0.9	3.7	153.2	0.0	0.1	5.3	66.7	1.8	11.9	53.7	43.2	27.2	0.0	0.0	0.3	0.4
WS-7	02/15/07	6.9	16.0	29			4.6	10	0.2	0.9	2.9	120.6	0.0	0.0	4.0	49.5	1.5	10.5	48.8	40.3	24.9	0.1	0.0	0.3	0.1
WS-8	03/01/07	7.1	21.2	37			2.4	15	<0.1	1.4	3.6	151.8	0.0	0.0	4.8	79.7	1.8	8.8	64.8	47.6	30.3	0.1	0.0	0.3	0.2
WS-9	03/19/07	7.2	16.0	76			1.1	19	0.8	1.8	3.1	118.4	0.0	0.0	3.1	57.4	1.3	10.2	56.3	44.7	28.6	0.1	0.0	0.4	0.0
WS-10	04/03/07	6.9	23.3	-95			1.6	402	0.1	0.9	4.0	152.6	0.0	0.0	6.0	79.7	1.8	12.6	65.5	51.3	33.9	0.0	0.0	0.4	0.6
WS-11	04/18/07	6.7	20.0	-119			0.9	900	<0.1	0.9	3.3	126.7	0.0	0.0	3.3	54.0	1.6	12.1	60.8	48.8	30.7	0.0	0.0	0.4	1.3
WS-12	05/02/07	7.0	24.3	-6			3.2	4	<0.1	1.3	4.1	157.1	0.0	0.0	3.2	79.8	1.9	13.0	65.0	53.1	32.7	0.0	0.0	0.4	0.9
WS-13	05/17/07	7.1	28.5	-33			2.6	10	<0.1	1.0	4.3	146.1	0.0	0.0	0.0	75.3	0.9	13.7	69.8	56.1	35.5	0.0	0.0	0.5	1.6
WS-14	05/31/07	7.2	25.3	-44	1002		2.4	0	0.1	0.9	0.8	23.8	0.0	0.0	0.0	4.9	1.4	14.6	79.2	63.0	39.5	0.0	0.0	0.5	0.9
WS-15	06/15/07	7.2	26.7	-37	929		1.3	14	0.3	0.9	1.0	40.3	0.0	0.0	0.8	20.7	0.5	13.7	74.0	56.5	36.7	0.0	0.0	0.5	1.1
WS-16	07/03/07	6.9	26.7	-133	950		0.2	900	0.4	0.7	3.9	154.4	0.0	0.0	2.4	52.4	1.4	14.1	74.2	56.5	37.3	0.1	0.0	0.5	1.5
WS-17	07/16/07	7.2	27.3	0	381	273	3.6	3	0.1	13.1	1.7	48.5	0.0	0.0	5.4	19.9	0.6	5.5	27.7	24.9	13.8	0.1	0.0	0.2	1.2

Sample	Date	pH	Temp	ORP	Cond	TDS	DO	H_2S	Fe^{2+}	As	F	Cl	NO_2	NO_3	PO_4	SO_4	Br	K	Na	Ca	Mg	Fe	Mn	Sr	Si
			° C	mV	uS/cm	mg/L	mg/L	ug/L	mg/l	ug/L															
WS-18	08/07/07	6.7	27.1	-166	770	565	0.1	900	0.6	1.1	0.2	5.6	0.0	0.0	0.4	0.6	0.1	9.5	58.4	53.4	30.3	0.2	0.0	0.4	3.8
WS-19	08/15/07	6.9	28.9	-98	694	505	0.6	900	0.1	0.4	2.3	80.0	0.0	0.0	8.1	20.5	1.0	8.0	58.3	44.4	28.6	0.0	0.0	0.4	2.0
WS-20	08/30/07	7.1	31.1	-57	752	548	2.9	31	0.1	0.2	3.1	111.3	0.0	0.0	2.0	31.7	1.5	9.6	58.4	43.6	27.8	0.1	0.0	0.4	1.7
WS-21	09/20/07	6.8	25.7	-74			0.4	900	0.1	0.2	2.9	106.1	0.0	0.0	7.1	23.4	1.2	8.9	53.1	40.6	26.9	0.0	0.0	0.3	2.0
WS-22	10/03/07	7.0	27.4	-76	771	567	1.3	25	0.2	0.7	2.8	109.9	0.0	0.0	2.9	29.3	1.3	9.3	52.3	42.4	26.3	0.1	0.0	0.3	1.8
WS-23	10/16/07	7.3	26.1	101	888	659	3.8	10	0.1	2.6	3.2	126.2	0.0	0.0	2.6	66.5	2.0	13.7	52.0	63.3	35.5	0.0	0.1	0.5	0.7
WS-24	10/30/07	7.1	24.0	-7	805	596	1.6	7	0.0	10.8	2.8	114.8	0.0	0.0	3.9	40.1	1.6	13.1	46.3	59.8	31.0	0.0	0.1	0.4	1.6
Filter Basin North Pump (FBN)																									
FBN-1	08/10/06	6.6	30.1	4	448		4.7	4	0.4	1.1	1.5	66.2	0.0	0.2	3.0	5.7	0.6	6.3	51.6	31.4	13.7	0.3	0.0	0.3	1.5
FBN-2	08/31/06	6.3	27.5	43			2.4	0	0.1	1.1	1.6	39.9	0.0	1.6	2.9	7.4	0.4	4.9	37.4	24.9	10.1	0.1	0.0	0.2	1.7
FBN-3	09/14/06	6.3	26.5	87	275	1	3.6	0	0.2	0.6	1.9	38.9	0.0	5.8	5.1	5.6	0.3	4.1	30.4	22.0	8.9	0.2	0.0	0.2	1.6
FBN-4	11/01/06	6.3	23.5	20	619	310	1.3	0	0.3	0.6	1.2	75.7	0.0	0.5	1.7	33.8	0.8	7.0	42.9	35.4	20.0	0.2	0.0	0.2	1.2
FBN-5	11/07/06	6.5	21.8	-23			1.2	6	0.4	0.7	1.9	111.1	0.0	0.1	3.1	57.7	1.2	8.9	49.7	41.7	24.0	0.2	0.1	0.3	1.2
FBN-6	11/20/06	6.7	20.6	65			3.4	0	0.5	0.8	1.5	104.5	0.0	0.4	2.8	54.9	1.2	10.0	54.9	44.2	26.4	0.1	0.1	0.3	1.3
FBN-7	12/07/06	6.7	18.2	-9	756	379	6.4	0	0.3	0.9	1.9	128.5	0.0	0.4	2.3	60.1	1.4	10.5	53.6	42.2	25.9	0.1	0.0	0.2	1.0
FBN-8	01/09/07	6.9	19.4	-26	653	328	5.8	6	0.4	1.3	2.2	115.8	0.0	0.4	2.6	45.6	1.2	11.6	51.4	42.9	25.5	0.2	0.0	0.3	0.9
FBN-9	01/16/07	6.6	21.4	15	698	346	5.9	0	0.5	1.2	2.1	113.0	0.0	0.4	2.6	46.1	1.2	13.0	51.5	42.0	26.2	0.2	0.0	0.3	1.1
FBN-10	01/31/07	6.9	16.8	-5	718	360	5.4	6	0.2	0.9	3.1	158.4	0.0	0.4	4.0	68.6	1.9	11.3	52.3	41.2	27.1	0.1	0.0	0.3	0.5
FBN-11	03/01/07	6.7	18.7	41			6.2	1	0.2	2.2	2.1	107.1	0.0	0.5	1.8	53.4	1.1	9.0	64.3	44.5	27.6	0.0	0.0	0.3	0.7
FBN-12	03/19/07	7.2	18.9	16			6.5	0	0.3	2.0	3.2	139.8	0.2	0.7	3.2	70.6	2.0	10.0	54.4	42.2	27.0	0.0	0.0	0.3	0.0
FBN-13	04/03/07	6.7	22.8	7			3.0	0	0.2	1.9	2.5	131.9	0.0	1.6	3.6	65.2	1.6	11.9	60.9	46.0	29.9	0.1	0.0	0.3	0.6
FBN-14	04/18/07	6.7	21.6	-38			1.3	16	0.9	2.2	3.4	135.4	0.0	0.2	3.3	63.5	1.6	12.2	60.3	45.9	30.6	0.3	0.1	0.3	1.0
FBN-15	05/02/07	6.9	23.2	-108			6.4	35	1.5	2.2	3.3	146.4	0.0	0.2	2.1	76.6	1.7	12.1	61.8	47.3	31.2	0.8	0.1	0.3	1.0
FBN-16	06/15/07	7.5	26.4	-93	913		5.9	21	0.8	2.2	0.3	23.5	0.2	0.3	0.2	24.9	2.7	13.7	73.8	51.7	35.1	0.6	0.1	0.4	1.1
FBN-17	07/03/07	7.0	26.4	-90	925		5.5	7	1.5	2.1	2.5	123.2	0.0	0.1	1.4	51.9	1.4	13.9	74.8	51.6	35.7	1.3	0.1	0.4	1.4
FBN-18	07/16/07	7.3	28.5	20	815	599	5.0	2	0.4	0.8	0.7	26.6	0.0	0.1	0.0	13.9	0.3	11.1	65.5	45.4	29.8	0.1	0.0	0.4	1.3
FBN-19	08/07/07	6.9	27.7	-18	754	553	4.2	0	0.2	0.9	1.6	60.6	0.0	3.0	1.0	28.6	0.8	10.9	60.7	49.4	29.9	0.2	0.0	0.4	1.8
FBN-20	08/15/07	7.3	27.7	11	703	514	4.5	7	0.3	0.9	2.8	97.9	0.0	0.7	2.4	24.9	1.2	9.2	58.8	45.8	28.5	0.2	0.0	0.4	2.0
FBN-21	08/30/07	6.5	28.3	-50	729	533	4.9	10	0.5	0.7	3.0	110.1	0.0	0.1	2.0	30.9	1.4	8.5	55.8	41.9	27.6	0.3	0.1	0.4	1.8
FBN-22	09/20/07	7.1	27.2	-30			4.8	27	0.5	0.7	2.9	106.6	0.0	0.7	2.2	32.2	1.4	8.4	50.9	39.6	26.4	0.4	0.0	0.3	1.8
FBN-23	10/03/07	7.1	26.4	-75	757	556	5.7	14	0.8	0.5	2.7	113.5	0.0	0.3	1.9	32.1	1.3	10.1	57.6	43.9	29.5	0.5	0.0	0.3	2.0
FBN-24	10/16/07	7.2	26.5	-79	828	612	5.8	40	0.6	2.0	2.6	120.4	0.0	0.1	2.9	52.7	1.7	12.0	47.3	56.5	31.4	0.5	0.1	0.4	1.4

Sample	Date	pH	Temp	ORP	Cond	TDS	DO	H_2S	Fe^{2+}	As	F	Cl	NO_2	NO_3	PO_4	SO_4	Br	K	Na	Ca	Mg	Fe	Mn	Sr	Si
			° C	mV	uS/cm	mg/L	mg/L	ug/L	mg/l	ug/L									mg/L						
FBN-25	10/30/07	7.1	24.5	-66	804	595	5.8	14	0.8	0.9	3.3	146.4	0.0	0.1	3.6	52.5	2.0	13.2	49.1	55.5	32.0	0.7	0.1	0.4	1.7
Filter Basin South Pump (FBS)																									
FBS-1	08/31/06	6.4	27.7	-48			0.9	17	1.8	2.3	1.4	39.0	0.0	0.3	1.9	6.0	0.5	4.9	38.6	26.3	10.9	1.6	0.1	0.2	1.8
FBS-2	09/14/06	6.4	26.9	-35	385	2	1.3	8	2.5	1.0	2.0	45.7	0.0	4.0	1.7	6.1	0.3	4.3	33.9	25.6	10.5	2.3	0.1	0.2	1.8
FBS-3	09/28/06	6.8	25.2	-72			0.9	18	2.5	1.2	1.3	35.6	0.0	0.0	0.0	5.3	0.3	4.6	34.0	29.0	12.0	2.0	0.1	0.2	2.5
FBS-4	10/11/06	6.3	25.8	-97	319	159	2.2	7	2.0	0.8	1.8	37.6	0.0	0.3	0.0	6.4	0.4	3.9	31.6	26.2	11.4	2.3	0.1	0.2	2.0
FBS-5	11/01/06	6.3	24.1	-34	589	294	1.2	0	2.0	0.5	1.7	86.9	0.0	0.4	1.5	38.6	1.0	6.2	38.1	31.3	17.6	0.5	0.0	0.2	1.3
FBS-6	11/07/06	6.6	22.6	-56			1.1	15	2.0	0.6	1.9	104.4	0.0	0.2	1.6	52.0	1.1	9.7	52.2	48.8	25.8	0.1	0.0	0.4	1.3
FBS-7	11/20/06	6.4	24.7	-62	463	231	2.7	0	3.0	0.6	2.0	59.2	0.0	0.4	0.0	21.9	0.6	6.4	28.5	33.1	15.6	0.8	0.1	0.2	2.2
FBS-8	12/07/06	6.7	18.9	-13	782	391	2.8	0	0.3	1.3	2.1	117.9	0.0	0.4	1.9	54.3	1.4	10.6	52.9	43.0	26.0	0.1	0.0	0.3	1.0
FBS-9	12/14/06	6.5	19.7	-11	250	372	1.9	6	1.0	0.9	2.0	113.5	0.0	0.1	1.2	52.8	1.2	9.2	48.4	43.0	22.6	0.4	0.0	0.2	1.2
FBS-10	12/18/06	6.6	21.0	-7			4.7	13	1.0	0.5	1.4	78.6	0.0	0.4	0.6	36.9	0.9	9.0	51.0	41.9	24.0	0.3	0.0	0.2	1.3
FBS-11	01/09/07	6.8	19.8	-53	706	353	1.5	48	1.5	0.7	2.2	107.2	0.0	0.3	1.7	36.7	1.1	11.3	49.7	40.1	24.4	0.5	0.0	0.3	1.0
FBS-12	01/16/07	6.6	19.0	-95	698	352	3.4	160	1.5	0.7	1.8	85.6	0.0	0.1	2.2	29.8	0.9	12.9	50.9	42.3	25.6	0.3	0.0	0.3	0.9
FBS-13	01/31/07	6.9	16.5	-33	732	366	1.9	21	0.7																
FBS-14	02/15/07	6.5	15.9	2			4.5	21	0.5	0.8	2.2	115.8	0.0	0.1	2.3	49.5	1.4	8.8	48.3	37.2	23.2	0.1	0.0	0.2	0.5
FBS-15	03/01/07	6.6	18.5	-9			2.4	28	0.9	1.8	2.2	119.2	0.0	0.1	1.9	59.5	1.3	8.0	57.3	46.0	27.2	0.2	0.0	0.3	0.7
FBS-16	03/19/07	6.9	19.6	-11			2.9	3	1.5	1.3	2.0	93.4	0.2	0.3	1.0	47.1	1.2	10.3	52.2	42.4	25.6	0.6	0.0	0.3	0.7
FBS-17	04/03/07	6.8	23.5	-30			1.9	3	0.7	2.0	3.4	158.6	0.1	1.1	4.3	81.8	1.8	12.0	62.8	47.8	30.8	0.3	0.0	0.3	0.6
FBS-18	05/02/07	6.7	22.7	-97			2.6	90	1.5	1.3	3.2	143.9	0.0	0.2	2.4	69.8	1.7	12.0	60.5	47.3	30.1	1.6	0.0	0.3	1.1
FBS-19	05/17/07	6.7	23.7	-2			1.9	22	1.0	1.8	2.1	142.7	0.0	0.0	0.0	65.3	0.5	12.8	64.6	48.9	31.3	0.7	0.0	0.3	1.5
FBS-20	05/31/07	7.1	24.7	-100	932		6.2	16	0.6	1.2	1.0	23.3	0.0	0.0	0.0	11.3	0.7	13.3	75.5	53.1	34.6	0.1	0.0	0.4	1.3
FBS-21	06/15/07	7.3	27.2	-85	916		2.9	11	1.0	2.3	2.1	10.1	0.0	0.0	2.7	0.6	0.0	13.8	73.5	51.3	35.1	0.4	0.1	0.4	1.1
FBS-22	07/03/07	7.0	26.5	-90	919		2.2	11	2.0	2.1	2.6	122.3	0.0	0.0	1.3	51.2	1.4	13.4	73.8	51.6	34.6	1.4	0.1	0.4	1.4
FBS-23	07/16/07	7.0	27.5	-72	839	619	1.7	3	1.5	1.6	2.8	129.3	0.1	0.7	1.6	57.4	1.5	12.0	67.0	48.0	31.0	1.3	0.1	0.4	1.5
FBS-24	08/07/07	6.9	28.0	-48	759	556	2.8	17	0.8	1.3	1.6	54.0	0.2	0.7	1.2	26.4	0.7	10.9	60.1	49.3	32.1	0.7	0.1	0.4	1.9
FBS-25	08/15/07	7.2	28.2	-74	699	510	1.7	66	1.5	0.9	2.8	92.2	0.0	0.2	2.5	22.3	1.2	9.0	60.0	44.9	28.3	1.2	0.1	0.4	2.0
FBS-26	08/30/07	6.9	28.2	-74	732	536	3.8	14	1.0	0.6	2.9	107.2	0.2	0.3	2.0	31.2	1.5	8.9	56.1	41.2	27.0	1.3	0.0	0.4	1.8
FBS-27	09/20/07	6.9	26.7	-32			2.3	41	1.5	0.9	2.6	103.2	0.0	0.0	1.9	26.8	1.3	8.5	50.6	39.7	25.2	1.4	0.0	0.3	1.8
FBS-28	10/03/07	7.1	26.5	-84	745	547	4.1	26	1.0	0.5	2.7	107.3	0.0	0.2	1.4	30.4	1.2	9.6	54.5	40.4	27.7	1.0	0.0	0.3	1.9
FBS-29	10/16/07	7.2	27.2	-76	811	598	2.2	24	1.0	2.7	2.5	110.3	0.0	0.1	2.5	49.4	1.7	12.1	46.9	57.4	31.8	1.0	0.1	0.4	1.4
FBS-30	10/30/07	7.1	24.8	-84	788	582	4.8	5	2.0	0.8	3.4	138.4	0.0	0.0	2.7	53.3	2.0	13.0	48.0	56.9	31.3	1.0	0.1	0.4	1.7

Sample	Date	pH	Temp	ORP	Cond	TDS	DO	H_2S	Fe^{2+}	As	F	Cl	NO_2	NO_3	PO_4	SO_4	Br	K	Na	Ca	Mg	Fe	Mn	Sr	Si
			° C	mV	uS/cm	mg/L	mg/L	ug/L	mg/l	ug/L															
Monitor Well (MW-1)																									
MW-1-1	04/28/06	6.1	25.5	1	660		3.6	41	4.0	1.2	0.6	49.4	0.0	0.4	0.0	20.7	0.9	5.4	13.7	71.8	34.5	2.4	0.1	0.2	7.7
MW-1-2	05/19/06	5.9	26.4	17	578		2.2	13	>10	2.8	0.5	32.1	0.0	0.8	0.0	11.6	1.1	1.7	9.1	63.8	30.4	18.1	0.2	0.2	9.8
MW-1-3	06/16/06	6.0	25.8	112	186		0.9	10	0.2	1.1	1.5	7.4	0.0	0.9	0.7	15.6	0.0	3.5	4.1	21.2	8.3	0.3	0.0	0.1	4.5
MW-1-4	06/27/06	6.1	27.1	7	251		1.5	29	5.0	2.1	1.1	8.8	0.0	0.0	0.0	11.9	0.2	3.2	4.8	26.4	10.9	4.1	0.1	0.1	6.1
MW-1-5	07/12/06	6.0	28.2	11	281		4.4	22	7.0	2.5	1.1	10.8	0.0	0.0	0.0	13.9	0.2	2.6	4.4	26.9	11.6	6.1	0.1	0.1	6.1
MW-1-6	07/28/06	5.8	28.7	5	331		1.9	0	>10	3.2	3.5	12.6	0.0	0.0	3.0	97.4	2.0	2.4	5.9	36.1	16.2	12.8	0.1	0.1	7.6
MW-1-7	08/31/06	5.7	27.8	20	210	106	3.9	36	>10	3.0	1.0	6.9	0.0	0.1	0.0	6.6	0.4	2.7	3.6	23.7	7.7	10.1	0.1	0.1	4.5
MW-1-8	09/28/06	5.9	26.6	23			2.4	76	9.0	3.4	0.9	5.3	0.0	0.0	0.0	4.7	0.0	2.2	3.1	25.3	6.9	7.1	0.1	0.1	4.5
MW-1-9	11/07/06	5.7	24.2	12			3.2	65	>10	3.4	0.9	6.2	0.0	0.0	0.0	4.7	0.3	1.9	4.4	28.5	10.3	8.6	0.1	0.1	5.8
MW-1-10	12/14/06	5.9	22.8	4	270	9	5.6	33	>10	3.0	0.7	6.6	0.0	0.1	0.0	3.4	0.3	1.3	4.3	27.3	10.4	4.4	0.1	0.0	5.4
MW-1-11	01/09/07	5.8	21.2	120	311	155	3.3	2	>10	2.9	0.7	14.3	0.3	61.8	0.0	19.0	0.1	2.6	4.3	33.7	10.1	0.2	0.0	0.0	3.7
MW-1-12	01/31/07	5.7	19.8	114			4.6	2	0.3	3.5	1.0	17.6	0.3	149.8	0.4	27.7	0.2	3.3	5.4	43.1	13.1	0.1	0.0	0.1	3.9
MW-1-13	03/01/07	5.7	21.4	152			3.9	3	0.1	2.1	0.7	13.6	0.5	127.7	0.0	24.2	0.0	3.7	5.4	46.4	12.7	0.0	0.1	0.1	3.9
MW-1-14	04/03/07	5.5	22.9	147			3.6	0	0.1	3.6	1.0	20.1	1.0	75.2	0.0	27.6	0.2	3.2	5.1	38.8	11.4	0.0	0.0	0.0	3.9
MW-1-15	05/02/07	5.5	24.2	80			3.4	6	2.0	2.1	0.9	17.0	0.0	3.7	0.0	19.3	0.6	2.1	6.2	36.8	12.6	2.5	0.1	0.0	5.2
MW-1-16	05/31/07	5.9	24.9	128	439		4.2	3	0.1	1.3	0.6	48.1	0.5	0.5	0.0	49.7	5.3	4.6	27.5	36.0	12.2	0.1	0.1	0.2	4.1
MW-1-17	07/03/07	6.4	26.8	3	725		2.0	0	0.6	3.7	0.8	147.4	0.0	0.3	0.6	42.5	1.7	8.0	63.7	42.6	16.7	0.5	0.1	0.1	3.7
MW-1-18	08/07/07	6.1	26.4	-13	229	162	2.7	25	>10	3.4	0.7	4.8	0.0	0.0	0.3	6.5	0.1	3.3	4.3	30.3	8.9	11.8	0.1	0.1	5.3
MW-1-19	08/30/07	6.6	27.9	-39	288	205	1.6	29	8.0	2.1	1.1	6.9	0.0	0.0	0.0	11.1	0.2	3.4	4.1	28.0	9.1	7.3	0.1	0.1	5.0
MW-1-20	10/03/07	6.0	27.3	23	226	160	1.2	8	3.0	1.2	1.1	8.1	0.1	5.8	0.0	18.0	0.0	3.2	4.0	27.1	7.9	2.5	0.0	0.0	4.4
MW-1-21	10/30/07	5.9	25.2	54	269	191	1.5	3	1.0	0.4	0.9	9.1	0.0	36.3	0.8	18.3	0.0	4.3	4.0	37.4	9.2	0.9	0.1	0.1	5.4
Monitor Well (MW-2)																									
MW-2-1	04/28/06	6.0	26.5	-30	384		4.6	16	>10	3.1	0.4	55.9	0.0	1.5	0.0	10.0	1.1	20.4	15.2	48.7	22.3	21.2	0.2	0.2	17.7
MW-2-2	05/19/06	5.8	28.0	-25	567		1.3	58	>10	4.9	0.5	24.7	0.2	6.1	0.0	5.4	1.0	3.1	14.1	41.4	19.6	20.4	0.2	0.1	17.7
MW-2-3	06/16/06	6.1	26.6	62	633		1.8	10	1.5	0.6	0.8	13.2	0.7	281.5	0.0	27.8	0.2	3.4	7.0	66.6	26.5	1.7	0.1	0.1	6.7
MW-2-4	06/27/06	6.1	28.0	164	630		2.2	6	0.3	0.5	1.2	17.9	1.1	341.0	0.0	32.3	0.2	2.7	7.9	68.7	28.2	0.3	0.1	0.2	5.6
MW-2-5	07/12/06	6.0	28.2	51	675		4.1	4	1.0	0.7	1.0	18.3	0.2	195.8	0.0	22.8	0.5	2.2	6.9	56.8	24.9	0.7	0.1	0.1	5.4
MW-2-6	07/28/06	5.7	28.2	96	501		0.8	0	0.5	0.4	0.8	15.7	0.1	88.9	0.0	17.6	0.4	2.1	7.5	58.1	26.4	0.4	0.1	0.1	6.1
MW-2-7	08/31/06	5.6	27.3	88	330	163	2.1	0	1.0	1.6	1.0	10.2	0.0	3.0	0.0	26.0	0.2	1.7	5.3	39.8	16.6	0.9	0.1	0.1	7.6
MW-2-8	09/28/06	5.9	26.3	34			3.0	17	>10	6.6	1.3	16.3	0.0	0.0	0.0	24.9	0.4	2.0	6.6	49.2	22.0	8.7	0.1	0.1	7.3
MW-2-9	11/07/06	5.8	23.9	17			3.2	5	>10	5.9	1.2	23.1	0.0	0.1	0.0	18.3	0.4	1.7	6.9	56.4	26.0	13.6	0.2	0.1	7.6

Sample	Date	pH	Temp	ORP	Cond	TDS	DO	H_2S	Fe^{2+}	As	F	Cl	NO_2	NO_3	PO_4	SO_4	Br	K	Na	Ca	Mg	Fe	Mn	Sr	Si
			° C	mV	uS/cm	mg/L	mg/L	ug/L	mg/l	ug/L								mg/L								
MW-2-10	12/14/06	6.0	22.3	-12	455	231	3.8	8	>10	5.8	0.9	19.0	0.0	0.1	0.0	16.9	0.5	1.0	6.3	46.0	22.5	9.0	0.1	0.1	6.2
MW-2-11	01/09/07	6.1	20.4	54	452	227	3.9	2	>10	3.5	0.8	16.4	0.1	4.1	0.0	15.4	0.4	0.9	6.0	43.8	20.9	3.5	0.1	0.1	5.9
MW-2-12	01/31/07	6.0	19.2	51			4.3	2	2.0	5.0	1.1	22.0	0.2	14.6	0.0	19.1	0.4	1.5	6.4	44.7	21.0	2.4	0.1	0.1	5.3
MW-2-13	03/01/07	6.1	21.1	15			3.6	0	3.0	4.9	1.0	25.2	0.0	0.0	0.0	17.6	0.6	1.6	6.7	58.2	29.4	2.7	0.1	0.1	6.2
MW-2-14	04/03/07	5.8	22.9	1			2.4	4	>10	6.9	0.9	20.2	0.0	0.0	0.0	12.5	0.5	1.0	7.9	58.7	30.5	11.6	0.1	0.1	6.7
MW-2-16	05/02/07	5.9	24.5	-6			3.1	0	>10	7.1	1.4	30.1	0.0	0.1	0.0	12.8	0.8	1.2	9.9	66.1	34.2	16.1	0.2	0.1	7.7
MW-2-16	05/31/07	6.2	25.3	-45	578		2.9	4	>10	7.2	0.6	61.5	0.0	4.6	0.0	10.2	0.7	1.6	9.7	63.7	32.4	13.0	0.2	0.1	7.7
MW-2-17	07/03/07	6.2	26.8	-35	616		1.9	0	>10	7.6	1.0	35.7	0.0	0.0	0.1	10.3	0.7	1.6	12.1	67.9	34.8	8.7	0.2	0.1	8.0
MW-2-18	08/07/07	6.1	27.0	-23	528	384	1.7	1	10.0	3.9	0.9	25.2	0.0	0.0	0.0	10.3	0.5	1.6	10.2	63.4	31.4	9.0	0.2	0.1	8.1
MW-2-19	08/30/07	5.9	27.3	-37	768	565	1.4	31	10.0	3.4	1.2	39.1	0.0	0.0	0.0	11.1	1.2	1.7	14.0	73.0	38.3	7.6	0.2	0.2	7.9
MW-2-20	10/03/07	6.0	26.7	-7	734	538	1.5	4	8.0	3.2	1.0	40.7	0.0	0.0	0.0	10.2	1.1	1.6	17.1	76.4	40.6	7.6	0.2	0.1	8.5
MW-2-21	10/30/07	6.0	24.9	-24	657	481	1.5	9	10.0	4.1	1.3	29.2	0.0	0.2	0.0	9.9	1.0	1.9	12.4	81.1	34.1	10.0	0.2	0.2	8.3
Monitor Well (MW-3)																									
MW-3-1	04/28/06	5.9	27.0	40	253		6.2	28	1.5	0.5	0.3	12.9	0.2	20.0	0.0	18.7	0.0	4.0	6.0	26.3	9.3	1.2	0.1	0.1	4.9
MW-3-2	05/19/06	6.0	26.8	102	250		3.1	19	4.0	1.1	0.5	18.1	0.0	3.7	0.0	34.7	0.0	1.0	6.0	28.7	8.0	0.1	0.1	0.1	4.2
MW-3-3	06/16/06	6.0	27.6	96	287		1.6	2	0.2	1.1	0.6	21.8	0.1	17.8	0.5	21.2	0.0	1.9	9.6	30.7	8.5	0.1	0.1	0.1	4.1
MW-3-4	06/27/06	6.0	27.3	90	274		3.5	16	1.0	1.2	0.5	21.3	0.0	17.6	0.0	17.2	0.0	2.1	8.7	28.8	7.7	0.1	0.1	0.1	3.9
MW-3-5	07/12/06	6.0	27.8	233	283		3.6	11	1.0	0.6	0.6	26.6	0.0	17.4	0.3	18.9	0.2	1.8	9.2	26.0	7.4	0.1	0.1	0.1	3.7
MW-3-6	07/28/06	5.8	26.6	106	284		1.3	0	0.3	1.2	0.3	15.0	0.0	6.1	0.0	10.5	0.0	2.0	12.2	31.1	8.8	0.1	0.1	0.1	3.8
MW-3-7	08/31/06	5.8	26.9	91	213	108	3.8	5	0.9	1.4	0.8	14.9	0.1	1.5	1.0	12.9	0.2	3.1	7.7	23.0	6.0	0.1	0.1	0.1	5.0
MW-3-8	09/28/06	5.9	25.4	77			4.8	13	0.6	2.4	0.6	24.2	0.0	0.0	0.4	13.9	0.0	3.4	10.9	28.4	8.0	0.3	0.1	0.1	4.5
MW-3-9	11/07/06	5.8	23.1	210			4.1	3	0.3	1.8	0.7	23.8	0.0	2.5	0.3	17.8	0.0	2.9	10.3	27.3	7.7	0.7	0.1	0.1	5.4
MW-3-10	12/14/06	6.1	22.9	52			4.3	15	0.7	1.7	0.6	50.6	0.0	0.1	0.0	16.0	0.4	2.8	17.3	30.4	10.4	0.4	0.1	0.1	3.3
MW-3-11	01/09/07	6.0	20.8	105	407	203	5.4	4	0.6	1.1	0.7	52.8	0.0	1.7	0.0	12.9	0.4	4.0	21.1	31.4	11.4	0.3	0.1	0.1	3.4
MW-3-12	01/31/07	5.9	21.1	118			6.3	3	0.4	1.3	0.9	74.8	0.0	9.5	0.6	13.4	0.6	5.7	19.7	30.9	11.2	0.2	0.1	0.1	3.3
MW-3-13	03/01/07	6.1	22.5	67			5.0	2	0.2	3.0															
MW-3-14	04/03/07	5.7	22.4	118			3.6	2	0.4	3.0	0.6	66.0	0.0	4.2	0.0	10.2	0.7	3.7	24.0	31.7	12.0	0.2	0.1	0.1	3.5
MW-3-15	05/02/07	5.6	23.3	160			4.2	0	<0.1	1.4	0.6	24.4	0.0	58.2	0.0	21.6	0.2	2.7	10.2	39.0	10.4	0.1	0.1	0.1	4.7
MW-3-16	05/31/07	6.0	25.3	0	376		3.7	0	8.0	5.0	1.9	28.1	0.0	0.0	0.0	0.5	0.0	3.4	6.3	46.2	15.9	6.5	0.1	0.1	5.2
MW-3-17	07/03/07	6.2	26.4	0	323		1.8	4	3.0	3.2	0.9	15.7	0.0	1.0	0.0	18.9	0.3	4.2	5.8	40.8	13.1	4.1	0.1	0.1	4.6
MW-3-18	08/07/07	6.4	26.5	8	670	489	3.1	9	0.8	2.7	0.7	126.6	0.0	1.5	0.0	34.6	1.4	7.1	58.5	46.1	16.8	0.8	0.1	0.1	4.8
MW-3-19	08/30/07	6.5	26.7	-32	711	517	1.4	8	2.5	3.4	0.8	115.1	0.0	0.2	0.0	38.2	1.4	7.3	56.3	36.9	14.6	2.8	0.1	0.1	4.1

Sample	Date	pH	Temp	ORP	Cond	TDS	DO	H_2S	Fe^{2+}	As	F	Cl	NO_2	NO_3	PO_4	SO_4	Br	K	Na	Ca	Mg	Fe	Mn	Sr	Si
			° C	mV	uS/cm	mg/L	mg/L	ug/L	mg/l	ug/L								mg/L								
MW-3-20	10/03/07	6.0	26.2	30	601	439	2.0	7	1.0	2.5	0.8	98.1	0.0	0.3	0.0	19.8	1.2	6.8	51.9	34.4	13.3	1.1	0.1	0.0	4.0
MW-3-21	10/30/07	6.2	24.8	38	744	548	1.2	1	2.0	3.6	0.8	136.6	0.0	0.0	0.0	18.9	1.9	10.6	57.4	47.2	16.4	1.7	0.2	0.2	3.4
Monitor Well (MW-4)																									
MW-4-1	05/19/06	5.6	26.6	31	404		1.9	114	10.0	3.0	0.7	30.1	0.0	0.7	0.0	1.7	3.0								
MW-4-2	06/16/06	5.7	28.6	72	119		3.7	41	10.0	1.7	1.5	37.0	0.0	0.0	5.4	6.6	0.2	2.0	3.7	14.5	3.9	0.8	0.1	0.1	3.8
MW-4-3	06/27/06	5.7	27.4	-37	210		3.1	181	10.0	1.4	0.7	22.2	0.0	0.1	0.0	7.6	0.6	2.0	6.3	19.2	6.2	1.3	0.1	0.1	5.0
MW-4-4	07/12/06	5.5	26.5	68	198		3.6	31	10.0	0.3	0.9	27.4	0.0	0.1	0.0	14.6	0.7	1.6	5.8	17.3	5.4	1.0	0.1	0.1	3.7
MW-4-5	07/28/06	5.4	26.8	23	269		1.9	0	10.0	1.3	0.5	16.7	0.0	0.0	0.0	1.9	1.3	2.2	7.8	24.6	10.5	8.4	0.1	0.1	7.8
MW-4-6	08/31/06	5.5	25.8	64			1.4	24	3.5	2.0	0.8	3.6	0.0	0.0	3.2	2.4	0.2	1.2	1.8	15.6	2.6	1.4	0.0	0.1	5.0
MW-4-7	09/28/06	5.6	26.6	51			3.6	184	8.0	1.1	3.1	123.9	0.0	0.0	4.2	56.8	1.4	1.3	3.2	18.4	4.5	3.1	0.0	0.1	3.9
MW-4-8	11/07/06	5.4	24.1	56			3.4	77	10.0	2.1	0.9	10.5	0.1	0.1	0.0	1.3	0.8	1.5	3.9	21.2	5.7	5.7	0.1	0.1	5.7
MW-4-9	12/14/06	5.6	22.9	65	207	105	3.5	2	10.0	1.4	0.6	9.7	0.0	0.0	0.0	0.9	0.6	1.0	3.9	19.6	6.1	1.8	0.0	0.0	4.3
MW-4-10	01/09/07	5.6	20.5	63	260	130	5.1	166	10.0	1.1	0.6	44.3	0.0	0.3	0.3	2.0	0.5	0.7	9.8	27.3	6.4	4.2	0.0	0.1	4.1
MW-4-11	01/31/07	5.7	22.3	32			7.0	34	4.0	2.2	0.8	23.5	0.0	0.1	1.6	3.6	0.6	0.8	7.4	17.0	3.1	1.3	0.0	0.1	3.1
MW-4-12	03/01/07	5.5	21.8	55			3.7	157	7.0	3.5	0.6	40.8	0.0	0.0	0.0	0.6	0.6	1.5	10.2	27.9	7.2	4.6	0.0	0.1	2.3
MW-4-13	04/03/07	5.5	22.3	37			3.7	26	10.0	1.2	0.6	32.9	0.0	0.0	0.0	0.0	0.9	0.9	9.5	28.2	9.9	12.2	0.0	0.0	3.4
MW-4-14	05/02/07	5.3	22.9	57			3.9	18	10.0	3.1	0.7	35.4	0.0	0.0	0.0	0.4	0.9	1.0	10.1	31.8	9.7	10.8	0.0	0.1	5.7
MW-4-15	05/31/07	5.8	24.0	0	301		4.0	15	10.0	3.0	1.0	27.8	0.0	0.1	0.0	0.0	1.3	1.6	10.2	30.3	9.0	10.7	0.1	0.1	7.6
MW-4-16	07/03/07	5.8	26.0	14	439		3.9	20	10.0	5.8	0.6	72.9	0.0	0.0	0.0	3.6	0.7	1.6	18.3	39.3	12.7	17.4	0.1	0.1	4.2
MW-4-17	08/07/07	5.8	25.8	29	148	442	3.0	101	10.0	1.7	0.6	5.3	0.0	0.0	1.9	0.0	0.1	1.0	4.6	19.3	4.8	10.2	0.0	0.1	2.9
MW-4-18	08/30/07	5.7	27.7	36	278	198	1.6	175	10.0	0.1	0.9	55.9	0.0	0.1	0.0	5.3	0.8	1.1	12.9	28.1	5.6	9.4	0.0	0.1	3.1
MW-4-19	10/03/07	5.5	26.8	0	416	300	0.9	24	10.0	5.1	0.8	57.3	0.0	0.1	0.0	0.6	1.0	1.1	18.9	43.5	9.3	23.0	0.2	0.0	4.1
MW-4-20	10/30/07	6.0	25.1	-61	714	525	1.2	40	10.0	2.8	0.5	76.1	0.0	0.0	0.0	1.7	1.5	3.3	22.6	88.8	18.2	37.3	0.5	0.2	5.8
Monitoring Well MW-5																									
MW-5-1	04/28/06	no sample																							
MW-5-2	05/19/06	5.7	28.6	37	438		3.2	7	10.0	1.6	0.4	48.9	0.0	0.0	0.0	23.3	3.2	2.3	12.5	41.9	18.7	11.3	0.2	0.1	5.3
MW-5-3	06/16/06	6.1	30.8	8	240		5.6	4	10.0	1.6	0.7	17.0	0.0	0.1	0.0	9.5	1.2	3.4	7.0	24.3	11.3	5.0	0.1	0.1	4.2
MW-5-4	06/27/06	6.0	33.2	4	337		5.3	1	10.0	0.9	0.7	30.3	0.0	1.8	0.0	17.2	2.0	4.0	10.1	30.2	14.7	4.1	0.1	0.1	4.6
MW-5-5	07/12/06	6.1	28.8	-23	488		6.7	12	10.0	1.9	0.5	37.5	0.0	0.2	0.0	11.5	3.4	1.7	10.5	39.0	20.2	23.1	0.1	0.1	3.9
MW-5-6	08/31/06	6.0	27.1	-28			6.6	11	10.0	2.2	1.0	11.3	0.0	0.0	0.0	4.9	0.9	1.6	4.4	24.9	11.7	11.3	0.3	0.1	3.5
MW-5-7	09/28/06	6.2	26.6	20			5.9	49	10.0	2.0	0.8	8.7	0.0	0.0	0.0	3.9	0.5	1.6	4.8	24.0	11.8	5.7	0.3	0.1	3.6
MW-5-8	11/07/06	6.0	23.1	-44			5.4	119	10.0	5.6	0.9	29.3	0.1	0.1	0.0	3.7	2.6	1.5	10.3	47.2	25.3	45.2	0.2	0.1	3.8

Sample	Date	pH	Temp	ORP	Cond	TDS	DO	H_2S	Fe^{2+}	As	F	Cl	NO_2	NO_3	PO_4	SO_4	Br	K	Na	Ca	Mg	Fe	Mn	Sr	Si
			° C	mV	uS/cm	mg/L	mg/L	ug/L	mg/l	ug/L								mg/L								
MW-5-9	12/14/06	6.2	23.3	16	493	246	4.9	6	10.0	3.4	0.6	27.5	0.0	0.1	0.0	2.3	2.4	0.9	11.0	44.9	25.3	0.7	0.1	0.0	3.0
MW-5-10	01/09/07	6.2	20.0	-8	325	162	5.1	39	10.0	1.5	0.9	15.8	0.0	0.2	0.0	8.9	0.9	1.0	5.9	26.9	14.6	14.3	0.1	0.1	3.1
MW-5-11	01/31/07	6.1	21.6	45			7.5	30	2.5	0.5	1.3	10.1	0.0	0.6	1.9	8.0	0.4	0.9	3.2	19.1	8.1	5.6	0.0	0.1	3.5
MW-5-12	03/01/07	6.3	22.2	5			5.9	6	3.0	1.7	1.1	15.3	0.0	0.2	0.0	19.6	0.5	1.6	5.2	29.6	18.9	1.2	0.1	0.1	2.3
MW-5-13	04/03/07	6.2	23.8	3			4.9	0	10.0	2.5	1.0	24.5	0.0	0.0	0.0	19.6	1.2	0.8	6.9	27.9	16.9	8.2	0.1	0.0	2.4
MW-5-14	05/02/07	5.9	24.9	8			5.7	7	10.0	3.3	1.2	18.9	0.0	0.0	0.0	8.7	0.9	1.1	6.1	25.0	13.5	12.4	0.1	0.0	3.2
MW-5-15	05/31/07	6.4	26.4	-71	392		6.4	0	10.0	3.5	3.1	139.7	0.0	0.4	1.6	69.9	1.6	1.3	8.7	35.4	18.4	24.8	0.1	0.1	3.2
MW-5-16	07/03/07	6.3	27.5	47	396		6.0	2	10.0	5.8	0.9	29.7	0.0	0.0	0.0	4.1	1.6	1.8	9.8	36.3	18.1	23.8	0.1	0.1	3.2
MW-5-17	08/07/07	6.1	28.2	-19	292	207	4.2	14	10.0	2.3	0.6	9.0	0.0	0.0	0.0	0.8	0.6	1.5	6.7	29.8	14.7	21.1	0.2	0.1	3.2
MW-5-18	08/30/07	6.2	28.3	-42	315	224	3.8	8	10.0	0.7	1.0	15.5	0.0	0.0	0.0	3.1	0.9	1.7	6.4	25.9	13.4	14.6	0.1	0.1	3.0
MW-5-19	10/03/07	5.9	28.2	-22	310	221	2.9	9	10.0	1.8	1.1	15.5	0.0	5.9	0.0	2.5	1.0	1.2	7.0	29.4	15.0	16.3	0.1	0.0	2.7
MW-5-20	10/30/07	5.9	25.8	-7	273	195	1.2	17	10.0	1.6	1.0	14.6	0.0	0.1	0.0	1.7	1.0	1.5	4.7	30.3	12.8	10.7	0.1	0.1	3.1
Monitor Well (MW-6)																									
MW-6-1	04/28/06	5.9		-38	916		1.7	0	10.0	14.8	0.7	51.2	0.0	0.0	0.0	0.0	2.0	4.9	22.6	76.4	38.0	56.4	0.3	0.1	5.1
MW-6-2	05/19/06	5.9	25.2	-33	684		2.1	25	10.0	2.1	1.1	28.4	0.0	0.0	0.0	7.0	1.6	3.9	15.7	64.2	31.4	13.8	0.2	0.1	4.5
MW-6-3	06/16/06	5.9	26.0	-5	413		0.5	46	10.0	10.1	1.1	28.9	0.0	0.3	0.0	12.1	0.5	0.5	11.6	38.7	16.3	22.3	0.1	0.0	3.6
MW-6-4	06/27/06	6.1	30.1	-58	734		2.3	94	10.0	5.6	1.0	28.1	0.0	0.0	0.0	0.6	1.6	0.9	17.9	69.0	30.3	56.8	0.2	0.1	3.7
MW-6-5	07/12/06	6.0	26.6	-31	914		1.9	73	10.0	3.6	1.1	31.3	0.0	0.1	0.0	0.2	1.8	1.2	17.0	66.3	29.5	41.8	0.2	0.1	3.3
MW-6-6	08/31/06	5.9	26.1	-55			1.7	143	10.0	8.8	1.2	9.3	0.0	0.0	0.0	2.6	0.4	1.4	7.8	40.1	16.3	20.2	0.1	0.2	8.1
MW-6-7	09/28/06	6.1	25.7	-44			1.8	45	10.0	2.4	0.5	10.9	0.0	0.0	0.0	0.4	1.0	1.2	19.7	75.9	32.1	56.3	0.2	0.1	3.6
MW-6-8	11/07/06	5.9	23.6	-65			2.4	20	0.0	5.6	1.2	34.1	0.0	0.0	0.0	0.6	1.6	1.2	18.5	71.4	31.2	47.3	0.2	0.1	3.2
MW-6-9	12/14/06	6.2	24.1	-58	781	392	2.6	10	10.0	7.6	1.0	28.0	0.0	0.0	0.0	0.7	1.4	1.4	18.6	72.5	34.1	31.5	0.2	0.0	3.4
MW-6-10	01/09/07	6.2	20.2	-57	726	362	3.8	56	10.0	10.2	0.9	29.2	0.0	0.3	0.0	0.4	1.3	0.6	17.9	69.8	31.2	41.1	0.2	0.0	2.9
MW-6-11	01/31/07	5.9	21.7	-34			1.8	166	10.0	8.5	1.4	30.1	0.0	0.2	0.0	8.4	1.7	0.7	15.1	57.7	25.2	26.9	0.1	0.0	2.7
MW-6-12	03/01/07	6.0	21.9	-50			2.1	59	10.0	7.2	0.9	28.3	0.0	0.0	0.0	2.1	1.1	1.5	21.2	77.1	35.4	45.1	0.2	0.0	3.0
MW-6-13	04/03/07	5.9	22.6	-67			1.2	18	10.0	9.0	0.9	26.7	0.0	0.0	0.0	1.1	1.3	0.6	19.2	73.0	34.6	61.8	0.2	0.0	3.0
MW-6-14	05/02/07	5.9	22.7	-61			2.3	21	10.0	15.5	0.9	26.3	0.0	0.0	0.0	0.8	1.4	0.6	19.6	79.1	35.9	67.9	0.2	0.0	3.2
MW-6-15	05/31/07	6.3	21.6	-109	834		1.8	20	10.0	13.3	0.8	17.0	0.0	1.1	0.0	17.3	0.5	1.1	22.0	84.9	39.2	67.1	0.2	0.1	3.8
MW-6-16	07/03/07	6.2	23.9	-89	780		1.9	43	10.0	17.9	0.9	23.7	0.0	0.0	0.0	0.1	1.2	1.4	21.0	78.8	35.8	68.0	0.2	0.1	3.6
MW-6-17	08/07/07	6.1	25.3	-61	697	510	1.3	55	10.0	9.2	0.9	18.8	0.0	0.0	0.2	0.2	0.8	1.1	20.7	81.5	33.9	57.8	0.2	0.1	3.7
MW-6-18	08/30/07	6.2	28.1	-88	718	526	1.8	36	10.0	8.8	1.4	23.9	0.0	0.0	0.0	13.6	1.1	1.1	19.5	73.3	30.8	54.0	0.2	0.1	3.4
MW-6-19	10/03/07	6.0	26.4	-84	736	540	1.1	13	10.0	7.0	1.0	23.6	0.0	0.0	0.0	1.0	1.1	0.8	20.2	74.1	32.5	62.3	0.2	0.0	2.9

Sample	Date	pH	Temp	ORP	Cond	TDS	DO	H_2S	Fe^{2+}	As	F	Cl	NO_2	NO_3	PO_4	SO_4	Br	K	Na	Ca	Mg	Fe	Mn	Sr	Si
			° C	mV	uS/cm	mg/L	mg/L	ug/L	mg/l	ug/L										mg/L						
MW-6-20	10/30/07	6.1	24.9	-72	766	565	1.2	11	10.0	8.6	1.1	29.0	0.0	0.1	0.0	1.3	1.5	1.3	16.9	93.6	34.8	58.7	0.2	0.1	3.3
N-15																									
N-15-2-1	04/28/06	7.5	28.1	-78	269		8.3	25	0.3	0.7	1.9	48.9	0.0	0.0	0.0	4.1	0.0	7.1	26.5	48.6	25.1	0.1	0.1	0.2	1.4
N-15-1-1	04/28/06	7.0	26.2	-8	573		2.9	71	0.4	0.7	2.0	42.8	0.0	0.5	0.0	2.7	0.2	6.8	25.8	44.3	25.4	0.2	0.1	0.2	0.7
N-15-3-1	04/28/06	7.9	30.0	-30	619		8.2	59	<0.1	0.5	1.6	36.9	0.0	0.7	0.0	8.1	0.0	6.4	24.0	50.9	25.8	0.0	0.0	0.2	0.3
N-15-3-2	05/19/06	7.2	28.0	15	502		6.1	23	0.1	1.2	1.5	22.1	0.0	0.0	0.0	4.3	0.0	3.1	21.2	47.2	24.1	0.1	0.2	0.2	0.5
N-15-2-2	05/19/06	7.3	28.1	186	537		5.1	4	0.6	0.8	1.8	32.6	0.0	3.3	0.3	3.4	0.0	3.6	28.1	52.0	26.7	0.1	0.1	0.2	0.9
N-15-1-2	05/19/06	6.7	25.2	135	505		1.0	30	0.4	1.3	2.3	28.9	0.0	3.1	0.0	2.2	0.0	1.1	26.3	44.4	25.6	0.4	0.1	0.2	1.0
N-15-1-3	06/16/06	6.6	25.0	-50	317		1.0	399	2.0	3.3	1.6	17.6	0.0	0.0	0.8	2.1	0.0	3.5	14.1	25.5	14.1	2.1	0.2	0.1	0.9
N-15-2-3	06/16/06	7.1	26.9	212	469		1.8	6	0.4	1.1	1.6	26.8	0.0	0.1	0.0	4.7	0.1	2.9	21.4	41.1	21.5	0.2	0.2	0.2	1.0
N-15-3-3	06/16/06	7.7	31.4	100	455		8.1	7	0.2	0.8	0.6	6.1	0.0	0.0	1.3	3.5	0.2	2.7	19.7	38.6	21.7	0.0	0.0	0.2	0.6
N-15-3-4	06/27/06	7.4	31.4	318	468		6.2	8	<0.1	0.7	1.8	27.9	0.0	0.1	0.3	6.3	0.2	2.7	19.9	39.3	21.8	0.1	0.1	0.2	0.5
N-15-1-4	06/27/06	6.7	27.1	-70			1.3	132	3.0	4.1	2.4	28.9	0.0	0.0	0.0	1.7	0.2	2.5	19.3	34.8	19.9	0.4	0.1	0.2	1.0
N-15-2-4	06/27/06	7.0	27.5	128			0.7	7	0.6	0.9	1.9	31.2	0.0	0.0	0.0	2.6	0.2	3.0	22.0	42.5	22.6	0.4	0.2	0.2	1.3
N-15-1-5	07/12/06	6.6	27.6	-31	441		1.7	59	2.0	1.3	2.0	31.2	0.0	0.0	0.0	1.4	0.3	3.5	19.4	31.1	18.7	0.5	0.1	0.1	0.6
N-15-2-5	07/12/06	7.0	28.5	58	483		0.7	6	0.2	0.3	2.1	35.5	0.0	0.0	0.4	1.8	0.3	2.9	19.7	38.1	20.3	0.2	0.2	0.2	1.3
N-15-3-5	07/12/06	7.1	28.9	125	449		4.9	5	0.2	0.8	1.7	25.8	0.0	0.1	0.4	4.3	0.3	2.8	17.9	33.4	20.1	0.1	0.1	0.1	0.7
N-15-3-6	07/28/06	7.0	29.6	67	475		2.8	0		0.6	1.6	26.4	0.0	2.1	0.0	1.9	0.2	3.1	35.2	45.0	24.3	0.2	0.4	0.1	1.1
N-15-2-6	07/28/06	6.5	28.7	-69	558		1.2	0	2.0	1.5	1.5	24.2	0.0	0.6	0.0	0.6	0.2	3.4	23.8	53.8	26.9	2.1	0.3	0.2	2.3
N-15-1-6	07/28/06	6.6	29.0	-45	420		1.2	0	0.9	0.7	2.0	21.4	0.0	0.0	0.0	2.1	0.0	2.3	35.7	37.6	23.3	0.8	0.1	0.1	0.9
N-15-2-7	08/31/06	6.5	27.3	-104	409	204	1.7	233	0.5	1.0	1.2	16.3	0.0	0.0	1.2	0.9	0.0	3.5	16.3	42.3	20.4	0.4	0.4	0.1	1.2
N-15-2-8	09/28/06	6.6	25.5	-77			1.2	433	0.8	1.1	1.2	18.7	0.0	0.0	0.0	0.5	0.0	5.9	20.2	50.6	24.7	0.6	0.5	0.1	1.9
N-15-2-9	11/07/06	6.7	21.7	20			1.2	14	0.4	0.7	2.1	30.5	0.0	0.0	2.2	1.1	0.1	3.4	20.5	46.8	23.4	0.3	0.3	0.2	2.3
N-15-2-10	12/14/06	7.2	21.5	22	509	252	6.7	1	0.2	1.4	1.6	26.4	0.0	0.1	0.9	1.2	0.1	3.6	21.4	44.0	22.8	0.1	0.0	0.1	1.6
N-15-2-11	01/31/07	7.0	15.2	17			2.3	10	0.4	1.0	1.7	28.3	0.0	0.0	0.5	0.9	0.1	3.3	21.2	43.3	22.7	0.1	0.1	0.1	1.1
N-15-2-12	03/01/07	7.3	21.8	-21			4.8	5	0.3	1.2	1.6	27.8	0.0	0.0	0.4	1.2	0.1	3.2	27.8	49.5	25.4	0.1	0.1	0.1	0.5
N-15-2-13	03/19/07	7.4	21.2	124			2.7	6	0.1	1.0	1.4	21.3	0.0	0.7	0.6	2.4	0.1	2.8	22.3	41.5	22.0	0.1	0.1	0.1	0.3
N-15-2-14	04/03/07	7.0	23.7	5			3.4	0	0.5	1.0	2.3	35.4	0.0	0.0	1.3	1.0	0.1	3.1	23.3	45.4	24.9	0.1	0.2	0.1	0.5
N-15-2-15	04/18/07	7.2	23.8	29			5.1	0	0.3	1.8	1.9	28.1	0.0	0.0	0.1	1.5	0.1	3.1	23.6	45.6	25.0	0.1	0.2	0.1	0.7
N-15-2-15	05/02/07	7.0	24.7	135			2.7	0	<0.1	1.9	2.1	32.2	0.0	0.1	0.8	0.6	0.1	3.1	25.1	48.3	26.7	0.1	0.2	0.1	0.6
N-15-2-17	05/31/07	7.2	25.1	98	540		2.5	0	0.3	1.1	0.2	21.7	0.3	0.3	0.0	23.9	2.6	3.7	27.5	49.5	27.8	0.1	0.2	0.2	1.5
N-15-2-18	06/15/07	7.5	27.7	-7	534		3.5	5	0.3	1.3	3.3	144.6	0.0	0.0	2.7	67.7	1.6	4.0	27.4	48.1	27.1	0.1	0.3	0.2	1.2

Sample	Date	pH	Temp	ORP	Cond	TDS	DO	H_2S	Fe^{2+}	As	F	Cl	NO_2	NO_3	PO_4	SO_4	Br	K	Na	Ca	Mg	Fe	Mn	Sr	Si
			° C	mV	uS/cm	mg/L	mg/L	ug/L	mg/l	ug/L								mg/L								
N-15-2-19	07/03/07	7.2	27.2	-24	510		1.6	0	0.4	1.6	1.5	25.2	0.0	0.1	0.4	0.7	0.1	4.4	27.5	46.0	27.1	0.2	0.3	0.2	1.5
N-15-2-20	07/16/07	7.6	28.3	20	463	336	2.3	0	0.5	1.8	1.7	25.7	0.0	0.1	0.6	7.9	0.1	3.7	22.3	41.1	22.5	0.2	0.2	0.1	1.7
N-15-2-21	08/07/07	7.0	28.5	-71	465	336	1.8	113	0.7	1.2	1.5	23.3	0.0	0.0	0.6	1.7	0.0	4.0	23.4	47.6	24.8	0.6	0.2	0.1	2.3
N-15-2-22	08/15/07	7.3	29.0	-23	464	336	1.6	5	0.6	1.1	1.5	21.6	0.0	0.0	0.7	1.3	0.1	4.3	23.7	44.9	25.1	0.2	0.3	0.1	2.1
N-15-2-23	08/30/07	6.8	28.1	-95	522	379	1.7	19	1.5	1.1	1.5	20.5	0.0	0.0	0.0	2.7	0.0	4.1	21.1	44.6	22.8	1.1	0.4	0.1	2.7
N-15-2-24	09/20/07	7.4	28.1	73			4.6	1	0.4	0.7	1.4	19.1	0.0	0.0	0.3	2.0	0.0	3.8	20.1	41.4	23.0	0.2	0.2	0.0	1.9
N-15-2-24	10/03/07	7.3	27.1	-36	447	323	3.2	2	0.4	0.8	1.5	20.5	0.0	0.0	0.0	1.5	0.0	3.6	19.6	40.3	22.3	0.1	0.2	0.0	1.8
N-15-2-25	10/16/07	7.3	25.0	131	434	316	2.6	0	0.5	1.9	1.3	19.7	0.0	0.0	0.0	2.6	0.0	4.4	15.1	49.6	21.7	0.2	0.2	0.1	1.9
N-15-2-26	10/30/07	7.2	24.0	24	459	335	2.7	3	0.4	0.7	1.4	23.2	0.0	0.0	0.0	1.8	0.1	5.1	17.5	51.1	22.7	0.2	0.1	0.1	1.9
SA-8																									
SA-8-1	12/14/06	7.9	20.6	61	366	184	7.3	54	0.0	4.7	0.7	4.5	0.1	0.0	1.4	3.0	0.0	3.6	9.5	35.3	18.3	0.1	0.0	0.1	2.2
SA-8-2	01/31/07	8.4	18.3	88			12.2	2	0.0	6.4	2.4	13.4	0.0	0.0	4.6	2.4	0.0	3.5	10.4	36.1	19.7	0.0	0.0	0.1	2.3
SA-8-3	02/15/07	8.0	16.8	195			8.9	2	0.1	6.3	2.6	14.8	0.0	0.0	4.7	3.6	0.0	3.1	9.6	35.6	18.7	0.0	0.0	0.1	2.2
SA-8-4	03/01/07	7.8	23.2	128			7.3	1	0.1	6.8	1.9	11.0	0.0	0.0	4.4	1.8	0.0	3.2	12.6	41.8	22.9	0.0	0.1	0.1	2.0
SA-8-5	03/19/07	8.4	20.8	52			9.5	2	0.0	6.6	2.5	12.4	0.0	0.0	4.9	1.5	0.0	2.5	10.5	36.6	20.3	0.0	0.0	0.1	0.6
SA-8-6	04/03/07	8.0	25.2	132			7.8	0	0.0	6.2	2.5	12.8	0.0	0.0	6.2	1.4	0.0	3.7	11.9	40.2	23.0	0.0	0.0	0.1	0.2
SA-8-7	04/18/07	8.0	19.6	167			9.8	0	0.0	6.2	2.6	13.7	0.0	0.0	3.6	1.8	0.0	3.6	12.3	41.1	23.2	0.0	0.0	0.1	0.1
SA-8-8	05/02/07	8.3	25.2	132			8.6	0	0.1	5.9	2.8	13.1	0.0	0.0	3.2	1.0	0.0	3.8	13.1	44.6	25.3	0.0	0.0	0.1	0.3
SA-8-9	05/17/07	8.3	29.4	138			5.8	18	0.2	6.0	3.5	13.2	0.0	0.0	0.6	0.9	1.6	3.6	12.1	41.0	23.7	0.0	0.0	0.1	0.5
SA-8-10	05/31/07	8.3	26.1	-82	440		4.6	0	0.0	6.3	3.9	147.8	0.0	0.0	3.1	77.0	1.7	4.0	13.8	46.4	26.1	0.0	0.0	0.1	0.6
SA-8-11	06/15/07	8.0	30.6	-7	439		6.2	4	0.2	6.1	0.6	50.8	0.6	0.7	0.4	51.4	5.3	3.9	13.8	46.7	25.9	0.0	0.0	0.1	0.1
SA-8-12	07/03/07	7.8	28.8	91	451		4.0	0	0.1	6.7	2.3	11.3	0.0	0.0	2.6	0.8	0.0	3.7	14.4	47.4	27.0	0.0	0.0	0.1	0.7
SA-8-13	07/16/07	7.6	31.8	71	441	317	5.6	0	0.1	6.5	1.0	5.4	0.0	0.2	1.7	0.4	0.0	3.7	14.2	46.0	26.5	0.0	0.0	0.1	0.1
SA-8-14	08/07/07	6.7	29.5	23	470	339	2.5	9	0.0	3.7	2.9	13.8	0.0	0.1	3.3	1.0	0.0	4.4	14.6	51.9	28.1	0.0	0.1	0.1	0.8
SA-8-15	08/15/07	7.0	30.7	78	432	312	4.1	0	0.1	3.3	2.7	12.5	0.0	0.0	2.8	1.6	0.0	3.8	14.2	47.3	28.0	0.0	0.0	0.1	0.6
SA-8-16	08/30/07	6.7	31.2	-124	413	296	7.3	11	0.3	2.9	2.7	13.3	0.0	0.0	2.0	1.3	0.0	3.4	13.2	42.9	25.0	0.0	0.0	0.1	0.3
SA-8-17	09/20/07	7.4	29.6	205			5.9	2	0.1	3.4	2.6	12.6	0.0	0.1	1.9	1.5	0.0	3.5	13.2	44.3	27.2	0.0	0.0	0.0	0.5
SA-8-17	10/03/07	8.3	29.3	-127	426	307	9.1	1	0.1	2.9	2.9	14.1	0.0	0.3	1.4	3.2	0.0	3.6	12.9	43.8	26.3	0.1	0.0	0.0	0.2
SA-8-18	10/16/07	8.0	26.4	103	432	313	5.8	0	0.1	8.0	2.6	13.0	0.0	0.1	3.0	2.1	0.0	4.3	10.5	54.4	26.9	0.1	0.1	0.1	0.2
SA-8-19	10/30/07	8.2	25.3	-55	438	319	7.7	0	0.0	4.6	2.5	12.1	0.0	0.0	2.1	2.1	0.0	4.7	10.6	55.4	26.9	0.0	0.0	0.1	0.4

Sample	Date	pH	Temp	ORP	Cond	TDS	DO	H_2S	Fe^{2+}	As	F	Cl	NO_2	NO_3	PO_4	SO_4	Br	K	Na	Ca	Mg	Fe	Mn	Sr	Si
			° C	mV	uS/cm	mg/L	mg/L	ug/L	mg/l	ug/L	mg/L														
Effluent (EF)																									
EF-1	04/28/06	7.1	27.0	74	750		8.2	0																	
EF-2	05/19/06	6.5	27.9	414	692		8.1	1	0.0																
EF-3	06/16/06	6.8	31.7	219	598		8.0	0	<0.1																
EF-4	06/27/06	6.7	32.6	280	541		7.6	3	<0.1																
EF-5	07/12/06	6.7	29.7	335	586		8.3	0	<0.1																
EF-6	07/28/06	6.7	32.9	265	555		7.7	0	<0.1																
EF-7	08/10/06	7.5	32.1	354	569		7.5	0	<0.1																
EF-8	08/31/06	6.7	28.4	82			8.3	0	<0.05																
EF-9	09/28/06	7.0	28.0	301			8.1	0	0.0																
EF-10	10/11/06	6.9	28.5	331	582	291	8.2	0																	
EF-11	11/01/06	6.9	29.5	186			7.9	0	<0.1																
EF-12	11/07/06	6.5	26.1	770			9.0	0	<0.1																
EF-13	11/20/06	6.9	24.4	236			9.0	0	0.0																
EF-14	12/07/06	6.3	24.5	341	508	254	8.6	0	<0.1																
EF-15	12/14/06	7.0	24.2	205			8.9	0																	
EF-16	01/09/07	7.0	23.1	213			9.4	0	0.0																
EF-17	01/16/07	6.7	26.0	264	469	234	8.5	0	0.0																
EF-18	02/15/07	6.7	18.4	220			9.5	0	0.0																
EF-19	03/01/07	7.0	23.5	235			8.8	0	0.0																
EF-20	03/19/07	7.0	23.2	230			9.4	0	0.0																
EF-21	04/03/07	6.8	26.5	193			8.9	0	0.0																
EF-22	04/18/07	6.7	24.4	240			8.3	0	0.0																
EF-23	05/02/07	6.6	27.8	180			8.4	0	0.0																
EF-24	05/17/07	6.8	29.1	221			7.7	0	0.0																
EF-25	05/31/07	7.1	28.1	256	618		7.8	0	0.0	0.2	3.6	131.3	0.0	0.0	0.0	85.4	1.6	14.0	53.6	30.8	12.8	0.0	0.0	0.3	7.6
EF-26	06/15/07	7.4	30.7	292	632		7.3	0	0.0	0.3	1.3	43.6	0.0	0.0	1.5	21.7	0.6	16.7	56.1	30.2	11.3	0.0	0.0	0.4	7.9
EF-27	07/03/07	8.0	29.5	-22	550		6.8	0	0.0	0.4	0.6	85.8	0.3	7.4	15.5	37.7	0.0	14.2	47.0	28.4	11.0	0.0	0.0	0.3	7.3
EF-28	07/16/07	7.4	31.3	120	557	404	6.4	0	0.0	0.3	0.8	111.8	0.0	12.2	25.7	41.9	0.0	15.0	48.6	30.0	10.0	0.0	0.0	0.3	7.6
EF-29	08/07/07	7.9	30.9	-10	574	416	6.4	0	0.0	0.4	0.7	106.2	0.0	14.1	19.6	36.5	0.0	14.5	51.8	32.1	10.6	0.0	0.0	0.4	7.4
EF-30	08/15/07	7.9	31.4	34	548	396	6.3	0	0.0	0.4	0.6	91.5	0.0	7.0	16.9	32.8	0.0	14.8	51.2	30.1	10.0	0.0	0.0	0.4	7.8
EF-31	08/30/07	8.0	33.0	140	611	442	5.8	0	0.0																
EF-32	09/20/07	7.3	30.2	127			6.3	0																	

APPENDIX B.

CHEMICAL AND ISOTOPIC COMPOSITION OF WATERS USED FOR THE MASS-BALANCE APPROACH

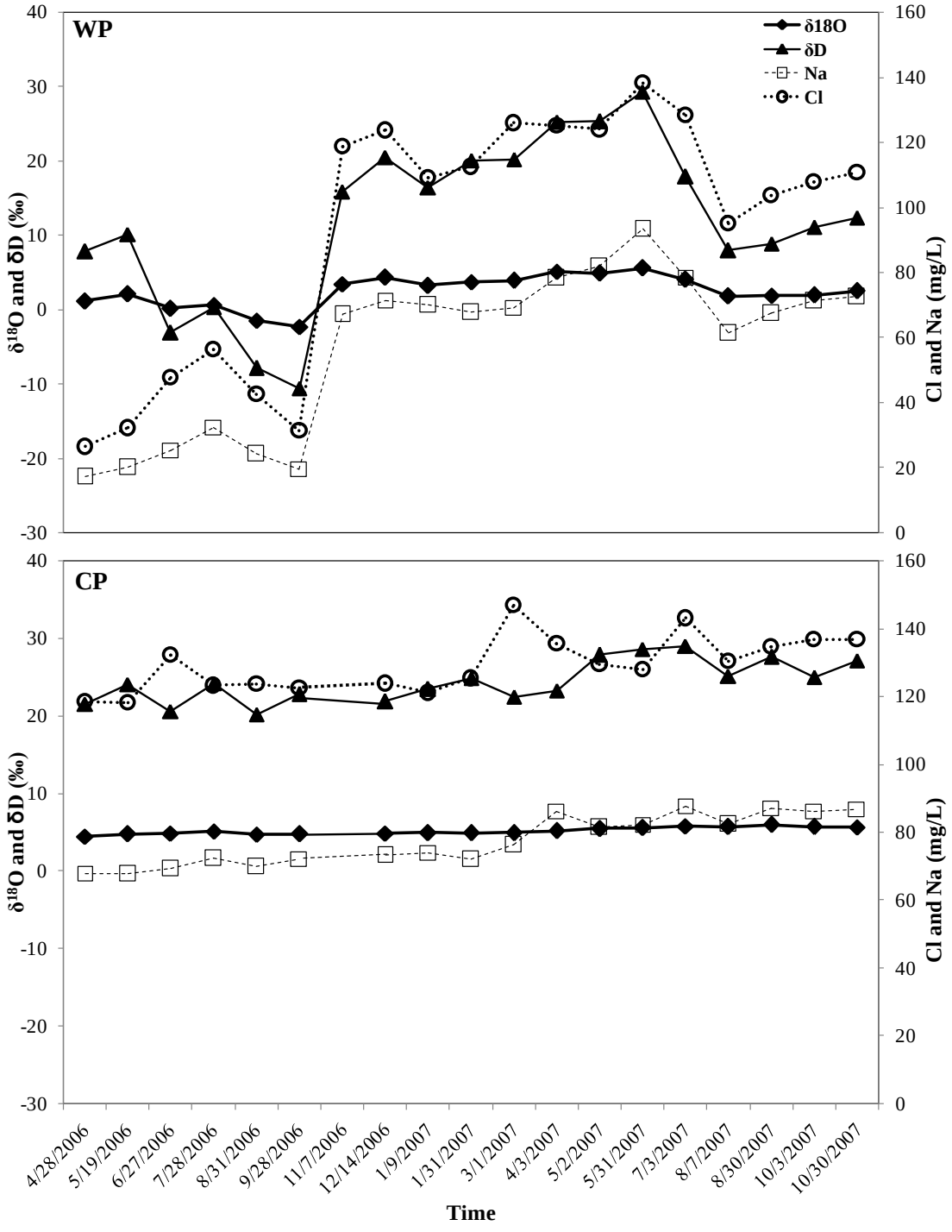
Sample	Date	$\delta^{18}O$*	δD*	Na'	Sample	Date	$\delta^{18}O$*	δD*	Na'	Sample	Date	$\delta^{18}O$*	δD*	Na'
CP	4/28/06	4.42	21.5	67.9	N-15	4/28/2006	2.09	11.4	28.2	SA-8	12/14/2006	1.97	10.8	13.3
	5/19/06	4.75	24.0	67.7		5/19/2006	2.70	12.7	31.3		1/31/2007	1.98	10.4	13.7
	6/27/06	4.86	20.6	69.3		6/27/2006	1.79	5.0	25.7		3/1/2007	1.99	10.4	14.0
	7/28/06	5.11	24.2	72.3		7/28/2006	1.83	6.0	27.0		4/3/2007	2.70	13.3	14.5
	8/31/06	4.70	20.2	69.8		8/31/2006	0.03	-1.9	18.8		5/2/2007	3.39	17.3	15.3
	9/28/06	4.74	22.8	72.2		9/28/2006	0.75	3.0	22.0		5/31/2007	3.84	19.9	15.0
	11/7/06	no sample				11/7/2006	1.21	6.5	26.9		7/3/2007	3.94	19.7	15.6
	12/14/06	4.84	21.8	73.1		12/14/2006	1.52	7.3	27.7		8/7/2007	3.20	16.6	15.8
	1/9/07	4.93	23.5	74.0		1/31/2007	1.15	7.5	27.1		8/30/2007	3.19	13.6	15.3
	1/31/07	4.92	24.8	72.0		3/1/2007	1.38	8.3	28.7		10/3/2007	3.20	14.3	15.5
	3/1/07	4.93	22.5	76.3		4/3/2007	1.84	11.0	30.0		10/30/2007	2.74	14.3	15.6
	4/3/07	5.19	23.2	86.3		5/2/2007	2.37	12.5	29.6					
	5/2/07	5.48	27.9	81.6		5/31/2007	2.84	12.9	29.8					
	5/31/07	5.55	28.6	82.3		7/3/2007	2.15	10.8	28.6					
	7/3/07	5.76	29.0	87.7		8/7/2007	1.40	5.8	25.1					
	8/7/07	5.72	25.1	82.4		8/30/2007	0.84	3.8	24.1					
	8/30/07	5.98	27.6	87.1		10/3/2007	0.69	4.2	23.2					
	10/3/07	5.71	25.0	86.2		10/30/2007	0.64	3.9	24.7					
	10/30/07	5.63	27.1	86.9										

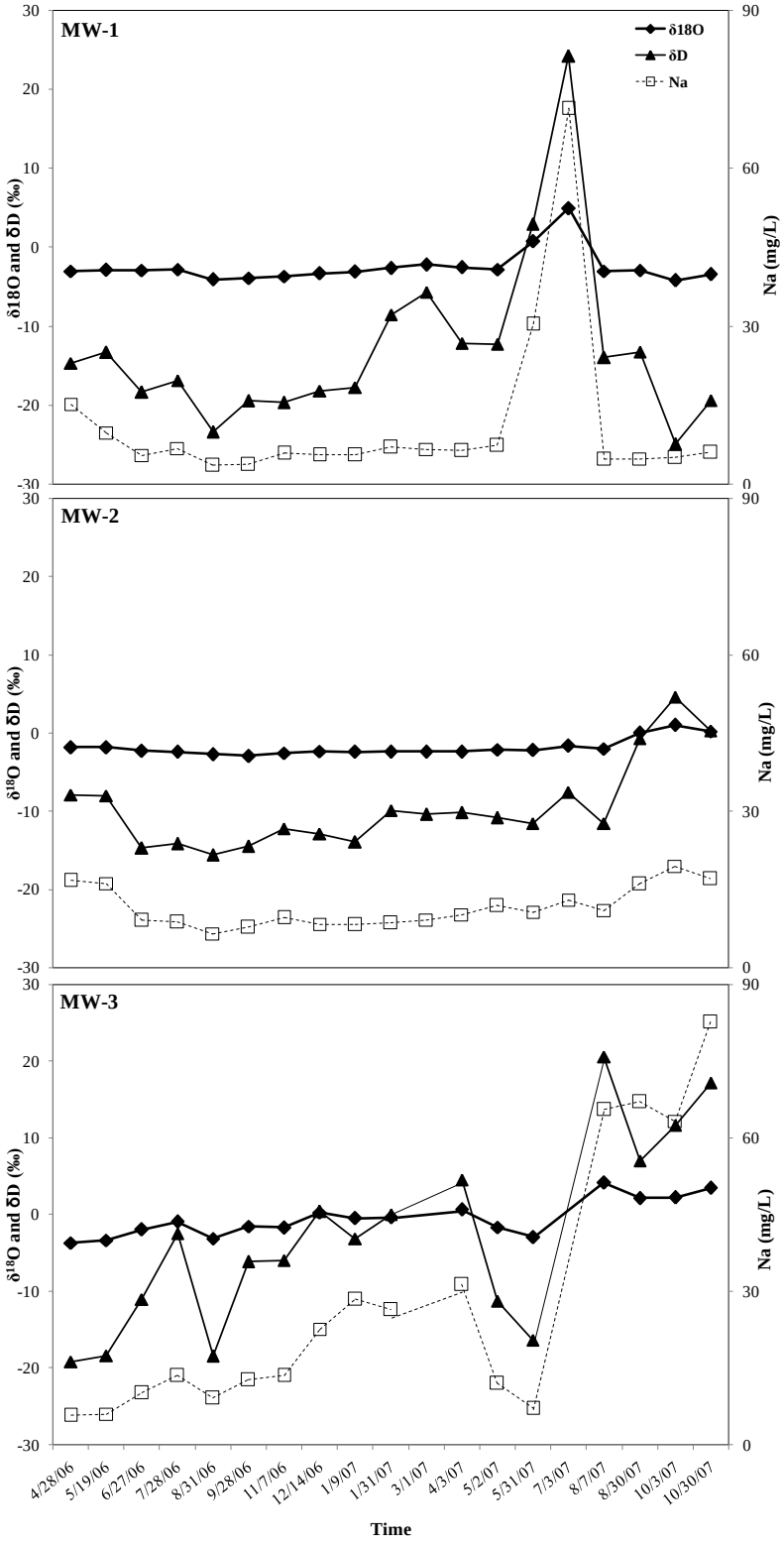
Sample	Date	$\delta^{18}O$*	δD*	Na'	*mCP*	*mGW*	*mN-15*	*mSA-8*
WP	4/28/06	1.17	7.8	17.3	4	18	47	31
	5/19/06	2.10	10.1	20.1	5	8	50	37
	6/27/06	0.19	-3.1	25.4	18	41	28	13
	7/28/06	0.63	0.3	32.4	30	41	20	9
	8/31/06	-1.47	-7.9	24.3	26	74	0	0
	9/28/06	-2.31	-10.6	19.6	22	78	0	0
	11/7/06	3.45	15.9	67.1	88	12	0	0
	12/14/06	4.36	20.5	71.4	92	8	0	0
	1/9/07	3.27	16.4	70.0	96	4	0	0
	1/31/07	3.72	20.1	67.8	88	12	0	0
	3/1/07	3.92	20.2	69.3	90	10	0	0
	4/3/07	5.12	25.2	78.3	100	0	0	0
	5/2/07	4.92	25.3	81.8	100	0	0	0
	5/31/07	5.62	29.3	93.5	100	0	0	0
	7/3/07	4.02	17.9	78.5	100	0	0	0
	8/7/07	1.80	8.0	61.5	87	13	0	0
	8/30/07	1.88	8.9	67.5	95	5	0	0
	10/3/07	1.92	11.1	71.3	99	1	0	0
	10/30/07	2.54	12.4	72.5	99	1	0	0

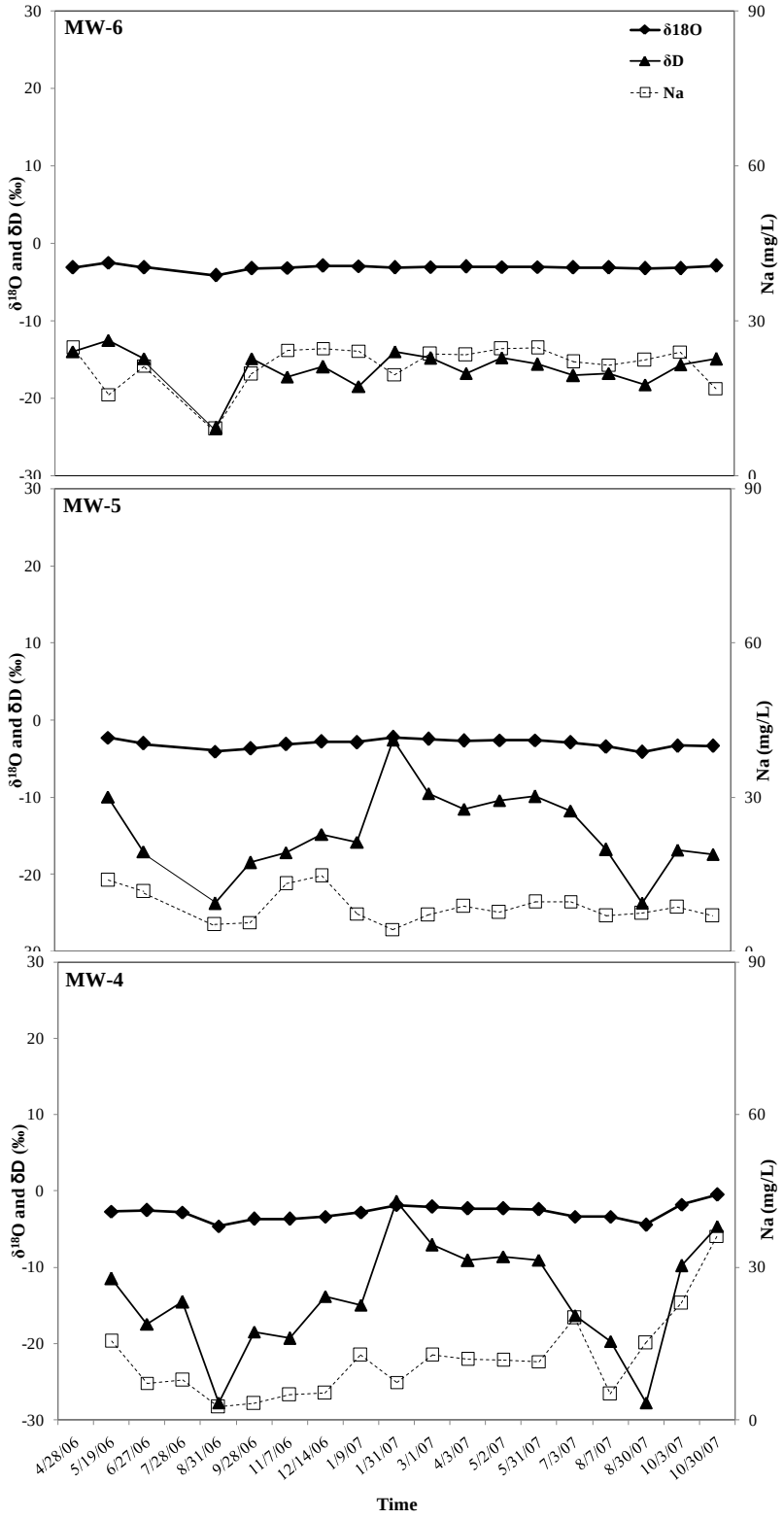
Note: CP- cooling pond; SA-8 and N-15 - water bodies to the north and south of the wetland; WP – wetland water from pump; GW - groundwater (based on well ROMP 45 data from Sacks and Tihansky, 1996); (*) - values in ‰; (′) – values in mg/L; *m* - mass or percentage of each end-member in the WP.

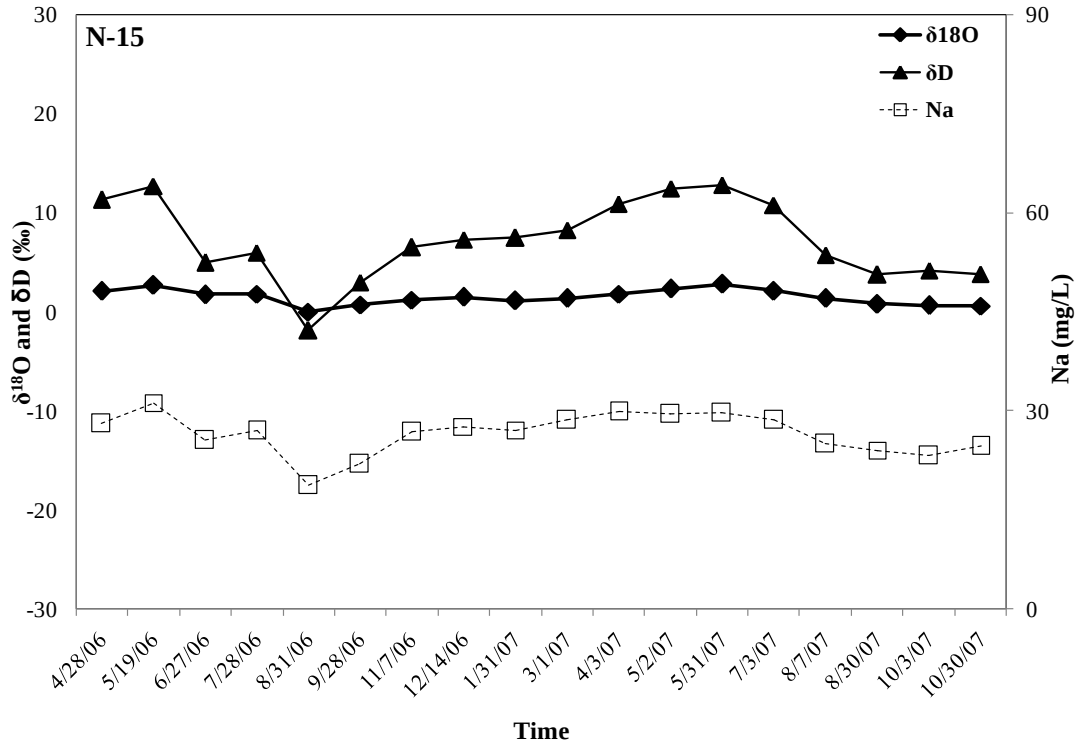
Sample	Date	$\delta^{18}O$*	δD*	Na'	*mWP*	*mN-15*	*mGW*	Sample	Date	$\delta^{18}O$*	δD*	Na'	*mWP*	*mSA-8*	*mGW*
MW-1	4/28/06	-3.04	-14.7	15.2	24	0	76	MW-4	4/28/06	no sample					
	5/19/06	-2.85	-13.3	9.7	2	14	84		5/19/06	-2.71	-11.5	15.4	19	0	81
	6/27/06	-2.92	-18.4	5.5	0	15	85		6/27/06	-2.52	-17.5	7.2	0	18	82
	7/28/06	-2.79	-16.9	6.8	0	17	83		7/28/06	-2.80	-14.6	7.8	2	12	86
	8/31/06	-4.10	-23.4	3.6	0	0	100		8/31/06	-4.63	-27.8	2.5	0	0	100
	9/28/06	-3.89	-19.4	3.8	0	0	100		9/28/06	-3.69	-18.5	3.2	0	0	100
	11/7/06	-3.69	-19.7	5.9	0	0	100		11/7/06	-3.68	-19.3	4.9	0	0	100
	12/14/06	-3.33	-18.2	5.6	0	7	93		12/14/06	-3.37	-13.9	5.3	0	5	95
	1/9/07	-3.07	-17.8	5.5	0	12	88		1/9/07	-2.80	-15.0	12.8	13	1	85
	1/31/07	-2.62	-8.6	7.1	0	21	79		1/31/07	-1.87	-1.4	7.4	0	28	72
	3/1/07	-2.18	-5.7	6.6	0	29	71		3/1/07	-2.11	-7.1	12.7	11	14	75
	4/3/07	-2.55	-12.1	6.4	0	22	78		4/3/07	-2.32	-9.1	11.9	10	12	78
	5/2/07	-2.81	-12.3	7.4	0	17	83		5/2/07	-2.30	-8.6	11.8	10	12	78
	5/31/07	0.74	2.9	30.4	25	56	19		5/31/07	-2.41	-9.1	11.5	9	11	80
	7/3/07	4.95	24.2	71.4	100	0	0		7/3/07	-3.40	-16.3	20.1	32	0	68
	8/7/07	-3.01	-14.0	4.8	0	13	87		8/7/07	-3.38	-19.8	5.0	0	5	95
	8/30/07	-2.93	-13.3	4.8	0	15	85		8/30/07	-4.43	-27.8	15.1	24	0	76
	10/3/07	-4.18	-24.9	5.1	5	0	95		10/3/07	-1.78	-9.8	22.9	34	0	66
	10/30/07	-3.40	-19.4	6.0	0	6	94		10/30/07	-0.53	-4.7	36.1	60	0	40
MW-2	4/28/06	-1.83	-7.9	16.7	12	21	66	MW-5	4/28/06	no sample					
	5/19/06	-1.83	-8.0	16.1	10	24	66		5/19/06	-2.24	-9.9	14.0	14	9	77
	6/27/06	-2.27	-14.7	9.0	0	27	73		6/27/06	-2.97	-17.0	11.7	12	0	88
	7/28/06	-2.43	-14.2	8.7	0	24	76		7/28/06	no sample					
	8/31/06	-2.72	-15.6	6.5	0	19	81		8/31/06	-4.04	-23.8	5.3	0	0	100
	9/28/06	-2.93	-14.5	7.7	0	15	85		9/28/06	-3.68	-18.5	5.7	0	0	100
	11/7/06	-2.59	-12.2	9.5	0	21	79		11/7/06	-3.12	-17.2	13.3	16	0	84
	12/14/06	-2.35	-12.9	8.3	0	26	74		12/14/06	-2.75	-14.8	14.8	18	0	82
	1/9/07	-2.40	-14.0	8.3	0	25	75		1/9/07	-2.84	-15.8	7.4	1	12	87
	1/31/07	-2.38	-9.9	8.5	0	25	75		1/31/07	-2.19	-2.5	4.3	0	23	77
	3/1/07	-2.38	-10.4	9.2	0	25	75		3/1/07	-2.44	-9.5	7.1	0	19	81
	4/3/07	-2.38	-10.2	10.1	0	25	75		4/3/07	-2.65	-11.5	8.9	4	12	84
	5/2/07	-2.12	-10.8	11.9	0	30	70		5/2/07	-2.57	-10.4	7.7	1	16	83
	5/31/07	-2.22	-11.6	10.6	0	28	72		5/31/07	-2.60	-9.9	9.7	6	11	83
	7/3/07	-1.62	-7.6	12.9	0	40	60		7/3/07	-2.90	-11.7	9.8	7	6	87
	8/7/07	-2.01	-11.6	11.0	0	32	68		8/7/07	-3.39	-16.8	7.0	2	3	95
	8/30/07	0.02	-0.7	16.1	0	71	29		8/30/07	-4.12	-23.7	7.5	5	0	95
	10/3/07	1.03	4.6	19.5	0	91	9		10/3/07	-3.28	-16.8	8.6	5	1	93
	10/30/07	0.19	0.3	17.0	0	75	25		10/30/07	-3.33	-17.4	7.0	2	4	94
MW-3	4/28/06	-3.66	-19.2	5.7	0	1	99	MW-6	4/28/06	-3.14	-14.0	24.8	42	0	58
	5/19/06	-3.35	-18.4	6.0	0	7	93		5/19/06	-2.51	-12.5	15.7	19	0	81
	6/27/06	-1.94	-11.1	10.1	0	34	66		6/27/06	-3.11	-14.9	21.2	34	0	66
	7/28/06	-0.93	-2.5	13.6	0	53	47		7/28/06	no sample					
	8/31/06	-3.11	-18.4	9.2	4	7	89		8/31/06	-4.15	-23.8	9.0	9	0	91
	9/28/06	-1.54	-6.1	12.7	0	41	59		9/28/06	-3.22	-14.9	19.7	31	0	69
	11/7/06	-1.67	-5.9	13.5	0	39	61		11/7/06	-3.16	-17.2	24.3	41	0	59
	12/14/06	0.27	0.4	22.6	3	72	24		12/14/06	-2.93	-16.0	24.6	41	0	59
	1/9/07	-0.45	-3.1	28.4	34	22	44		1/9/07	-2.96	-18.5	24.1	40	0	60
	1/31/07	-0.36	0.1	26.4	26	33	41		1/31/07	-3.14	-14.0	19.6	30	0	70
	3/1/07	no sample							3/1/07	-3.06	-14.8	23.5	39	0	61
	4/3/07	0.68	4.6	31.4	29	50	21		4/3/07	-3.04	-16.8	23.4	39	0	61
	5/2/07	-1.63	-11.2	12.0	0	40	60		5/2/07	-3.06	-14.8	24.6	42	0	58
	5/31/07	-2.91	-16.3	7.1	0	15	85		5/31/07	-3.06	-15.6	24.8	42	0	58
	7/3/07	no sample							7/3/07	-3.14	-17.1	22.0	36	0	64
	8/7/07	4.15	20.6	65.6	100	0	0		8/7/07	-3.14	-16.8	21.4	35	0	65
	8/30/07	2.17	7.1	67.1	100	0	0		8/30/07	-3.25	-18.3	22.3	37	0	63
	10/3/07	2.25	11.7	63.3	100	0	0		10/3/07	-3.20	-15.7	23.9	41	0	59
	10/30/07	3.52	17.3	82.7	100	0	0		10/30/07	-2.92	-15.0	16.9	23	0	77

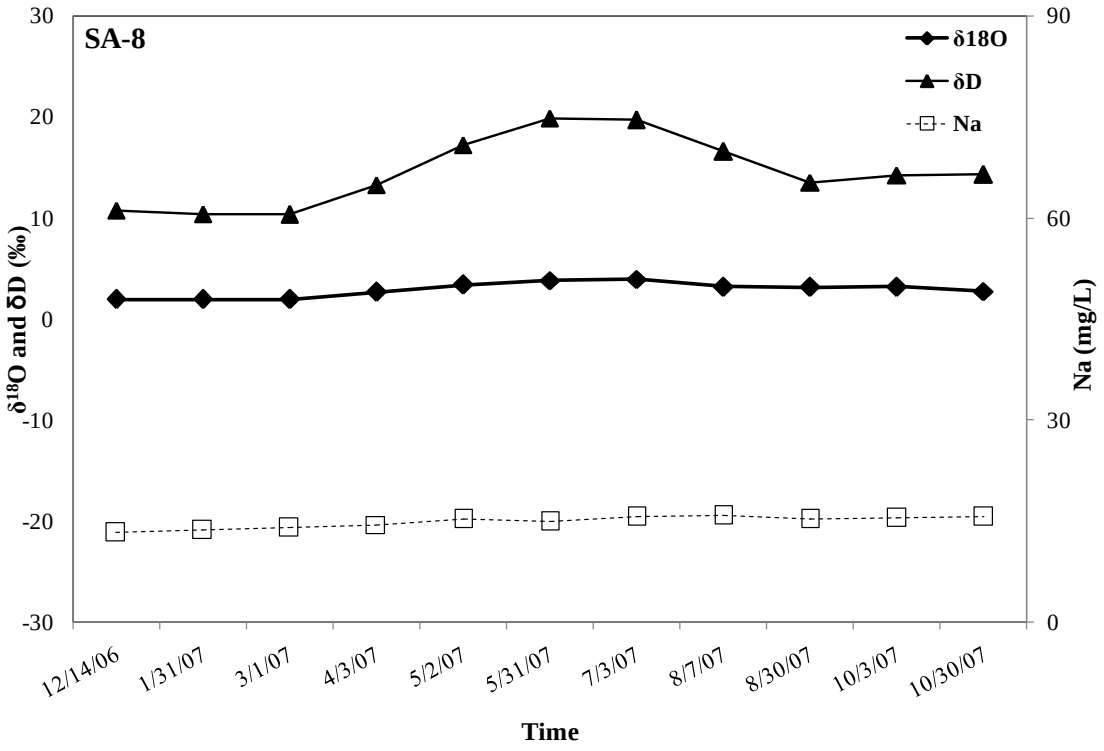
Note: MW - monitor wells; (*) - values in ‰; (´) – values in mg/L; *m* - mass or percentage of each end-member in MW; WP – wetland water from pump; GW – groundwater (based on well ROMP 45 data from Sacks and Tihansky, 1996); SA-8 and N-15 - water bodies to the north and south of the wetland.


WP
CP
δ18O
δD
Na
Cl
δ18O and δD (‰)
Cl and Na (mg/L)
Time
4/28/2006
5/19/2006
6/27/2006
7/28/2006
8/31/2006
9/28/2006
11/7/2006
12/14/2006
1/9/2007
1/31/2007
3/1/2007
4/3/2007
5/2/2007
5/31/2007
7/3/2007
8/7/2007
8/30/2007
10/3/2007
10/30/2007


MW-1
MW-2
MW-3
δ18O
δD
Na
δ18O and δD (‰)
Na (mg/L)
Time
4/28/06
5/19/06
6/27/06
7/28/06
8/31/06
9/28/06
11/7/06
12/14/06
1/9/07
1/31/07
3/1/07
4/3/07
5/2/07
5/31/07
7/3/07
8/7/07
8/30/07
10/3/07
10/30/07


MW-6
δ18O
δD
Na
MW-5
MW-4
δ18O and δD (‰)
Na (mg/L)
30
20
10
0
-10
-20
-30
90
60
30
0
4/28/06
5/19/06
6/27/06
7/28/06
8/31/06
9/28/06
11/7/06
12/14/06
1/9/07
1/31/07
3/1/07
4/3/07
5/2/07
5/31/07
7/3/07
8/7/07
8/30/07
10/3/07
10/30/07
Time


N-15
δ18O
δD
Na
30
20
10
0
-10
-20
-30
90
60
30
0
δ18O and δD (‰)
Na (mg/L)
4/28/06
5/19/06
6/27/06
7/28/06
8/31/06
9/28/06
11/7/06
12/14/06
1/31/07
3/1/07
4/3/07
5/2/07
5/31/07
7/3/07
8/7/07
8/30/07
10/3/07
10/30/07
Time


SA-8
δ18O
δD
Na
30
20
10
0
-10
-20
-30
90
60
30
0
δ18O and δD (‰)
Na (mg/L)
12/14/06
1/31/07
3/1/07
4/3/07
5/2/07
5/31/07
7/3/07
8/7/07
8/30/07
10/3/07
10/30/07
Time

APPENDIX C.

CHEMICAL AND MINERALOGICAL ANALYSIS OF THE SAMPLES FROM THE SUWANNEE LIMESTONE (IN MG/KG)

Sample	Ca	Fe	Mg	Si	S	P	Al	Na	K	As	Mineralogy
98-101(1)	336025	6250	28687	1972	3712	11922	5123	1090	223	10.1	ls+Q-ph-c mtrx.(95/5)
98-101(2)	318663	6221	28619	1965	3841	11146	4876	1068	218	10.0	ls+Q-ph-c mtrx.(95/5)
98-101(a)	399126	461	2594	308	889	208	<5	140	19	1.5	ls
98-101(b)	355001	20579	2928	1922	8108	404	18986	254	155	15.4	Q-ph-c mtrx.
101-104(1)	321179	3582	15867	1324	3079	1562	1830	244	308	7.9	ls+Q-ph-c mtrx.+ch. (90/7/3)
101-104(2)	349911	3677	13202	2948	3034	1692	1885	279	307	7.7	ls+Q-ph-c mtrx.+ch. (90/7/3)
101-104(a)	401033	640	2346	343	862	175	<5	99	17	1.8	ls,Q
101-104(b)	176245	9158	87682	1054	614	8928	1799	556	200	3.5	ls,i_ox, p, Q
101-104(c)	396391	21333	3632	2447	7964	386	19792	235	140	11.6	Q-ph-c mtrx.
104-107(1)	388624	2812	2565	7143	1896	253	1863	219	77	2.7	ls+Q-ph-c mtrx.(95/5)
104-107(2)	419183	2943	3327	4689	1943	283	1989	213	83	3.0	ls+Q-ph-c mtrx.(95/5)
104-107(a)	384124	742	2107	463	946	154	<5	98	33	3.0	ls
104-107(b)	380177	21534	2655	2440	9188	320	18875	649	512	11.6	Q-ph-c mtrx.
107-110(1)	422894	1462	3984	2593	1138	270	744	130	35	2.4	ls+ds+Q-ph-c mtrx.(90/7/3)
107-110(1.1)	402075	1471	3519	1656	1155	251	786	129	23	1.8	ls+ds+Q-ph-c mtrx.(90/7/3)
107-110(2)	387000	650	3606	643	803	236	70	113	12	1.1	ls+ds+Q-ph-c mtrx.(90/7/3)
107-110(a)	397074	338	3606	350	773	203	<5	121	18	0.9	ls,p,ph
107-110(b)	420664	215	3402	186	703	210	<5	89	<5	0.2	ls,p,ph
107-110(c)	353391	19722	2416	1842	13504	306	17743	1079	959	10.0	Q-ph-c mtrx.
110-114(1)	395897	1950	3531	3841	1247	316	1300	155	50	0.5	ls+ds+Q-ph-c mtrx.(85/10/5)
110-114(2)	413195	1672	3686	1529	1011	652	793	164	33	1.4	ls+ds+Q-ph-c mtrx.(85/10/5)
110-114(2.1)	405356	1362	3176	3684	1011	441	723	145	26	1.5	ls+ds+Q-ph-c mtrx.(85/10/5)
110-114(a)	396094	93	3969	191	555	380	<5	102	<5	0.4	ls,p, i_ox
110-114(b)	416380	21813	3366	1929	8837	315	20611	1124	919	11.9	Q-ph-c mtrx.
110-114(c)	390311	173	3320	324	623	551	<5	135	28	2.4	ls,p
114-117(1)	416380	1154	3961	1145	1038	257	584	198	47	1.3	ls+Q-ph-c mtrx.(95/5)
114-117(2)	402201	1111	3487	1781	1019	247	506	206	44	2.5	ls+Q-ph-c mtrx.(95/5)
114-117(a)	407264	166	3359	268	637	290	<5	219	37	0.1	ls
114-117(b)	391828	20714	3083	1523	9038	307	19399	663	529	11.9	Q-ph-c mtrx.
117-120(1)	447687	502	3287	1301	746	189	56	213	19	0.7	ls+Q-ph-c mtrx.(95/5)
117-120(2)	397694	457	3364	878	710	187	6	197	24	0.7	ls+Q-ph-c mtrx.(95/5)
117-120(a)	407152	17	3299	150	467	189	<5	197	13	0.2	ls
117-120(b)	387890	21776	2557	2116	8657	299	19916	695	544	14.4	Q-ph-c mtrx.
120-123(1)	398055	2683	2524	8049	1572	221	1950	237	83	2.0	ls+Q-ph-c mtrx.(95/5)
120-123(2)	392931	2628	3027	2155	1565	219	1941	238	91	2.0	ls+Q-ph-c mtrx.(95/5)
120-123(a)	391296	96	2920	223	550	207	<5	238	27	0.5	ls
120-123(b)	388572	21378	2642	2198	8465	302	18473	667	500	13.8	Q-ph-c mtrx.
123-126(1)	396581	2157	3212	1463	1448	241	1416	244	62	1.9	ls+Q-ph-c mtrx.(95/5)
123-126(2)	390150	2079	2979	4539	1408	221	1488	241	59	2.0	ls+Q-ph-c mtrx.(95/5)
123-126(a)	395897	110	2754	396	776	195	<5	517	49	0.4	ls
123-126(b)	374561	21279	2642	2136	8548	306	18366	634	480	13.7	Q-ph-c mtrx.
126-129(1)	402201	123	3153	264	631	200	<5	225	7	0.9	ls+Q-ph-c mtrx.(99/1)
126-129(2)	401333	98	3161	259	633	219	<5	242	17	0.4	ls+Q-ph-c mtrx.(99/1)
126-129(a)	406882	170	3736	77	762	103	<5	135	<5	0.8	ls
129-133(1)	412207	140	3156	318	734	203	<5	307	9	1.8	ls+Q-ph-c mtrx.(99/1)
129-133(2)	418138	163	3161	331	741	200	<5	313	6	0.5	ls+Q-ph-c mtrx.(99/1)
129-133(a)	404355	98	3060	346	703	209	<5	293	33	0.4	ls
133-136(1)	439141	166	3052	295	735	194	<5	349	11	0.7	ls+Q-ph-c mtrx.(99/1)
133-136(2)	423367	172	2600	336	716	183	<5	344	10	0.9	ls+Q-ph-c mtrx.(99/1)
133-136(a)	415879	197	3440	181	634	336	<5	106	<5	1.5	ls
136-139(1)	390803	305	2779	247	763	210	<5	328	6	0.9	ls+Q-ph-c mtrx.(99/1)
136-139(2)	406554	355	2733	253	744	207	<5	297	<5	16.1	ls+Q-ph-c mtrx.(99/1)
136-139(a)	413063	105	3111	300	598	235	<5	232	13	0.8	ls

Sample	Ca	Fe	Mg	Si	S	P	Al	Na	K	As	Mineralogy
139-142(1)	394908	144	3140	187	505	237	<5	181	<5	0.4	ls+Q-ph-c mtrx.(99/1)
139-142(2)	397952	141	2858	181	517	229	<5	174	<5	0.0	ls+Q-ph-c mtrx.(99/1)
139-142(a)	405141	53	3020	186	552	252	<5	189	13	0.3	ls
142-145(1)	415561	141	3206	199	578	245	<5	205	<5	1.0	ls+Q-ph-c mtrx.(95/5)
142-145(2)	405571	147	2989	207	605	247	<5	205	3	0.7	ls+Q-ph-c mtrx.(95/5)
142-145(a)	466051	78	3265	237	552	256	<5	207	15	0.1	ls
142-145(b)	394334	21758	3270	1734	10042	310	20391	614	500	10.9	Q-ph-c mtrx.
145-148(1)	423751	92	3011	153	449	184	<5	154	<5	0.2	ls+Q-ph-c mtrx.(99/1)
145-148(2)	407862	87	3332	172	461	194	<5	152	<5	0.2	ls+Q-ph-c mtrx.(99/1)
145-148(a)	391788	90	3277	353	523	224	<5	170	28	1.0	ls
148-152(1)	464464	103	3759	186	475	162	<5	168	1	0.5	ls+Q-ph-c mtrx.(99/1)
148-152(2)	414245	74	3031	197	462	203	<5	139	2	0.2	ls+Q-ph-c mtrx.(99/1)
148-152(1)	421878	60	2756	205	480	201	<5	172	12	0.2	ls
152-155(1)	400155	243	3261	164	611	185	<5	137	5	2.5	ls+Q-ph-c mtrx.(99/1)
152-155(2)	445351	264	3441	187	616	197	<5	137	5	2.4	ls+Q-ph-c mtrx.(99/1)
152-155(a)	417908	370	3292	397	765	235	<5	151	40	2.1	ls
155-158(1)	398055	199	3287	209	532	211	<5	127	15	1.2	ls+Q-ph-c mtrx.(99/1)
155-158(2)	416220	183	3856	216	545	219	<5	130	<5	2.1	ls+Q-ph-c mtrx.(99/1)
155-158(a)	438628		3337		368	159	<5	115	<5	0.0	ls
158-161(1)	411283	290	3219	117	582	192	<5	117	<5	1.9	ls+Q-ph-c mtrx.(99/1)
158-161(2)	396217	244	3326	117	561	175	<5	123	<5	1.8	ls+Q-ph-c mtrx.(99/1)
158-161(a)	407152	298	3921	208	693	239	<5	130	24	2.2	ls
161-164(1)	392280	328	3358	380	623	187	<5	133	<5	1.4	ls+Q-ph-c mtrx.(95/5)
161-164(2)	411952	338	2841	436	607	173	<5	124	<5	1.5	ls+Q-ph-c mtrx.(95/5)
161-164(a)	394249	240	4160	227	605	209	<5	121	14	1.3	ls
161-164(b)	416702	22069	3304	1982	9975	321	19914	721	579	13.3	Q-ph-c mtrx.
164-167(1)	413690	633	3777	154	762	191	<5	113	<5	2.0	ls+Q-ph-c mtrx.(95/5)
164-167(2)	398607	609	3412	180	806	189	<5	110	<5	2.6	ls+Q-ph-c mtrx.(95/5)
164-167(a)	417081	199	4227	136	651	242	<5	125	10	0.8	ls
167-171(1)	392280	352	3511	175	685	196	<5	116	0	1.7	ls,p
167-171(2)	404209	340	3594	162	704	160	<5	121	3	2.1	ls,p
167-171(a)	418558	328	4802	186	752	238	<5	132	7	1.5	ls,p
171-174(1)	411173	528	3701	474	731	204	<5	138	1	5.5	ls+Q-ph-c mtrx.(95/5)
171-174(2)	390803	407	3586	603	699	189	<5	134	<5	0.9	ls+Q-ph-c mtrx.(95/5)
171-174(2)	452979	229	3472	209	564	211	<5	117	20	1.2	dolom.ls,p, Q
171-174(b)	396081	22326	3365	2037	10293	317	19609	679	510	12.5	Q-ph-c mtrx.,c,p
174-177(1)	404299	283	3632	141	592	172	<5	128	<5	0.5	ls+ds(99/1)
174-177(2)	429011	291	3975	119	594	174	<5	126	<5	0.5	ls+ds(99/1)
174-177(a)	408568	99	3471	87	606	177	<5	120	<5	0.5	ls,Q,p,i_ox.
177-180(1)	398055	280	2966	110	648	172	<5	133	<5	0.6	ls+ds(99/1)
177-180(2)	417883	286	4052	115	669	175	<5	136	<5	0.7	ls+ds(99/1)
177-180(a)	410925	216	3550	86	773	158	<5	147	<5	0.6	ls,Q,p,i_ox.
180-183(1)	405782	276	3611	131	706	228	<5	134	<5	0.7	ls+ds(99/1)
180-183(2)	433294	282	3274	103	679	195	<5	136	<5	0.6	ls+ds(99/1)
180-183(a)	404847	230	3501	134	762	142	<5	151	5	0.5	ls,Q,p,i_ox.
183-186(1)	401850	455	5553	241	870	213	<5	162	16	1.2	ls,Q,p,i_ox.
183-186(2)	395591	497	5203	241	894	222	<5	160	32	1.2	ls,Q,p,i_ox.
183-186(a)	407485	297	4407	171	893	196	<5	159	11	1.2	ls,Q,p,i_ox.
186-189(1)	381069	192	3643	192	727	161	<5	124	<5	0.7	ls+ds (97/3)
186-189(2)	377709	275	3471	205	828	169	<5	124	<5	0.1	ls+ds (97/3)
186-189(a)	394004	317	3739	217	953	128	<5	148	<5	0.9	ls

APPENDIX D.

CHEMICAL AND MINERALOGICAL ANALYSIS OF THE SAMPLES FROM THE OCALA LIMESTONE (IN MG/KG)

Sample	Ca	Fe	Mg	Si	S	P	Al	Na	K	As	Mineralogy
189-192(1)	342638	241	13196	137	520	201	<5	77	<5	0.4	ls+ds (97/3)
189-192(2)	355004	287	11687	109	487	141	<5	73	<5	0.5	ls+ds (97/3)
189-192(a)	265630	83	24127	142	426	234	<5	49	4	0.2	ls, i_ox.
192-195(1)	367889	412	3481	46	626	106	<5	95	<5	0.6	ls+ds (97/3)
192-195(2)	352528	420	3263	58	598	141	<5	82	<5	0.4	ls+ds (97/3)
192-195(a)	389471	35	5625	75	564	145	<5	81	<5	0.3	ls, i_ox.
195-199(1)	400345	112	3290	326	734	292	<5	275	24	1.3	ls+ds (99/1)
195-199(2)	396391	80	4136	87	796	141	<5	131	<5	0.8	ls+ds (99/1)
195-199(a)	403269	33	3735	65	647	82	<5	112	<5	0.6	ls, i_ox., p
199-202(1)	396094	649	4216	114	830	144	<5	125	<5	0.4	ls+ds (99/1)
199-202(2)	389559	129	4184	108	798	140	<5	118	<5	0.4	ls+ds (99/1)
199-202(a)	405852	34	5438	106	761	147	<5	100	<5	0.2	ls, i_ox., p
202-205(1)	398446	51	4346	112	783	150	<5	117	1	0.0	ls+ds (99/1)
202-205(2)	397841	56	4981	112	770	135	<5	107	<5	0.3	ls+ds (99/1)
202-205(a)	397218	22	4280	42	672	89	<5	93	<5	0.3	ls
205-208(1)	387315	84	4863	120	755	110	<5	125	<5	0.6	ls+ds (97/3)
205-208(2)	425749	138	5792	171	876	159	<5	145	1	0.7	ls+ds (97/3)
205-208(a)	392437	7	4088	38	935	129	<5	141	<5	0.2	ls
208-211(1)	301224	141	74683	287	725	329	<5	176	11	0.9	ds+ls (50/50)
208-211(2)	309402	174	93758	296	769	295	<5	232	23	1.7	ds+ls (50/50)
208-211(a)	440966	158	2950	421	682	288	<5	198	19	0.7	ls, Q
208-211(b)	245296	168	123374	322	784	328	<5	213	32	0.6	ds sucrosic, i_ox.
211-213(1)	321759	199	64291	325	789	287	<5	171	14	1.1	ds+ls (70/30),p,i_ox.
211-213(2)	311671	145	67307	294	784	311	<5	177	10	1.1	ds+ls (70/30),p,i_ox.
211-213(a)	390591	11	3186	65	523	179	<5	141	<5	0.2	dolom. ls, p
211-213(b)	267885	59	126439	359	654	304	<5	228	2	0.1	ds sucrosic, i_ox.
213-217(1)	421729	67	3277	152	1221	160	<5	168	1	1.4	ls, Q, i_ox
213-217(2)	392931	121	2861	225	1288	146	<5	159	10	1.9	ls, Q, i_ox
213-217(a)	417081	73	2981	267	1179	123	<5	143	9	1.1	ls, Q, i_ox
217-220(1)	446750	69	4959	107	1109	110	<5	159	<5	1.1	ls, Q, p, i_ox
217-220(2)	441193	58	5035	111	1089	134	<5	158	<5	1.1	ls, Q, p, i_ox
217-220(a)	340365	49	5058	94	1141	116	<5	155	<5	0.9	ls, Q, p, i_ox
220-223(1)	427434	<5	3616	33	1018	96	<5	172	<5	0.8	ls
220-223(2)	400423	56	3158	42	1026	108	<5	176	<5	0.7	ls
220-223(a)	408932	27	3215	64	959	101	<5	130	<5	0.6	ls
223-226(1)	414754	10	3338	38	794	102	<5	115	<5	0.5	ls+Q-ph-c mtrx.(95/5)
223-226(2)	378895	10	2951	34	739	107	<5	108	<5	0.6	ls+Q-ph-c mtrx.(95/5)
223-226(a)	391000	22000	2575	3545	9650	357	16800	620	480	14.7	Q+ph-c mtrx.
223-226(b)	406500	<5	3020	25	795	90	<5	109	<5	0.2	ls
226-230(1)	406631	233	5104	46	825	103	<5	139	<5	0.4	ls
226-230(2)	422976	419	5296	42	814	106	<5	136	<5	0.5	ls
226-230(a)	386029	<5	2902	6	702	91	<5	102	<5	0.8	ls
230-231(1)	405000	179	6600	426	1005	112	<5	165	<5	0.6	ls+Q-ph-c mtrx.(95/5)
230-231(2)	447500	79	8200	147	915	114	<5	165	<5	1.0	ls+Q-ph-c mtrx.(95/5)
230-231(a)	404428	<5	3642	9	815	98	<5	131	<5	0.3	ls
230-231(b)	355481	21818	2435	3471	11655	333	17013	594	473	14.6	Q+ph-c mtrx.

Sample	Ca	Fe	Mg	Si	S	P	Al	Na	K	As	Mineralogy
231-236(1)	394917	40	11951	73	918	148	<5	159	<5	0.5	ls
231-236(2)	393259	55	11507	83	905	134	<5	160	<5	0.5	ls
231-236(a)	298293	8	7761	72	752	162	<5	115	<5	0.3	ls
236-239(1)	321347	1702	47745	5640	1417	222	1042	289	52	1.7	ls+ds+Q-ph-c mtrx.(40/40/20)
236-239(2)	334147	1366	49447	729	1280	300	771	281	47	1.5	ls+ds+Q-ph-c mtrx.(40/40/20)
236-239(a)	377899	11	2457	42	887	99	<5	127	<5	2.6	ls
236-239(b)	244177	65	111222	265	894	226	<5	408	45	0.4	ds sucrosic, i_ox.
236-239(c)	367000	21200	2595	3320	9100	330	17150	630	494	13.8	Q+ph-c mtrx.
239-242(1)	329500	136	58000	307	945	203	<5	303	<5	1.2	ls+ds(50/50)
239-242(2)	326523	111	59932	209	881	214	<5	274	<5	1.2	ls+ds(50/50)
239-242(a)	394167	<5	9537	23	873	145	<5	203	<5	0.8	ls
239-242(b)	253092	4	118926	165	787	225	<5	378	17	0.2	ds sucrosic, p
239-242(c)	255625	163	113750	303	1344	271	<5	517	3	8.6	ls.ds,p
242-246(1)	296065	124	89044	270	1029	325	<5	342	25	1.2	ds+ls(65/35), Q
242-246(2)	311265	180	71919	271	1001	222	<5	329	<5	1.5	ds+ls(65/35), Q
242-246(a)	381326	490	3957	425	1279	122	<5	171	<5	1.4	ls,Q
242-246(b)	273950	111	127158	284	1186	284	<5	495	54	1.0	ds, p, i_ox.
246-249(1)	288500	175	98000	453	1075	227	<5	401	13	1.7	ds+ls (75/25), Q, i_ox.
246-249(2)	279500	59	102000	235	1005	240	<5	422	25	1.6	ds+ls (75/25), Q, i_ox.
246-249(a)	171284	<5	1425	28	325	104	<5	13	<5	0.2	ls,Q,i_ox.
246-249(b)	245765	54	104473	227	998	229	<5	423	36	1.1	ds, p, i_ox.
249-252(1)	356500	221	38000	425	1070	184	<5	234	4	1.4	ls+ds (60/40)
249-252(2)	417562	240	31414	588	1051	188	<5	240	7	0.9	ls+ds (60/40)
249-252(a)	320000	69	63000	279	970	196	<5	318	8	0.6	dolom. ls
249-252(b)	235023	90	127292	470	1077	330	<5	427	22	1.1	ds

APPENDIX E.

CHEMICAL AND MINERALOGICAL ANALYSIS OF THE SAMPLES FROM THE AVON PARK FORMATION (IN MG/KG)

Sample	Ca	Fe	Mg	Si	S	P	Al	Na	K	As	Mineralogy
252-255(1)	470457	158	5843	210	1006	116	<5	149	<5	1.4	ls, dolom.ls,p, i_ox
252-255(1)	406554	100	7367	180	1066	181	<5	139	<5	1.1	ls, dolom.ls,p, i_ox
252-255(a)	424000	58	2190	71	1150	97	<5	143	<5	0.8	ls, dolom.ls,p, i_ox
255-257(1)	260225	515	103345	613	1548	336	83	690	65	4.8	ls+ds(75/25), gy
255-257(2)	262277	432	92004	617	1590	251	<5	621	67	5.2	ls+ds(75/25)
255-257(a)	233087	193	112509	389	1432	237	<5	604	52	3.7	l.b ds
255-257(b)	275500	285	139000	446	1760	246	<5	720	82	5.2	d.b ds sucrosic
257-260(1)	277361	1281	92444	2992	1746	226	952	670	83	1.7	ls+ds+Q-ph-c mtrx.(75/24/1)
257-260(2)	256434	477	107706	517	1534	325	275	733	76	1.2	ls+ds+Q-ph-c mtrx.(75/24/1)
257-260(1a)	229318	<5	118444	111	1178	218	<5	811	<5	0.8	l.b ds sucrosic, p
260-261(1)	307825	789	87736	801	1610	300	569	498	191	4.8	ds+ls(90/10)
260-261(2)	301630	854	97259	1175	1692	259	706	539	199	3.7	ds+ls(90/10), c
260-261(a)	269138	821	142548	888	1869	286	1016	765	247	3.2	d.b ds sucrosic,p, c
261-265(1)	275154	223	98389	442	1394	226	<5	538	12	4.1	ds+ls(80/20)
261-265(2)	269559	175	100386	456	1424	221	<5	622	40	2.6	ds+ls(80/20)
261-265(a)	297454	194	135200	421	1324	245	<5	604	54	4.5	d.b ds sucrosic,p,i_ox
265-268(1)	305593	201	91000	477	1783	206	<5	539	17	1.1	ds+ls(50/50)
265-268(2)	268000	214	96000	545	2060	223	<5	565	36	1.8	ds+ls(50/50)
265-268(a)	399202	71	3414	146	573	330	<5	112	<5	0.7	ls,Q, p, ph
265-268(b)	233776	93	116037	503	1917	202	<5	1103	114	1.4	ds, p, i_ox
265-268(c)	384761	20489	2574	1558	9344	311	18390	626	491	12.2	Q+ph-c mtrx.
268-269(1)	286458	739	81250	740	1892	262	350	390	12	1.4	ds+ls+Q-ph-c mtrx.(75/24/1)
268-269(2)	274290	55	92479	323	1467	224	<5	427	<5	0.6	ds+ls+Q-ph-c mtrx.(75/24/1)
268-269(a)	234994	72	126652	398	1622	233	<5	760	52	1.5	l.b ds, i_ox
268-269(b)	372000	21300	2790	3570	9600	384	16600	610	456	14.2	Q+ph-c mtrx.
269-271(1)	303793	172	60036	289	2158	197	<5	323	<5	1.3	ds+ls(50/50)
269-271(2)	291602	167	62873	195	1803	196	<5	330	5	1.1	ds+ls(50/50)
269-271(a)	220898	137	122296	308	4520	208	<5	389	39	1.2	ds, p, i_ox
271-271(1)	298916	143	99273	314	1832	207	<5	454	<5	1.1	ds+ls(50/50)
271-271(2)	304322	162	101964	309	1625	226	<5	461	22	1.6	ds+ls(50/50)
271-271(a)	397558	49	2854	114	1101	131	<5	140	<5	1.3	ls
271-271(b)	230309	1052	110741	1089	2303	233	1204	554	308	4.4	ds, p, i_ox
271-274(1)	298763	254	83067	399	1143	230	<5	337	21	1.8	ds+ls(60/40)
271-274(2)	378605	322	98674	409	1340	273	<5	380	26	1.5	ds+ls(60/40)
271-274(a)	229242	182	117614	403	1267	226	<5	408	49	1.4	ds, p, i_ox

APPENDIX F.

DATA FROM THE BENCH-SCALE LEACHING EXPERIMENTS INCLUDING THE COMPOSITION OF ORIGINAL WATERS AND RECOVERED LEACHATES

Suwannee Limestone; Interval 136 m - 139 m; 0.3 m columns

Sample	Date/Time	Volume of leachate	pH	ORP	T	H_2S	As	DO	Fe^{2+}	F	Cl	SO_4	NO_3	PO_4	NO_2	Br	Na	Mg	K	Ca	Sr	Mn	Fe	Si
		mL		mV	˚C	mg/L	µg/L													mg/L				
DW	10/24/06; 9:35 AM	0	6.7	320	21.2	0.0	0.0	2.9	0.0	0.0	5.8	39.0	2.5	0.0	0.0	0.0	12.9	5.2	1.6	108.6	0.7	0.0	0.0	4.0
1	10:02-10:44 AM	60	7.4	122	21.1	0.0	2.0		0.0	0.2	33.0	345.9	8.3	0.0	0.5	0.1	29.3	38.4	13.0	139.4	1.9	0.0	0.0	6.1
2	10:44-11:26 AM	120	7.3	111	22.0	0.0	1.8		0.0	0.6	17.6	109.4	6.9	0.0	0.0	0.0	13.7	16.8	2.4	138.3	1.6	0.0	0.0	4.7
3	11:26-12:11 AM	180	7.1	125	21.9	0.0	1.4		0.0	0.5	16.6	99.3	6.5	0.0	0.0	0.0	13.7	13.6	2.0	191.5	1.6	0.0	0.1	4.8
4	12:11-1:06 PM	240	7.1	122	21.8	0.0	2.0		0.0	0.5	17.3	104.2	6.7	0.0	0.0	0.0	13.4	10.1	1.8	159.7	1.3	0.0	0.0	4.5
5	1:06-1:51 PM	300	7.2	144	21.9	0.0	2.3		0.0	0.5	16.1	97.8	6.4	0.0	0.0	0.0	13.3	9.7	1.8	234.8	1.2	0.0	0.0	4.7
6	1:51-2:35 PM	360	7.2	147	22.4	0.0	1.4		0.0	0.5	17.0	104.7	6.8	0.0	0.0	0.0	13.3	9.4	1.8	300.2	1.1	0.0	0.1	4.6
WW	3/11/08; 11:00 AM	0	6.8	-143	18.0	3.0	1.2	0.4	0.1	3.0	136.4	43.4	0.0	5.3	0.0	2.0	58.8	35.3	18.8	56.8	0.5	0.0	0.0	0.8
1	3:10-3:45 PM	60	7.3	-88	21.2	0.3	3.9		0.0	1.2	159.3	298.1	1.4	0.0	0.3	2.0	65.5	44.5	19.1	124.9	1.6	0.0	0.0	1.1
2	3:45-4:40 PM	120	7.4	-70	30.8	0.1	4.6		0.0	1.5	150.1	152.6	0.6	0.0	0.2	1.9	63.6	38.8	19.2	96.7	1.2	0.0	0.0	1.1
3	4:40-5:10 PM	180	7.4	-86	21.0	0.2	4.3		0.0	2.0	147.0	95.1	0.3	0.0	0.1	2.1	61.1	36.3	19.1	73.9	0.9	0.0	0.0	1.0
4	5:10-5:45 PM	240	7.4	-89	20.8	0.2	4.6		0.0	2.4	150.8	74.1	0.2	0.0	0.1	2.0	62.1	36.1	18.5	67.5	0.7	0.0	0.0	0.9
5	5:45-6:10 PM	300	7.4	-102	20.8	0.1	4.6		0.0	2.6	150.6	64.5	0.0	0.0	0.2	1.9	60.3	35.5	18.6	64.4	0.7	0.0	0.0	0.9
6	6:10-6:45 PM	360	7.3	-88	21.0	0.1	4.3		0.0	2.7	150.3	60.2	0.0	0.0	0.1	2.1	56.6	36.2	18.8	64.1	0.6	0.0	0.0	0.9
7	6:45-7:35 PM	420	7.3	38	21.2	0.0	3.9		0.0	2.8	149.1	59.3	0.0	0.0	0.2	2.1	68.7	51.1	11.4	70.8	0.5	0.0	0.0	0.4
8	11:50 AM-12:30 PM	480	7.5	108	19.1	0.0	5.3		0.0	1.9	119.1	71.2	0.0	0.0	0.0	1.8	61.7	38.2	18.3	75.2	0.7	0.0	0.0	1.7
9	12:30-1:15 PM	540	7.5	80	19.8	0.0	5.3		0.0	2.8	151.5	59.8	0.1	0.0	0.0	2.3	60.6	34.9	18.7	64.5	0.6	0.0	0.0	0.9
10	1:15-1:55 PM	600	7.4	87	19.8	0.0	4.0		0.0	2.7	129.2	47.5	0.0	0.0	0.0	2.0	80.6	54.6	16.3	81.8	0.6	0.0	0.0	0.5
11	1:55-2:40 PM	660	7.4	88	19.9	0.0	3.9		0.0	3.2	156.3	55.7	0.2	0.0	0.0	2.4	59.2	35.8	18.2	61.1	0.5	0.0	0.0	0.8
12	2:40-3:35 PM	720	7.4	88	19.8	0.0	3.1		0.0	4.4	210.5	77.6	0.3	0.0	0.0	3.1	60.3	35.7	18.9	60.3	0.5	0.0	0.0	0.8
13	3:35-4:55 PM	780	7.3	89	19.8	0.0	3.7		0.0	3.0	132.1	50.1	0.2	0.0	0.0	2.0	60.6	36.1	18.3	61.5	0.5	0.0	0.0	0.8
14	4:55-5:15 PM	840	7.5	79	19.6	0.0	2.8		0.0	3.7	169.7	57.9	0.2	0.0	0.0	2.3	61.8	36.5	18.4	60.1	0.5	0.0	0.0	0.8
BW	1/29/08; 10:00 AM	0	6.7	-56	17.3	0.0	0.7	1.7	1.0	2.4	107.4	46.3	0.6	0.0	0.0	1.9	51.2	34.9	16.2	52.5	0.4	0.0	0.5	0.7
1	12:48-1:36 PM	60	7.0	94	19.6	0.0	4.6		0.0	0.5	95.9	251.0	2.3	0.0	0.0	1.5	53.3	44.9	17.4	151.6	1.8	0.0	0.0	1.4
2	1:36-2:30 PM	120	7.0	198	19.6	0.0	3.9		0.0	0.6	61.1	44.5	0.5	0.0	0.0	1.2	44.6	29.6	14.3	79.0	0.9	0.0	0.0	0.9
3	2:30-3:19 PM	180	7.0	132	19.3	0.0	3.9		0.0	1.4	108.0	60.4	0.6	0.0	0.0	2.1	51.3	30.7	16.4	65.4	0.7	0.0	0.0	0.9
4	3:19-3:50 PM	240	7.3	150	19.3	0.0	4.0		0.0	1.3	86.1	41.5	0.6	0.0	0.0	1.6	48.0	31.9	15.3	61.1	0.6	0.0	0.0	0.8
5	3:50-4:35 PM	300	7.1	160	19.3	0.0	4.9		0.0	1.5	85.5	39.8	0.6	0.0	0.0	1.8	47.9	32.4	15.4	60.8	0.5	0.0	0.1	0.8
6	4:35-5:10 PM	360	6.9	150	19.3	0.0	3.0		0.0	1.8	97.8	44.9	0.7	0.0	0.0	1.9	50.8	33.3	16.1	59.8	0.5	0.0	0.1	0.8
7	5:10-6:05 PM	420	7.0	181	19.3	0.0	3.3		0.0	2.2	113.1	54.3	0.7	0.0	0.0	2.0	51.1	33.0	15.6	59.9	0.5	0.0	0.0	0.8
8	6:05-6:40 PM	480	7.2	108	19.3	0.0	3.0		0.0	2.0	94.8	43.6	0.6	0.0	0.0	1.8	49.1	32.8	15.5	60.3	0.5	0.0	0.1	0.8

Sample	Date/Time	Volume of leachate	pH	ORP	T	H_2S	As	DO	Fe^{2+}	F	Cl	SO_4	NO_3	PO_4	NO_2	Br	Na	Mg	K	Ca	Sr	Mn	Fe	Si
		mL		mV	˚C	mg/L	µg/L												mg/L					
BW before UV	1/29/08; 10:00 AM	0	6.7	-56	17.3	0.0	0.7	1.7	1.0	2.4	107.4	46.3	0.6	0.0	0.0	1.9	51.2	34.9	16.2	52.5	0.4	0.0	0.5	0.7
BW-UV	1:05 PM	0	6.9	11	19.3	0.0	0.8	3.4	0.4	2.4	106.1	45.7	0.6	0.0	0.0	1.9	49.5	35.1	15.7	53.2	0.4	0.0	0.2	0.7
1	1:32-2:10 PM	60	7.1	175	20.1	0.0	6.1		0.0	0.6	99.8	292.5	2.5	0.0	0.1	0.0	55.7	48.3	19.4	138.4	1.9	0.0	0.0	1.3
2	2:10-2:40 PM	120	7.3	122	20.1	0.0	3.3		0.0	1.0	100.6	78.5	0.7	0.0	0.0	2.0	49.8	32.2	15.2	67.9	0.9	0.0	0.0	0.9
3	2:40-4:00 PM	180	7.4	114	20.1	0.0	4.4		0.0	1.1	76.3	42.3	0.6	0.0	0.0	1.5	50.9	30.9	15.1	53.4	0.7	0.0	0.0	0.9
4	4:00-4:40 PM	240	7.4	112	20.1	0.0	2.8		0.0	1.4	77.8	38.5	0.5	0.0	0.0	1.3	49.2	31.5	16.2	47.5	0.6	0.0	0.0	0.8
5	4:40-5:50 PM	300	7.4	109	20.1	0.0	2.9		0.0	1.4	77.5	36.8	0.5	0.0	0.0	1.4	49.7	32.8	15.2	47.5	0.5	0.0	0.0	0.8
6	5:50-6:41 PM	360	7.6	174	20.1	0.0	2.9		0.0	1.8	93.8	44.0	0.7	0.0	0.0	1.6	50.3	34.1	16.4	49.8	0.5	0.0	0.0	0.8
GW	2/11/08; 9:55 AM	0	7.0	-120	26.1	0.2	0.4	1.2	0.6	0.0	5.0	556.4	0.0	0.0	0.0	0.0	2.7	15.6	1.4	262.0	6.1	0.0	0.3	5.4
1	10:15-11:10 AM	60	6.8	-156	18.4	0.0	1.5		0.0	0.5	22.6	665.9	3.2	0.0	0.2	0.2	13.9	57.0	10.2	402.6	5.1	0.0	0.1	6.2
2	11:20-11:50 AM	120	7.2	-126	18.4	0.0	0.3		0.0	0.4	5.8	590.1	0.2	0.0	0.1	0.0	3.2	21.4	2.5	293.1	5.6	0.0	0.1	6.2
3	11:50 AM-12:30 PM	180	7.3	-96	18.8	0.0	0.4		0.0	0.3	5.3	558.7	0.0	0.0	0.1	0.0	2.9	18.8	1.6	258.3	6.4	0.0	0.0	5.9
4	12:30-1:15 PM	240	7.2	-106	20.1	0.0	0.4		0.0	0.4	5.7	543.4	0.1	0.0	0.1	0.0	2.9	18.5	1.7	296.6	6.3	0.0	0.0	5.9
5	1:15-1:50 PM	300	7.1	-150	20.3	0.0	0.3		0.0	0.3	5.5	503.5	0.0	0.0	0.1	0.0	3.0	17.4	1.6	274.0	6.2	0.0	0.0	5.8
6	1:50-2:20 PM	360	6.9	-126	20.5	0.0	0.3		0.0	0.3	6.5	568.2	0.1	0.0	0.1	0.0	3.0	17.8	1.6	280.7	6.6	0.0	0.0	5.9
7	2:20-3:15 PM	420	7.2	-139	20.2	0.0	0.3		0.0	0.2	4.9	525.7	0.0	0.0	0.1	0.0	3.0	17.6	1.7	323.7	6.7	0.0	0.0	6.1
8	3:15-3:55 PM	480	7.0	-114	20.3	0.0	0.3		0.0	0.2	4.9	527.7	0.1	0.0	0.1	0.0	2.7	17.8	1.6	282.1	6.6	0.0	0.0	6.0
9	3:55-4:30 PM	540	7.0	-106	20.7	0.0	0.2		0.0	0.2	4.9	527.4	0.0	0.0	0.0	0.0	2.9	17.3	1.6	272.3	6.5	0.0	0.0	5.9
GW/air	2/13/08; 9:25:00 AM	0	7.5	161	20.3	0.0	0.4	7.6	0	0.0	5.0	556.4	0.0	0.0	0.0	0.0	2.7	15.6	1.4	262.0	6.1	0.0	0.3	5.4
1	9:45 -10:29 AM	60	7.1	145	21.1	0.0	4.3		0	0.5	14.3	870.5	0.8	0.0	0.6	0.0	8.8	44.9	4.5	285.2	5.2	0.0	0.0	5.9
2	10:29-11:00 AM	120	7.2	119	21.0	0.0	3.9		0	0.5	6.5	765.6	0	0.0	0.1	0.0	2.9	20.9	1.7	259.8	5.8	0.0	0.0	5.7
3	11:00-11:30 AM	180	7.2	129	21.4	0.0	3.7		0	0.4	6.1	723.7	0	0.0	0.1	0.0	2.9	24.2	1.6	277.9	6.6	0.0	0.0	5.4
4	11:30 AM-12:00 PM	240	7.2	122	21.2	0.0	2.6		0	0.3	5.1	558.5	0	0.0	0.1	0.0	3.1	18.2	1.6	265.0	6.5	0.0	0.0	6.0
5	12:00-12:35 PM	300	7.1	135	21.5	0.0	2.2		0	0.3	5.2	590.1	0	0.0	0.1	0.0	3.0	17.9	1.6	263.3	6.5	0.0	0.0	5.9
6	12:35-1:05 PM	360	7.2	133	21.4	0.0	2.3		0	0.3	6.3	745.1	0	0.0	0.1	0.0	2.8	17.6	1.5	265.3	6.4	0.0	0.0	5.7
7	1:05-1:35 PM	420	7.2	140	21.7	0.0	2.2		0	0.2	5.7	671.3	0	0.0	0.1	0.0	3.0	17.4	1.6	265.0	6.5	0.0	0.0	6.1
8	1:35-2:05 PM	480	6.9	162	21.1	0.0	2.4		0	0.2	5.0	545.3	0	0.0	0.1	0.0	3.0	18.0	1.6	266.4	6.8	0.0	0.0	5.9
9	2:05-2:35 PM	540	7.1	149	21.6	0.0	1.3		0	0.2	5.9	705.7	0	0.0	0.0	0.0	2.9	17.1	1.5	255.5	6.4	0.0	0.0	5.9
10	2:35-3:05 PM	600	7.2	149	21.2	0.0	2.0		0	0.2	6.2	733.2	0	0.0	0.1	0.0	3.0	17.4	1.5	265.6	6.6	0.0	0.0	5.9

Suwannee Limestone; Interval 171 m - 176 m; 1 m columns

Sample	Time	Volume of leachate	pH	ORP	T	H_2S	As	DO	Fe^{2+}	F	Cl	SO_4	NO_3	PO_4	NO_2	Br	Na	Mg	K	Ca	Sr	Mn	Fe	Si
		mL		mV	˚C	mg/L	µg/L												mg/L					
DW	2/12/08; 10:10 AM	0	7.0	223	22.9	0	0.1	5.0	0	0.1	14.3	58.1	0.0	0.0	5.5	0.0	6.4	5.3	1.3	121.5	0.7	0.0	0.0	4.4
1	10:35-11:50 AM	60	7.7	107	21.1	0	8.1		0	0.0	26.0	491.6	7.4	0.0	0.3	0.2	41.4	10.2	65.3	117.8	1.7	0.0	0.0	5.0
2	11:50 AM-12:20 PM	120	7.5	109	21.1	0	8.3		0	0.1	18.1	247.1	5.8	0.0	0.2	0.0	15.7	8.0	27.2	103.5	1.4	0.0	0.0	6.0
3	12:20-12:45 PM	180	7.4	108	21.2	0	8.3		0	0.1	15.7	166.8	5.2	0.0	0.0	0.0	10.4	7.0	15.1	102.1	1.3	0.0	0.0	6.3
4	12:45-1:15 PM	240	7.4	112	21.1	0	8.6		0	0.0	18.1	178.1	6.3	0.0	0.2	0.0	8.2	6.3	9.4	103.2	1.2	0.0	0.0	6.2
5	1:15-1:45 PM	300	7.7	115	21.2	0	7.1		0	0.1	18.8	165.5	6.3	0.0	0.2	0.0	7.1	6.1	6.5	93.2	1.1	0.0	0.0	7.1
6	1:45-2:15 PM	360	7.4	118	21.1	0	7.7		0	0.1	18.1	144.7	6.3	0.0	0.1	0.0	6.9	5.8	5.1	94.2	1.0	0.0	0.0	7.2
7	2:15-2:45 PM	420	7.3	124	21.4	0	7.1		0	0.0	17.5	129.6	6.1	0.0	0.1	0.0	6.7	5.8	4.1	95.1	0.9	0.0	0.0	8.2
8	2:45-3:15 PM	480	7.3	125	21.5	0	8.1		0	0.1	16.7	116.7	5.7	0.0	0.1	0.0	6.6	5.5	3.4	93.8	0.9	0.0	0.0	8.2
WW	3/11/08; 11:00 AM	0	6.8	-143	18.0	3.0	1.2	0.4	0.1	3.0	136.4	43.4	0.0	5.3	0.0	2.0	58.8	35.3	18.8	56.8	0.5	0.0	0.0	0.8
1	3:25-3:55 PM	60	8.1	96	21.3	0.0	9.0		0	0.0	142.0	511.1	2.2	0.0	1.3	2.1	92.6	17.1	84.2	110.5	2.4	0.0	0.0	2.4
2	3:55-4:30 PM	120	7.8	-104	20.7	0.0	9.1		0	0.0	132.8	274.9	0.6	0.0	0.5	1.9	72.1	20.2	53.6	88.4	1.7	0.0	0.0	3.5
3	3:30-5:05 PM	180	7.7	-104	20.6	0.0	10.7		0	0.1	144.5	196.7	0.3	0.0	0.4	1.9	65.0	23.3	37.2	75.7	1.4	0.0	0.0	4.7
4	5:05-5:45 PM	240	7.6	-106	20.6	0.0	11.3		0	0.0	139.5	141.3	0.2	0.0	0.3	2.0	62.9	24.7	29.9	70.1	1.2	0.0	0.0	5.2
5	5:45-6:15 PM	300	7.6	-93	20.8	0.0	11.3		0	0.2	147.1	123.6	0.1	0.0	0.2	2.1	61.1	25.7	25.7	63.8	1.1	0.0	0.0	5.8
6	6:15-6:55 PM	360	7.6	-98	20.8	0.0	14.8		0	0.4	136.3	97.8	0.2	0.0	0.3	1.9	68.9	34.3	19.6	67.3	0.9	0.0	0.0	4.0
7	6:55-7:35 PM	420	7.6	61	20.2	0.0	12.3		0	0.4	126.2	81.3	0.0	0.0	0.2	1.8	69.6	42.8	22.0	79.1	1.0	0.0	0.0	4.5
8	11:50-12:25 PM	480	8.7	101	18.6	0.0	2.8		0	0.4	127.9	176.9	0.0	0.0	0.5	1.9	61.9	13.4	23.2	55.1	0.9	0.0	0.0	11.8
9	12:25-1:00 PM	540	8.6	96	20.1	0.0	3.9		0	0.6	139.4	174.6	0.0	0.0	0.3	2.1	60.6	13.0	20.0	51.2	0.8	0.0	0.0	11.7
10	1:00-1:40 PM	600	7.9	93	19.7	0.0	13.8		0	0.7	143.1	102.6	0.1	0.0	0.0	2.0	61.6	20.2	19.9	48.0	0.7	0.0	0.0	9.4
11	1:40-2:30 PM	660	7.7	94	19.9	0.0	16.6		0	0.8	131.6	64.4	0.3	0.0	0.0	1.9	63.3	26.2	20.1	52.6	0.8	0.0	0.0	6.9
12	2:30-3:15 PM	720	7.7	91	20.0	0.0	16.1		0	0.8	140.4	59.6	0.0	0.0	0.0	2.1	61.8	30.1	19.0	54.4	0.7	0.0	0.0	5.7
13	3:15-4:00 PM	780	7.7	88	20.0	0.0	17.5		0	1.1	141.6	56.5	0.1	0.0	0.0	2.0	61.5	31.1	18.8	55.5	0.7	0.0	0.0	5.3
14	4:00-4:50 PM	840	7.6	78	20.0	0.0	19.4		0	1.3	143.6	55.7	0.0	0.0	0.0	2.5	61.6	32.8	19.2	56.7	0.7	0.0	0.0	5.0
15	4:50-5:15 PM	900	7.6	82	19.6	0.0	16.0		0	1.5	148.9	55.8	0.0	0.0	0.2	2.3	59.1	33.1	19.1	55.3	0.6	0.0	0.0	4.8

Sample	Time	Volume of leachate	pH	ORP	T	H_2S	As	DO	Fe^{2+}	F	Cl	SO_4	NO_3	PO_4	NO_2	Br	Na	Mg	K	Ca	Sr	Mn	Fe	Si
		mL		mV	˚C	mg/L	µg/L																	
GW	6/6/06; 1:51 PM	0	7.2	-19	27.7	0.1	1.1	1.6	0.4	0.1	13.7	524.2	0.2	0.0	0.0	0.2	13.5	12.8		217.6	4.2	0.1	8.3	4.6
1	5:20-6:02 PM	60	10.8	-35	22.5	0.0	0.2		0.1	0.5	35.4	207.0	4.5	0.0	1.0	0.4	87.9	0.2		200.8	5.6	0.0	0.0	4.3
2	6:03-6:47 PM	120	11.2	-5	21.7	0.0	0.1		0.0	0.8	46.6	217.5	3.7	0.0	0.7	0.3	55.4	0.0		242.6	4.4	0.0	0.0	2.6
3	6:47 PM-8:20 AM	180	11.1	18	21.0	0.0	0.2		0.0	0.5	30.5	209.5	2.6	0.0	0.7	0.3	50.9	0.3		251.7	4.0	0.0	0.0	2.5
4	8:21-9:45 AM	240	11.4	-3	21.0	0.0	0.2		0.0	0.3	16.3	120.2	0.4	0.0	0.2	0.1	38.5	0.7		370.4	4.6	0.0	0.0	2.1
5	9:45-10:50 AM	300	11.5	-8	21.6	0.0	0.3		0.0	0.3	16.7	143.8	0.2	0.0	0.0	0.1	23.2	1.0		410.9	3.4	0.0	0.1	1.8
6	10:50-11:56 AM	360	11.5	-12	20.9	0.0	0.2		0.0	0.3	14.1	119.1	0.2	0.0	0.0	0.1	18.4	1.2		404.8	2.2	0.0	0.1	1.9
7	11:56AM-1:10 PM	420	11.5	-17	21.3	0.0	0.3		0.0	0.4	18.1	184.1	0.0	0.0	0.0	0.0	17.3	1.8		418.8	1.7	0.0	0.1	2.1
8	1:10-2:25 PM	480	11.5	-2	21.2	0.0	0.2		0.0	0.3	20.8	176.7	0.1	0.0	0.0	0.0	16.9	1.3		366.8	1.5	0.0	0.1	2.3
9	2:25-3:43 PM	540	11.4	-2	21.3	0.0	0.4		0.0	0.2	13.5	144.4	0.0	0.0	0.0	0.0	16.5	0.9		319.9	1.3	0.0	0.1	2.3
10	3:43-4:57 PM	600	11.4	-16	21.8	0.0	0.2		0.0	0.2	15.6	179.3	0.0	0.0	0.0	0.0	16.9	1.2		326.6	1.2	0.0	0.1	2.4
11	4:57-6:08 PM	660	11.3	18	21.1	0.0	0.2		0.0	0.2	14.5	160.8	0.0	0.0	0.0	0.0	16.3	1.2		324.7	1.1	0.0	0.1	2.6
12	6:08-7:20 PM	720	11.3	18	23.1	0.0	0.1		0.0	0.2	14.6	164.1	0.0	0.0	0.0	0.0	16.2	0.5		246.1	1.0	0.0	0.0	2.6
13	7:20 PM- 10:42 AM	780	11.1	25	22.0	0.0	0.2		0.0	0.2	15.9	188.6	0.0	0.0	0.0	0.0	17.9	0.4		262.3	1.4	0.0	0.0	2.5

Ocala Limestone; Interval 195 m - 199 m; 0.3 m columns

Sample	Date/Time	Volume of leachate	pH	ORP	T	H_2S	As	DO	Fe^{2+}	F	Cl	SO_4	NO_3	PO_4	NO_2	Br	Na	Mg	K	Ca	Sr	Mn	Fe	Si
		mL		mV	˚C	mg/L	µg/L												mg/L					
DW	1/25/07; 11:05 AM	0	7.0	268	22.5	0.0	0.3	5.0	0	0.0	2.3	11.9	0.9	0.0	0.0	0.0	5.7	5.7	1.3	77.9	0.7	0.0	0.0	4.2
1	11:26 AM-12:10 PM	60	7.4	182	21.2	0.0	17.1		0	0.5	28.0	275.2	8.5	0.0	0.2	0.2	8.8	17.4	2.7	128.2	1.3	0.0	0.0	4.1
2	12:10-1:05 PM	120	7.2	202	20.7	0.0	11.5		0	0.3	18.2	108.1	6.9	0.0	0.0	0.1	5.7	7.3	1.4	102.4	0.9	0.0	0.0	4.2
3	1:05-1:50 PM	180	7.2	223	20.9	0.0	9.1		0	0.2	17.5	97.7	6.7	0.0	0.0	0.0	5.6	6.3	1.3	109.2	0.8	0.0	0.0	3.9
4	1:50-2:35 PM	240	7.2	188	21.2	0.0	5.9		0	0.3	22.0	127.0	8.5	0.0	0.0	0.0	5.7	5.7	1.3	103.3	0.7	0.0	0.0	4.2
5	2:35-3:20 PM	300	7.2	176	21.1	0.0	6.8		0	0.2	19.1	104.3	7.5	0.0	0.0	0.0	5.4	5.9	1.3	105.9	0.8	0.0	0.0	4.2
WW	3/11/08; 11:00 AM	0	6.8	-143	18.0	3.0	1.2	0.4	0.1	3.0	136.4	43.4	0.0	5.3	0.0	2.0	58.8	35.3	18.8	56.8	0.5	0.0	0.0	0.8
1	3:10-3:40 PM	60	7.4	-95	20.8	0.5	23.6		0.0	1.5	143.4	124.6	0.1	0.0	0.0	2.0	60.5	36.3	18.3	78.8	1.0	0.0	0.0	0.9
2	3:40-4:10 PM	120	7.4	-172	21.3	0.5	20.8		0.0	2.2	157.4	75.9	0.0	0.0	0.1	2.1	61.0	35.4	18.7	67.6	0.7	0.0	0.0	0.8
3	4:10-4:55 PM	180	7.4	-130	20.4	0.3	19.5		0.0	2.4	141.0	58.8	0.0	0.0	0.1	2.0	59.5	35.6	18.6	68.9	0.6	0.0	0.0	0.8
4	4:55-5:25 PM	240	7.3	-132	20.6	0.5	16.0		0.0	2.7	145.7	55.6	0.0	0.0	0.2	1.9	58.7	35.8	18.1	59.7	0.5	0.0	0.0	0.8
5	5:25-5:52 PM	300	7.3	-122	20.7	0.4	15.5		0.0	2.8	143.5	55.0	0.0	0.0	0.2	2.0	60.7	36.0	18.1	60.2	0.5	0.0	0.0	0.8
6	5:52-6:20 PM	360	7.3	-120	20.9	0.3	12.8		0.0	3.1	150.5	65.4	0.0	0.0	0.2	2.1	58.4	34.8	17.7	58.6	0.5	0.0	0.0	0.8
7	6:20-6:55 PM	420	7.3	-106	20.6	0.2	12.5		0.0	3.6	179.4	67.8	0.0	1.6	0.2	2.3	61.1	36.2	18.3	61.4	0.5	0.0	0.0	0.8
8	6:55-7:35 PM	480	7.4	36	20.6	0.0	11.7		0.0	3.6	167.7	60.1	0.0	0.0	0.2	2.3	59.2	35.4	18.3	58.0	0.5	0.0	0.0	0.8
GW	2/11/08; 9:55 AM	0	7.0	-120	26.1	0.2	0.4	1.2	0.6	0.0	5.0	556.4	0.0	0.0	0.0	0.0	2.7	15.6	1.4	262.0	6.1	0.0	0.3	5.4
1	10:18-11:20 AM	60	7.2	-138	18.5	0.0	2.8		0.0	0.4	11.1	688.9	0.4	0.0	0.0	0.1	6.9	31.0	3.9	314.4	5.4	0.0	0.1	5.9
2	11:20 AM-12:15 PM	120	7.1	-77	19.8	0.0	0.2		0.0	0.4	6.5	543.8	0.0	0.0	0.0	0.0	3.0	18.3	1.7	273.7	5.8	0.0	0.0	5.5
3	12:15-12:45 PM	180	7.2	-56	20.2	0.0	0.1		0.0	0.2	5.3	578.3	0.0	0.0	0.1	0.0	3.0	17.6	1.5	267.2	6.3	0.0	0.0	5.4
4	12:45-1:45 PM	240	7.0	-150	20.3	0.0	0.1		0.0	0.2	5.2	575.3	0.0	0.0	0.1	0.0	2.9	16.8	1.4	265.4	6.1	0.0	0.0	5.5
5	1:45-2:20 PM	300	7.3	-127	20.3	0.0	0.9		0.0	0.1	4.7	502.6	0.0	0.0	0.0	0.0	3.0	16.4	1.4	262.6	6.5	0.0	0.0	5.6
6	2:20-3:20 PM	360	7.1	-126	20.2	0.0	0.1		0.0	0.1	5.2	570.5	0.0	0.0	0.0	0.0	2.9	17.0	1.5	266.5	6.4	0.0	0.0	5.9
7	3:20-4:00 PM	420	7.0	-100	20.1	0.0	0.1		0.0	0.2	5.3	598.0	0.0	0.0	0.1	0.0	2.8	16.6	1.5	255.8	6.5	0.0	0.0	5.9
8	4:00-4:30 PM	480	7.1	-110	20.6	0.0	0.1		0.0	0.1	6.7	592.7	0.0	0.0	0.1	0.0	2.8	16.4	1.5	264.0	6.7	0.0	0.0	5.7

Sample	Date/Time	Volume of leachate	pH	ORP	T	H_2S	As	DO	Fe^{2+}	F	Cl	SO_4	NO_3	PO_4	NO_2	Br	Na	Mg	K	Ca	Sr	Mn	Fe	Si
		mL		mV	˚C	mg/L	µg/L												mg/L					
BW	1/29/08; 10:00 AM	0	6.7	-56	17.3	0.0	0.7	1.7	1.0	2.4	107.4	46.3	0.6	0.0	0.0	1.9	49.5	35.1	15.7	53.2	0.4	0.0	0.2	0.7
1	12:47-1:35 PM	60	7.2	82	19.6	0.0	35.6		0.0	0.7	97.0	153.3	0.8	0.0	0.0	1.6	51.7	41.8	18.0	97.9	1.3	0.0	0.0	1.0
2	1:35-2:30 PM	120	6.7	167	19.6	0.0	24.3		0.0	1.2	92.2	56.2	0.6	0.0	0.0	1.4	49.9	33.6	14.9	74.1	0.7	0.0	0.1	0.8
3	2:30-3:10 PM	180	6.8	129	19.6	0.0	21.7		0.0	2.0	112.3	59.0	0.7	0.0	0.0	2.2	48.9	33.4	15.7	62.9	0.6	0.0	0.1	0.8
4	3:10-3:40 PM	240	6.9	152	19.5	0.0	20.4		0.0	1.6	83.6	43.1	0.5	0.0	0.0	1.5	49.3	34.0	15.9	62.1	0.5	0.0	0.1	0.8
5	3:40-4:30 PM	300	6.8	142	19.5	0.0	17.1		0.0	1.9	99.0	46.3	0.7	0.0	0.1	1.8	50.5	33.0	16.1	60.3	0.5	0.0	0.1	0.7
6	4:30-5:10 PM	360	6.8	168	19.5	0.0	16.2		0.0	2.3	114.3	56.1	0.7	0.0	0.1	1.9	51.0	35.1	16.5	65.5	0.5	0.0	0.1	0.8
7	5:10-6:05 PM	420	6.9	172	19.5	0.0	13.2		0.0	2.0	97.2	44.5	0.6	0.0	0.2	1.7	49.9	34.5	15.8	63.4	0.5	0.0	0.1	0.7
8	6:05-6:40 PM	480	7.3	105	19.5	0.0	13.4		0.0	2.2	104.3	47.7	0.6	0.0	0.0	1.8	49.9	33.9	15.6	62.2	0.5	0.0	0.1	0.7
BW before UV	1/29/08; 10:00 AM	0	6.7	-56	17.3	0.0	0.7	1.7	1.0	2.4	107.4	46.3	0.6	0.0	0.0	1.9	49.5	35.1	15.7	53.2	0.4	0.0	0.2	0.7
BW-UV	12:41 PM	0	6.9	11	19.3	0.0	0.8	3.4	0.4	2.4	106.1	45.7	0.6	0.0	0.0	1.9	49.5	35.1	15.7	53.2	0.4	0.0	0.2	0.7
1	1:12-1:46 PM	60	6.6	102	19.6	0.0	23.6		0.0	1.0	113.2	153.7	0.7	0.0	0.1	1.8	52.5	37.5	16.4	82.9	1.0	0.0	0.1	0.9
2	1:46-2:30 PM	120	6.9	179	19.6	0.0	20.3		0.0	1.6	114.2	72.9	0.6	0.0	0.0	2.0	50.5	33.0	15.7	56.1	0.6	0.0	0.1	0.8
3	2:30-3:10 PM	180	7.3	154	19.7	0.0	20.7		0.0	1.6	93.4	47.8	0.5	0.0	0.0	1.9	49.7	33.6	15.2	50.4	0.5	0.0	0.1	0.7
4	3:10-3:40 PM	240	7.5	159	19.1	0.0	14.3		0.0	2.4	131.8	66.7	0.8	0.0	0.2	2.2	47.1	32.2	16.2	50.5	0.5	0.0	0.1	0.7
5	3:40-4:30 PM	300	7.3	143	19.1	0.0	13.5		0.0	2.6	130.4	64.0	0.8	0.0	0.1	2.2	51.2	32.4	16.6	48.9	0.5	0.0	0.1	0.7
6	4:30-5:10 PM	360	6.9	147	19.1	0.0	12.0		0.0	1.9	94.1	43.2	0.6	0.0	0.0	1.7	46.0	33.7	17.0	49.2	0.5	0.0	0.1	0.7
7	5:10-6:05 PM	420	7.1	169	19.1	0.0	10.9		0.0	1.9	94.9	42.9	0.6	0.0	0.0	1.6	47.5	32.6	16.2	46.8	0.4	0.0	0.1	0.7
8	6:05-6:41 PM	480	7.2	100	19.1	0.0	11.0		0.0	2.2	99.7	45.7	0.6	0.0	0.1	1.8	50.2	33.3	16.7	48.3	0.5	0.0	0.1	0.7

Avon Park Formation; Interval 255 m - 257 m; 0.3 and 0.5 m columns

Sample	Date/Time	Volume of leachate	pH	ORP	T	H_2S	As	DO	Fe^{2+}	F	Cl	SO_4	NO_3	PO_4	NO_2	Br	Na	Mg	K	Ca	Sr	Mn	Fe	Si
		mL		mV	˚C	mg/L	µg/L									mg/L								
GW	2/11/08; 9:55 AM	0	7.0	-120	26.1	0.2	0.4	1.2	0.6	0.0	5.0	556.4	0.0	0.0	0.0	0.0	2.7	15.6	1.4	262.0	6.1	0.0	0.3	5.4
1	10:15-11:05 AM	60	6.8	131	19.2	0.0	4.2		0.0	0.2	7.2	776.4	1.9	0.0	0.2	0.0	6.0	122.6	3.9	358.1	7.6	0.0	0.2	5.9
2	10:05-11:45 AM	120	7.0	125	19.4	0.0	0.3		0.0	0.2	6.4	570.3	0.0	0.0	0.0	0.0	2.9	30.4	1.9	306.9	6.5	0.0	0.1	6.1
3	11:45 AM-12:30 PM	180	7.3	92	18.2	0.0	0.2		0.0	0.8	5.9	566.4	0.1	0.0	0.1	0.0	2.9	24.4	1.6	293.5	6.8	0.0	0.1	6.0
4	12:30-1:10 PM	240	7.3	93	19.7	0.0	0.2		0.0	0.1	5.0	527.3	0.0	0.0	0.1	0.0	2.8	21.4	1.5	288.5	6.7	0.0	0.0	5.7
5	1:10-2:20 PM	300	7.2	125	20.1	0.0	0.2		0.0	0.1	5.4	578.4	0.0	0.0	0.0	0.0	2.9	22.3	1.6	299.7	6.9	0.0	0.1	5.9
6	2:20-3:15 PM	360	6.9	135	20.2	0.0	0.1		0.0	0.1	4.5	546.0	0.0	0.0	0.1	0.0	2.8	19.5	1.5	270.8	6.8	0.0	0.0	5.5
7	3:15-3:55 PM	420	7.2	114	19.9	0.0	0.1		0.0	0.1	6.4	558.5	0.0	0.0	0.0	0.0	2.9	18.5	1.5	277.5	6.8	0.0	0.0	5.8
8	3:55-4:30 PM	480	7.0	103	20.5	0.0	0.1		0.0	0.1	5.3	507.1	0.0	0.0	0.1	0.0	2.9	18.4	1.4	276.2	6.6	0.0	0.0	5.7
GW/air	2/13/08; 9:55 AM	0	7.5	161	20.3	0.0	0.4	7.6	0.0	0.0	5.0	556.4	0.0	0.0	0.0	0.0	2.7	15.6	1.4	262.0	6.1	0.0	0.3	5.4
1	9:45-10:29 AM	60	7.1	139	21.1	0.0	40.7		0.0	0.3	9.2	1246.9	2.3	0.0	0.2	0.0	6.1	128.0	3.7	388.5	8.3	0.0	0.0	5.6
2	10:29-11:00 AM	120	7.2	121	21.0	0.0	24.1		0.0	0.2	5.4	722.8	0.0	0.0	0.1	0.0	3.1	31.8	1.8	302.5	6.8	0.0	0.0	5.6
3	11:00-11:30 AM	180	7.2	129	21.4	0.0	19.9		0.0	0.2	6.4	854.5	0.1	0.0	0.1	0.0	2.9	19.1	1.7	265.0	5.6	0.0	0.0	6.0
4	11:30 AM-12:00 PM	240	7.2	128	21.1	0.0	17.0		0.0	0.1	6.4	839.2	0.1	0.0	0.1	0.0	2.9	21.5	1.6	288.8	7.0	0.0	0.0	5.7
5	12:00-12:30 PM	300	7.3	133	21.1	0.0	15.7		0.0	0.1	5.9	758.1	0.1	0.0	0.2	0.0	2.9	20.8	1.6	279.1	6.5	0.0	0.0	5.6
6	12:30-1:00 PM	360	7.4	135	21.1	0.0	13.3		0.0	0.1	5.3	631.0	0.0	0.0	0.1	0.0	3.0	20.3	1.5	289.7	7.1	0.0	0.0	5.8
7	1:00-1:30 PM	420	7.3	140	21.2	0.0	13.6		0.0	0.1	5.0	577.7	0.0	0.0	0.1	0.0	3.0	19.8	1.5	282.8	6.9	0.0	0.0	5.7
8	1:30-2:00 PM	480	7.3	152	21.1	0.0	11.3		0.0	0.1	6.2	775.9	0.1	0.0	0.1	0.0	2.9	18.8	1.5	275.6	6.8	0.0	0.0	5.7
9	2:00-2:30 PM	540	7.3	147	21.1	0.0	10.6		0.0	0.1	5.3	621.5	0.0	0.0	0.1	0.0	2.7	18.6	1.5	267.9	6.9	0.0	0.0	5.6
10	2:30-3:00 PM	600	7.3	149	21.1	0.0	10.9		0.0	0.1	6.1	714.0	0.0	0.0	0.0	0.0	2.7	17.6	1.4	258.3	6.7	0.0	0.0	5.6
WW	4/4/06; 12:58 PM	0	6.9	-82	20.5	0.3	0.6	0.1	0.1	3.3	133.3	69.6	0.0	4.0	0.0	1.5	80.3	36.5	9.4	55.5	0.4	0.0	0.0	0.5
1	1:15-1:53 PM	60	7.0	141	21.1	0.0	47.1		0.0	2.3	133.3	439.8	16.9	0.0	0.0	1.5	78.9	79.3	10.4	136.7	2.0	0.0	0.0	0.9
2	1:53-2:33 PM	120	7.1	102	19.9	0.0	33.7		0.0	2.7	124.8	166.2	4.3	1.1	0.0	1.5	77.7	47.5	9.3	86.7	1.1	0.0	0.0	0.7
3	2:33-3:13 PM	180	7.1	122	19.6	0.0	28.8		0.0	2.9	128.8	126.3	2.6	1.2	0.0	1.5	76.0	42.4	9.1	73.5	0.9	0.0	0.0	0.6
4	3:13-3:52 PM	240	7.1	112	19.3	0.0	23.2		0.0	3.0	125.1	105.7	1.8	2.2	0.0	1.6	78.3	41.7	9.8	71.3	0.8	0.0	0.0	0.6
5	3:52-4:33 PM	300	7.1	113	20.4	0.0	22.5		0.0	3.3	140.1	107.2	1.5	2.4	0.0	1.7	83.2	40.2	9.2	69.5	0.8	0.0	0.0	0.6
6	4:33-5:15 PM	360	7.2	130	19.6	0.0	22.2		0.0	3.2	132.8	92.7	1.1	3.2	0.0	1.6	77.5	37.9	8.8	63.8	0.6	0.0	0.0	0.6
7	5:15-6:02 PM	420	7.0	136	19.8	0.0	20.2		0.0	3.7	152.2	105.9	1.1	3.2	0.0	1.8	73.1	38.2	9.2	63.8	0.6	0.0	0.0	0.6

Sample	Date/Time	Volume of leachate	pH	ORP	T	H_2S	As	DO	Fe^{2+}	F	Cl	SO_4	NO_3	PO_4	NO_2	Br	Na	Mg	K	Ca	Sr	Mn	Fe	Si
		mL		mV	˚C	mg/L	µg/L												mg/L					
WW before UV	5/1/07; 10:30 AM	0	6.7	-145	22.8	2.8	0.6	0.2	0.1	3.5	129.2	55.1	0.0	3.1	0.0	1.6	64.7	32.0	12.5	48.8	0.4	0.0	0.0	1.2
WW-UV	12:50 PM	0	6.9	-67	24.1	0.0	1.0	4.6	0.0	3.2	122.3	54.4	0.0	2.8	0.0	1.5	63.8	31.3	12.3	48.1	0.4	0.0	0.1	1.3
1	3:15-3:50 PM	60	7.6	136	20.4	0.0	35.3		0.0	2.3	133.8	334.7	4.0	0.0	0.0	1.7	62.3	43.5	15.4	123.7	1.9	0.0	0.0	1.9
2	3:50-4:23 PM	120	7.4	148	22.4	0.0	28.3		0.0	2.7	131.4	155.0	1.0	1.0	0.0	1.7	62.5	36.3	12.9	76.8	1.2	0.0	0.0	1.9
3	4:23-4:58 PM	180	7.4	135	22.5	0.0	25.6		0.0	2.3	102.5	86.6	0.4	0.5	0.0	1.3	62.2	34.4	12.3	66.2	1.0	0.0	0.0	1.9
4	4:58-5:39 PM	240	7.3	139	22.3	0.0	21.5		0.0	3.2	141.3	104.5	0.4	1.7	0.0	1.7	63.1	34.1	12.3	63.2	0.9	0.0	0.0	1.8
5	5:39-6:20 PM	300	7.3	112	22.1	0.0	19.1		0.0	2.9	134.6	91.3	0.2	2.0	0.0	1.6	61.9	33.7	12.3	60.8	0.8	0.0	0.0	1.8
BW	1/23/07; 1:18 PM	0	6.7	-38	20.3	0.1	0.8	1.3	0.7	3.6	164.6	62.0	0.1	5.5	0.0	1.9	53.5	26.5	11.8	40.7	0.3	0.0	0.1	0.7
1	1:50-3:17 PM	60	7.3	124	20.4	0.0	65.5		0.1	1.1	142.3	1144.8	2.4	n.a.	0.1	1.6	57.1	127.9	16.9	270.5	5.3	0.0	0.0	1.2
2	3:17-4:12 PM	120	7.1	168	21.0	0.0	48.6		0.0	2.7	164.7	340.2	0.1	n.a.	0.0	1.9	54.4	32.3	13.1	114.3	1.9	0.0	0.0	0.8
3	4:12-5:10 PM	180	7.4	148	23.4	0.0	35.4		0.0	2.5	134.3	146.1	0.0	0.5	0.0	1.6	53.9	28.0	12.9	83.6	1.3	0.0	0.0	0.7
4	5:10-6:01 PM	240	7.4	164	23.9	0.0	27.9		0.0	2.5	125.7	80.5	0.0	1.3	0.0	1.5	54.9	28.2	13.1	66.9	1.0	0.0	0.0	0.7
5	6:01-6:40 PM	300	7.2	164	21.9	0.0	23.9		0.0	2.8	143.8	72.9	0.0	1.9	0.0	1.7	55.6	28.6	13.4	62.4	0.9	0.0	0.0	0.7
6	6:40-7:17 PM	360	7.4	152	22.1	0.0	20.3		0.0	3.6	171.3	82.3	0.0	2.9	0.0	2.0	54.1	27.7	13.0	58.0	0.8	0.0	0.0	0.7
7	7:17-7:58 PM	420	7.3	160	22.1	0.0	23.8		0.0	3.2	154.0	69.7	0.0	2.8	0.0	1.9	54.4	27.8	13.0	56.3	0.8	0.0	0.0	0.7
BW before UV	5/4/07; 10:25 PM	0	6.4	-35	23.5	0.0	0.4	1.3	0.7	2.9	144.7	65.1	0.3	2.5	0.0	1.7	66.9	32.3	14.1	51.2	0.4	0.0	0.5	1.2
BW-UV	5/4/07; 10:40 PM	0	6.6	7	25.1	0.0	0.3	4.7	0.4	3.4	156.7	70.5	0.2	3.3	0.0	1.9	64.1	30.1	12.7	47.2	0.3	0.0	0.4	1.1
1	1:40-2:18 PM	60	7.5	64	22.9	0.0	56.2		0.0	2.2	160.2	537.0	6.1	0.0	0.0	1.9	61.7	69.5	13.8	127.9	2.4	0.0	0.0	1.3
2	2:18-3:02 PM	120	7.2	141	22.2	0.0	41.7		0.0	2.6	153.9	184.0	1.5	0.6	0.0	1.9	62.9	41.3	12.7	79.7	1.3	0.0	0.0	1.2
3	3:02-3:38 PM	180	7.2	162	21.9	0.0	29.1		0.0	2.3	127.8	104.7	0.9	0.9	0.0	1.4	60.9	36.3	12.1	69.2	1.0	0.0	0.0	1.1
4	3:38-4:18 PM	240	7.1	165	22.1	0.0	26.1		0.0	3.0	160.5	117.8	0.8	1.5	0.0	1.9	62.7	35.2	12.6	65.4	0.9	0.0	0.0	1.2
5	4:18-5:00 PM	300	7.1	169	21.7	0.0	21.0		0.0	3.0	160.5	108.6	0.8	0.0	0.4	2.4	62.0	33.6	12.4	62.3	0.8	0.0	0.0	1.2

Sample	Date/Time	Volume of leachate	pH	ORP	T	H_2S	As	DO	Fe^{2+}	F	Cl	SO_4	NO_3	PO_4	NO_2	Br	Na	Mg	K	Ca	Sr	Mn	Fe	Si
		mL		mV	˚C	mg/L	µg/L																	
DW-0.3	7/18/06; 11:47 AM	0	6.9	223	22.3	0.0	0.1	5.0	0	0.1	14.3	58.1	5.5	0.0	0.0	0.0	22.0	4.7	1.7	101.4	0.4	0.0	0.0	3.6
1	11:47 AM-12:37 PM	60	7.7	175	22.3	0.0	26.2		0	0.7	25.0	678.5	9.4	0.0	0.0	0.0	11.0	118.0	3.4	130.0	4.6	0.0	0.0	4.0
2	12:37-1:15 PM	120	7.7	103	23.4	0.0	21.8		0	0.6	25.8	169.7	8.7	0.0	0.0	0.0	5.3	30.0	0.8	40.6	2.7	0.0	0.0	2.0
3	1:15-1:50 PM	180	7.6	129	23.3	0.0	20.9		0	0.5	20.9	103.1	8.1	0.0	0.0	0.0	8.0	34.8	1.1	75.6	5.0	0.0	0.0	4.1
4	1:50-2:26 PM	240	7.8	114	23.2	0.0	19.6		0	0.4	21.6	90.3	8.3	0.0	0.0	0.0	7.6	24.5	1.0	74.5	4.6	0.0	0.0	3.7
5	2:26-3:05 PM	300	7.5	120	23.5	0.0	19.1		0	0.4	23.1	79.7	7.6	0.0	0.0	0.0	7.6	21.9	1.0	86.5	4.4	0.0	0.0	3.8
6	3:05-3:49 PM	360	7.6	111	23.1	0.0	15.4		0	0.4	21.7	87.2	8.4	0.0	0.0	0.0	7.5	20.3	1.0	88.9	3.6	0.0	0.0	3.6
7	3:49-4:27 PM	420	7.5	115	23.0	0.0	16.6		0	0.3	22.2	88.9	8.7	0.0	0.0	0.0	7.4	15.8	1.0	84.0	3.6	0.0	0.0	3.8
8	7/21/06;2:33-3:05 PM	480	7.3	221	22.0	0.0	20.5		0	0.5	26.9	182.1	9.8	0.0	0.0	0.0	7.8	39.9	1.1	82.1	7.5	0.0	0.0	4.1
9	3:05-3:42 PM	540	7.3	182	22.2	0.0	16.4		0	0.5	63.2	116.2	12.2	0.0	0.0	0.0	7.5	18.3	1.0	81.4	5.9	0.0	0.0	3.7
10	3:42-4:16 PM	600	7.4	152	22.2	0.0	15.0		0	0.3	24.6	87.0	9.8	0.0	0.0	0.0	68.4	15.6	2.0	111.6	4.2	0.0	0.0	4.3
11	4:16-4:51 PM	660	7.3	149	21.9	0.0	15.2		0	0.3	23.5	84.3	9.2	0.0	0.0	0.0	7.5	9.6	0.9	91.6	2.9	0.0	0.0	3.7
12	4:51-5:25 PM	720	7.4	154	22.4	0.0	13.7		0	0.2	24.0	87.0	9.3	0.0	0.0	0.0	7.5	10.6	0.9	98.5	2.2	0.0	0.0	3.7
13	5:25-6:00 PM	780	7.4	155	22.4	0.0	12.7		0	0.2	23.5	86.5	9.1	0.0	0.0	0.0	7.3	8.1	0.9	92.5	2.0	0.0	0.0	3.6
14	8/09/06;9:50-10:21 AM	840	6.9	163	21.7	0.0	41.7		0	0.3	20.4	154.5	4.3	0.0	0.0	0.0	13.3	37.5	1.8	89.7	10.4	0.0	0.0	4.4
15	10:21-10:51 AM	900	7.3	119	22.2	0.0	19.2		0	0.3	18.1	88.4	7.7	0.0	0.0	0.0	12.9	21.2	1.7	101.0	8.1	0.0	0.0	4.0
16	10:51-11:22 AM	960	7.3	155	22.3	0.0	16.4		0	0.2	17.9	89.3	7.9	0.0	0.0	0.0	12.2	12.7	1.6	102.0	5.3	0.0	0.0	3.8
17	11:22-11:52 AM	1020	7.3	178	22.4	0.0	8.4		0	0.2	17.7	88.7	7.9	0.0	0.0	0.0	12.2	9.3	1.6	101.1	3.8	0.0	0.0	3.8
18	11:52 AM-12:22 PM	1080	7.3	188	22.4	0.0	9.6		0	0.2	17.4	85.6	7.8	0.0	0.0	0.0	12.2	8.1	1.6	102.6	3.0	0.0	0.0	3.8
19	12:22-12:53 PM	1140	7.4	212	22.7	0.0	11.0		0	0.2	17.7	84.9	7.9	0.0	0.0	0.0	12.1	8.3	1.6	105.2	2.5	0.0	0.0	3.8
20	12:53-1:22 PM	1200	7.3	211	22.5	0.0	17.6		0	0.2	27.6	88.1	8.9	0.0	0.0	0.0	12.7	8.3	1.6	109.4	2.2	0.0	0.0	3.9
21	8/29/06;12:04-12:34 PM	1260	7.0	151	22.3	0.0	28.6		0	0.3	18.0	129.6	3.4	0.0	0.0	0.0	12.1	23.5	5.6	130.5	11.3	0.0	0.0	3.9
22	12:34-1:25 PM	1320	7.2	194	22.3	0.0	17.5		0	0.2	17.8	92.6	6.5	0.0	0.0	0.0	11.6	27.9	3.1	134.4	7.1	0.0	0.2	3.9
23	1:25-2:30 PM	1380	7.3	156	23.0	0.0	9.0		0	0.2	18.2	92.8	6.8	0.0	0.0	0.0	12.3	12.9	3.1	106.9	6.5	0.0	0.0	4.2
24	2:30-2:47 PM	1440	7.4	164	23.1	0.0	9.9		0	0.2	17.1	88.7	6.6	0.0	0.0	0.0	12.5	10.3	3.1	105.8	5.1	0.0	0.0	3.8
25	9/19/06;10:31-11:05 AM	1500	7.0	107	22.1	0.0	19.7		0	0.2	14.6	103.1	3.3	0.0	0.0	0.0	14.3	25.0	1.7	98.7	9.4	0.0	0.0	4.4
26	11:05 AM-12:14 PM	1560	7.3	150	22.4	0.0	9.8		0	0.2	14.3	75.2	6.1	0.0	0.0	0.0	14.3	15.1	1.7	97.0	7.9	0.0	0.0	4.2
27	12:14-1:30 PM	1620	7.4	135	22.7	0.0	14.9		0	0.2	11.7	59.8	4.9	0.0	0.0	0.0	13.9	15.9	1.7	97.3	11.0	0.0	0.0	4.4
28	1:30-2:45 PM	1680	7.5	141	23.0	0.0	14.6		0	0.1	10.3	50.5	4.6	0.0	0.0	0.0	13.9	8.6	1.7	106.5	4.0	0.0	0.0	4.2
29	2:45-4:07 PM	1740	7.4	142	23.5	0.0	15.3		0	0.2	11.8	61.1	5.1	0.0	0.0	0.0	13.9	10.5	1.7	102.3	6.8	0.0	0.0	4.3
30	10/3/06;10:08-11:42 AM	1800	6.4	144	21.9	0.0	12.9		0	0.2	16.9	115.1	5.1	0.0	0.0	0.0	12.8	18.8	1.6	100.8	5.5	0.0	0.0	3.8
31	11:42 AM-12:14 PM	1860	7.0	103	22.1	0.0	17.6		0	0.2	17.2	93.9	7.5	0.0	0.0	0.0	13.1	10.9	1.6	97.8	4.9	0.0	0.0	3.8
32	12:14-12:52 PM	1920	7.1	133	22.0	0.0	12.3		0	0.1	14.9	76.5	6.7	0.0	0.0	0.0	13.4	8.7	1.6	106.1	3.3	0.0	0.0	3.9
33	12:52-1:28 PM	1980	7.2	141	22.5	0.0	9.9		0	0.2	19.2	104.1	8.5	0.0	0.0	0.0	13.3	7.9	1.6	106.7	2.2	0.0	0.0	3.9
34	1:28-2:12 PM	2040	7.1	155	22.3	0.0	8.6		0	0.2	20.6	112.3	8.9	0.0	0.0	0.0	13.2	8.9	1.6	112.3	1.8	0.0	0.0	3.8
35	2:12-2:45 PM	2100	7.1	150	22.1	0.0	8.4		0	0.1	15.1	78.7	6.7	0.0	0.0	0.0	13.1	7.9	1.6	110.5	1.5	0.0	0.0	3.8

Sample	Date/Time	Volume of leachate	pH	ORP	T	H_2S	As	DO	Fe^{2+}	F	Cl	SO_4	NO_3	PO_4	NO_2	Br	Na	Mg	K	Ca	Sr	Mn	Fe	Si
		mL		mV	˚C	mg/L	µg/L										mg/L							
36	10/17/06;12:00-12:33 PM	2160	7.0	148	22.6	0.0	10.6		0	0.2	17.3	109.3	4.5	0.0	0.0	0.0	13.2	16.8	1.6	111.3	2.5	0.0	0.0	3.8
37	12:33-1:06 PM	2220	7.2	155	23.3	0.0	10.0		0	0.1	14.5	72.2	5.2	0.0	0.0	0.0	13.3	10.2	1.6	98.6	3.6	0.0	0.0	3.8
38	1:06-1:40 PM	2280	7.3	172	23.4	0.0	8.1		0	0.1	15.0	74.5	5.6	0.0	0.0	0.0	13.6	10.0	1.6	109.5	3.0	0.0	0.0	3.9
39	1:40-2:15 PM	2340	7.3	139	23.3	0.0	9.2		0	0.3	16.8	125.0	4.7	0.0	0.0	0.0	13.7	7.7	1.6	107.4	2.3	0.0	0.0	4.0
40	2:15-2:50 PM	2400	7.3	158	23.4	0.0	9.6		0	0.1	17.3	90.1	6.4	0.0	0.0	0.0	14.2	8.1	1.6	108.9	1.9	0.0	0.0	4.1
41	2:50-3:28 PM	2460	7.3	148	23.4	0.0	7.2		0	0.1	17.9	94.0	6.6	0.0	0.0	0.0	12.8	6.9	1.6	104.9	1.5	0.0	0.0	3.8
42	11/02/06;3:02-3:45 PM	2520	7.6	63	22.9	0.0	14.2		0	0.2	18.2	111.9	3.5	0.0	0.0	0.0	7.4	15.7	1.8	101.7	4.4	0.0	0.0	4.0
43	3:45-4:33 PM	2580	7.4	63	23.2	0.0	12.7		0	0.1	16.8	90.0	5.4	0.0	0.0	0.0	7.6	9.5	1.7	103.8	3.6	0.0	0.0	4.0
44	4:33-5:14 PM	2640	7.2	110	23.0	0.0	15.6		0	0.1	17.5	93.0	5.3	0.0	0.0	0.0	7.4	12.5	1.7	106.9	6.0	0.0	0.0	4.0
45	5:14-6:00 PM	2700	7.2	124	22.9	0.0	13.3		0	0.1	16.0	91.1	5.2	0.0	0.0	0.0	7.3	6.8	1.7	102.9	2.0	0.0	0.0	3.9
46	6:00-6:47 PM	2760	7.2	117	23.1	0.0	12.5		0	0.1	16.2	89.7	4.2	0.0	0.0	0.0	7.6	6.1	1.7	103.9	1.7	0.0	0.0	3.9
47	11/20/06;1:19-2:-5 PM	2820	7.2	155	21.4	0.0	12.6		0	0.2	15.9	109.8	5.2	0.0	0.0	0.0	7.5	14.7	1.7	102.5	4.2	0.0	0.0	3.7
48	2:05-2:53 PM	2880	7.3	167	21.2	0.0	10.5		0	0.1	16.0	87.9	5.0	0.0	0.0	0.0	7.4	8.1	1.6	97.2	2.9	0.0	0.0	3.7
49	2:53-3:35 PM	2940	7.3	190	21.1	0.0	10.4		0	0.1	16.3	89.0	4.9	0.0	0.0	0.0	7.4	6.4	1.7	96.5	2.1	0.0	0.0	3.7
50	3:35-4:26 PM	3000	7.2	182	21.7	0.0	10.0		0	0.1	16.8	87.9	4.4	0.0	0.0	0.0	7.5	6.1	1.7	100.8	1.8	0.0	0.0	3.6
51	4:26-5:19 PM	3060	7.3	176	21.6	0.0	8.7		0	0.1	16.0	88.0	4.7	0.0	0.0	0.0	7.5	5.5	1.6	96.2	1.4	0.0	0.0	3.5
52	5:19-6:12 PM	3120	7.3	166	21.4	0.0	9.4		0	0.1	16.0	87.8	4.9	0.0	0.0	0.0	7.3	5.3	1.6	95.4	1.3	0.0	0.0	3.9
DW-0.5	7/18/06;11:47 AM	0	6.9	223	22.3	0.0	0.1	5.0	0	0.1	14.3	58.1	5.5	0.0	0.0	0.0	22.0	4.7	1.7	101.4	0.4	0.0	0.0	3.6
1	11:47 AM-12:49 PM	60	7.9	148	23.5	0.0	35.4		0	0.7	27.1	1051.2	9.3	0.0	0.2	0.1	17.8	231.0	5.5	196.2	5.9	0.0	0.1	6.1
2	12:49-1:22 PM	120	7.9	142	23.4	0.0	27.4		0	0.6	21.2	301.1	8.0	0.0	0.1	0.0	8.9	83.2	2.4	55.1	6.0	0.0	0.0	4.8
3	1:22-1:59 PM	180	7.9	134	23.5	0.0	28.3		0	0.5	19.6	125.7	7.5	0.0	0.0	0.0	12.0	81.3	1.8	48.9	8.2	0.0	0.0	5.0
4	1:59-2:37 PM	240	8.0	129	23.4	0.0	27.9		0	0.5	20.5	94.0	7.9	0.0	0.0	0.0	9.3	55.2	1.2	51.0	9.8	0.0	0.0	4.5
5	2:37-3:16 PM	300	7.8	123	23.5	0.0	23.1		0	0.5	20.8	89.5	8.0	0.0	0.0	0.1	7.6	47.6	1.0	61.5	9.7	0.0	0.0	4.1
6	3:16-3:52 PM	360	7.8	123	23.2	0.0	20.9		0	0.5	20.8	86.4	8.7	0.0	0.0	0.0	7.7	54.2	1.0	96.2	10.1	0.0	0.1	4.1
7	3:52-4:27 PM	420	7.7	121	23.5	0.0	23.8		0	0.5	21.0	86.9	8.9	0.0	0.0	0.0	7.6	46.1	1.0	96.2	10.0	0.0	0.1	4.0
8	7/21/06; 2:34-3:10 PM	480	7.6	202	21.9	0.0	24.7		0	0.6	25.5	209.5	7.9	0.0	0.1	0.3	8.3	72.0	1.1	104.0	12.6	0.0	0.1	4.8
9	3:10-3:46 PM	540	7.6	173	22.5	0.0	22.1		0	0.5	23.5	99.6	8.8	0.0	0.0	0.0	7.6	35.8	1.0	55.6	11.9	0.0	0.0	4.1
10	3:46-4:20 PM	600	7.5	189	22.2	0.0	19.8		0	0.4	23.9	92.3	9.2	0.0	0.0	0.0	7.6	26.5	1.0	71.3	11.2	0.0	0.0	3.9
11	4:20-4:54 PM	660	7.5	160	22.2	0.0	18.3		0	0.4	24.3	93.0	9.3	0.0	0.0	0.0	7.5	22.0	0.9	77.7	10.2	0.0	0.0	3.9
12	4:54-5:29 PM	720	7.5	163	22.5	0.0	18.1		0	0.3	23.8	90.0	8.9	0.0	0.0	0.0	7.6	19.4	1.0	84.0	8.7	0.0	0.0	3.9
13	5:29-6:06 PM	780	7.5	167	22.7	0.0	15.7		0	0.4	28.7	118.3	10.8	0.0	0.0	0.0	7.7	19.1	0.9	85.9	8.1	0.0	0.0	3.8
14	8/09/06;9:50-10:26 AM	840	7.3	153	22.1	0.0	30.4		0	0.5	19.7	203.5	2.9	0.0	0.0	0.0	13.9	52.3	1.9	73.9	12.7	0.0	0.0	5.4
15	10:26-11:04 AM	900	7.5	131	22.2	0.0	17.6		0	0.4	18.2	105.3	7.2	0.0	0.0	0.0	12.8	36.9	1.7	84.8	12.1	0.0	0.0	4.3
16	11:04-11:38 AM	960	7.4	150	22.2	0.0	11.3		0	0.3	24.7	96.6	8.0	0.0	0.0	0.0	12.4	21.1	1.7	82.9	11.9	0.0	0.0	4.0
17	11:38 AM-12:16 PM	1020	7.4	196	22.0	0.0	11.4		0	0.3	18.5	96.0	8.1	0.0	0.0	0.0	12.5	23.4	1.7	112.9	9.0	0.0	0.0	4.0
18	12:16-12:51 PM	1080	7.4	221	22.1	0.0	14.5		0	0.3	23.9	129.0	10.4	0.0	0.0	0.0	12.1	16.9	1.7	108.3	7.2	0.0	0.0	3.9

Sample	Date/Time	Volume of leachate	pH	ORP	T	H_2S	As	DO	Fe^{2+}	F	Cl	SO_4	NO_3	PO_4	NO_2	Br	Na	Mg	K	Ca	Sr	Mn	Fe	Si
		mL		mV	˚C	mg/L	µg/L													mg/L				
19	12:51-1:22 PM	1140	7.4	221	22.6	0.0	9.3		0	0.2	18.5	91.0	8.1	0.0	0.0	0.0	12.7	15.2	1.7	112.7	6.2	0.0	0.0	4.1
20	8/29/06;12:04-12:40 PM	1200	7.2	124	22.5	0.0	19.1		0	0.4	17.5	151.5	3.6	0.0	0.0	0.0	10.9	55.4	8.6	147.7	15.9	0.0	0.1	5.4
21	12:40-1:32 PM	1260	7.4	178	22.3	0.0	7.6		0	0.3	17.5	104.2	5.7	0.0	0.0	0.0	15.2	128.9	3.4	193.6	13.5	0.0	0.5	4.8
22	1:32-2:47 PM	1320	7.4	162	22.8	0.0	15.9		0	0.3	19.2	111.9	6.7	0.0	0.0	0.0	14.1	31.5	2.4	134.4	12.3	0.0	0.0	4.1
23	9/19/06;10:32-11:07 AM	1380	7.3	118	22.2	0.0	22.6		0	0.3	14.6	123.4	3.4	0.0	0.0	0.0	14.1	33.5	1.8	88.0	13.0	0.0	0.0	5.0
24	11:07 AM-12:18 PM	1440	7.4	143	22.5	0.0	16.2		0	0.2	12.1	64.2	4.7	0.0	0.0	0.0	14.3	21.2	1.7	86.8	12.2	0.0	0.0	4.5
25	12:18-1:32 PM	1500	7.4	142	23.0	0.0	13.2		0	0.1	10.6	51.2	4.7	0.0	0.0	0.0	13.9	10.4	1.7	103.3	6.0	0.0	0.0	4.1
26	1:32-2:49 PM	1560	7.5	139	23.3	0.0	15.0		0	0.2	13.4	71.4	5.6	0.0	0.0	0.0	14.4	12.2	1.7	95.6	8.5	0.0	0.0	4.3
27	2:49-4:07 PM	1620	7.5	142	23.1	0.0	12.4		0	0.1	11.2	57.4	5.0	0.0	0.0	0.0	14.0	7.4	1.7	107.4	3.0	0.0	0.0	4.2
28	10/3/06;11:10-11:45 AM	1680	6.9	124	22.5	0.0	14.0		0	0.3	20.1	174.0	6.1	0.0	0.0	0.0	13.2	39.2	1.7	137.7	10.8	0.0	0.1	4.2
29	11:45 AM-12:19 PM	1740	7.1	126	22.6	0.0	21.9		0	0.2	15.4	87.5	6.5	0.0	0.0	0.0	13.1	25.8	1.7	124.4	9.6	0.0	0.0	3.9
30	12:19-12:55 PM	1800	7.1	133	22.5	0.0	13.0		0	0.2	16.5	89.9	7.1	0.0	0.0	0.0	13.3	24.9	1.7	135.8	7.0	0.0	0.0	3.9
31	12:55-1:30 PM	1860	7.1	142	22.7	0.0	10.7		0	0.2	15.2	85.3	6.5	0.0	0.0	0.0	13.1	38.8	1.7	183.7	5.5	0.0	0.1	3.9
32	1:30-2:12 PM	1920	7.2	149	22.8	0.0	16.6		0	0.1	14.9	78.9	6.5	0.0	0.0	0.0	13.3	26.4	1.7	149.5	4.5	0.0	0.0	4.0
33	2:12-2:48 PM	1980	7.1	143	22.6	0.0	9.9		0	0.1	16.5	87.7	7.1	0.0	0.0	0.0	12.7	17.1	1.6	127.7	3.8	0.0	0.0	3.8
34	10/17/06;12:04-12:33 PM	2040	7.0	154	22.5	0.0	13.0		0	0.2	17.3	96.3	5.9	0.0	0.0	0.0	13.7	35.7	1.8	133.0	10.6	0.0	0.0	4.4
35	12:33-1:05 PM	2100	7.2	155	23.0	0.0	11.4		0	0.2	17.5	94.3	6.1	0.0	0.0	0.0	13.1	23.7	1.6	132.8	5.9	0.0	0.0	3.9
36	1:05-1:38 PM	2160	7.2	152	23.3	0.0	11.4		0	0.2	16.4	87.6	6.0	0.0	0.0	0.0	13.2	15.3	1.6	117.3	4.9	0.0	0.0	3.9
37	1:38-2:14 PM	2220	7.3	139	23.4	0.0	7.5		0	0.2	17.1	90.7	6.2	0.0	0.0	0.0	13.5	20.1	1.7	134.0	4.5	0.0	0.0	4.0
38	2:14-2:46 PM	2280	7.3	162	23.1	0.0	9.1		0	0.2	15.3	81.9	5.7	0.0	0.0	0.0	13.2	11.1	1.6	111.8	3.9	0.0	0.0	3.9
39	2:46-3:28 PM	2340	7.3	135	23.5	0.0	7.3		0	0.2	16.4	84.3	6.1	0.0	0.0	0.0	13.1	13.0	1.7	110.1	3.9	0.0	0.0	3.9
40	11/02/06;3:04-3:46 PM	2400	6.9	85	23.3	0.0	20.4		0	0.3	17.5	124.8	6.0	0.0	0.0	0.0	7.5	22.7	1.8	103.2	10.3	0.0	0.0	4.3
41	3:46-4:33 PM	2460	7.2	164	23.5	0.0	18.0		0	0.2	17.5	86.9	6.3	0.0	0.0	0.0	7.3	21.6	1.8	122.0	8.4	0.0	0.0	4.0
42	4:33-5:15 PM	2520	7.2	113	23.2	0.0	14.7		0	0.2	17.3	87.5	6.2	0.0	0.0	0.0	7.4	7.4	1.7	100.7	2.6	0.0	0.0	3.9
43	5:15-6:00 PM	2580	7.2	127	23.5	0.0	14.5		0	0.2	16.9	86.6	6.1	0.0	0.0	0.0	7.4	11.2	1.7	109.6	4.7	0.0	0.0	4.0
44	6:00-6:48 PM	2640	7.1	120	23.3	0.0	10.2		0	0.2	16.5	88.5	6.3	0.0	0.0	0.0	7.6	11.9	1.7	113.7	3.9	0.0	0.0	3.8
45	11/20/06;1:21-2:05 PM	2700	7.2	165	21.5	0.0	15.3		0	0.2	16.7	90.5	5.9	0.0	0.0	0.0	7.0	18.9	1.7	98.8	9.4	0.0	0.0	3.9
46	2:05-2:53 PM	2760	7.3	169	20.8	0.0	14.3		0	0.2	16.5	87.5	6.2	0.0	0.0	0.0	7.5	13.3	1.7	102.1	7.2	0.0	0.0	3.7
47	2:53-3:35 PM	2820	7.3	190	21.1	0.0	11.9		0	0.1	16.4	82.6	6.2	0.0	0.0	0.0	7.5	10.7	1.6	103.7	5.2	0.0	0.0	3.6
48	3:35-4:26 PM	2880	7.3	178	21.4	0.0	11.0		0	0.1	16.3	83.7	6.0	0.0	0.0	0.0	7.1	8.4	1.7	94.9	3.8	0.0	0.0	3.7
49	4:26-5.19 PM	2940	7.2	169	21.2	0.0	7.4		0	0.2	15.5	81.7	6.1	0.0	0.0	0.0	7.0	8.0	1.6	96.2	3.2	0.0	0.0	3.7
50	5:19-6:12 PM	3000	7.4	167	21.1	0.0	9.1		0	0.1	15.6	82.6	6.2	0.0	0.0	0.0	7.4	7.8	1.7	98.3	3.1	0.0	0.0	3.8

Consecutive injection of BW and DW (0.3 m column)

Sample	Date/Time	Volume of leachate	pH	ORP	T	H_2S	As(III)	As (V)	DO	Fe^{2+}	F	Cl	SO_4	NO_3	PO_4	NO_2	Br	Na	Mg	K	Ca	Sr	Mn	Fe	Si
		mL		mV	˚C	mg/L	µg/L			mg/L															
BW	2/1/07;1:54 PM	0	6.7	-13	22.0	15.0	0.6	0.2	5.0	0.4	2.0	105.4	43.8	0.1	3.1	0.0	1.5	51.3	32.0	15.3	52.7	0.3	0.0	0.9	0.7
2	2:20-2:52 PM	60	7.2	116	20.4	0.0	0.9	58.3		0.1	2.2	173.5	756.8	2.5	0.3	0.0	1.9	52.9	83.7	19.9	168.5	3.2	0.0	0.1	1.1
3	2:52-3:32 PM	120	7.1	153	20.0	0.0	0.5	44.8		0.0	2.4	146.1	199.7	0.4	1.0	0.0	1.7	52.2	42.7	16.4	100.5	1.6	0.0	0.1	0.9
4	3:32-4:16 PM	180	7.2	148	20.0	0.0	0.4	37.2		0.0	2.7	153.1	133.1	0.3	1.5	0.0	1.7	53.9	36.4	16.0	84.4	1.2	0.0	0.0	0.8
5	4:16-4:57 PM	240	7.2	189	20.0	0.0	0.4	29.2		0.0	3.0	165.8	115.0	0.4	2.2	0.0	1.9	50.5	34.0	15.2	73.6	1.0	0.0	0.0	0.7
6	4:57-5:38 PM	300	7.0	186	19.8	0.0	0.4	25.5		0.0	3.0	156.2	94.9	0.2	2.8	0.0	1.7	52.0	32.7	15.0	68.2	0.9	0.0	0.0	0.8
7	5:38-6:20 PM	360	6.9	202	20.1	0.0	0.3	23.5		0.0	2.7	140.3	79.7	0.2	2.5	0.0	1.7	51.2	33.5	15.0	68.1	0.8	0.0	0.0	0.8
DW	2/2/07;12:56 PM	420	6.8	268	22.5	0.0	0.0	0.4		0.0	0.1	19.2	111.8	6.3	0.0	0.0	0.0	6.2	5.2	1.2	119.8	0.8	0.0	0.0	4.4
8	12:56-1:38 PM	480	7.0	190	21.4	0.0	7.7	59.1		0.0	2.1	100.7	183.0	3.2	0.7	0.0	1.1	34.6	36.5	10.5	93.7	2.1	0.0	0.0	2.7
9	1:38-2:20 PM	540	7.0	234	21.0	0.0	1.2	26.6		0.0	0.8	23.6	126.7	7.0	0.5	0.0	0.0	8.0	15.3	2.7	108.8	1.6	0.0	0.0	4.3
10	2:20-3:02 PM	600	7.0	234	20.9	0.0	0.4	19.2		0.0	0.5	20.5	120.6	6.5	0.4	0.0	0.0	6.6	11.1	1.8	116.7	1.4	0.0	0.0	4.5
11	3:02-4:12PM	660	6.8	222	21.0	0.0	0.2	15.1		0.0	0.3	16.5	94.0	5.1	0.4	0.0	0.0	6.3	8.7	1.6	118.4	1.3	0.0	0.0	4.5
12	4:12-4.50 PM	720	7.2	208	21.8	0.0	0.0	13.4		0.0	0.3	16.7	96.7	5.1	0.3	0.0	0.0	6.2	7.7	1.5	117.1	1.2	0.0	0.0	4.4
13	4:50-5:36 PM	780	7.0	185	23.0	0.0	0.0	13.8		0.0	0.3	15.9	94.5	4.7	0.7	0.0	0.0	6.1	7.3	1.4	123.5	1.3	0.0	0.0	4.5
BW	2/3/07;1:40 PM	840	6.6	-10	22.4	0.0	0.8	0.0		0.0	2.6	126.4	53.1	0.0	3.6	0.0	1.6	51.7	31.0	15.1	54.2	0.3	0.0	0.1	0.9
15	1:40-2:19 PM	900	6.9	214	20.0	0.0	1.8	35.4		0.0	1.3	83.2	110.0	0.2	0.7	0.4	0.9	28.8	19.1	6.9	100.9	2.1	0.0	0.0	2.5
16	2:19-3:00 PM	960	6.9	182	22.1	0.0	0.7	25.7		0.0	2.4	149.4	71.8	0.1	1.4	0.0	1.8	141.4	47.3	18.8	115.6	1.7	0.0	0.0	0.8
17	3:00-3:40 PM	1020	7.0	177	22.1	0.0	0.6	19.5		0.0	2.9	161.6	72.4	0.0	2.7	0.0	1.9	53.0	29.1	14.9	66.8	1.0	0.0	0.0	0.8
18	3:40-4:14 PM	1080	7.1	179	20.6	0.0	0.6	16.7		0.0	3.0	158.1	70.4	0.1	3.2	0.0	1.8	51.5	28.3	14.2	62.5	0.9	0.0	0.0	0.8
DW	2/4/2007; 12:27 PM	1140	6.8	268	21.5	0.0	0.0	0.3		0.0	0.1	22.6	123.8	8.4	0.0	0.0	0.0	6.4	5.3	1.3	121.5	0.7	0.0	0.0	4.4
19	12:27-1:33 PM	1200	6.6	186	19.9	0.0	38.7	28.9		0.0	1.2	75.8	82.0	2.1	0.7	0.0	0.9	31.4	24.9	9.0	81.8	2.5	0.0	0.0	2.7
20	1:33-3:32 PM	1260	7.0	191	19.9	0.0	7.8	12.5		0.0	0.7	25.5	127.9	8.0	0.7	0.0	0.1	7.7	12.7	2.6	106.0	1.9	0.0	0.0	4.3
21	3:32-4:10 PM	1320	7.1	180	19.9	0.0	3.9	9.5		0.0	0.4	21.0	113.7	7.5	0.3	0.0	0.0	6.6	9.6	1.9	113.1	1.6	0.0	0.0	4.3
22	4:41-4:51 PM	1380	7.2	178	19.5	0.0	2.6	7.7		0.0	0.3	18.4	94.9	6.7	0.5	0.0	0.0	6.4	7.8	1.6	113.8	1.4	0.0	0.0	4.4

Avon Park Formation; Interval 260 m - 261 m; 0.3 m columns

Sample	Time	Volume of leachate	pH	ORP	T	H_2S	As	DO	Fe^{2+}	F	Cl	SO_4	NO_3	PO_4	NO_2	Br	Na	Mg	K	Ca	Sr	Mn	Fe	Si
		mL		mV	˚C	mg/L	µg/L																	
GW	10/19/06; 9:20 AM	0	6.8	-108	26.5	0.1	0.1	1.6	2.0	0.1	3.1	522.4	0.0	0.0	0.0	0.0	4.0	20.0	2.0	317.4	8.1	0.0	2.1	6.1
1	10:20-11:02 AM	60	10.1	-25	23.4	0.0	1.4		0.2	0.2	97.1	2054.2	6.4	0.0	3.4	0.3	46.9	5.2	29.6	674.9	9.2	0.0	0.0	8.7
2	11:02-11:42 AM	120	10.5	-22	22.2	0.0	0.2		<0.1	0.3	8.0	1179.8	3.0	0.0	0.8	0.0	7.8	11.0	17.5	437.9	7.9	0.0	0.1	9.5
3	11:42 AM-12:22 PM	180	10.4	-46	23.6	0.0	0.1		0.0	0.3	7.9	1135.8	0.9	0.0	0.7	0.0	7.4	8.9	10.3	394.3	8.3	0.0	0.0	9.1
4	12:22-1:04 PM	240	10.3	11	22.8	0.0	0.2		0.0	0.3	6.6	999.9	0.7	0.0	0.5	0.0	9.3	10.2	6.9	357.3	8.3	0.0	0.1	7.9
5	1:04-1:47 PM	300	10.2	61	23.5	0.0	0.5		0.0	0.3	6.6	979.8	0.6	0.0	0.4	0.0	9.6	7.5	5.0	338.8	8.6	0.0	0.0	7.6
6	1:47-2:27 PM	360	9.9	82	23.5	0.0	0.4		0.0	0.3	6.4	950.3	0.6	0.0	0.4	0.0	7.0	16.3	4.0	344.1	9.0	0.0	0.0	7.6
7	2.27-3:07 PM	420	9.7	69	23.5	0.0	0.2		0.0	0.1	6.6	980.4	0.6	0.0	0.4	0.0	9.5	21.4	3.4	309.8	9.0	0.0	0.0	7.5
8	3:07-3:51 PM	480	9.6	72	23.7	0.0	1.1		0.0	0.3	7.7	1108.4	0.8	0.0	0.4	0.1	9.6	26.5	3.1	295.1	8.6	0.0	0.0	9.8
9	3:51-4.35 PM	540	9.3	-101	23.7	0.0	3.0		0.0	0.1	6.6	940.3	0.5	0.0	0.3	0.0	9.9	27.2	2.9	282.1	8.5	0.0	0.0	12.6
10	4:35-5:18 PM	600	9.1	-13	21.6	0.0	7.5		0.0	0.2	6.3	898.0	0.4	0.0	0.2	0.0	9.6	29.0	2.7	271.7	8.6	0.0	0.0	14.2
11	5:18-5:56 PM	660	9.1	16	23.0	0.0	5.9		0.0	0.3	7.5	1115.2	0.4	0.0	0.3	0.0	6.9	30.9	2.5	264.4	8.7	0.0	0.0	16.4
12	5:56-8:53 PM	720	9.3	50	23.4	0.0	4.2		0.0	0.3	6.1	920.2	0.7	0.0	0.4	0.0	7.2	20.4	2.6	304.8	9.6	0.0	0.0	12.1
DW	10/24/06; 9:35 AM	0	6.7	320	21.2	0.0	0.0	2.9	0.0	0.0	5.8	39.0	2.5	0.0	0.0	0.0	12.9	5.2	1.6	108.6	0.7	0.0	0.0	4.0
1	9:56-10:36 AM	60	10.8	1	20.3	0.0	7.8		0.2	0.3	30.0	1199.1	9.5	0.0	2.7	0.4	48.5	46.9	28.1	642.8	9.2	0.0	0.5	10.1
2	10:36-11:18 AM	120	10.9	-23	21.3	0.0	5.9		<0.1	0.4	14.7	372.9	6.2	0.0	0.5	0.0	20.2	28.8	10.8	362.5	8.6	0.0	0.4	10.0
3	11:18 AM-12:02 PM	180	10.8	-16	21.8	0.0	9.0		0.0	0.4	17.6	333.7	7.3	0.0	0.4	0.0	18.3	38.3	7.4	345.1	8.9	0.0	0.4	12.1
4	12:02-12:53 PM	240	10.8	-14	21.0	0.0	4.4		0.0	0.3	15.8	244.8	6.5	0.0	0.3	0.0	17.2	12.6	4.9	203.6	8.5	0.0	0.1	11.4
5	12:53-1:40 PM	300	10.6	18	22.2	0.0	1.5		0.0	0.3	16.1	218.0	6.6	0.0	0.3	0.0	17.5	15.2	3.7	199.2	8.5	0.0	0.1	12.8
6	1:40-2:21 PM	360	10.6	10	22.3	0.0	1.1		0.0	0.3	16.4	204.2	6.7	0.0	0.3	0.0	17.7	9.0	2.9	166.9	7.9	0.0	0.1	14.2
7	2:21-3:03 PM	420	10.6	13	22.5	0.0	3.2		0.0	0.3	16.9	201.2	7.0	0.0	0.3	0.0	17.4	7.9	2.6	154.9	7.4	0.0	0.1	13.9
8	3:03-3:45 PM	480	10.4	25	22.6	0.0	3.0		0.0	0.2	12.7	138.3	5.4	0.0	0.2	0.0	17.5	4.6	2.4	137.8	7.0	0.0	0.0	14.2
9	3:45-4:30 PM	540	10.6	15	21.6	0.0	2.2		0.0	0.2	17.1	191.4	7.2	0.0	0.2	0.0	17.4	3.4	2.2	131.2	6.8	0.0	0.0	14.6
10	4:30-5:11 PM	600	10.4	20	22.3	0.0	2.1		0.0	0.1	14.1	163.5	6.1	0.0	0.2	0.0	15.8	3.7	2.1	122.9	6.2	0.0	0.0	14.9
11	5:11-5:58 PM	660	10.4	31	23.2	0.0	0.4		0.0	0.2	14.3	160.3	6.1	0.0	0.2	0.0	15.0	3.6	2.0	115.2	5.9	0.0	0.0	14.8
12	11:17AM-12:03 PM	720	10.4	67	21.8	0.0	0.7		0.0	0.3	17.1	311.6	7.1	0.0	0.6	0.0	17.6	7.1	0.8	190.9	10.8	0.0	0.1	11.7
13	12:03-12:43 PM	780	10.5	104	21.1	0.0	0.1		0.0	0.2	17.2	150.1	7.6	0.0	0.1	0.0	18.2	2.2	2.1	107.9	6.1	0.0	0.0	13.8
14	12:43-1:28 PM	840	10.2	75	22.2	0.0	2.1		0.0	0.2	17.8	153.3	7.8	0.0	0.1	0.0	17.9	2.3	2.0	96.4	5.6	0.0	0.0	14.9
15	1:28-2:14 PM	900	10.1	62	22.3	0.0	0.8		0.0	0.2	17.4	155.4	7.6	0.0	0.1	0.0	17.7	1.9	0.8	93.1	5.6	0.0	0.0	15.5
16	2:14-2:57 PM	960	10.0	59	22.3	0.0	3.8		0.0	0.1	8.0	69.6	3.6	0.0	0.1	0.0	10.6	1.9	0.9	90.0	5.5	0.0	0.0	16.1
17	5:00-5:43 PM	1020	10.0	20	22.4	0.0	4.4		0.0	0.1	16.6	174.4	7.2	0.0	0.2	0.0	18.0	2.4	1.9	99.3	6.4	0.0	0.0	14.9
18	5:43-6:16 PM	1080	9.9	51	22.1	0.0	2.6		0.0	0.0	1.7	13.4	0.8	0.0	0.0	0.0	0.0	2.8	0.8	85.1	5.5	0.0	0.0	16.0

Sample	Time	Volume of leachate	pH	ORP	T	H_2S	As	DO	Fe^{2+}	F	Cl	SO_4	NO_3	PO_4	NO_2	Br	Na	Mg	K	Ca	Sr	Mn	Fe	Si
		mL		mV	˚C	mg/L	µg/L													mg/L				
WW	4/9/08; 1:00 PM	0	6.6	-214	22.9	8.3	0.0	0.1	0.8	2.6	101.0	21.7	0.0	6.3	0.0	1.4	78.3	34.3	12.6	55.3	0.5	0.0	0.0	1.2
1	2:50-3:40 PM	60	7.4	-125	23.1	0.5	28.8	0.0		1.0	110.4	917.1	9.5	0.0	0.5	1.8	77.5	78.6	28.6	634.6	2.2	0.0	0.0	3.5
2	3:40-4:15 PM	120	7.5	-155	21.4	0.9	42.4	0.0		1.7	105.7	277.8	0.0	0.0	0.0	1.6	76.6	40.6	13.5	356.7	1.3	0.0	0.0	2.6
3	4:15-4:54 PM	180	7.4	-148	21.4	2.6	46.5	0.0		2.4	131.9	162.7	0.0	0.0	0.3	1.9	75.5	39.5	14.6	210.7	1.1	0.0	0.0	2.4
4	4:54-5:30 PM	240	7.3	-154	24.1	2.2	46.7	0.0		2.1	106.0	82.3	0.2	1.0	0.3	1.5	76.7	39.5	13.5	173.6	1.0	0.0	0.0	2.0
5	5:30-6:00 PM	300	7.3	-157	24.2	0.9	48.4	0.0		2.2	105.8	61.2	0.3	1.6	0.2	1.6	75.4	38.5	12.6	171.8	1.0	0.0	0.0	1.9
6	6:00-6:40 PM	360	7.3	-152	21.0	0.7	52.0	0.0		2.2	103.6	47.3	0.3	2.1	0.1	1.5	76.6	38.8	13.7	149.6	0.9	0.0	0.0	1.9
7	6:40:7:20 PM	420	7.2	-151	21.0	0.7	57.7	0.0		2.3	106.6	40.1	0.7	2.5	0.2	1.5	77.5	37.5	13.2	133.5	0.8	0.0	0.0	1.5
8	7:20-7:55 PM	480	7.3	-90	21.0	0.6	62.5	0.0		2.3	103.3	33.1	0.2	3.5	0.2	1.4	75.6	36.6	12.6	124.5	0.8	0.0	0.0	1.4
9	7:55-8:33 PM	540	7.2	-146	21.0	0.6	66.9	0.0		2.2	98.1	27.7	0.0	3.6	0.2	1.4	76.5	35.4	12.2	119.6	0.7	0.0	0.0	1.3
WW_filt_0.2 um	5/8/08; 11:20 AM	0	6.8	-200	24.1	3.8	0.0	0.5	0.2	3.2	132.0	27.6	0.0	5.9	0.0	1.9	46.9	27.7	13.4	47.2	0.4	0.0	0.0	1.7
1	5:30-6:45 PM	60	7.5	45	21.3	0.1	16.4		0.0	0.8	146.1	1402.9	17.6	0.0	0.4	1.9	57.7	30.5	27.6	502.6	5.9	0.0	0.0	3.5
2	6:45-7:40 PM	120	7.7	-43	20.6	0.1	20.6		0.0	2.4	161.1	450.9	3.3	0.0	0.0	2.2	53.1	15.4	14.9	200.1	2.3	0.0	0.1	2.8
3	7:40-9:25 PM	180	7.6	20	20.0	0.0	23.6		0.0	2.3	140.9	317.2	0.7	0.0	0.0	2.0	54.2	17.4	15.0	171.2	2.1	0.0	0.1	2.9
4	9:25-10:20 PM	240	7.6	18	20.9	0.0	30.0		0.0	3.1	167.0	188.7	0.4	0.0	0.0	2.2	51.8	17.1	13.6	119.6	1.6	0.0	0.0	2.5
BW	11/15/06; 11:38 AM	0	6.5	-66	24.9	0.0	0.5	1.0	1.0	1.8	91.5	39.5	0.3	0.6	0.0	0.9	39.4	20.8	7.2	37.9	0.3	0.1	0.9	1.7
1	12:05-12:52 PM	60	9.4	-20	23.2	0.0	6.7		0.2	0.2	147.0	1553.2	12.9	0.0	2.5	1.4	43.1	29.5	41.5	524.9	6.5	0.0	0.2	10.7
2	12:52-1:42 PM	120	9.7	-9	21.6	0.0	2.9		0.2	0.3	99.2	562.5	3.2	0.0	0.7	1.0	38.3	10.8	15.4	191.4	4.6	0.0	0.1	11.2
3	1:42-4:09 PM	180	10.0	-9	21.6	0.0	4.6		0.1	0.5	83.2	391.8	2.5	0.4	0.7	1.1	38.3	11.8	12.7	185.5	5.5	0.0	0.1	11.5
4	4:09-5:15 PM	240	9.3	37	20.8	0.0	8.0		0.1	0.6	84.9	210.3	1.5	0.0	0.4	1.1	38.2	10.2	9.2	114.4	4.0	0.0	0.1	12.6
5	5:15-6:15 PM	300	9.3	47	21.6	0.0	20.7		0.0	0.6	75.9	138.7	1.2	0.0	0.2	0.7	39.2	15.7	8.6	107.3	4.2	0.0	0.1	13.9
6	6:15-7:25 PM	360	8.8	84	21.4	0.0	28.1		0.0	0.8	74.1	113.9	0.7	0.0	0.2	0.8	39.9	18.6	8.3	90.5	4.5	0.0	0.1	13.8
7	7:25-8:32 PM	420	8.4	107	21.4	0.0	22.9		0.0	1.3	96.9	139.7	1.1	0.0	0.2	1.2	42.1	15.4	8.7	59.7	5.3	0.0	0.0	13.9
8	8:32-9:16 PM	480	8.1	125	21.1	0.0	29.1		0.0	1.0	72.3	88.5	0.7	0.0	0.0	0.9	37.2	25.0	7.6	89.2	4.8	0.0	0.1	12.0

APPENDIX G

GEOCHEMICAL REACTIVE TRANSPORT MODELING DATA

(1) Water-rock interaction between the aquifer matrix and surface water (Closed System).

Injectant volume and composition	H_2O	60	mL
	Ca^{2+}	101.4	mg/L
	Mg^{2+}	4.7	
	Na^{+}	22.0	
	HCO_3^{-}	81.9	
	Cl^{-}	14.3	
	Fe^{2+}	0.0	
	K+	1.7	
	SO_4^{2-}	58.1	
	O_2(aq)	5.0	
	NO_3^{-}	5.5	
	$As(OH)_4^{-}$	0.11	μg/L
	pH	6.9	
	T	22.3	˚C
Rock composition (reactants)	Calcite	258	g
	Dolomite	35.2	
	Pyrite	0.2	
	Arsenopyrite	0.002	
	Gypsum	10	

Note: reactants 0.003 times

(2) Water-rock interaction between the aquifer matrix and surface water (Open System).

Injectant volume and composition	H_2O	60	mL
	Ca^{2+}	101.4	mg/L
	Mg^{2+}	4.7	
	Na^{+}	22.0	
	HCO_3^{-}	81.9	
	Cl^{-}	14.3	
	Fe^{2+}	0.0	
	K+	1.7	
	SO_4^{2-}	58.1	
	O_2(aq)	5.0	
	NO_3^{-}	5.5	
	$As(OH)_4^{-}$	0.11	μg/L
	pH	6.9	
	T	22.3	˚C
Rock composition (reactants)	Calcite	258	g
	Dolomite	35.2	
	Pyrite	0.2	
	Arsenopyrite	0.002	
	Gypsum	10	

Note: reactants times 0.003; activity of O_2(aq) was fixed

(3) Water-rock interaction between the aquifer matrix and surface water (Open System; high amount of pyrite).

Injectant volume and composition	H_2O	60	mL
	Ca^{2+}	101.4	mg/L
	Mg^{2+}	4.7	
	Na^{+}	22.0	
	HCO_3^{-}	81.9	
	Cl^{-}	14.3	
	Fe^{2+}	0.0	
	K+	1.7	
	SO_4^{2-}	58.1	
	O_2(aq)	5.0	
	NO_3^{-}	5.5	
	$As(OH)_4^{-}$	0.11	µg/L
	pH	6.9	
	T	22.3	˚C
Rock composition (reactants)	Calcite	258	g
	Dolomite	35.2	
	Pyrite	0.7	
	Arsenopyrite	0.007	
	Gypsum	10	

Note: reactants 1 times; activity of O_2(aq) was fixed

(4) 1D reaction-transport model of water-rock interaction between the aquifer matrix and surface water (Closed System).

Initial and Injectant volume and composition	H_2O	60	mL
	Ca^{2+}	101.4	mg/L
	Mg^{2+}	4.7	
	Na^{+}	22.0	
	HCO_3^{-}	81.9	
	Cl^{-}	14.3	
	Fe^{2+}	0.0	
	K+	1.7	
	SO_4^{2-}	58.1	
	O_2(aq)	5.0	
	NO_3^{-}	5.5	
	$As(OH)_4^{-}$	0.11	µg/L
	pH	6.9	
	T	22.3	˚C
Rock composition (reactants)	Calcite	258	g
	Dolomite	35.2	
	Pyrite	0.2	
	Arsenopyrite	0.002	
	Gypsum	10	

Note:

- Reaction: from 0 hours to 5 hours
- Reactants 0.003 times
- Domain: 50 cm long and divided into 10 nodes along x
- Domain: 2 cm wide (along y)
- Discharge: 0.01 cm/sec
- log Permeability (darcy) = (-5) + (15)*Porosity
- Dispersivity: domain length/100
- Diffusion coefficient (cm2/sec): 1e-6
- Initial porosity: 0.15

5) 1D reaction-transport model of water-rock interaction between the aquifer matrix, groundwater and surface water (Closed System).

Initial system composition (rock+groundwater)	H_2O	60.0000427	mL	**Injectant volume and composition**	H_2O	60.00	mL
	Ca^{2+}	1.6076250E-04			Ca^{2+}	101.40	
	Mg^{2+}	1.9352990E-05			Mg^{2+}	4.70	
	Na^{+}	6.0019500E-04			Na^{+}	22.00	
	HCO_3^{-}	1.9581910E-04			HCO_3^{-}	81.90	
	Cl^{-}	7.8098330E-04			Cl^{-}	14.30	mg/L
	Fe^{2+}	1.9085308E-06	mol		Fe^{2+}	1.0E-07	
	K+	1.0000000E-25			K+	1.7	
	H^{+}	3.0709813E-05			SO_4^{2-}	58.1	
	SO_4^{2-}	7.0439599E-25			O_2(aq)	4.98	
	O_2(aq)	7.1992095E-69			NO_3^{-}	5.5	
	NO_3^{-}	1.0000000E-60			$As(OH)_4^{-}$	0.1137	µg/L
	$As(OH)_4^{-}$	2.3233080E-11	µg/L		pH	6.9	
	T	27.7	˚C		T	22.3	˚C
Rock composition (reactants)	Calcite	258	g				
	Dolomite	35.2					
	Pyrite	0.2					
	Arsenopyrite	0.002					
	Gypsum	10					

Note:

- Reaction: from 0 hours to 5 hours
- Reactants 0.008 times
- Domain: 50 cm long and divided into 10 nodes along x
- Domain: 1.9 cm wide (along y)
- Discharge: 0.01 cm/sec
- log Permeability (darcy) = (-5) + (15)*Porosity
- Dispersivity: domain length/100
- Diffusion coefficient (cm2/sec): 1e-6
- Initial porosity: 0.15

ABOUT THE AUTHOR

Olesya Lazareva earned a B.S. Degree in Geology, Advanced Degree ("Specialist") in Geology and Environmental Geology from Lomonosov Moscow State University (Moscow, Russia), a M.S. Degree in Environmental Geochemistry and Ph.D. in Geology from at the University of South Florida (Tampa, USA). During the graduate studies (2002 - 2010), she was a Teaching and Research Associate collaborating with the FIPR, SWFWMD, EPA, FGS, and FDEP, and the University of Bremen. She was a Lab Manager in the Center for Water and Environmental Analysis at the University of South Florida from 2006 to 2008. Her main research interests include hydrogeology, environmental, aqueous, and isotope geochemistry, as well as the sustainability and environmental quality of water resources. She participated in the international conferences on geochemistry (i.e., Goldschmidt, AGU, and ACS) and had peer-reviewed publications in the Applied Geochemistry and Chemical Geology.