Geochemical Factors Controlling the Mobilization of Arsenic at an Artificial Recharge Site, Clearwater, Florida

Bruce K. Darling

Geosyntec Consultants, Austin, Texas, USA

Abstract: Aquifer storage and recovery and artificial recharge projects are common methods of developing and managing groundwater resources for future use by cities that face pressure to maintain sustainable supplies of water for growing populations. Such projects, however, are often accompanied by water-quality problems that can be mitigated by careful attention to geological and geochemical factors that account for the occurrence and mobilization of contaminants such as arsenic in storage zones. Investigations of artificial recharge systems in Florida, for example, have identified oxidative dissolution of pyrites by treated injectate waters as the principal factor causing the mobilization of arsenic from the matrix of an aquifer. This paper describes major-ion chemistry and associated reduction-oxidation factors that account for the occurrence of arsenic in groundwater at an artificial recharge site under development by the City of Clearwater, Florida. The results of this investigation are fully consistent with those of previous studies. Of particular significance is the apparent sensitivity of arsenical sulfides to slight changes in the redox conditions under which those minerals are otherwise stable.

Keywords: *aquifer storage and recovery, artificial recharge, arsenic, reduction-oxidation potential, oxidative dissolution*

As many cities consider the need to develop sustainable sources of water for growing populations, strategies such as aquifer storage and recovery (ASR) and artificial recharge (AR) have become central components of long-term water-resource management plans. Without thorough characterization of local geology and groundwater chemistry, such strategies are often accompanied by problems with the potential to limit the effectiveness of ASR and AR systems. One problem associated with such unconventional water-supply programs is the potential for the liberation of arsenic from minerals that are otherwise stable in subsurface environments before the injection of treated water.

Arsenic concentrations greater than the U.S. Environmental Protection Agency's prescribed maximum contaminant level (MCL) of 10 micrograms per liter (μg/L) have been detected in recovery water at ASR sites in Florida (Arthur, Dabous, and Cowart 2002; Price and Pichler 2006;

Jones and Pichler 2007). Investigations of the association of arsenic and pyrite have consistently identified oxidation of iron sulfides, specifically pyrite (FeS_2), as the principal factor accounting for the occurrence of arsenic in recovery water (Arthur, Dabous, and Cowart 2002; Jones and Pichler 2007).

Jones and Pichler (2007) studied this association in the Suwannee Limestone of the Upper Floridan Aquifer. Their findings are summarized as follows:

Geochemical modeling was employed to examine pyrite stability in limestone during simulated injections of surface water into wells open only to the Suwannee Limestone with known mineralogy and water chemistry. The goal was to determine if aquifer redox conditions could be altered to the degree of pyrite instability. Increasing amounts of injection water were added to native storage-zone water, and resulting reaction paths were plotted on pyrite stability diagrams. Native

storage-zone water plotted within the pyrite stability field, indicating that conditions were sufficiently reducing to allow for pyrite stability. Thus, arsenic is immobilized in pyrite, and its groundwater concentration should be low. This was corroborated by analysis of water samples, none of which had arsenic concentrations above 0.036 microg/L. During simulation, however, as injection/native storage-zone water ratios increased, conditions became less reducing and pyrite became unstable. The result would be release of arsenic from limestone into storage-zone water (Jones and Pichler 2007, 723).

Clearwater Groundwater Replenishment Project

Geosyntec Consultants (Geosyntec) conducted a groundwater geochemical modeling investigation (Darling 2014) as part of the Clearwater Groundwater Replenishment Project (Project) to evaluate the suitability of the Suwannee Limestone (Floridan aquifer) to be an injection zone for up to three million gallons per day (MGD) of purified reclaimed water from the City of Clearwater Northeast Water Reclamation Facility (NEWRF). This paper is a highly condensed summary of the geochemical investigation (Darling 2014). The work was conducted for Leggett, Brashears & Graham, Inc. (LBG) as part of the hydrogeologic services conducted for the Project on behalf of the City of Clearwater, Florida (City). The Southwest Florida Water Management District (SWFWMD) was a source of cooperative funding for the Project.

A principal matter of concern to the City and SWFWMD is the potential for the mobilization of arsenic and other metals within the injection zone. The primary objectives of this investigation were to describe the major-ion chemistry and hydrochemical facies of the groundwater system at the Project site, ascertain whether arsenic is a naturally occurring solute in groundwater, and identify probable mineralogical associations and geochemical controls on the occurrence of arsenic.

A parallel and complementary component of this investigation involved an assessment of rock cores to describe the bulk mineralogical makeup of the aquifer matrix and to identify associated metals that might be released to groundwater through rock-water interactions. Additionally, bench-scale column tests were conducted to determine whether arsenic and other metals can be leached from the matrix and associated minerals under variable pH and reduction-oxidation (redox) conditions (Norton et al. 2014). The results of the investigation by Norton et al. (2014) are summarized in the discussion section of this paper.

Groundwater Sample Collection and Laboratory Analyses

The investigation began with the collection of samples of groundwater from four monitor wells and one water supply well at the NEWRF. The four monitor wells are divided into two upper-zone (UZAMW-1 and UZAMW-2) and two lower-zone (LZAMW-1 and LZAMW-2) wells, all of which are located within the southern half of the Project area (Figure 1). The depth of each upper-zone well is approximately 150 feet below land surface (ft BLS), and the depth of each lower-zone well is approximately 340 ft BLS (Trommer 2014). The source well drilled to supply water for a long-term injection test is also a lower-zone well, but at a depth of approximately 360 ft BLS, and located near the northeast corner of the property (Figure 1). Water from the source well is pumped through a pipeline to a recharge well (RW-1) located north of the UZAMW-1 and LZAMW-1 monitor wells (Figure 1). The injection zone is designated "Lower Zone A" of the Suwannee Limestone (Figure 2). In this paper, the upper zone wells are referred to as UZA1 and UZA2, and the lower zone wells as LZA1, LZA2, and RW1.

Between April 9 and July 2, 2014, 13 sets of samples were collected from Wells UZA1, UZA2, LZA1, LZA2, and RW1, for a total of 65 samples. The sampling method involved the recording of temperature, conductivity, pH, dissolved oxygen (DO), and oxidation-reduction potential (ORP), along with the time at which the variables were recorded. At each well, water was diverted through a flowline to a closed flow cell with probes attached to a calibrated pH/ORP/temperature/conductivity meter. The above variables were recorded on field data sheets at five-minute intervals until the measurements changed by no more than five percent (plus or minus) over two consecutive five-minute intervals.
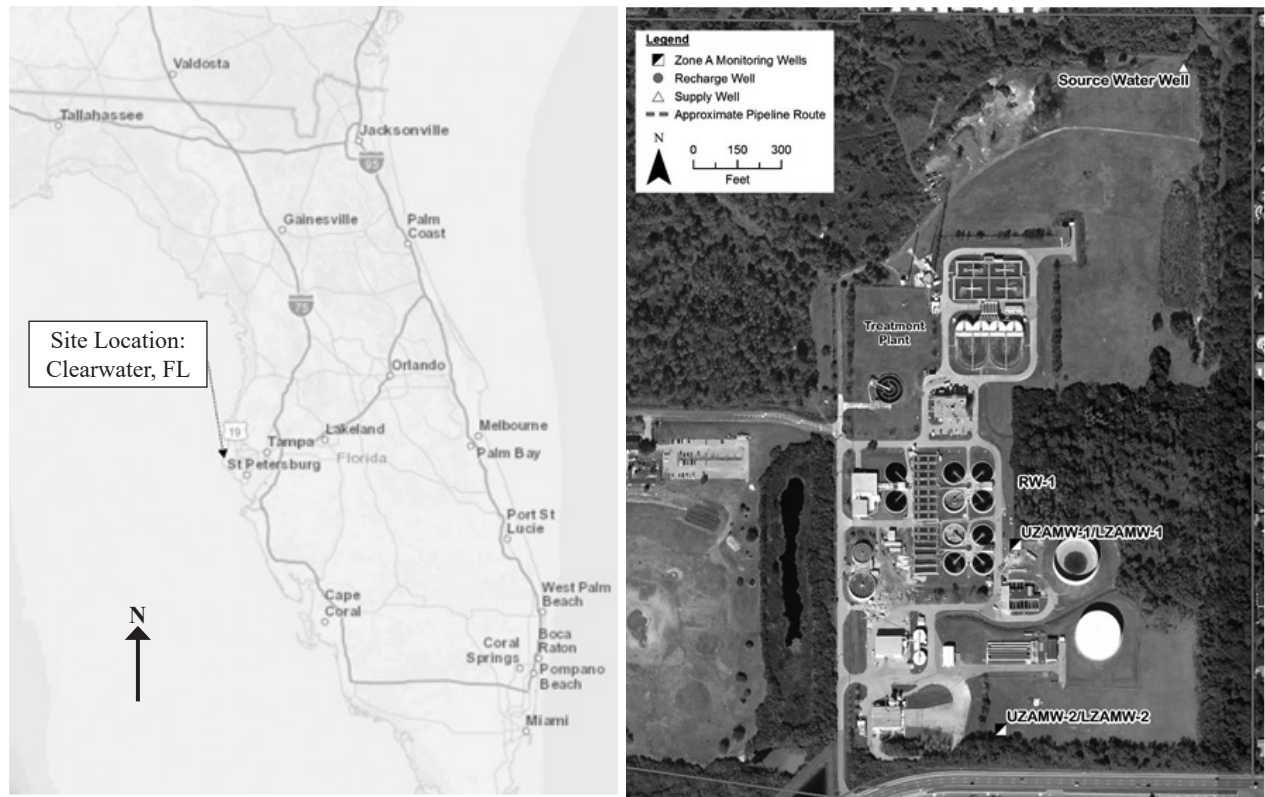
Figure 1. Location of Groundwater Replenishment Project and Project Site. Source: Darling 2014.
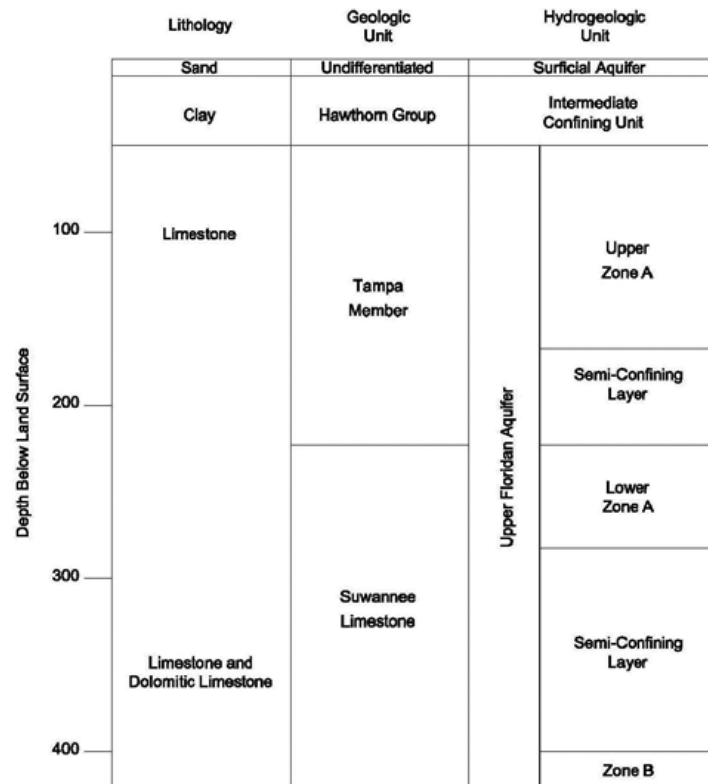

Figure 2. Stratigraphy of Clearwater Groundwater Replenish Project Site.

After the field parameter values were determined to be stable, the flowline was removed from the flow cell and the flow of water to the line was shut off at the outflow valve to which the flowline was attached at the wellhead. A 0.45-micron filter was attached to the end of the flowline and the outflow valve was reopened, allowing water to flow through the line again and to fill the 0.45-micron filter. Filtered water was then discharged to a 0.5-L Nalgene bottle to which nitric acid had been added by TestAmerica Laboratories of Tampa, Florida. That sample was designated for analysis of metals. A second 0.5-L Nalgene bottle without nitric acid was also filled. That sample was designated for analysis of nonmetals. Field measurements and the list of analytes were as follows:

- Temperature
- pH
- ORP
- Dissolved Oxygen
- Total Dissolved Solids (TDS)
- Calcium
- Magnesium
- Sodium
- Potassium
- Iron
- Arsenic
- Sulfate
- Sulfide
- Alkalinity (Bicarbonate)
- Fluoride

Major-Ion Analyses

The major-ion chemistry of all samples is represented by a Durov diagram (Figure 3). The basis of a Durov diagram is percentage plotting, in separate trilinear diagrams of cations and anions in units of milliequivalent per liter (meq/L). Lines from each pair of points in the cation and anion triangles are projected into the central rectangle to form a common point, which represents the composition of the samples with respect to cations and anions. The points in the central rectangle are projected into the TDS and pH fields, which offer additional dimensions for comparison and contrast of samples.

Figure 3 is based on the average concentrations of cations, anions, TDS, and pH for each of the five wells to avoid overlapping of symbols. The groundwater samples form distinct clusters, with hydrochemical compositions that range from calcium-sodium-chloride for the upper-zone wells (UZA1 and UZA2) to sodium-chloride for the lower-zone wells (RW1, LZA1, and LZA2). The clusters are further distinguished from each other, as illustrated by the loci of points within the TDS field. Water from the lower-zone wells has higher TDS than water from upper-zone wells, and the RW-1 samples exhibited the highest TDS. On a plot of sodium versus chloride (Figure 4), the clusters lie along a line with a sodium-to-chloride concentration ratio that is representative of the mixing of fresh groundwater and seawater.

With regard to the occurrence of arsenic in groundwater, there are four distinct clusters formed by the samples from the five wells (Figure 5). Figure 5 is not intended to indicate a causal link between arsenic and chloride. Figure 5 shows different ranges of arsenic for each group of samples. Arsenic concentrations decrease in the following order: UZA2 > RW1 > UZA1 > LZA1 = LZA2. Because arsenic concentrations among the LZA1 and LZA2 samples overlap, LZA1 and LZA2 are regarded as a single group.

Arsenic concentrations among the UZA1 samples and the LZA1 and LZA2 samples are less than the 10-µg/L MCL for arsenic in drinking water. The concentrations for the UZA1 samples are greater than 5 µg/L but less than 10 µg/L, and the concentrations among the LZA1 and LZA2 samples are less than 5 µg/L. Arsenic concentrations among the 13 RW1 samples are distributed around a mean of approximately 14 µg/L.

The association of dissolved arsenic and iron in groundwater samples is illustrated by Figure 6. In samples with iron concentrations less than 0.05 mg/L, arsenic forms three distinct clusters defined by the 26 LZA1 and LZA2 samples, the 13 UZA1 samples, and the 13 RW1 samples. A fourth group is formed by the 13 UZA2 samples. Iron concentrations for the latter group range from 0.05 to 0.19 mg/L.

The highest arsenic concentrations are associated with the UZA2 samples, the group with the largest concentrations of dissolved iron. Figure 7 illustrates that the highest iron concentrations are generally associated with the highest ORP measurements. This is a direct indication that reducing conditions

predominate within the lower zone and within the area of the upper zone in the vicinity of UZA1. Around UZA2, however, the ORP measurements indicate that conditions are more oxidizing and thus more likely to lead to the dissolution of pyrite and to the release of arsenic.

The predominance of reducing conditions is also found in figures of the concentration of sulfide with respect to ORP (Figure 8), dissolved oxygen and iron (Figure 9), dissolved oxygen and sulfide (Figure 10), sulfide and arsenic (Figure 11), and dissolved oxygen and arsenic (Figure 12).
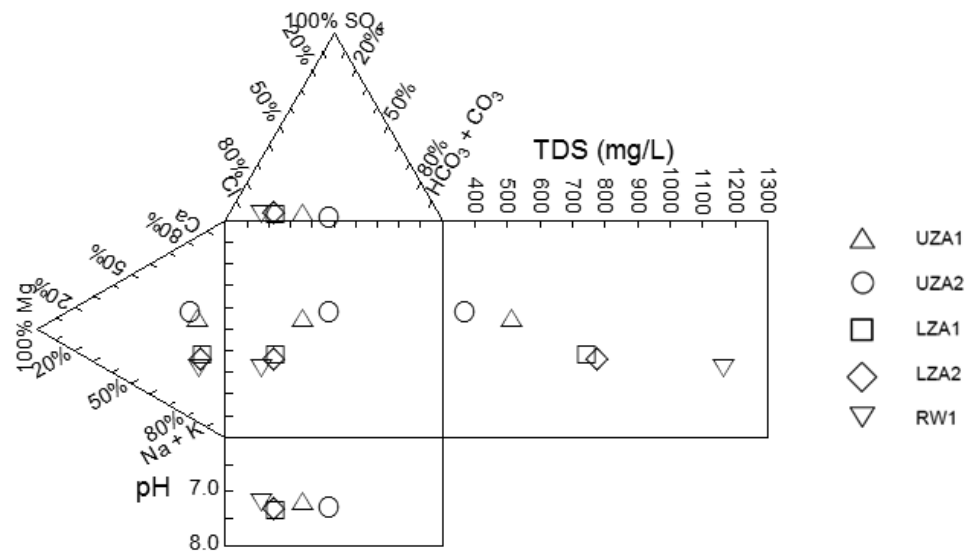
Figure 3. Durov diagram.
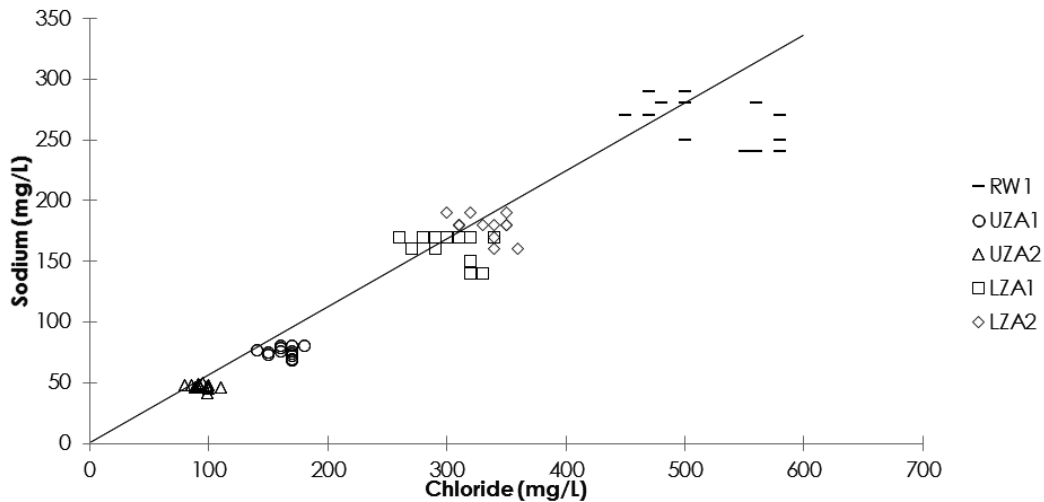
Figure 4. Plot of chloride versus sodium for Upper Zone and Lower Zone groundwaters.
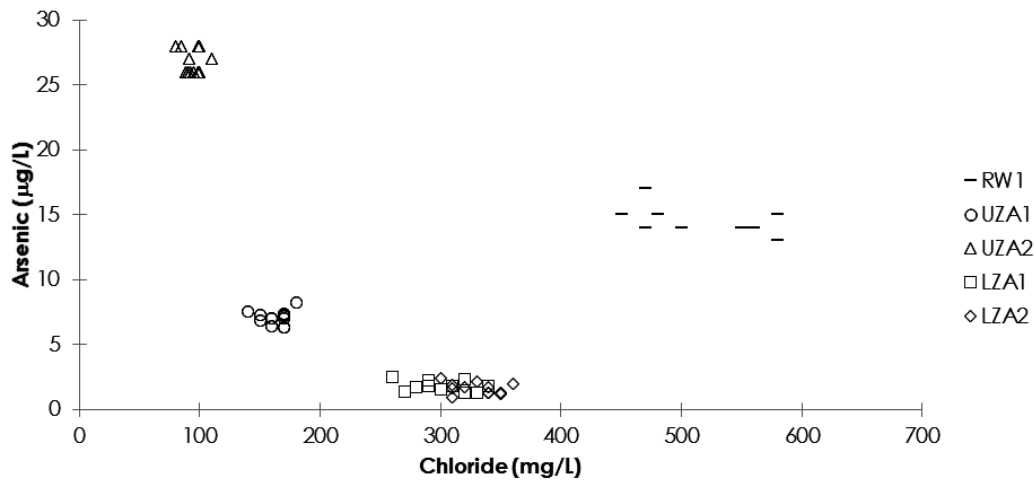
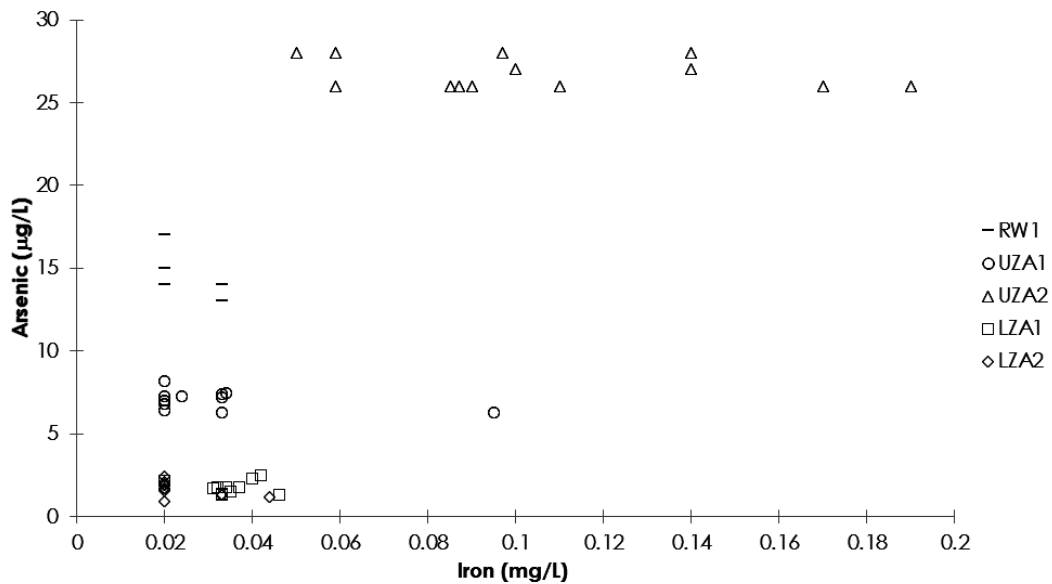**Figure 5.** Plot of arsenic clusters and concentrations of chloride for Upper Zone and Lower Zone groundwaters.

Figure 6. Plot of concentrations of arsenic and iron for Upper Zone and Lower Zone groundwaters.
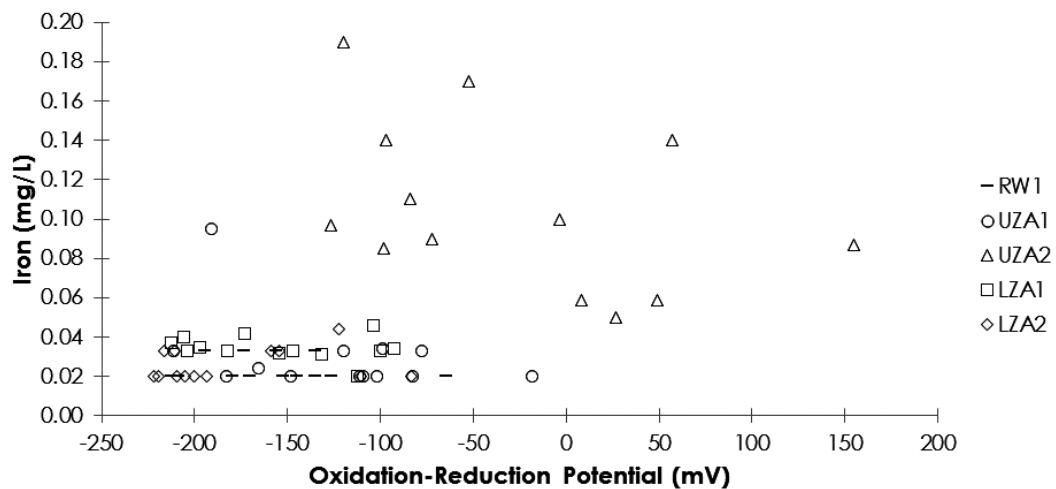

Figure 7. Plot of iron concentrations and measurements of oxidation-reduction potential for Upper Zone and Lower Zone groundwaters.
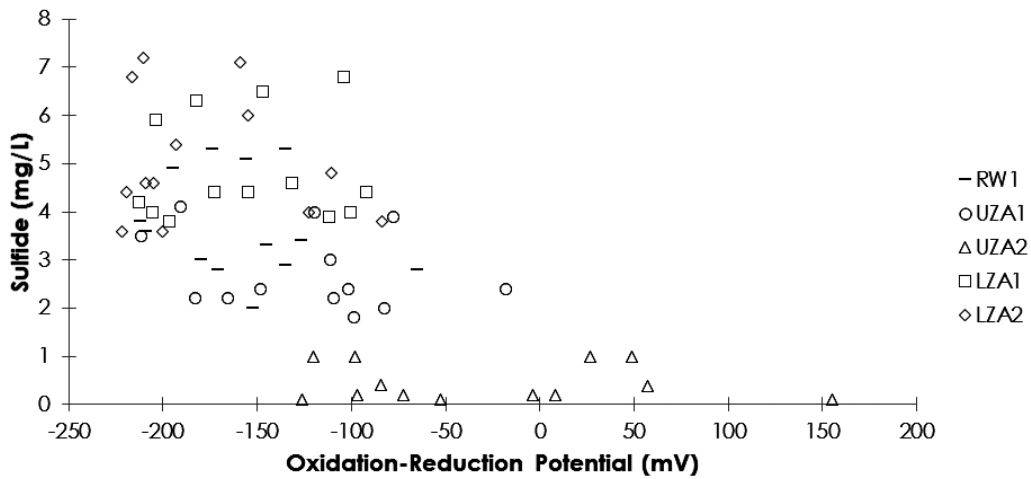
Figure 8. Plot of concentrations of sulfide and measurements of oxidation-reduction potential for Upper Zone and Lower Zone groundwaters.
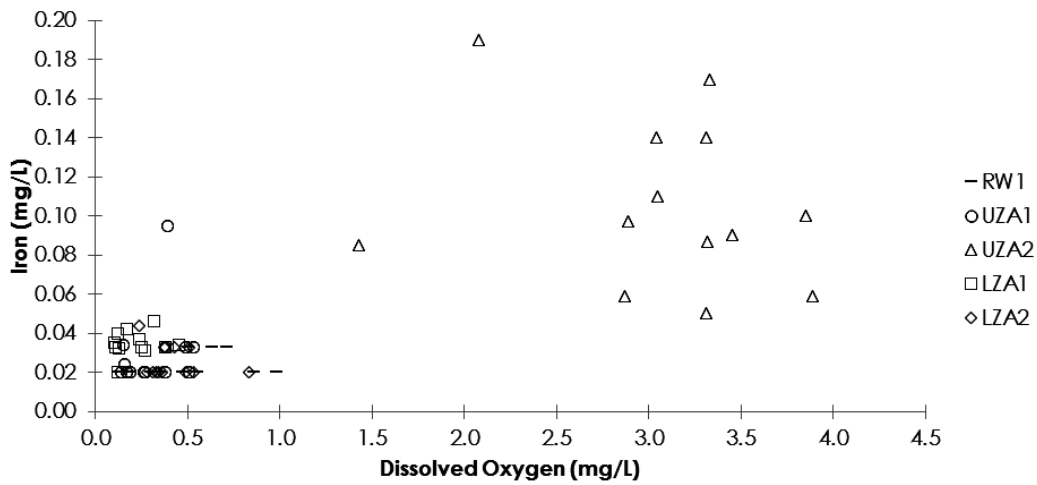

Figure 9. Plot of concentrations of iron and dissolved oxygen for Upper Zone and Lower Zone groundwaters.
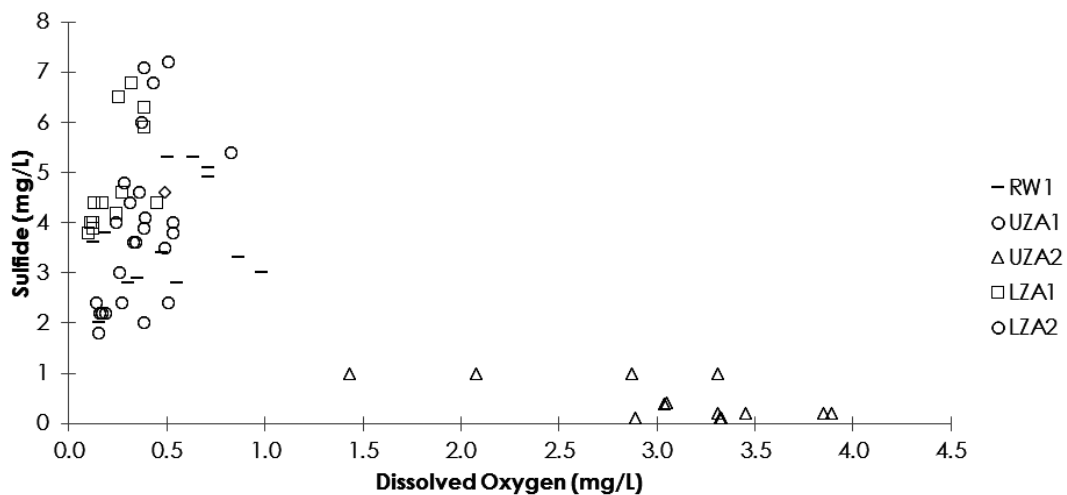

Figure 10. Plot of concentrations of sulfide and dissolved oxygen for Upper Zone and Lower Zone groundwaters.
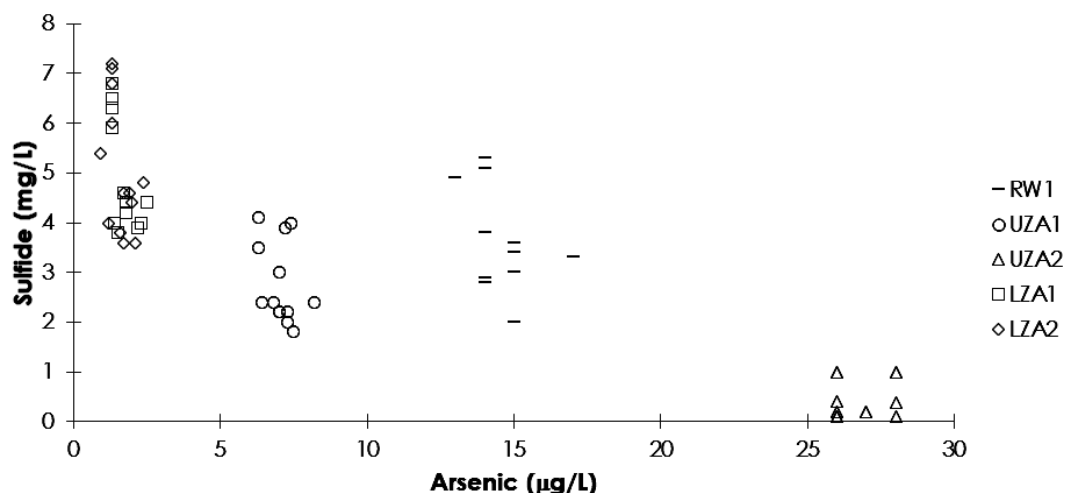
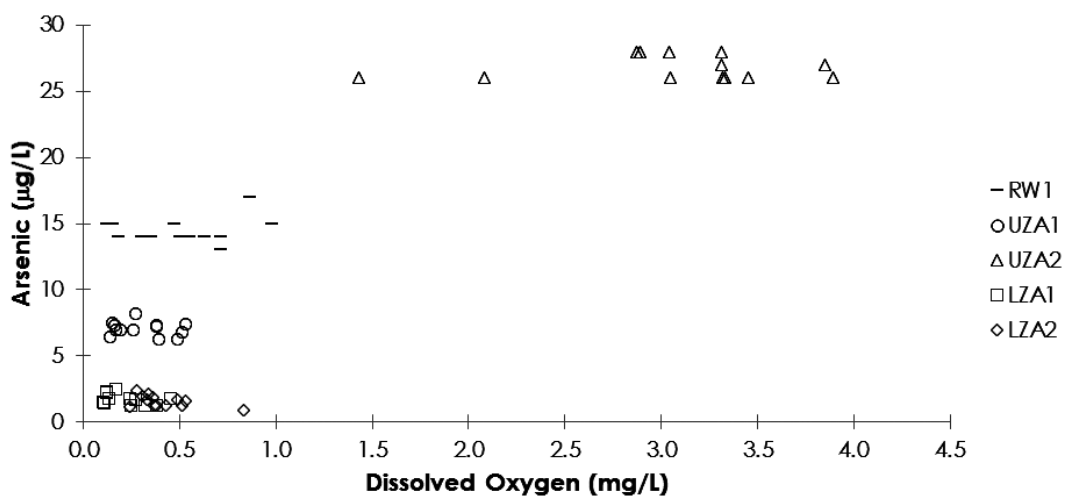**Figure 11.** Plot of concentrations of sulfide and arsenic for Upper Zone and Lower Zone groundwaters.

Figure 12. Plot concentrations of arsenic and dissolved oxygen in Upper Zone and Lower Zone groundwaters.

Discussion

Figures 6 through 12 show that anoxic conditions predominate with respect to the upper and lower zones. Anoxic conditions are most pronounced with respect to LZA1 and LZA2, and slightly less so with regard to UZA1 and RW1. Slight differences in ORP might account for much of the difference in arsenic concentrations among these wells, although the higher TDS and chloride concentrations (i.e., higher ionic strength) of RW1 might indicate the potential for a combination of reductive dissolution and competitive desorption as factors controlling the occurrence of arsenic in higher-TDS groundwaters of the area (Liu et al. 2014).

By any objective set of geochemical criteria, the local groundwater system, exclusive of UZA2, is anoxic. Where DO concentrations are reported as 0.50 mg/L or less, iron concentrations are typically less than 0.04 mg/L, ORP is negative, and sulfide concentrations range from 2 to 7 mg/L. It is noted that DO measurements at concentrations less than 0.5 mg/L in the presence of sulfide might not be reliable. However, the ORP measurements and other redox-related data indicate that geochemical conditions are moderately to strongly anoxic, and that conditions as represented by data from LZA1 and LZA2 underscore the high probability that pyrite, the mineral with which arsenic is most commonly associated in the Suwannee

Limestone, is stable and unlikely to yield arsenic at concentrations greater than 3 µg/L.

Additional support for the dominance of anoxic conditions is found in Eh-pH diagrams on which data from the wells are plotted (Figures 13 and 14). Eh is an electrochemical description of the oxidation state for a system in equilibrium (Bethke 2008). It can be derived from ORP by adding a correction factor (typically an average of 200 millivolts (mV)) to ORP. The correction factor is an empirical adjustment to account for the difference between measured and theoretical voltages of electrodes and electrode solutions at different temperatures.

Figures 13 and 14 show the stability fields of ferrous iron (Fe^{2+}) and ferric iron (Fe^{3+}) under different combinations of Eh and pH, within the stability boundaries of water. The figures were constructed with the Act2 module of Geochemist's Workbench©, v. 10, assuming a system temperature of 25 °C. Eh-pH diagrams can be constructed to include different solid mineral phases, such as pyrite and hematite. Solid phases are not included here because the figures are intended to show only the combinations of Eh and pH under which dissolved iron species predominate in aqueous systems at 25 °C.

In Figure 13, the data from UZA1 plot within the Fe^{2+} field – an indication that ferrous iron is the dominant species of dissolved iron. Data from UZA2, however, lie within the Fe^{2+} and $Fe(OH)_3$ fields – a response to conditions that vary between oxidizing ($Fe(OH)_3$) and reducing (Fe^{2+}) over the narrow pH range for those samples.

With regard to Figure 14, the points from RW1, LZA1, and LZA2 all lie within the Fe^{2+} stability field, over approximately the same narrow range of pH measurements. This indicates that the aqueous environment within the lower zone is reducing and relatively uniform between the LZA1/LZA2 locations and the deeper zone represented by the supply well that provides water for RW1.

Norton et al. (2014) examined potential mineralogical sources of arsenic in conjunction with the Project. The investigation involved examination of petrographic thin sections of 14 core samples from the Suwannee Limestone. The core samples were collected from a depth range of 274-289 feet below land surface, the intended recharge depth. Leaching tests were also conducted on selected samples from the same depth range.

The core samples are described as "peloidal packstone to grainstone with traces of quartz grains and clay" (Norton et al. 2014, 51). The specimens include "sparse grains of pyrite, ilmenite, rutile, iron oxide, chalcopyrite and possible pentlandite (nickel iron sulfide) as well as a few unidentified grains with higher concentrations of the rare earth elements" (Norton et al. 2014, 51). Based on data from associated bulk rock and leaching analyses, Norton et al. (2014) concluded:

- Arsenic concentrations in bulk samples range from below detection limits (< 1 mg/kg) to 2 mg/kg.

- Arsenic concentrations in pyrite range from below detection limits to 1400 (± 350) mg/kg – or near the lower end of the range of 100 to 11,200 mg/kg (the average is 2300 mg/kg) reported by others for the Suwannee Limestone.

- Leaching tests document arsenic concentrations increasing from approximately 2 to 13 µg/L in source water with DO concentrations ranging from less than 10 to 60 µg/L and sharply lower concentrations of arsenic at DO greater than 600 µg/L. Arsenic was detected in solution above 10 µg/L in five of nine leaching tests.

- There is a strong correlation ($R^2 = 0.914$) between the mass of leached arsenic and source water DO concentration up to 60 µg/L.

- The mass of arsenic released to groundwater is highly correlated with other redox-sensitive metals, especially molybdenum ($R^2 = 0.943$) and cadmium ($R^2 = 0.880$).

Conclusions

This paper is a highly condensed summary of work conducted to address a narrow range of questions related to the suitability of the Suwannee Limestone to be an injection zone for purified reclaimed water. The principal geochemical matter of concern is the potential for dissolution of minerals in which arsenic is sequestered either by precipitation/co-precipitation or adsorption. The iron sulfide mineral pyrite has been shown to be the most common source of arsenic at ASR sites in Florida (Arthur, Dabous, and Cowart 2002; Jones and Pichler 2007)
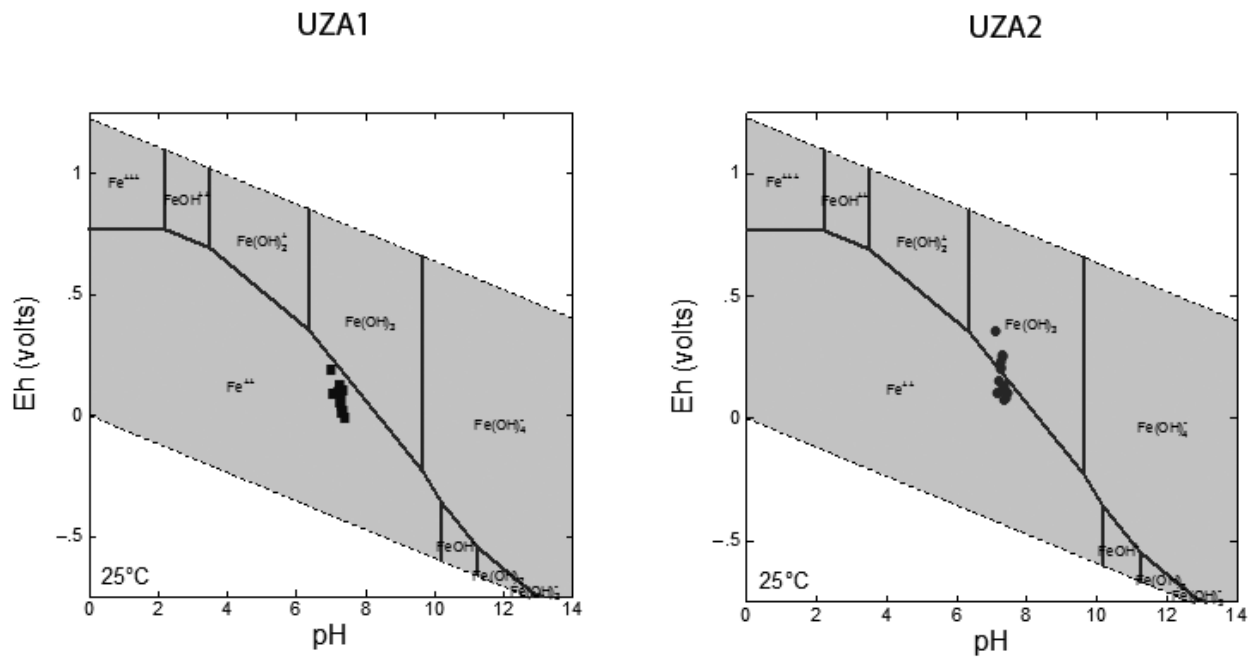
UZA1

UZA2

Figure 13. Eh-pH diagrams (iron-oxygen system), Upper Zone.
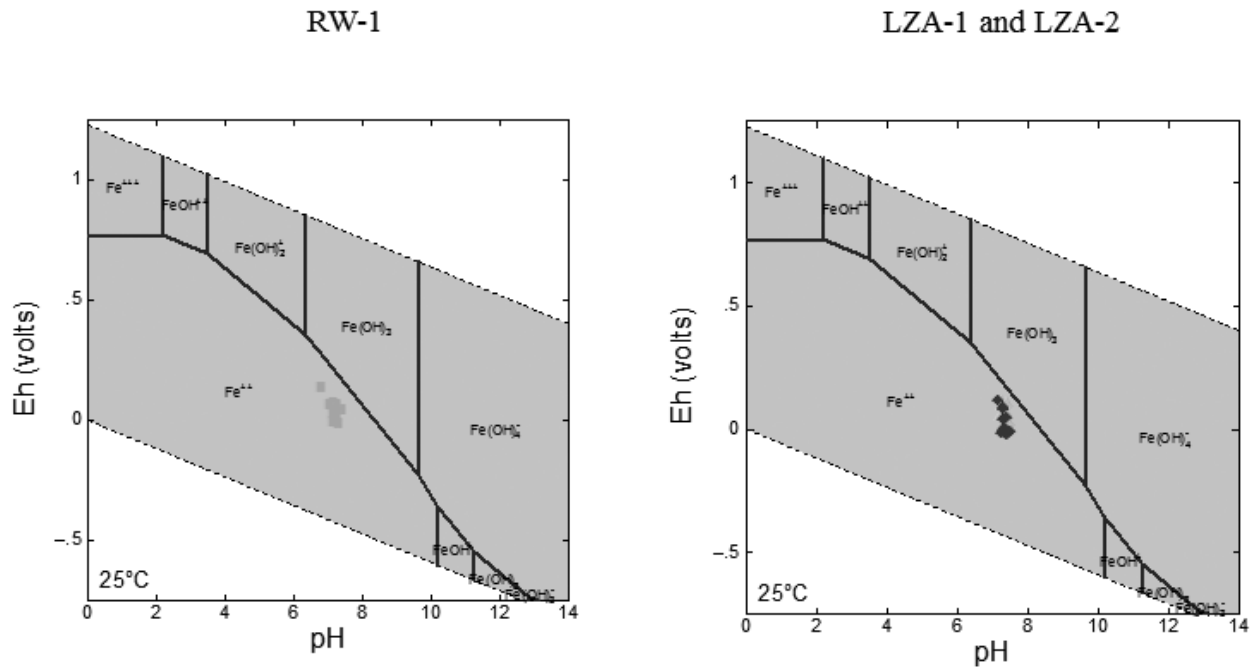
RW-1

LZA-1 and LZA-2

Figure 14. Eh-pH diagrams (iron-oxygen system), Lower Zone.

and at Clearwater (Norton et al. 2014). Other metals of significance at Clearwater are molybdenum and cadmium (Norton et al. 2014). The results of this investigation are consistent with those of other researchers (Arthur, Dabous, and Cowart 2002; Jones and Pichler 2007) and further identify and explain reduction-oxidation factors that control the stability of iron sulfide minerals disseminated within the matrix of the Suwannee Limestone. Significant observations and conclusions from this investigation are the following:

- Upper- and lower-zone groundwaters are calcium-sodium-chloride and sodium-chloride in composition, and all appear to be mixtures of freshwater and seawater. TDS and chloride concentrations are higher in lower-zone groundwaters than in upper-zone groundwaters.

- The lower zone of the Suwannee Limestone is anoxic. This is clearly indicated by negative ORP measurements and DO concentrations less than 0.5 mg/L, sulfide concentrations ranging from 2 to 7 mg/L, and iron concentrations less than 0.04 mg/L.

- Sulfide concentrations greater than 2 mg/L in samples of lower-zone groundwater indicate that the lower zone is anoxic and that DO has probably been exhausted within that part of the groundwater system.

- The upper zone is anoxic in the vicinity of UZA1, but positive ORP measurements and DO concentrations ranging from 1.4 to 3.9 mg/L in samples from UZA2 indicate oxidizing conditions in the vicinity of that well.

- Arsenic occurs naturally in groundwaters of the upper and lower zones. The lowest concentrations of arsenic (0.93 to 2.5 µg/L) are associated with LZA1 and LZA2, wells with consistently negative ORP measurements, elevated sulfide concentrations, and low concentrations of iron. The highest arsenic concentrations (26 to 28 µg/L) are found in samples from UZA2.

- The low iron concentrations (0.020 to 0.046 µg/L) of LZA1 and LZA2 indicate that pyrite, the iron sulfide mineral with which arsenic is most commonly associated in the Suwannee Limestone, is stable in the anoxic environment of the lower zone.

- The low arsenic concentrations associated with LZA1 and LZA2 are probably related to the sequestration of arsenic by pyrite, and the high arsenic concentrations associated with UZA2 are probably related to the release of arsenic through the dissolution of pyrite in that part of the upper zone.

- Arsenic concentrations of approximately 14 µg/L associated with RW1 could be related to competitive desorption in the higher-TDS groundwater produced by the source well. The TDS of this water ranged from 1100 to 1300 mg/L and was higher than the TDS for other lower-zone wells (690 to 860 mg/L).

With regard to the Clearwater AR project, this investigation is one of many components of the City's intensive program to assess the lithological, stratigraphic, hydrogeological, and geochemical characteristics of the Suwannee Limestone and groundwater. The results of this investigation are consistent with those of geochemical studies at other project sites in Florida. As such, the data and associated analyses form a sound basis to help the City's team of hydrogeologists, engineers, and consultants understand the availability of arsenic and the conditions under which it is liberated from the matrix of the Suwannee Limestone, and to design operational procedures to maintain the stability of the sulfide minerals with which arsenic is associated.

Author Bio and Contact Information

Bruce K. Darling is a Senior Hydrogeologist and Geochemist in the Austin, Texas, office of Geosyntec Consultants. He has dealt extensively with matters related to the mobilization and fate of arsenic, uranium, and radium in groundwater systems. He earned a M.S. in geology from the University of Louisiana at Lafayette, and a Ph.D. in geology from The University of Texas at Austin. He may be contacted at: Geosyntec Consultants, 8217 Shoal Creek Blvd., Austin, TX 78757; or bdarling@geosyntec.com.

References

Arthur, J.D., A.A. Dabous, and J.B. Cowart. 2002. Mobilization of arsenic and other trace elements during aquifer storage and recovery, southwest Florida. In: *U.S. Geological Survey Artificial Recharge Workshop Proceedings, Sacramento,*

California, April 2-4. G.R. Aiken and E.L. Kuniansky (Eds.). USGS Open-File Report 02-89: 47-50.

Bethke, C.M. 2008. *Geochemical and Biogeochemical Reaction Modeling*, 2nd ed. Cambridge University Press.

Darling, B.K. 2014. Geochemical Modeling Investigation – City of Clearwater Groundwater Replenishment Project. Geosyntec Consultants report prepared for Leggette, Brashears & Graham. The report is found in Appendix E of *City of Clearwater Groundwater Replenishment: Recharge Test, Geochemistry, and Groundwater Modeling Report*, prepared by Leggette, Brashears & Graham for the City of Clearwater.

Jones, G.W. and T. Pichler. 2007. Relationship between pyrite stability and arsenic mobility during aquifer storage and recovery in southwest central Florida. *Environmental Science & Technology* 41: 723-730.

Liu, C.W., K.L. Lu, Y.H. Kao, C.J. Wang, S.K. Maji, and J.F. Lee. 2014. Identifying sources and controlling factors of arsenic release in saline groundwater aquifers. *Hydrology and Earth System Sciences* 18: 1089-1103.

Norton, S., M. Annable, J. Cho, M. Miller, J. Harris, W. Harris, J. Arthur, and C. Fischler. 2014. Preliminary Evaluation of the Trace Metal Leaching Potential of Source Water from the Clearwater Groundwater Replenishment Project. Contract report prepared by Indewater, LLC, University of Florida, and Florida Geological Survey for the City of Clearwater, Florida. The report is found in Appendix D of *City of Clearwater Groundwater Replenishment: Recharge Test, Geochemistry, and Groundwater Modeling Report*, prepared by Leggette, Brashears & Graham for the City of Clearwater.

Price, R.E. and T. Pichler. 2006. Abundance and mineralogical association of arsenic in the Suwannee Limestone (Florida): Implications for arsenic release during water-rock interaction. *Chemical Geology* 228: 44-56.

Trommer, J. 2014. *City of Clearwater Groundwater Replenishment Test Recharge and Monitoring Well Construction and Testing Report*. Consulting report prepared by Leggette, Brashears & Graham, Inc. for City of Clearwater Engineering Department.