

Final Report

Evaluating Elevated Arsenic and Molybdenum Concentrations at the Pritcher Road Site, Lithia, Central Florida

Prepared for Florida Department of Environmental Protection, Site
Investigation Section

By Dr. Thomas Pichler

April 2010

Executive Summary

Following the discovery of more than 300 µg/L As in a newly installed irrigation well near the village of Lithia in central Florida FDEP SIS sampled and analyzed approximately 100 private supply wells. Of these, 19 showed arsenic concentrations above the current drinking water standard of 10 µg/L. The highest value was 344 µg/L As. In addition many wells had molybdenum (Mo) concentrations above 40 µg/L (the US EPA recommended value). Besides As and Mo, all other parameters were as expected for central Floridan groundwater.

With no obvious anthropogenic or agricultural sources present, the As and Mo are likely of natural (geogenic) origin and released from the aquifer matrix due to a change in physicochemical conditions, such as the rapid infiltration of oxygen-rich surface water into the aquifer. To test this hypothesis 5 multi-level monitoring well clusters were installed in the Lithia are. The cores from 3 wells were logged and sampled for chemical and mineralogical analyses. The monitoring wells and a subset of 40 private supply wells were selected for a comprehensive chemical study, including As speciation, stable isotope analyses and tritium-helium dating.

The chemical study of the water revealed that most groundwater parameters in the monitoring wells and the private supply wells were as expected for central Florida. Only As and Mo showed a distinct pattern of (a) decreasing concentrations with depth and (b) a geographical distribution, with highest values in the center of the study area. A similar pattern could also be observed for $\delta^{18}\text{O}$ and δD , where lighter values were generally found at shallow depth. Isotope values for those private wells with elevated As and Mo fall into the same range as the shallow monitoring wells. Age dates for shallow groundwater samples were younger. Rapid infiltration is likely since the ages between waters collected from very shallow wells (approximately 30 ft) is basically are same ages as those for samples collected from at depth around 150 ft to 170 ft, while samples from just 30 ft deeper are much older. This separation in age also correlates to a separation based on groundwater levels, which decrease with with depth.

In the 3 cores Mo and As varied significantly with depth and values were often significantly above the crustal average for As and Mo. Values were highest between approximately 130 and 250 ft, which is the interval that roughly corresponds to the Hawthorn and Tampa. Below 250 ft, which corresponds to the Suwannee Limestone values returned “normal”, i.e., expected values for crustal carbonate rocks. The mineral pyrite, which was identified in all cores, contained significant amounts of As and was thus identified as a potential source of As. In the core DEP-1 the calcium molybdate, powellite (CaMoO_4), was identified as a source of Mo and as a source of As, because powellite contained up to 18000 mg/kg As. In the subsurface As is elevated at three different depths and at each

of these depths it is associated with different elements. At 30 ft only As and Fe were elevated, while at 150 ft only As and Mo were elevated and at 200 ft only As, Fe and S were elevated. From this it is possible to deduce the mineralogical association of As. In the shallow subsurface where the conditions are still more oxygenated As is likely bound to hydrous ferric oxide (HFO). At the intermediate level off around 150 ft As seems to be more or less exclusively associated with powellite and at 200 ft where Fe and S were elevated, the source of As is likely As-rich pyrite. The inferred As mineralogy in the subsurface in the Lithia area follows an expected redox gradient for groundwater from oxygenated near the surface to more and more reducing conditions at depth.

There is no indication that Mo and As are of anthropogenic origin and thus they should be of geogenic origin and that a change in physicochemical conditions in the aquifer causes their release. However, what causes exactly this change in physicochemical conditions is still unclear. In summary, the combination of massive groundwater pumping to the west of Lithia combined with many private supply wells, which are open to several groundwater horizons in a karstic aquifer create an environment conducive to As and Mo release from the aquifer matrix.

Table of Contents

1. Introduction.....	5
1.1. Working Hypothesis	6
2. Work Plan and Methods.....	8
2.1. Analytical Methods: Water Chemistry.....	9
2.2. Analytical Methods: Rock/Sediment Mineralogy and Chemistry	10
2.3. Analytical Methods: Tritium-Helium Dating.....	12
3. Results and Discussion	13
3.1. Water Chemistry.....	13
3.1.1. Monitoring Well Clusters DEP-1 to DEP-5.....	14
3.1.2. Surficial Monitoring Wells.....	16
3.1.3. Private Supply Wells	17
3.2. Rock/Sediment Chemistry and Mineralogy	18
3.3. T-He Dating	21
3.4. Groundwater levels.....	23
4. Conclusions	23
5. Outlook and Recommendations	27
6. References	27
7. Figures.....	31
8. Tables	52
Appendix: Enchem Tasks	58
Appendix: Water Levels in DEP-1 to DEP-5.....	59
Appendix: Core Description DEP-1	62
Appendix: Core Description DEP-2.....	65
Appendix: Core Chemistry DEP-1	70
Appendix: Core Chemistry DEP-2	72
Appendix: Core Chemistry DEP-5	74

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 is geogenic, i.e., naturally occurring in the aquifer matrix. The release of As from the aquifer matrix, however, is generally caused by anthropogenic perturbations of the physicochemical conditions in the aquifer, such as a redox change. There are a multitude of scientific publications addressing the 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 (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 exist; 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 in addition to our own work (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.

The Pritcher Road site near the village of Lithia in central Florida affords an exceptional field site to study the contamination of groundwater with geogenic As in a limestone aquifer. There, approximately 100 private supply wells were sampled for As, after the discovery of more than 300 µg/L As in a newly installed irrigation well. Similarly high As concentrations were detected in many of the private supply wells. Surprisingly there was no pattern recognizable and wells with low concentrations were adjacent to wells with extremely high concentrations (Fig. 1). Plots of As distribution in private supply wells in Bangladesh show the same enigma and thus new insights from this study may further progress unraveling the As disaster there. In particular, if excessive groundwater withdrawal from select aquifers may cause a sufficient change in physicochemical conditions across the system to cause the release of As (e.g., Ahmed et al., 2006).

Of the approximately 100 private supply wells, 19 wells showed arsenic concentrations above the current drinking water standard of 10 µg/L. The highest value was 344 µg/L. Several wells were also high in molybdenum (Mo), although of lesser concern because Mo is not regulated by the US EPA. Nevertheless there exists a recommended value of 40 µg/L. Besides As and Mo, all other parameters were as expected for central Floridan groundwater.

1.1. Working Hypothesis

With no obvious anthropogenic or agricultural sources present, the arsenic is likely of natural (geogenic) origin, i.e., present in the mineral pyrite, which is part of the aquifer matrix, but released into groundwater due to a change in

physicochemical conditions. The assumption that pyrite is the likely source of As to groundwater was based on detailed investigations about the mineralogical associations of As in the Intermediate Floridan Aquifer (IFA) and Upper Floridan Aquifer (UFA) (Lazareva, 2004; Lazareva and Pichler, 2007; Price, 2003; Price and Pichler, 2002, 2006). The key findings of those studies were that (1) As was only very slightly elevated in the aquifer matrix (3.5 mg/kg vs. 2.6 mg/kg world average in limestone) and (2) As was mostly associated with pyrite as a substitute element for sulfur in the FeS_2 structure. These studies in conjunction with geochemical modeling and observations from aquifer storage and recovery operation (ASR) provided insight into the question whether the interaction (reaction) of water with an aquifer matrix of normal As concentration that can generate high-As groundwater (Pichler and Jones, 2006). A change in physicochemical conditions that selectively affects the stability of pyrite is sufficient to increase As concentrations by several orders of magnitude (Jones and Pichler, 2007).

Assuming that pyrite is the source of arsenic, 4 scenarios (A-D) were considered to explain the high concentrations of arsenic. Each of these scenarios involves a change of hydraulic conditions in the Lithia area, causing the rapid introduction of oxygenated groundwater into the Upper Floridan aquifer where most of the supply wells are screened.

(A) The removal of clays during the phosphate mining process east of the Lithia area, which is hydraulically upgradient of the site, has allowed water with different geochemical characteristics from the surface/surficial aquifer to penetrate into the Suwannee Limestone.

(B) Water from a gypsum stack associated with the former phosphate plant is drained into a creek that straddles the up gradient extent of the site. This creek may be a surface reflection of a fracture that allows the drainage water with different characteristics to migrate quickly into the Suwannee Limestone.

(C) The extensive pumping from the well field located on the western portion of the site has significantly altered the difference in hydraulic head between the

surficial/Intermediate aquifer and the underlying Floridan providing more potential for waters from shallow intervals to migrate into the Suwannee Limestone.

(D) Combination of one or more of the scenarios from above.

2. Work Plan and Methods

To test these hypotheses, 40 private supply wells were selected for further study. Selection was based on the premise of geographical coverage, high As and low As concentrations. These wells were sampled a second time and in addition to the parameters of the previous sampling (turbidity, pH, conductivity, dissolved oxygen, oxygen reduction potential, alkalinity, Al, Sb, As, Br, Cd, Ca, Cl, Cr, Cu, F, Fe, Kie-N, Pb, Mg, Mn, Mo, Ni, N, K, Se, Si, Na, Sr, SO₄, S, P, V, Zn) the following were added: (1) As was speciated (As³⁺, As⁵⁺, DMA and MMA), (2) sulfide was determined in the field and (3) oxygen and hydrogen isotopes ($\delta^{18}\text{O}$ and δD). Those elements of particular interest, such as, sulfide, As, Sb and Mo were analyzed by the FDEP laboratory and also by EnChem for the purpose of quality control. The private supply wells provided only poor information about well depth and screened interval. Thus, FDEP installed 5 monitoring well clusters, each cluster consisting of four screened sampling intervals of 20 ft length at a depth of approximately 150 ft, 200 ft, 260 ft and 300 ft below surface. The cluster locations were chosen in order to represent geographical coverage, as well as high and low As areas (Fig. 2). The cluster DEP-5 was installed away from the area of high As to serve as a reference site. Subsequently the monitoring well clusters were sampled in May, June, October of 2008 and April 2009. The reason for the multiple sample collection was to establish a time series, allowing to observe a potential variation of groundwater chemistry based on: (1) well installation or (2) pumping in the well field to the west of the Pritcher Road site.

In order to test if infiltration of water from the phosphate mine to the east of the Pritcher Road site or infiltration of shallow groundwater (< 30 ft) is a source of As 8 shallow groundwater samples were collected by Geoprobe during the April 2009 sampling event (Fig. 3).

In addition 3 of the 5 geologic cores were described and sampled in detail to delineate the presence of arsenic in the aquifer matrix. This included: (1) the chemical analyses of at least 20 samples per core for As, Sb, Al, Si, Fe, Mg, Ca, P, Sr, S, Mo, and Mn content and (b) preparation of at least 10 thin sections per core for electron microprobe analyses of mineral phases to determine arsenic and antimony concentrations. Sampling consisted of a two-step process, where samples were collected randomly and from areas potentially higher in arsenic, such as fracture zones, framboidal pyrite, iron-oxyhydroxide coatings on limestone/dolostone grains, and high porosity zones containing molds, fractures and various other dissolution features. This sampling approach was successfully applied by Lazareva and Pichler (2007) and Price and Pichler (2006) to assess the importance of pyrite as the source of As in the Upper Floridan Aquifer.

Based on data collected until October 2008, 20 private supply wells and the FDEP monitoring wells were selected and sampled in April 2009 for groundwater dating using the tritium-helium method (T-He) to better assess key questions such as:

- ∞ Is there a correlation of age with predicted flow direction?
- ∞ Is there an increase of ages with depths in the deep aquifer?
- ∞ Is there a correlation of age with Arsenic concentration?
- ∞ Is there young water in deeper aquifer?
- ∞ Where are the pathways from upper to lower aquifer?

2.1. Analytical Methods: Water Chemistry

The FDEP staff and laboratories carried out the bulk of the field measurements and chemical analyses. Exceptions were As-speciation, total As, Sb, Mo, stable isotope and field-based sulfide analyses, which were provided by EnChem and by the University of California at Davis Stable Isotope Facility. The stable oxygen and hydrogen isotopes were determined by simultaneous analysis of $^{18}\text{O}/^{16}\text{O}$ and D/H isotope ratios in liquid water samples using an LGR DLT-100 instrument (Los Gatos Research, Inc., Mountain View, CA, USA). Each sample was injected 6 times, the first 3 injections are discarded to eliminate memory effects, and the

average of injections 4, 5 and 6 was used for isotope ratio calculations. Working standard waters calibrated against NIST standard reference materials (VSMOW, GISP, SLAP), were inserted in the sample sequence (usually before and after each group of 6 unknowns). Sample isotope ratios are adjusted to working reference waters. Results are given in delta notation ($\delta^{18}\text{O}$ and δD) relative to Vienna Standard Mean Ocean Water (VSMOW). Precision was better than 0.3 ‰ and 0.8 ‰ for $\delta^{18}\text{O}$ and δD , respectively.

Total As and Sb concentrations were analyzed by hydride generation-atomic fluorescence spectrometry (HG-AFS) on a PSA Millenium instrument following procedures by (Price and Pichler, 2005, 2006). A 2% solution of potassium iodide was used to reduce As(V) to As(III) prior to hydride generation. The 4 arsenic species, As(III), DMA, MMA and As(V) were separated in a Hamilton PRP-X100 column using a potassium phosphate buffer prior to HG-AFS analysis. The quality of the speciation data was confirmed by comparing total As to the sum of As species. Molybdenum (Mo) was determined on a Perkin Elmer Optima 2000 DV inductively coupled plasma – optical emission spectrometer (ICP-OES). The accuracy and precision of the measurements were verified through the use of internal and external standards.

Sulfide was determined in the field by photo spectrometry using a HACH DR 2400 Portable Spectrophotometer following the USEPA approved Methylene Blue method.

2.2. Analytical Methods: Rock/Sediment Mineralogy and Chemistry

The cores from the well clusters DEP-1, DEP-2 and DEP-5 were described in hand sample, using hand lens and stereo-microscope. A total of 219 samples were selected for further chemical and mineralogical analyses: DEP-1 (56), DEP-2 (88) and DEP-5 (75). Those samples for chemical analyses were dried at room temperature and subsequently powdered by hand with an agate mortar and pestle, which was cleaned with pure quartz sand and rinsed with distilled water between samples to prevent cross contamination. Approximately $0.5 \text{ g} \pm .005 \text{ g}$ of powdered sample was weighed into vials for digestion with aqua

regia, a 3:1 mixture of HCl and HNO₃. The samples were capped with a ribbed plastic watch glass to prevent the escape of arsine gas and placed on a hot block for 30 minutes at 80 °C. The glasses were then removed and the condensation rinsed from each lid with DI. For each digestion batch, 54 samples, 2 internal standards (homogenous local limestone), 1 external standard (JLS-1), 2 spiked samples, and a blank were included for quality control. Once cooled the digestates were diluted to 50 mL with DI water and allowed to settle for at least 24 hours before being passed through a 2.0 µm Teflon. Two mL of the filtered samples were diluted with 8 mL of DI for the determination of on the Perkin Elmer Optima 2000 DV inductively coupled plasma – optical emission spectrometer (ICP-OES) for Al, Si, Fe, Mg, Ca, P, Sr, S, Mo, and Mn following procedures by (Price and Pichler, 2006).

A second aliquot of each sample was prepared for As and Sb analysis using hydride generation-atomic fluorescence spectrometry (HG-AFS) on a PSA 10.055 Millennium Excalibur instrument following procedures by (Price and Pichler, 2006). Ten (10) mL of digested sample were transferred to a new Teflon vial. Then 15 mL trace metal grade HCl and 1 mL saturated KI solution were added to reduce the As to As³⁺. Each aliquot was finally diluted to 50 mL with DI water.

To assure quality control duplicate samples were randomly selected for approximately 10% of the samples and had a reproducibility of ≥ 95% on the ICP-OES and ≥ 90% on the HG-AFS. Sample blanks, which were added every 5 to 10 samples did not show detectable concentrations of As or Sb. To test for recovery, 2 samples from each batch were spiked with 25 mg/kg As before digestion. Recovery of As was always between 90 % and 110 %.

Polished thin sections were made for 20 samples high in As and Mo for further analyses of discrete mineral phases by transmitted and reflective light microscopy as well as electron microprobe analysis (EMPA). The thin sections were analyzed with a Nikon Eclipse LV100 POL petrographic microscope to determine the presence and mineral associations of pyrite and to delineate targets for EMPA. The individual pyrites and other targets were then analyzed for

As, Mo, Ca, Zn, Fe, S, and Sb with a JEOL JXA-8900R instrument. Reference materials consisted of natural and synthetic sulfide, sulfate, silicate, and oxide. Calcium was analyzed as an excitation-volume monitor during sulfide analysis as some samples were small, irregular, and thin. The analyses were corrected for electron beam and matrix effects, and instrumental drift and dead time using a Phi-Rho-Z algorithm supplied with the JEOL WDS electron microprobe (Armstrong, 1995). Relative accuracy of the analyses, based upon comparison between measured and published compositions of standard reference materials, is ~1-2 % for concentrations >1 wt. % and ~5-10% for concentrations <1 wt.%. Analyzed elements and oxides and their detection limits (wt.%) at 3 sigma (background) are as follows: Sb (0.02), As (0.05), Fe (0.03), S (0.03), Zn (0.07), Mo (0.08), FeO (0.05), SrO (0.09), MnO (0.04), BaO (0.04), CaO (0.04), As₂O₅ (0.09), MgO (0.03), SO₄ (0.08).

2.3. Analytical Methods: Tritium-Helium Dating

To avoid atmospheric contamination the samples were taken after excessive well purging. Conductivity, temperature, pH and oxygen content were monitored and sampling took place only once values were stable. The samples to be used for helium and neon analyses, and determination of the ³He/⁴He isotope ratio ($\delta^3\text{He}$) of dissolved helium were collected (in duplicate) into specially prepared copper sample tubes. The copper tubes were flushed for 5 minutes prior to capping. During sampling, the copper tubes were attached with clear Tygon[®] tubing to visually observe whether air bubbles are present in the water line. The sample fraction to be used for tritium determination by helium ingrowth was collected in duplicate into Safety-coated 500 mL glass bottles with polycone seals.

Analysis of ³H, He isotopes and Ne for ³H-³He dating was conducted at the noble gas laboratory of the Institute of Environmental Physics, University of Bremen. For the He and Ne isotope analysis all gases were extracted from water. He and Ne were separated from other gases with a cryo system kept at 25 K and 14 K and ⁴He, ²⁰Ne and ²²Ne were measured with a quadrupole mass spectrometer. The helium isotopes were analyzed with a high-resolution sector

field mass spectrometer (MAP 215-50). The system was calibrated with atmospheric air and controlled for stable conditions for the He and Ne concentrations and the $^3\text{He}/^4\text{He}$ ratio. For groundwater samples, the precision of the He and Ne concentrations was better than 1 % and for the $^3\text{He}/^4\text{He}$ ratio better than 0.5 %.

Tritium (^3H) was analyzed with the ^3He -ingrowth method (Clarke et al. 1976). Samples of 500 g of water were degassed and stored to allow for the accumulation of the ^3He the ^3H decay product in dedicated He-free glass bulbs. After a period of 6 months ^3He was analyzed using the MAP 215-50 instrument. This method achieves a detection limit of 0.01 TU, which allowed the detection of the residue of pre-bomb ^3H . The uncertainty was typically less than 3 % for samples of > 1 TU and 0.01 TU for very low concentrations. For ideal samples, analytical conditions allow a time resolution of about 3 months for apparent ages of less than 10 years. Unknown hydrogeological conditions affecting gas exchange, as for example inaccurate temperatures assumed for gas exchange with the atmosphere (Solomon and Cook, 2000) lead to a time resolution of about 0.5 to 1.0 year (Kipfer et al., 2002). More details of the sampling, analysis and data evaluation of the method are given in (Sültenfuß et al., 2009).

3. Results and Discussion

3.1. Water Chemistry

The analytical quality of the data was very good. There is excellent agreement for As data between the EnChem and the FLDEP laboratories. This provides the necessary confidence for data interpretation, since the distribution of As, Sb and Mo did not show any logical pattern.

Sample duplicates and field blanks demonstrated good reproducibility and the absence of sampling related contamination. Major and trace elements and hydrogen and oxygen isotopes stayed well within their analytical uncertainty of around 3 to 5 %. With the exception of samples from well DEP-1-165 charge balances were better than 5 %. This well showed some grout problems, as indicated by low Mg values, high pH and high K values. However once OH^- was

added to the charge balance the error also dropped below 10 %. Based on the analyses of sample duplicates As speciation data was deemed reliable (better than 10 % deviation) for samples with total As concentrations of > 10 µg/L.

3.1.1. Monitoring Well Clusters DEP-1 to DEP-5

Following installation, the monitoring well clusters DEP-1, DEP-2, DEP-3, DEP-4 and DEP-5 were sampled in May, June, October of 2008 and April 2009. The water was of the HCO₃-Ca type and most monitored elements showed little variation (Fig. 4 and Table 1). Water Type and distribution in the Piper diagram were as expected for Floridan groundwater (compare to Fig. 10 in Sacks, 1996). Only those elements sensitive to changes in redox conditions, such as, sulfide, oxygen, iron and arsenic showed larger variations.

Field Measurements: Those measurements done in the field by electrode, such as, oxygen (DO), ORP and turbidity showed a somewhat erratic data distribution. Changing oxygen values, for example were not recorded in ORP and vice versa. Turbidity was low but also showed unexpected variation with time. One would have expected turbidity values to constantly drop with time. Only pH and conductivity showed stable readings.

Sulfide: There was excellent agreement between those sulfide measurements made in the field and those in the laboratory ($r^2=0.89$). This indicates that sulfide did not oxidize to sulfate from the time of sampling until its analysis in the laboratory. For all subsequent calculations the laboratory values will be used. All wells showed the same pattern of increasing sulfide concentrations with depth (Fig. 5). In wells DEP-1 and DEP-2, there was only very little variation with time, whereas the other three wells showed increasing or decreasing values of sulfide with time. This would indicate that the groundwater conditions were disturbed during well installation, but are slowly returning to pre-installation conditions. This is particularly evident in well DEP-4 and to a lesser degree in DEP-5 where sulfide and As are inversely correlated. This is an argument to use the data from the most recent sampling for further discussion of the site.

Vanadium (V): Vanadium concentrations remained below the detection limit of 5 µg/L, except for the shallow interval in DEP-1 and DEP-2, where values were approximately 25 and 10 µg/L, respectively. However, only the value in DEP-1 could be verified by a second sampling.

Nickel (Ni): Nickel concentrations weakly correlated with those of Mo. Whenever Mo was substantially elevated above the assumed background concentration of approximately 0.5 µg/L Ni was detected at concentration above the detection limit of 0.25 µg/L. Values were never above a level considered detrimental to drinking water quality. It is likely that Ni is a minor element in the mineral powellite (CaMoO_4) and released during powellite dissolution.

Arsenic (As): Arsenic values were generated by two laboratories, the FDEP laboratory and the USF Center for Water Analyses. There was good agreement between the two data sets ($r^2=0.989$). Arsenic showed a most erratic behavior and without confirmation by two independent laboratories there would have been doubt about the data quality. Generally those wells with high values had relatively stable As concentrations, some times they displayed a slight increase with time. Those samples with lower As concentrations often showed decreasing trends with time (see sulfide above). This trend was particularly strong for six monitoring intervals, DEP-1-270, DEP-2-276, DEP-4-228, DEP-4-275, DEP-5-173 and DEP-5-270 (Fig. 6). In this set of samples an even more pronounced trend of decreasing values could be observed for Mo (Fig. 6). With the exception of DEP-5-173 these observations are confined to the deeper intervals. The reason for the declining values could be that during well installation oxygenated surface water was introduced into the deeper aquifer where due to the associated change in groundwater conditions, powellite and pyrite became instable and released As and Mo. Once well installation was completed the groundwater conditions slowly returned to pre-installation, “normal” conditions. Hence, the observed decline in As and Mo concentrations.

There was no statistically significant linear correlation between sulfide and As, although those wells with high As concentrations (DEP-1, DEP-2 and DEP-3) showed a clear pattern of low sulfide and high As (Fig. 5). In well DEP-4 this

pattern is much less developed and it is absent in well DEP-5 (Fig. 5). Arsenic speciation data confirmed the presence of arsenate (As^{5+}) in the those samples collected from the shallow wells (Fig. 7), which would indicate either a redox disequilibrium with respect to $\text{As}^{3+}/\text{As}^{5+}$, but more likely that As was released under more oxygenated conditions as one would expect for groundwater from a depth of more than 150 ft. The deeper groundwater samples show virtually no As^{3+} . These observations correlate well with the results for sulfide concentrations and the sulfate to sulfide ($\text{SO}_4^{2-}/\text{S}^{2-}$) ratio (Fig.8).

In summary, most groundwater parameters compared to those of the private supply wells and were as expected for central Florida (Sacks, 1996; Sacks et al., 1995; Sacks and Tihansky, 1996). Only As and Mo showed a distinct pattern of (a) decreasing concentrations with depth (Fig. 9) and (b) a geographical distribution, with highest values in the center of the study area (Fig. 1).

A similar pattern could also be observed for $\delta^{18}\text{O}$ and δD , where lighter values were generally found at shallow depth; thus low $\delta^{18}\text{O}$ and δD did correlate to some degree with As and Mo. This becomes particularly evident in a comparison of monitoring and private wells, where most of the elevated As and Mo values fall into the isotopic range of the shallow monitoring wells (Fig. 10). This indicates that those supply wells with high As and Mo concentrations are likely screened shallower than those wells with lower to “normal” concentrations.

The observed separation (based on As, Mo and isotope values) between the shallow sampling depth of approximately 145-165 ft and the deeper intervals was also observed in the height of the groundwater table. In all monitoring well clusters (DEP-1 to DEP-5, Fig. 2) the water level in the shallow interval was consistently 3 to 6 ft higher than in the deeper intervals, indicating two different aquifers (APPENDIX: Water Levels).

3.1.2. Surficial Monitoring Wells

The chemical composition for the surficial wells MW-1, MW-2, MW-3, MW-4, MW-5, MW-6, MW-7 and MW-8 was as expected for water in the Surficial

Floridan Aquifer, where water composition is much more variable than in the confined Upper Floridan Aquifer (Table 2 and Fig. 4). The overall quality of the chemical analyses was excellent; all calculated charge balances were better than $\pm 5\%$. Particularly the two wells, MW-2 and MW-3, which were located on the Mosaic Phosphates Company property showed extreme values for $\delta^{18}\text{O}$, δD , SO_4 and Fe (Table 2). These values are due to extreme evaporation in the clay settling area of the Mosaic property. The well MW-6, which is located in an agricultural area between the well clusters DEP-2 and DEP-1 (Fig. 2), showed the highest N and Cl concentrations. These concentrations are likely the result of fertilizer use. After exclusion of these three wells the remaining 5 wells are of a comparable water type to the DEP well clusters (Fig. 4). The surficial wells, with the exception of MW-2 and MW-3 show the lowest δD and $\delta^{18}\text{O}$ values. This fits well with the observed values for the DEP monitoring wells, where the shallow intervals had lower isotope values (Table 1).

In all MW samples As and Mo were below their recommended abundance of less than 10 $\mu\text{g/L}$ and 40 $\mu\text{g/L}$, respectively. Thus infiltration of As or Mo from the Surficial into Upper Floridan Aquifer seems not to be a mechanism responsible for the elevated concentrations seen in the private supply wells in the Lithia area and in the monitoring well clusters, DEP-1 to DEP-5.

3.1.3. Private Supply Wells

Private supply wells were sampled up to two times (Table 3). Most measured parameters remained stable within their analytical uncertainty. Arsenic and Mo values varied more than other elements, but did not show a predictable pattern, values increased in some wells while they decreased in others. Some high values of Zn and V are likely a result of plumbing. Of real concern is the water quality at 8710 COUNTY LINE ROAD, where As is low, however, many other heavy metals were elevated. The second analyses of the subset of 40 private supply wells in December 2007 confirmed the values of the initial sampling in May 2007. Arsenic ranged from 0.1 to 350 $\mu\text{g/L}$ and the correlation of the values between the two laboratories was excellent ($r^2 = 0.998$). The As speciation data was inconclusive; in some samples As^{3+} was the dominating species, while in

other As^{5+} . There was no correlation between As speciation and those of other redox indicators, such as ORP, DO, S^{2-} or the sulfide to sulfate ratio. This should indicate that the water samples, as collected, are out of redox equilibrium, which may be a result of sampling or alternatively that different water mix in the well itself during extraction (see the different water types determined in the DEP monitoring wells and the surficial wells). However, to some degree, total As concentration showed a positive correlation with total SO_4^{2-} and $\text{SO}_4^{2-}/\text{S}^{2-}$ ratio (Fig. 11), indicating both the release of SO_4^{2-} from the aquifer matrix and potentially slightly oxygenated conditions, because under reducing conditions S released from the aquifer matrix would be present as S^{2-} . No reliable data for the screened interval was available for the private supply wells, thus it is concluded that data from these wells is not beneficial to the interpretation of groundwater processes in the Lithia area.

Oxygen and hydrogen isotope data from the public supply wells, as well as the 5 monitoring well clusters indicate that the bulk of the contamination is confined to the shallow aquifer between 140 and 170 ft. Thus we can assume that those private supply wells high in As and Mo are open to that depth. Furthermore the final concentration of Mo and As in each well may be a result of what percentage of the total screen is between 140 and 170 ft

3.2. Rock/Sediment Chemistry and Mineralogy

After the petrographic examination of cores from wells DEP-1 and DEP-2 the lithological boundaries in the study area were determined as follows: Surficial Sediments 0 to 55 ft, Hawthorn Group 55 to 200 ft, Tampa 200 to 230 ft and Suwannee Limestone below 230 ft (down to the maximum well depths of approximately 350 ft). A detailed description is attached as APPENDIX (Core Description). With exception of the uppermost sediments, calcium carbonates were the main lithology. Occasionally dolomite and clay minerals were present.

This lithology was also observed in the bulk sediment chemical composition, where Ca was generally above 300 000 mg/kg. A detailed chemical composition is presented as an APPENDIX (Core Chemistry). Molybdenum and

As varied significantly with depth (Fig. 12) and values were significantly above the crustal average for Mo of approximately 1.1 mg/kg (Li, 2000). Values were highest between approximately 130 and 250 ft, which is the interval that roughly corresponds to the Hawthorn and Tampa. Below 250 ft, which corresponds to the Suwannee Limestone values returned “normal”, i.e., expected values for crustal carbonate rocks. DEP-5, which was the reference core outside of the immediate area of contamination did not differ from DEP-1 and DEP-2. Surprisingly DEP-5 had higher Mo and As values than DEP-2, which is the core from the monitoring well cluster with much higher Mo and As values. However it is not advisable to compare the abundance of Mo and As in the aquifer matrix directly to those in the groundwater. It has been shown that even small amounts in the aquifer matrix can cause high values in groundwater, if the physicochemical conditions are changed (Pichler and Jones, 2006).

The high concentrations of Mo and As were also confirmed during the mineralogical analysis of the core material from DEP-1 and DEP-2. During the description of hand specimens, pyrite was identified in both cores and later verified by reflected light microscopy. Pyrite was present in euhedral, massive and framboidal forms (Fig. 13 B-D). Electron microprobe analyses revealed variable concentrations of As in pyrite ranging from approximately 200 to 9 000 mg/kg (Table 5). These values are in the same range as those previously reported for the Hawthorn Group (Lazareva and Pichler, 2007) and Suwannee Limestone (Price and Pichler, 2006). Thus oxidation of pyrite has the potential to release large amounts of As to the groundwater in the Lithia area. The bulk concentration of Fe and S in the three cores correlated well and plotted along the “pyrite” line (Fig. 14), indicating that pyrite is ubiquitous in the aquifer matrix.

The calcium molybdate powellite (CaMoO_4) was identified in DEP-1. It occurred as very small grains of approximately 20 μm diameter (Fig. 13A). Identification was made using EDX spectra obtained in the EMPA (Fig. 15). This is the first description of powellite in Florida and should be closely linked to the high Mo concentrations found in the monitoring and private supply wells. Powellite contained up to 18 000 mg/kg As (Table 5), which would explain the correlation

between Mo and As in the monitoring well water samples ($r^2 = 0.91$, Fig. 16), assuming that the dissolution of powellite is a possible source for elevated As and Mo in the private supply wells and the DEP monitoring wells. (Note: although powellite was only observed in the core from DEP-1 it is very likely that this mineral is present in all other cores where Mo concentrations are high.)

Taking a closer look at core DEP-2 (Fig. 12) it becomes evident that arsenic is elevated at three different depths, at around 30 ft (bls), at around 150 ft (bls) and at around 200 ft (bls). Surprisingly, at each of these depths arsenic is associated with different elements. At 30 ft only As and Fe were elevated, while at 150 ft only As and Mo were elevated and at 200 ft only As, Fe and S were elevated. From this it is possible to deduce the mineralogical association of As. In the shallow subsurface where the conditions are still more oxygenated As is likely bound to hydrous ferric oxide, which is common (Raven et al., 1998). At the intermediate level off around 150 ft As seems to be more or less exclusively associated with powellite and at 200 ft where Fe and S were elevated, the source of As is likely As-rich pyrite. Unfortunately the shallow sections were not analyzed in the cores from wells DEP-1 and DEP-5 and thus the presence of hydrous ferric oxide was not confirmed. Nevertheless, these two cores showed the same correlation of As and Mo at a depth of around 150 ft and Fe, S and As at a depth of approximately 200 ft. Interestingly the inferred As mineralogy in the subsurface in the Lithia area follows an expected redox gradient for groundwater from oxygenated near the surface to more and more reducing conditions at depth. Hydrous ferric oxides are generally stable under oxygen-rich conditions (Jambor and Dutrizac, 1998), while powellite is stable in intermediate conditions and pyrite under reducing conditions (Rickard, 1968).

In summary, stereo microscope and reflected light microscope analyses showed that pyrite was present in most samples, which were selected for microprobe analysis. The average concentration of As in approximately 90 pyrite crystals from all samples was more than 2000 mg/kg, which is more than sufficient As to account for the high As values seen in groundwater in the Lithia area. Those pyrites higher in the stratigraphy had generally higher As

concentrations. As part of this investigation the mineral powellite (CaMoO_4) was encountered in one core DEP-1. This mineral was not previously described in Florida. Although one of the more common molybdates, this is a relatively rare mineral. Its presence explains the extremely high Mo concentrations seen in the groundwater in the Lithia area, as well as the correlation between As and Mo for those samples high in the two elements. Arsenic concentrations in powellite were as high as 18,000 mg/kg. The occurrence of powellite correlated well with those sampling intervals highest in Mo in the monitoring wells and more importantly the ratios of As and Mo were similar in groundwater (18 to 25) and mineral (23). This indicates the likely dissolution of powellite as the source of Mo and As seen in those samples. The reverse that the high Mo values in groundwater cause the precipitation of powellite cannot be immediately ruled out, since evidently powellite is a very late phase (Fig. 15). However, unpublished data from a recent study of the Avon Park Formation showed the presence of powellite at a depth of more than 700 ft (bls). At this depth and location anthropogenic interference can be ruled out, therefore demonstrating the “natural” occurrence of powellite in the Floridan subsurface.

3.3. T-He Dating

The results of the Tritium-He dating should elucidate whether these changes in physicochemical conditions are caused by (a) forced lateral movement due to pumping or (b) forced vertical flow and the associated input of younger, potentially oxygen-rich water into the shallow aquifer.

In total 48 samples were analyzed for tritium (^3H) and for 39 samples Ne and He isotope data could be obtained. Most samples were analyzed twice and showed high reproducibility. Therefore the data was judged as very reliable. The focus was to use ^3H as a tracer for young water and the by alpha decay produced ^4He or so called radiogenic ^4He , as a tracer for old water. The achieved detection limit for ^3H was 0.025 TU (tritium units) and allowed to detect natural ^3H from before 1950. The precision for ^3He , ^4He and Ne was 1%. The resulting error for ^3He from ^3H decay (tritogenic ^3He) was 0.5 to 1 TU. The uncertainty for the

calculated ^3H - ^3He age resulting from analytical conditions was therefore about 1 to 2 years.

In general the calculated ages correlated with depth. All surficial wells, MW-1 to MW-8, displayed water ages of about 20 to 30 years (Table 6). The sum of ^3H (Fig. 17, red bars) and tritiogenic ^3He (blue bars) of the samples add up to the ^3H concentration in precipitation at the calculated infiltration time period. Thus a ^3H free component (older than 1950) can be ruled out.

The waters collected from the shallow interval in monitoring wells DEP-1, DEP-2, DEP-3 and DEP-5 were younger water in the range of about 30 to 40 years (Table 6). Nevertheless, those samples also contain an older ^3H -free water component. Decay corrected ^3H concentration in precipitation in Florida always exceeds 2 TU. Hence all samples with ^3H less than 2 TU contain older, ^3H -free waters. The ^3H concentrations of the deeper samples were below 1% of the concentration of ^3H in precipitation of the last decades, thus excluding an addition of younger water to those depths. Hence all samples with ^3H less than 2 TU contain older, ^3H -free waters. Because of the relatively short screen length that has was not expected for the shallow depths.

All surficial wells are free of radiogenic ^4He . From this we deduce a maximum ^4He accumulation rate $3\text{E-}8$ ccSTP/kg/yr. Hence the high radiogenic concentration in the private wells must point to very old water (> 1000 yrs). The predominant set of samples (Fig. 18, black diamonds) contained only atmospheric ^4He and Ne. Four samples displayed a significant concentration of radiogenic ^4He (Fig 14, no.: 39, 24, 27 & 21). Values of ^4He are used as an indicator for old water and typical ages derived from such ^4He values are some hundreds to some thousands years in age. Those 4 samples were all from private supply wells, which also contained significant concentrations of ^3H (0.65 – 1.63 TU). The presence of both, significant ^3H and ^4He , in those wells can only be explained by mixing between very old and younger waters in the well itself, i.e., a long filter screen. On the other hand several samples had low ^4He concentration, but did not contain significant ^3H .

Only one of the private wells was virtually ^3H -free (< 0.025 TU), whereas all samples from DEP wells with depths below 215 ft were free of ^3H . The same deep DEP monitoring well samples also contained As below $0.5\text{ }\mu\text{g/L}$.

3.4. Groundwater levels

The groundwater level measurements for the surficial monitoring wells and the DEP monitoring wells show a decrease of water level with depth, indicating three potential aquifers and a potential downward movement of groundwater (Appendix: Water Levels). Differences in water level between the surficial wells and the DEP wells are up to 30 ft, while the differences between the shallow and deep intervals in the DEP wells are only between 3 and 6 ft (Fig. 19). The well DEP-5 did not show the same separation. In DEP-5 the first two intervals showed more or less identical water levels, which were separated from the two deeper intervals by only 1 ft to 1.5 ft (Fig. 19). Despite this separation all DEP wells underwent the same water level fluctuation with time of up to 15 ft (Fig. 20), indicating that they are hydraulically connected. If the surficial wells undergo the same water level fluctuations remains unknown, because they were only measured once in April 2009. A natural process which would cause these large fluctuations is hard to imagine, particularly in the Lithia area, which is topographically flat and removed from the ocean by more than 30 miles. Thus pumping in the well field to the west of the study area should be the cause.

4. Conclusions

The large fluctuations in groundwater level, which are up to 15 ft, may be a potential trigger of As release in the unconfined surficial aquifer: (1) during the drop in water level, conditions in the upper part of the aquifer may change from saturated to vadose, (2) pyrite oxidizes and As is being released, (3) ferrous iron (FeII), which is also released oxidizes to ferric iron (FeIII) and hydrous ferric oxide (HFO) precipitates, (4) As is adsorbed to the HFO, (5) HFO remains stable as long as conditions are of a vadose nature, (6) pumping stops/shifts and the conditions slowly change to saturated again, (7) in the absence of oxygen HFO becomes unstable and As is being released, (8) this time As remains in solution

because the formation of pyrite, which could immobilize As, is much slower than the precipitation of HFO. Those private supply wells, which are open to the surficial aquifer may tap into this As reservoir. While the DEP wells undergo the same fluctuations, it is not likely that the aquifer changes from saturated to vadose.

Based on the interpretation of available data it becomes evident that despite its relatively small area, the geochemical and hydrogeological setting in Lithia is very complex. The combination of extensive cyclical pumping in the well field to the east cause large fluctuations in groundwater levels and may activate fracture flow, thus (1) facilitating the rapid recharge of surface water into the aquifer or (2) causing the upward movement of deeper groundwater into the shallow regions of the aquifer. During both processes the result is a change in redox conditions, which affects the stability of minerals present in the aquifer matrix. The exchange between different groundwater bodies, i.e., deep and shallow, is potentially enhanced due to the installation of more than 100 private supply wells in the Lithia area. Most of these wells have large open screened intervals, which allow water movement between the different water bodies. With respect to arsenic (As), the already complex situation is further complicated by its mineralogical association in the aquifer matrix. In the shallow aquifer As is mainly bound to hydrous ferric oxides (HFO), while in the intermediate aquifer it is bound to the mineral powellite (CaMoO_4) and in the deeper portions of the aquifer it is bound to pyrite. Of these minerals particularly HFO and pyrite are greatly affected by a change in redox conditions, such as the movement of reducing groundwater into the shallow aquifer or movement of oxygenated groundwater into the deeper aquifer. The calcium molybdate, powellite, likely form under somewhat oxygenated conditions, because under reducing conditions the molybdenum sulfide, molybdenite (MoS_2) would form. However after precipitation, the stability of powellite is not as readily affected by a change in redox anymore. Its stability is now more or less controlled by the ion activity product (IAP) of Ca and Mo. Thus groundwater movement and mixing of different groundwaters are likely the largest impact on its stability. The large fluctuations in

groundwater level in combination with a karsitic aquifer and more than 100 private supply wells are thus the four processes noted above which cause the release of As from the aquifer matrix.

- 1) Movement of reducing water into the shallow aquifer causes the dissolution of HFO due to the reduction of ferric to ferrous iron. The As which was adsorbed to the surface of the HFO is released to the groundwater. Should the condition remain reducing and sulfide be present, then pyrite can form and scavenge As from the groundwater. While this reduces the As loading of the groundwater under reducing conditions it will oxidize and release the As once conditions change back to oxygenated.
- 2) Movement of oxygenated water into the deeper aquifer causes the dissolution of pyrite due to oxidation of ferrous to ferric iron. The As, which is present in the pyrite structure is released to the groundwater. Should conditions remain oxygenated, then HFO can form and scavenge As from the groundwater. While this reduces the As loading of the groundwater under oxygenated conditions it will oxidize and release the As once conditions change back to reducing.
- 3) Due to water movement, either up or down, powellite can become instable. With time the system will equilibrate with respect to powellite, meaning that neither powellite precipitation nor dissolution takes place. Under these conditions As is likely bound in the powellite structure. However, if the equilibrated water is removed and replaced with groundwater, which is undersaturated with respect to powellite, dissolution takes place and causes the release of As until equilibrium is attained once more.
- 4) Undersaturation or over saturation of powellite can also be caused by simple mixing of groundwaters with a different chemical composition. For example groundwater A contains elevated Ca^{2+} , but no MoO_4^{2-} and groundwater B contains elevated MoO_4^{2-} , but only little Ca^{2+} . Mixing of

these two waters can increase the IAP to the degree of powellite precipitation.

Arsenic levels in many of the private supply wells are much higher than those found in the DEP monitoring wells, while Mo value are more or less comparable. This could indicate the above-mentioned addition of As which was released in the surficial aquifer. There the aquifer matrix is relatively low in Mo (Fig. 12) and As is thought to be bound to HFO.

The true enigma, however is that DEP-4 and DEP-5, which are geographically removed from the Pritcher Road area where As levels are highest, undergo the same water level fluctuations, but show much lower Mo and As values. Arsenic and Mo values in core samples from DEP-5 did not differ from those in DEP-1 and DEP-2, although water samples from the DEP-5 cluster did not show any As values above 3 µg/L and only one sample had Mo above 40 µg/L. Considering that DEP-5 undergoes the same water level fluctuations as the other 4 wells it becomes evident that in the Pritcher Road area restricted geological, hydrological and physicochemical conditions occur, which promote the release of Mo and As. At this time it seems that the only difference is the amount of private supply wells, which is much higher in the area where As and Mo contamination is highest. Since these wells are likely open to all three groundwater horizons, vertical water movement is facilitated. The mixing of waters from different water horizons in the private supply wells is indicated by their position in the $\delta^{18}\text{O}$ - δD plot (Fig. 10) and in the $\delta^{18}\text{O}$ -TU plot (Fig. 21), where they plot intermediate between the shallow and deep samples.

There is no indication that Mo and As are of anthropogenic origin and thus they should be of geogenic origin and that a change in physicochemical conditions in the aquifer causes their release. However, what causes exactly this change in physicochemical conditions is still unclear.

In summary, the combination of massive groundwater pumping to the west of Lithia combined with many private supply wells, which are open to several

groundwater horizons in a karstic aquifer create an environment conducive to As and Mo release from the aquifer matrix.

5. Outlook and Recommendations

Installation of water level monitors in each of the DEP wells to investigate the hydraulic conductivity between the upper and lower aquifer. Expansion of a local groundwater model, which should include the data from the 5 monitoring well clusters.

A potential remedy for the As and Mo problem in the Lithia area may be to install wells with discrete screens in the Suwannee Limestone or deeper.

This study at the Pritcher Road site turned out to be more difficult than expected, BUT therein lies a great opportunity to further both, our practical and our scientific understanding of geogenic contamination scenarios. Eventually results from this study should be made available to a broader audience to aid such investigations across Florida, across the US and across the world. Thus I recommend FDEP to keep this site as a priority.

6. References

- Ahmed, M.F., Ahuja, S., Alauddin, M., Hug, S.J., Lloyd, J.R., Pfaff, A., Pichler, T., Saltikov, C., Stute, M., and van Geen, A., 2006, Ensuring safe drinking water in Bangladesh: Science.
- Amini, M., Abbaspour, K.C., Berg, M., Winkel, L., Hug, S.J., Hoehn, E., Yang, H., and Johnson, C.A., 2008, Statistical modeling of global geogenic arsenic contamination in groundwater: Environmental Science & Technology, v. 42, p. 3669-3675.
- Armienta, M.A., and Segovia, N., 2008, Arsenic and fluoride in the groundwater of Mexico: Environmental Geochemistry and Health, v. 30, p. 345-353.
- Armstrong, J.T., 1995, CITZAF: A package of correction programs for the quantitative electron microbeam X-ray analysis of thick polished materials, thin films, and particles: Microbeam Analysis, v. 4, p. 177-200.
- Dhar, R.K., Zheng, Y., Stute, M., van Geen, A., Cheng, Z., Shanewaz, M., Shamsudduha, M., Hoque, M.A., Rahman, M.W., and Ahmed, K.M., 2008, Temporal variability of groundwater chemistry in shallow and deep aquifers of Araihaazar, Bangladesh: Journal of Contaminant Hydrology, v. 99, p. 97-111.

- Ducci, D., de Masi, G., and delli Priscoli, G., 2008, Contamination risk of the Alburni Karst System (Southern Italy): *Engineering Geology*, v. 99, p. 109-120.
- Ferguson, J.F., and Gavis, J., 1972, A review of the arsenic cycle in natural waters: *Water Research Pergamon Press*, v. 6, p. 1259-1274.
- Gbadebo, A.M., 2005, Arsenic pollution in aquifers located within limestone areas of Ogun State, Nigeria: *Natural Arsenic in Groundwater: Occurrence, Remediation and Management*, p. 85-92.
- Jambor, J.L., and Dutrizac, J.E., 1998, Occurrence and constitution of natural and synthetic ferrihydrite, a widespread iron oxyhydroxide: *Chemical Reviews*, v. 98, p. 2549-2585.
- Jones, G.W., and Pichler, T., 2007, The Relationship between Pyrite Stability and Arsenic Mobility During Aquifer Storage and Recovery in Southwest Central Florida: *Environmental Science and Technology*, v. 41, p. 723-730.
- Katz, B.G., 2004, Sources of nitrate contamination and age of water in large karstic springs of Florida: *Environmental Geology*, v. 46, p. 689-706.
- Korte, N.E., and Fernando, Q., 1991, A review of arsenic (III) in groundwater: *Critical Reviews in Environmental Control*, v. 21, p. 1-36.
- Kovacova, E., and Malik, P., 2007, Groundwater vulnerability of the karst-fissure hydrogeological structure of south-facing slopes of the Nizke Tatry Mts., Slovakia: *Acta Carsologica*, v. 36, p. 261-268.
- Lazareva, O., 2004, Detailed geochemical and mineralogical analyses of naturally occurring arsenic in the Hawthorn Group [MS thesis]: Tampa, University of South Florida.
- Lazareva, O., and Pichler, T., 2007, Naturally occurring arsenic in the Miocene Hawthorn Group, Southwestern Florida: implication for phosphate mining: *Applied Geochemistry*, v. 22, p. 953-973.
- Li, Y.-H., 2000, A compendium of geochemistry: from solar nebula to the human brain: Princeton, Princeton University Press, 476 p.
- McMahon, P.B., Bohlke, J.K., Kauffman, L.J., Kipp, K.L., Landon, M.K., Crandall, C.A., Burow, K.R., and Brown, C.J., 2008, Source and transport controls on the movement of nitrate to public supply wells in selected principal aquifers of the United States: *Water Resources Research*, v. 44, p. -.
- McNeill, L.S., Hsiao-wen, C., and Edwards, M., 2002, Aspects of arsenic chemistry in relation to occurrence, health and treatment, *in* Frankenberger, W.T., Jr, ed., *Environmental chemistry of arsenic*: New York, Marcel Dekker, p. 141-154.
- Obeidat, M.M., Ahmad, F.Y., Hamouri, N.A., Massadeh, A.M., and Athamneh, F.S., 2008, Assessment of nitrate contamination of karst springs, Bani Kanana, northern Jordan: *Revista Mexicana De Ciencias Geologicas*, v. 25, p. 426-437.
- Pichler, T., and Jones, G.W., 2006, Low-arsenic rocks can make high-arsenic water: Lessons learned from ASR in Florida: *Abstracts of Papers of the American Chemical Society*, v. 231, p. -.

- Polizzotto, M.L., Harvey, C.F., Sutton, S.R., and Fendorf, S., 2005, Processes conducive to the release and transport of arsenic into aquifers of Bangladesh: Proceedings National Academy of Sciences of the USA.
- Price, R.E., 2003, Abundance and mineralogical associations of naturally occurring arsenic in the Suwannee Limestone, Upper Floridan Aquifer [MS thesis]: Tampa, University of South Florida.
- Price, R.E., and Pichler, T., 2002, Naturally occurring arsenic in the Upper Floridan Aquifer, southwest Florida: Implications for aquifer storage and recovery, *in* Kenny, J.F., ed., GroundWater/Surface Water Interactions, Volume TPS-02-2: Middleburg, Virginia, American Water Resources Association, p. 387-392.
- , 2005, Distribution, speciation and bioavailability of arsenic in a shallow-water submarine hydrothermal system, Tutum Bay, Ambitle Island, PNG: Chemical Geology, v. 224, p. 122-135.
- , 2006, Abundance and mineralogical associations of naturally occurring arsenic in the Suwannee Limestone, Upper Floridan Aquifer: Chemical Geology, v. 228, p. 44-56.
- Raven, K.P., Jain, A., and Loeppert, R.H., 1998, Arsenite and arsenate adsorption on ferrihydrite: kinetics, equilibrium and adsorption envelopes: Environmental Science & Technology, v. 32, p. 344-349.
- Rickard, D.T., 1968, The chemistry of iron sulfide formation at low temperatures: Stockholm Contributions to Geology, v. 20, p. 67-95.
- Romero, F.M., Armienta, M.A., and Carrillo-Chavez, A., 2004, Arsenic sorption by carbonate-rich aquifer material, a control on arsenic mobility at Zimapan, Mexico: Archives of Environmental Contamination and Toxicology, v. 47, p. 1-13.
- Sacks, L.A., 1996, Geochemical and isotopic composition of ground water with emphasis on sources of sulfate in the Upper Floridan Aquifer in Parts of Marion, Sumter, and Citrus Counties, Florida: Tallahassee, U.S. Geological Survey, p. 47.
- Sacks, L.A., Herman, J.S., and Kauffman, S.J., 1995, Controls on high sulfate concentrations in the Upper Floridan aquifer in southwest Florida: Water Resources Research, v. 31, p. 2541-2551.
- Sacks, L.A., and Tihansky, A.B., 1996, Geochemical and isotopic composition of ground water with emphasis on sources of sulfate in the Upper Floridan Aquifer and Intermediate Aquifer System in Southwest Florida: Tallahassee, U.S. Geological Survey, p. 70.
- Simsek, C., Elci, A., Gunduz, O., and Erdogan, B., 2008, Hydrogeological and hydrogeochemical characterization of a karstic mountain region: Environmental Geology, v. 54, p. 291-308.
- Smedley, P.L., and Kinniburgh, D.G., 2002, A review of the source, behavior and distribution of arsenic in natural waters: Applied Geochemistry, v. 17, p. 517-568.
- Stute, M., Zheng, Y., Schlosser, P., Horneman, A., Dhar, R.K., Datta, S., Hoque, M.A., Seddique, A.A., Shamsudduha, M., Ahmed, K.M., and van Geen, A.,

- 2007, Hydrological control of As concentrations in Bangladesh groundwater: *Water Resources Research*, v. 43.
- Swartz, C.H., Blute, N.K., Badruzzman, B., Ali, A., Brabander, D., Jay, J., Besancon, J., Islam, S., Hemond, H.F., and Harvey, C.F., 2004, Mobility of arsenic in a Bangladesh aquifer: inferences from geochemical profiles, leaching data, and mineralogical characterization: *Geochimica et Cosmochimica Acta*, v. 68, p. 4539-4557.
- van Geen, A., Radloff, K., Aziz, Z., Cheng, Z., Huq, M.R., Ahmed, K.M., Weinman, B., Goodbred, S., Jung, H.B., Zheng, Y., Berg, M., Trang, P.T.K., Charlet, L., Metral, J., Tisserand, D., Guillot, S., Chakraborty, S., Gajurel, A.P., and Upreti, B.N., 2008, Comparison of arsenic concentrations in simultaneously-collected groundwater and aquifer particles from Bangladesh, India, Vietnam, and Nepal: *Applied Geochemistry*, v. 23, p. 3244-3251.
- Vesper, D.J., and White, W.B., 2003, Metal transport to karst springs during storm flow: an example from Fort Campbell, Kentucky/Tennessee, USA: *Journal of Hydrology*, v. 276, p. 20-36.
- Zheng, Y., van Geen, A., Stute, M., Dhar, R., Mo, Z., Cheng, Z., Horneman, A., Gavrieli, I., Simpson, H.J., Versteeg, R., Steckler, M., Grazioli-Venier, A., Goodbred, S., Shahnewaz, M., Shamsudduha, M., Hoque, M.A., and Ahmed, K.M., 2005, Geochemical and hydrogeological contrasts between shallow and deeper aquifers in two villages of Araihasar, Bangladesh: Implications for deeper aquifers as drinking water sources: *Geochimica et Cosmochimica Acta*, v. 69, p. 5203-5218.
- Zhou, W.F., and Beck, B.F., 2008, Management and mitigation of sinkholes on karst lands: an overview of practical applications: *Environmental Geology*, v. 55, p. 837-851.

7. Figures

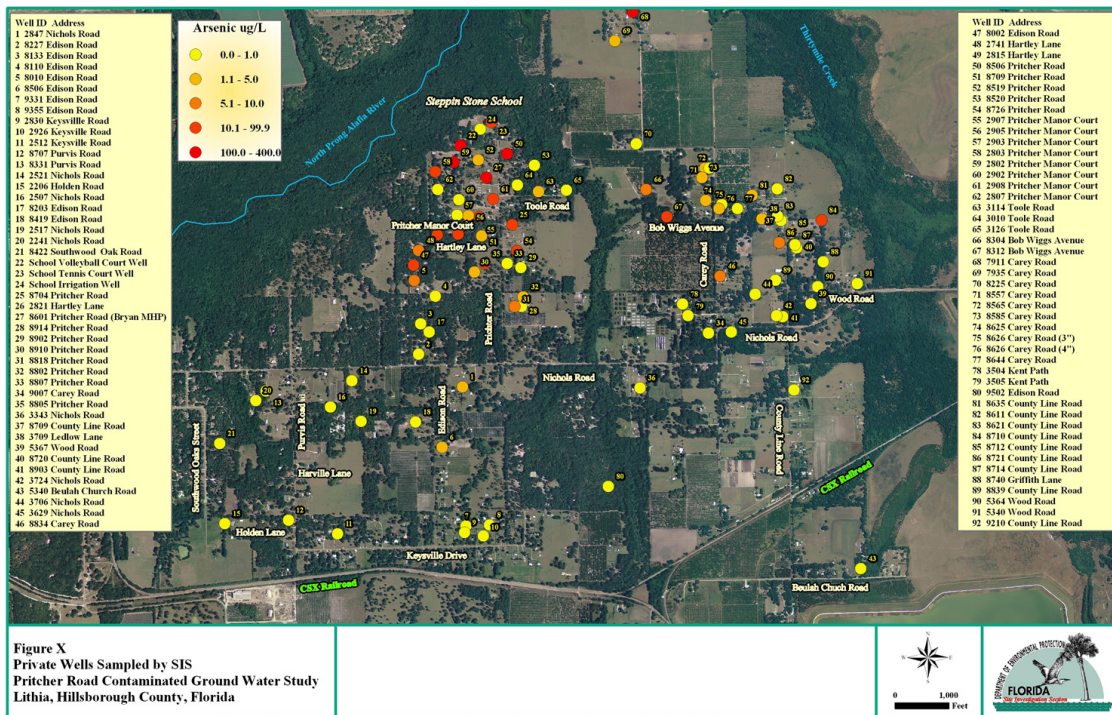


Fig.1 Location and distribution of private supply wells in the Lithia area, which were sampled in May 2007 by the Florida Department of Environmental Protection.

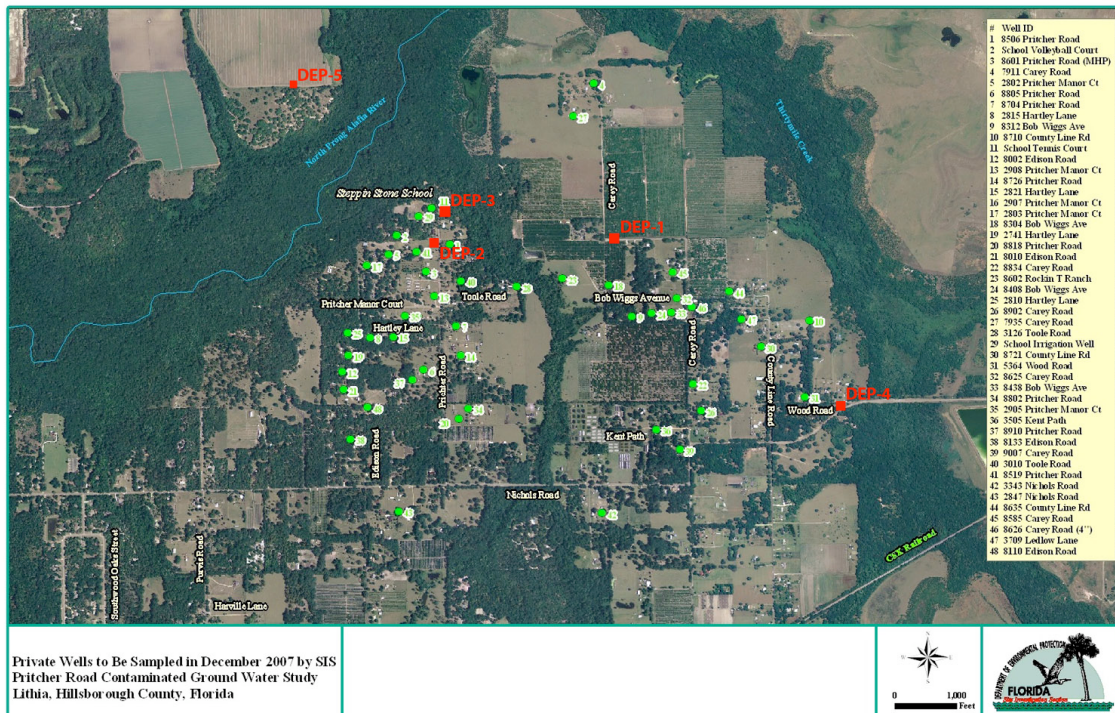


Fig.2 Location and distribution of those private supply wells, which were chosen for the second round of sampling, as well as the locations of the 5 monitoring well clusters DEP-1 to DEP-5.

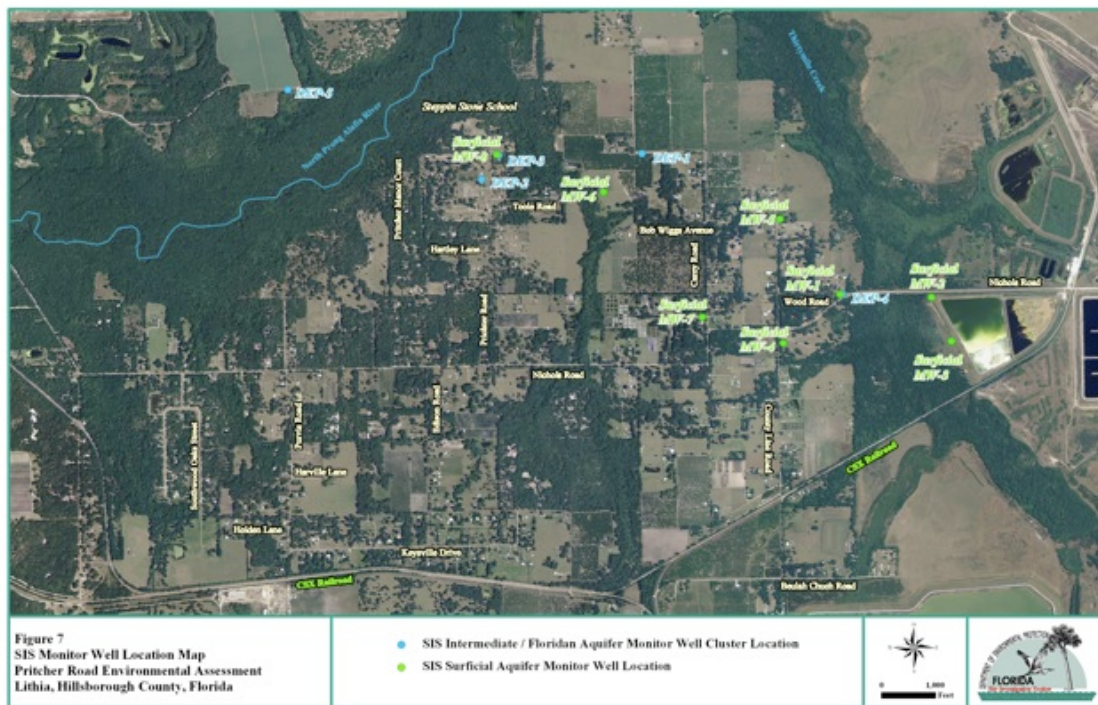


Fig.3 Location and distribution of the Surficial Aquifer Monitoring wells SW-1 to SW-5

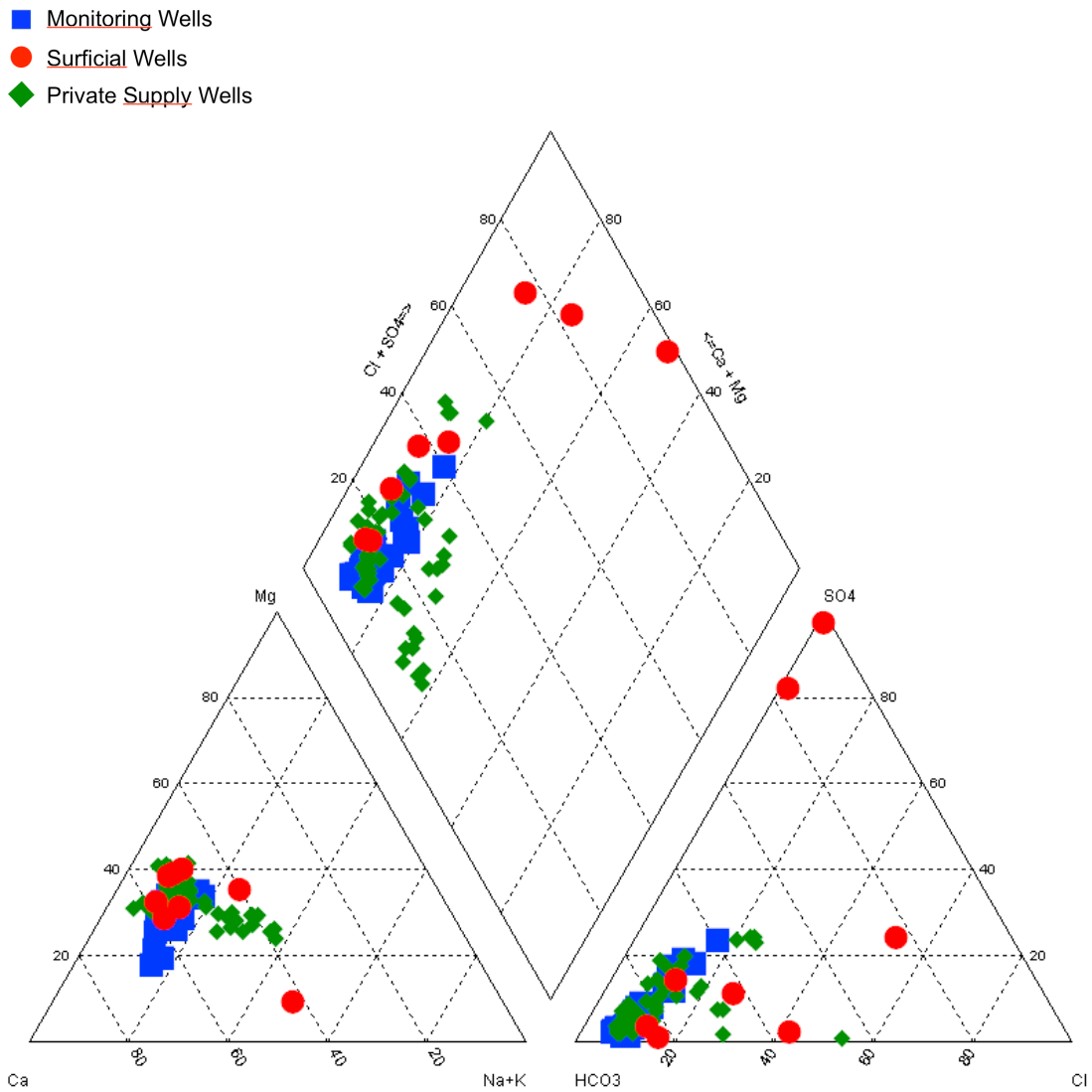


Fig. 4 Piper diagram of all water samples collected in from December 2007 until April 2009 from the DEP monitoring wells, private supply wells and shallow monitoring wells in the Lithia area.

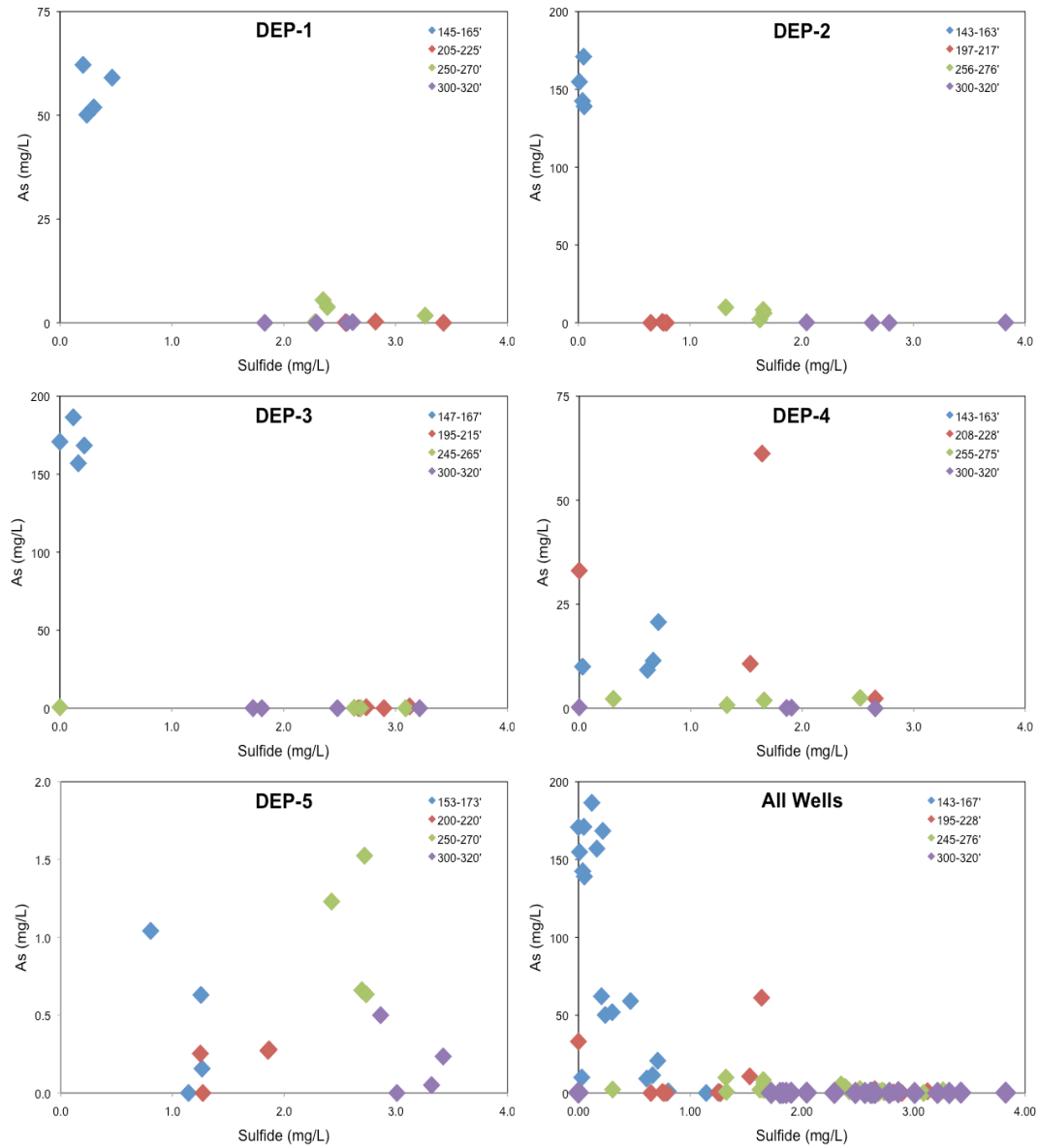


Fig. 5 Arsenic and sulfide concentrations for the 5 monitoring well clusters individually and for the whole data set.

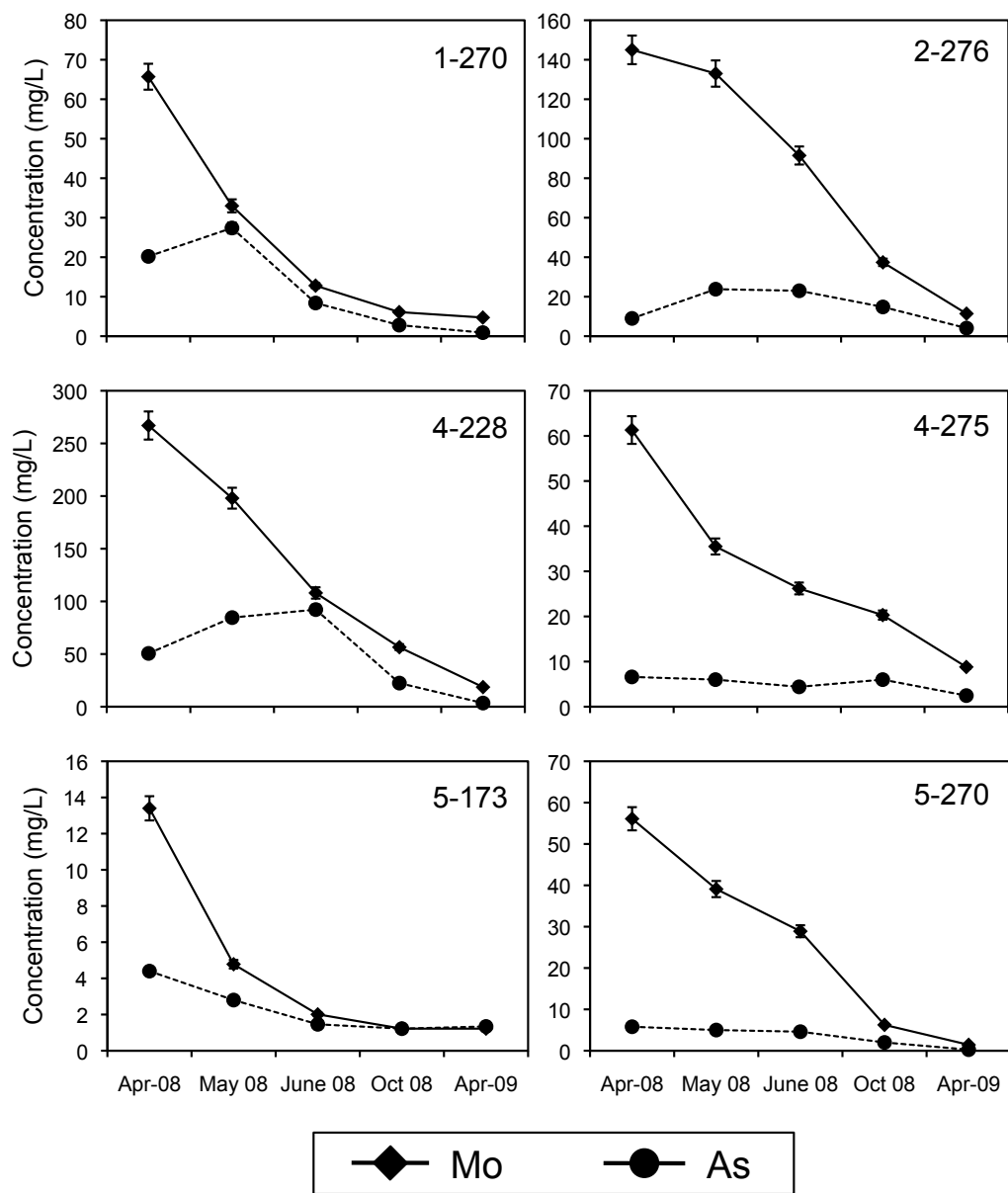


Fig. 6 Arsenic and Mo trends for selected DEP monitoring well intervals.

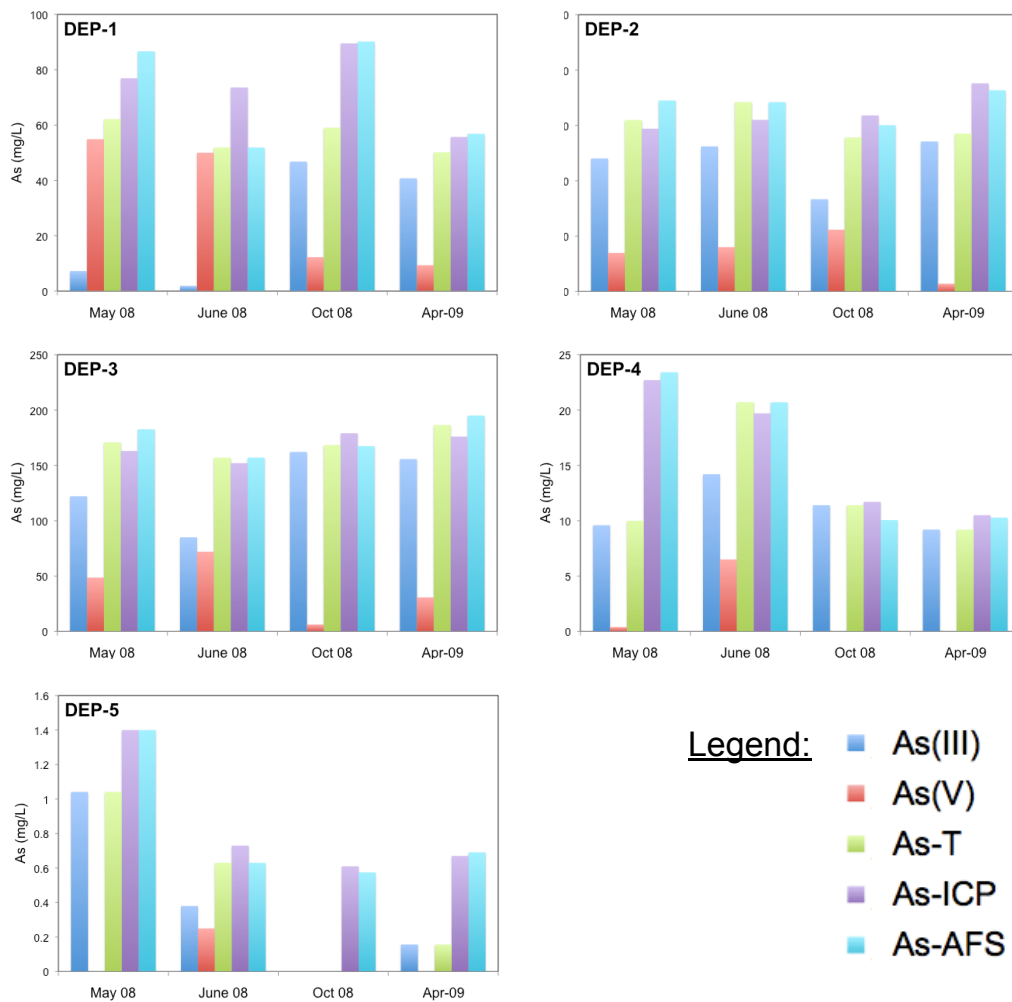


Fig. 7 Arsenic speciation results for As^{3+} and As^{5+} . Results are also compared to total As concentration determined by ICP and AFS

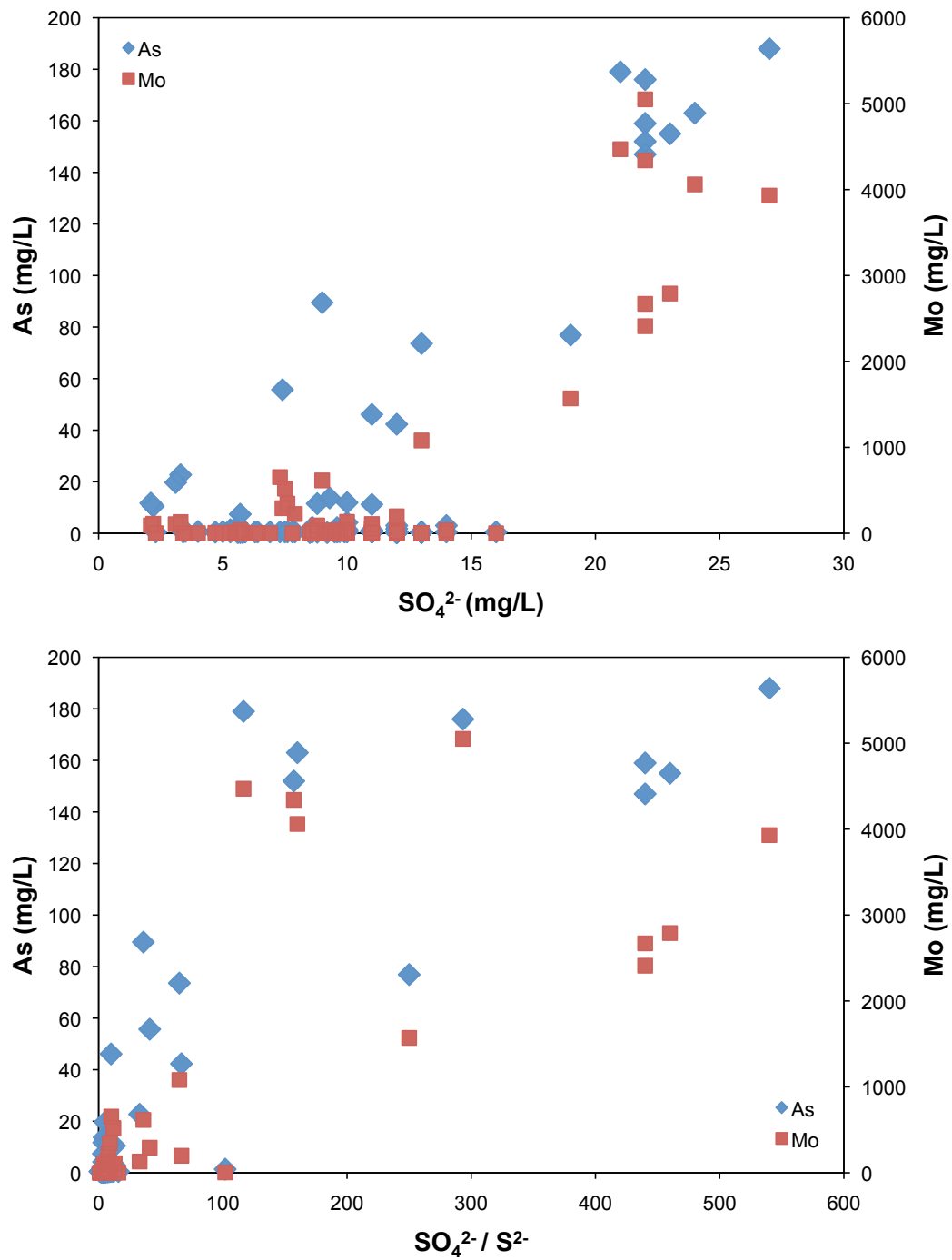


Fig. 8 Total sulfate and sulfate/sulfide ratios compared to As and Mo data in the DEP monitoring well clusters.

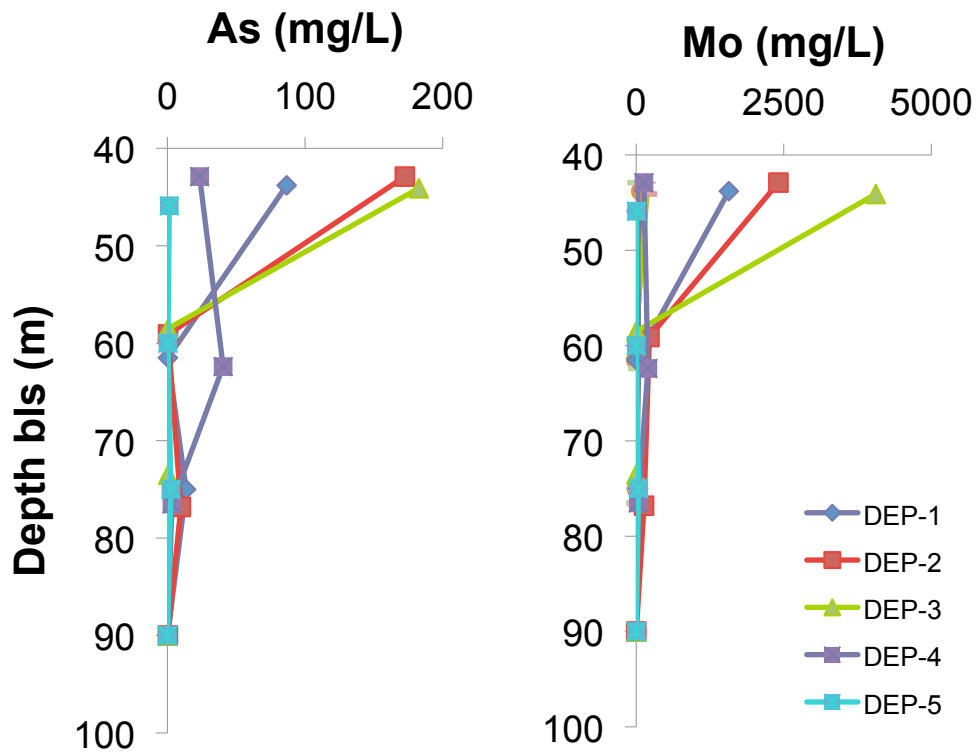


Fig. 9 As and Mo profiles with depth in the 5 monitoring well clusters in Lithia, Central Florida

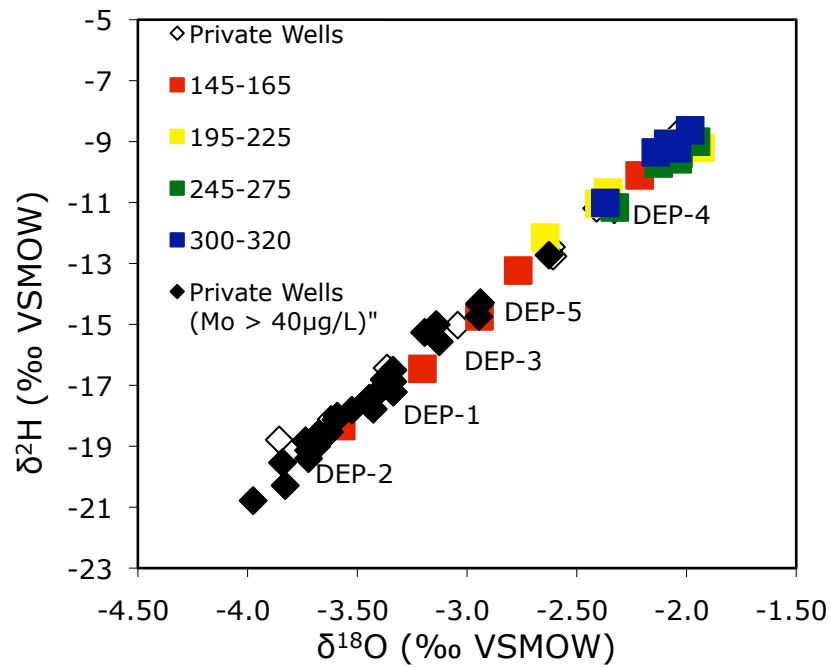
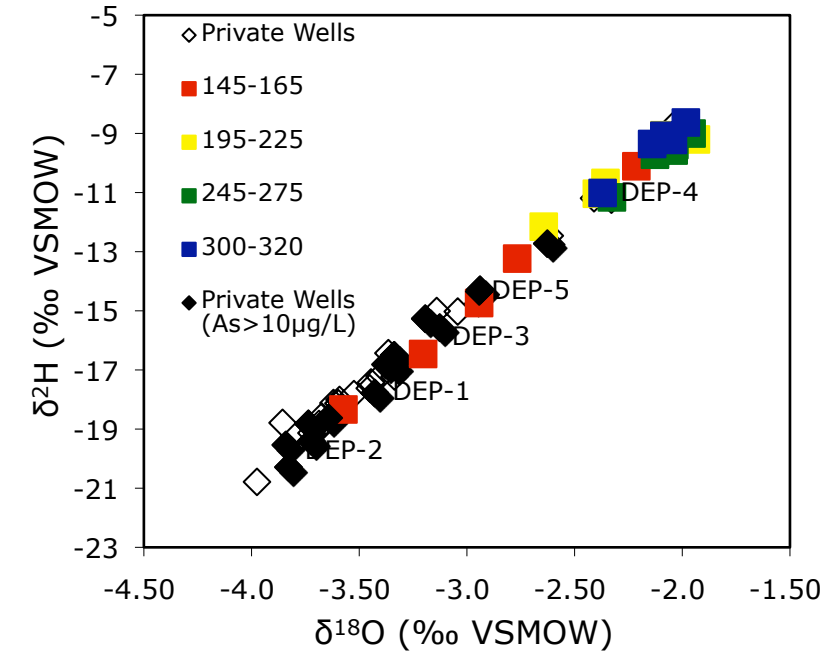


Fig. 10 Plot of $\delta^{18}\text{O}$ and δD for the 5 monitoring well clusters and 40 private supply wells in the Lithia area. The monitoring wells are color coded with depth. The private wells which show As values above the current drinking water standard are solid black. Most solid black diamonds fall within the range of the shallow interval in the monitoring wells (red color). Note: Well depths are in feet (ft).

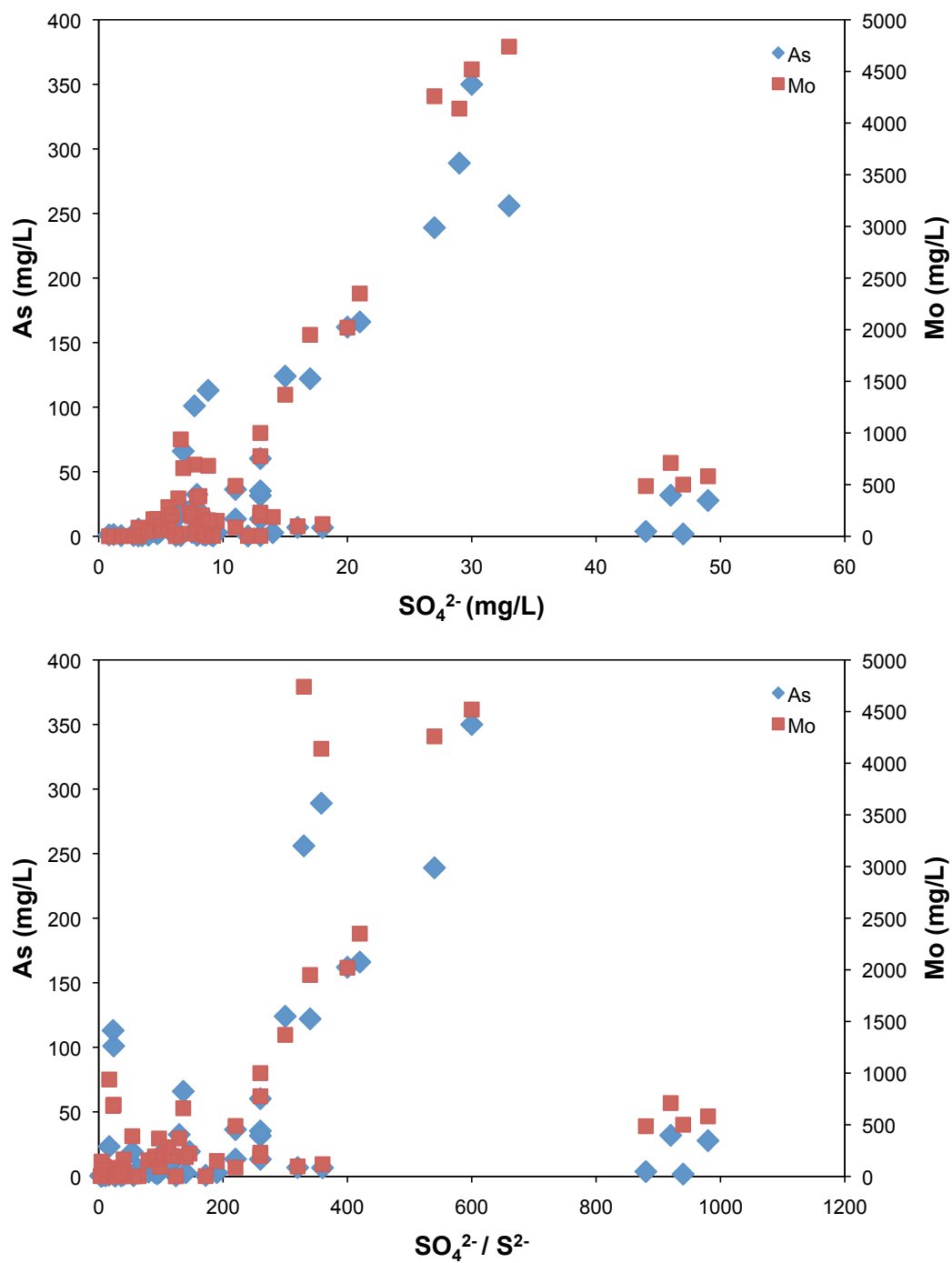


Fig. 11 Total sulfate and sulfate/sulfide ratios compared to As and Mo data in the private supply wells

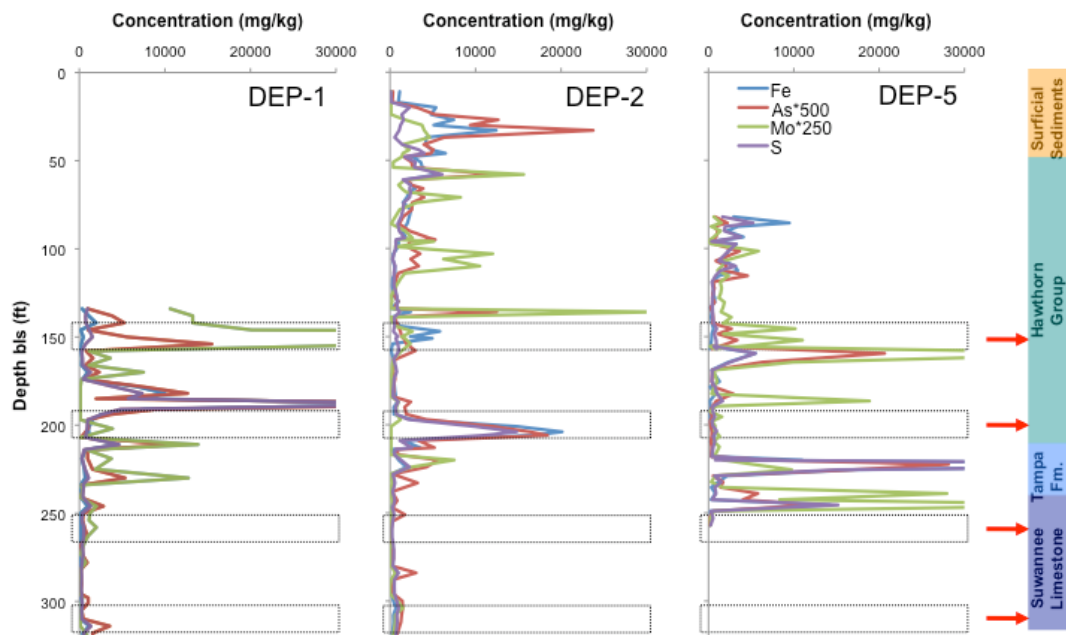


Fig. 12 Distribution of Mo and As with depth below surface (bls) for well clusters DEP-1, DEP-2 and DEP-5. The screened intervals are indicated by dashed boxes.

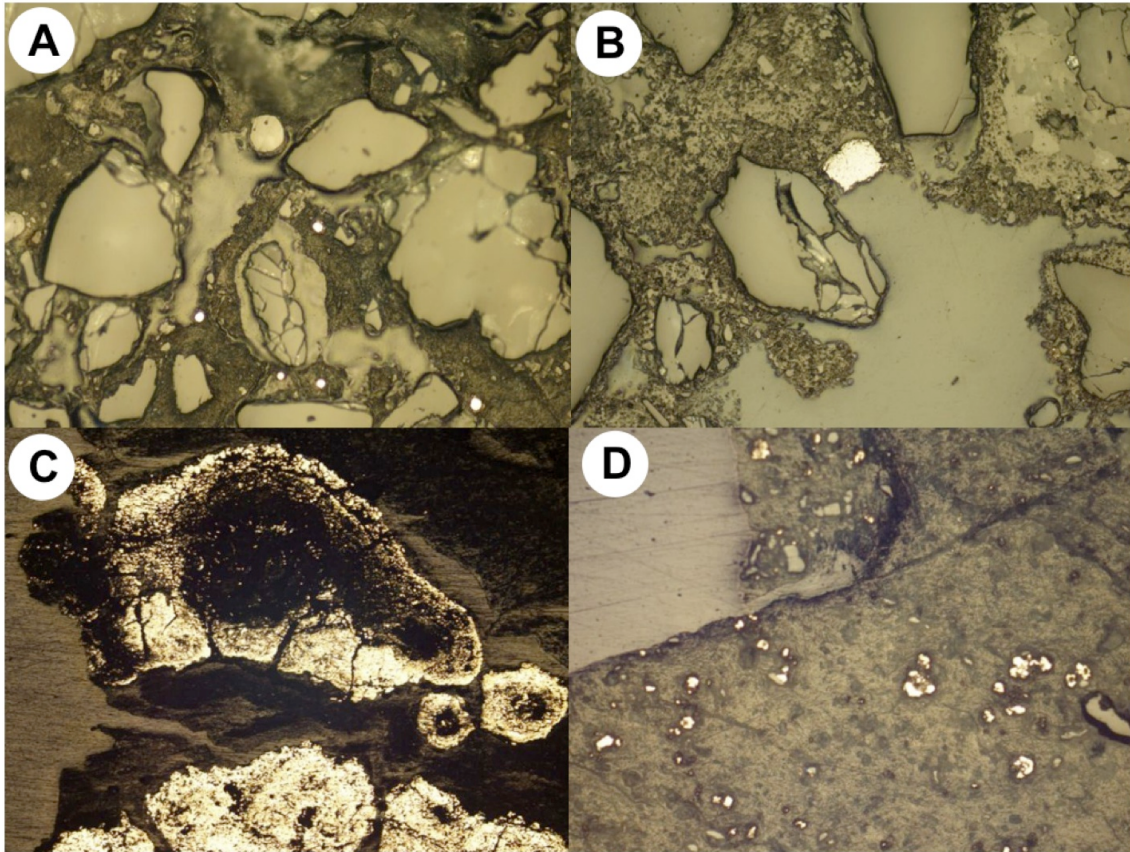


Fig. 13 Reflected light microscope images: (A) Small powellite crystals in a carbonate and clay matrix in core DEP-1 at 152 ft (20x magnification), (B) Larger euhedral pyrite in a carbonate and clay matrix in core DEP-1 at 156 ft (20x magnification), (C) Massive pyrite in core DEP-1 at 190 ft (2x magnification) and (D) Small framboidal pyrites in a carbonate matrix in core DEP-2 (20x magnification)

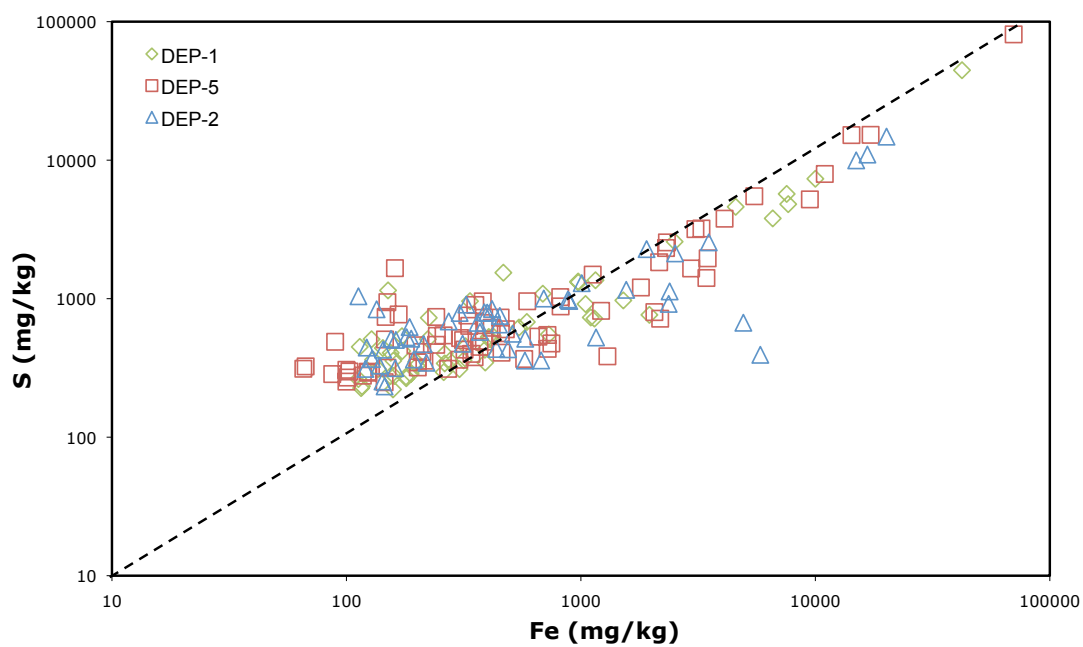


Fig. 14 Plot of Fe vs. S for the three monitoring well clusters DEP-1, DEP-2 and DEP-5. The dashed line represents the “pyrite line”, i.e., if pyrite would be the single source of Fe and S in a sample then all analyses would plot on this line.

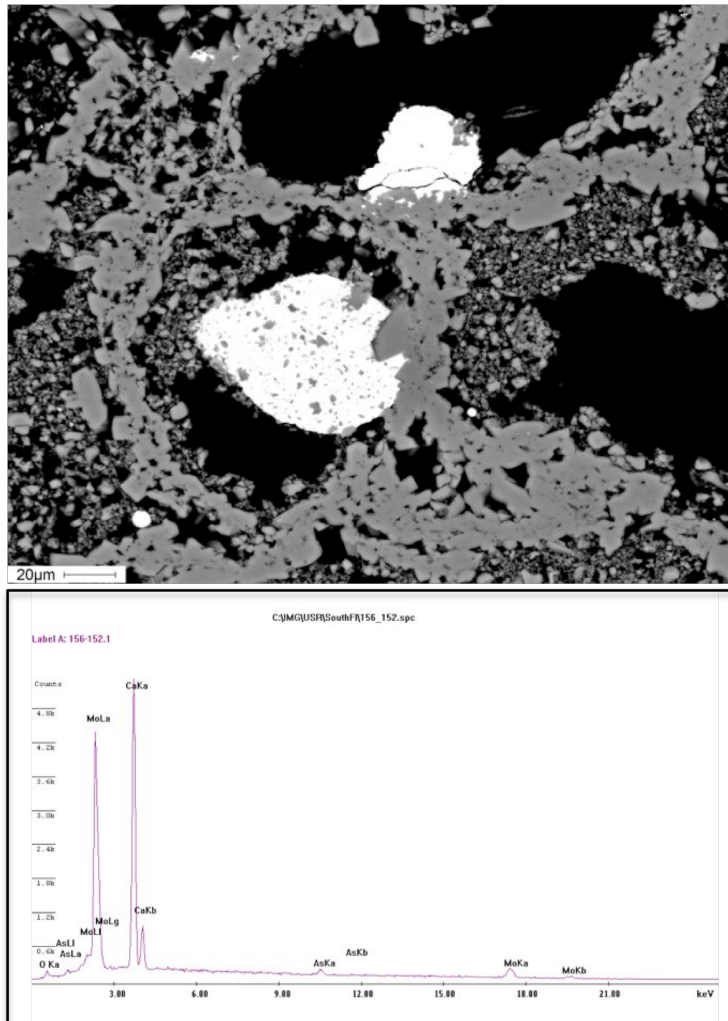


Fig. 15 Back scatter electron image from core DEP-1 (152 ft depth) of powellite in a clay/carbonate matrix. This type of image is based on density, the heavier a mineral phase the brighter it is displayed. Powellite is the latest stage of crystallization, not developing its own crystal shape, but filling pore space. The EDX spectra below was taken at a 5 μm-sized spot on the upper of the two powellites.

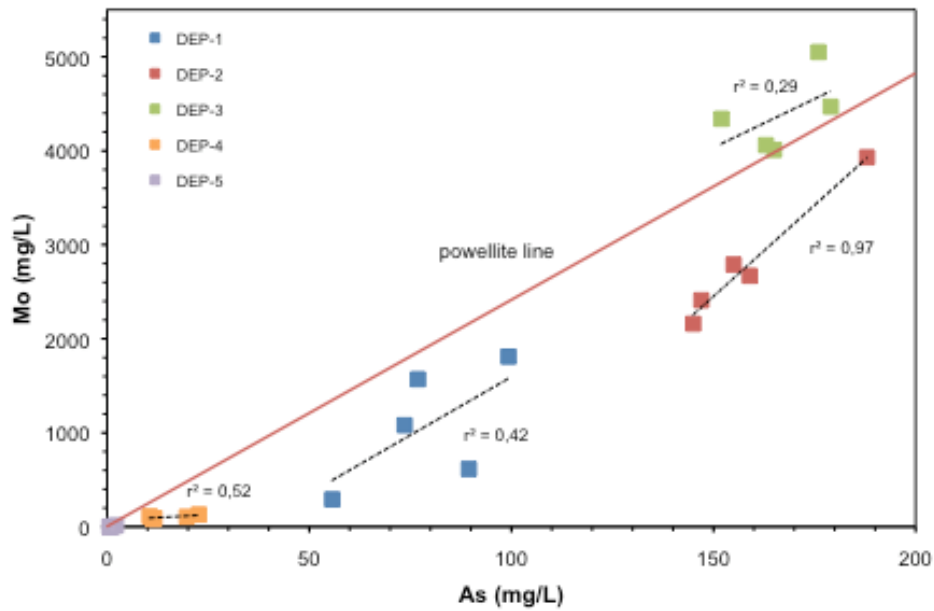
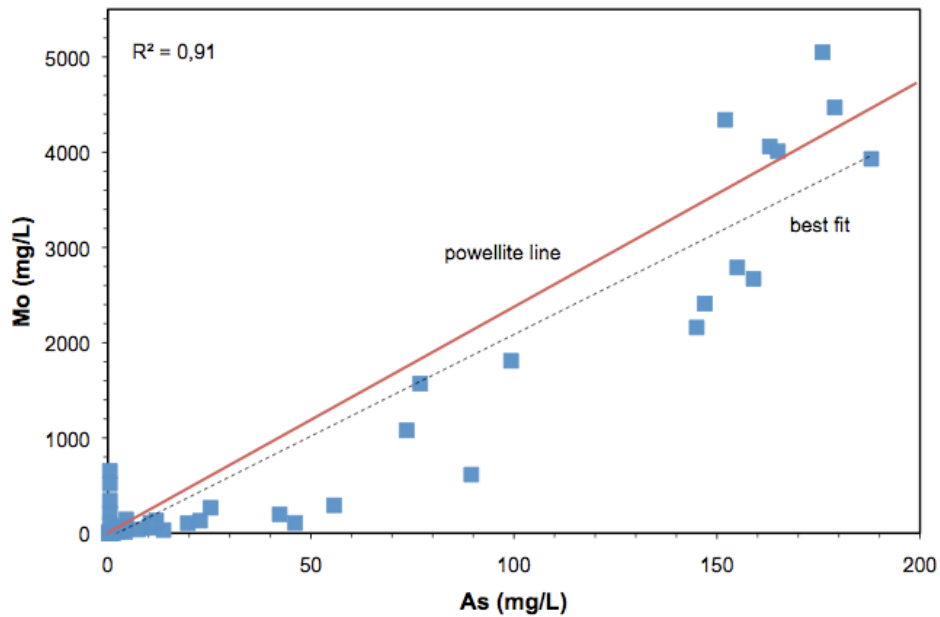


Fig. 16 Plot of As vs Mo for all FDEP monitoring well clusters. Above for the whole data set and below for the 5 well clusters individually. The powellite line was calculated based on the relative concentrations of Mo and As, which were determined by electron microprobe analysis (Table 5).

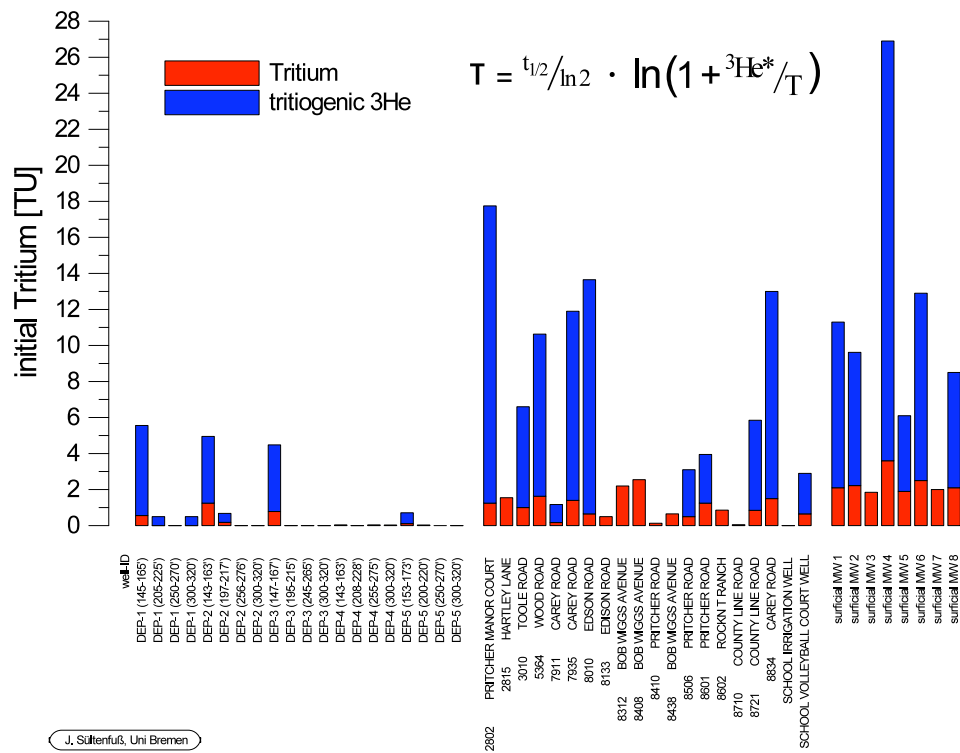


Fig. 17 Results of the tritium analyses and the calculated tritogenic ^3He for all samples. He isotopes were analyzed for samples where the blue bar on top of the red bar is missing.

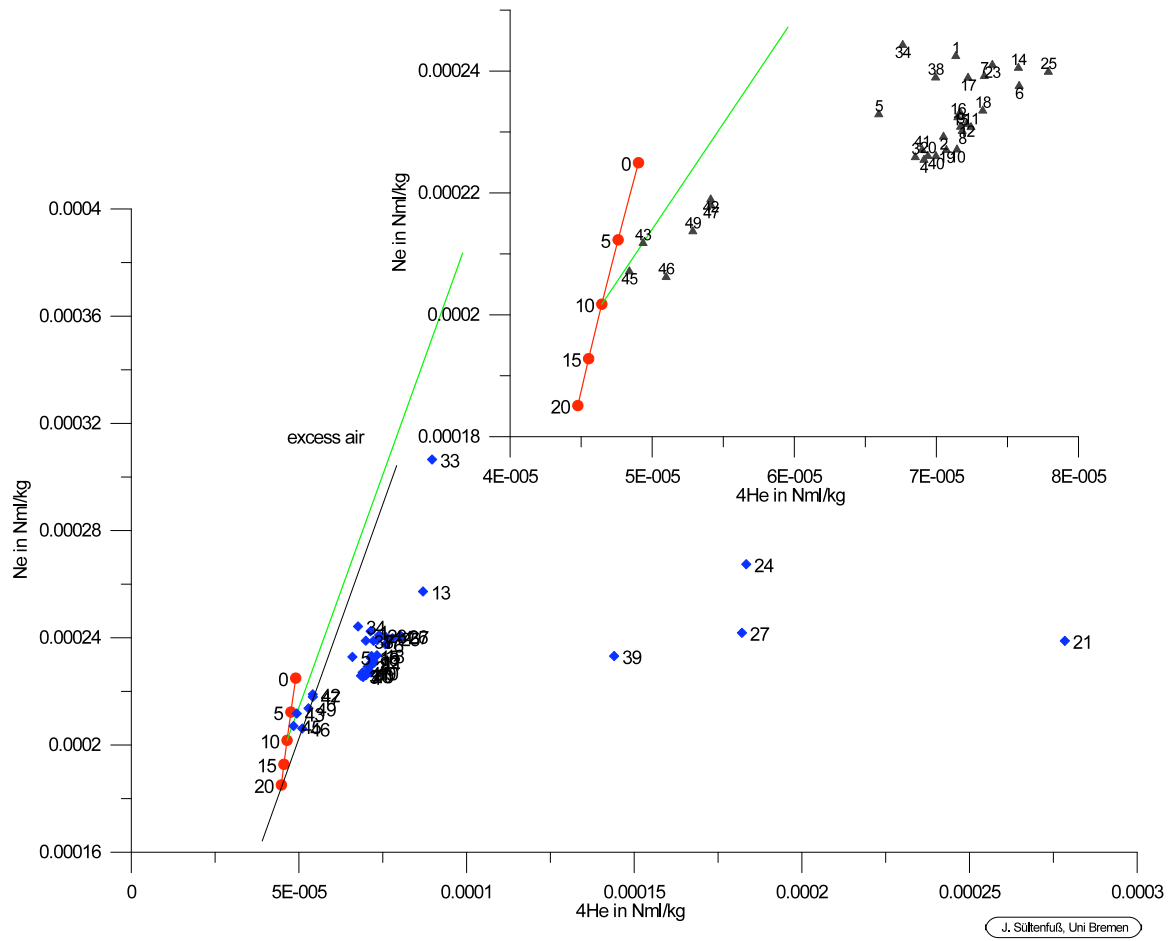


Fig. 18 Ne concentration vs. ^4He concentration. The upper right figure is an enlargement. Red line indicates solubility equilibrium concentration for different temperatures. Green line represents the addition of atmospheric air to a sample equilibrated at 10°C.

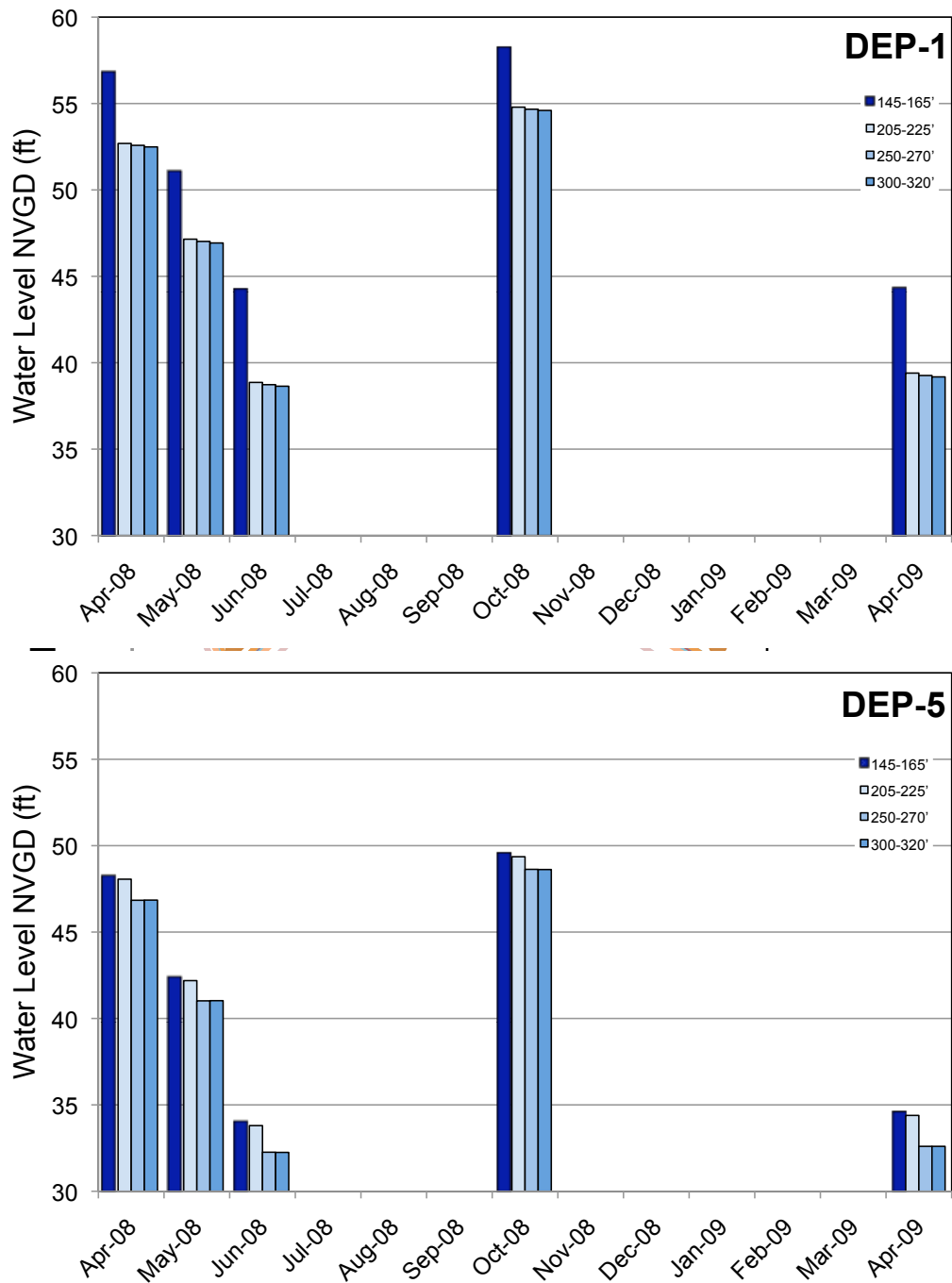


Fig. 19 Water level fluctuations with time in monitoring wells DEP-1 and DEP-5

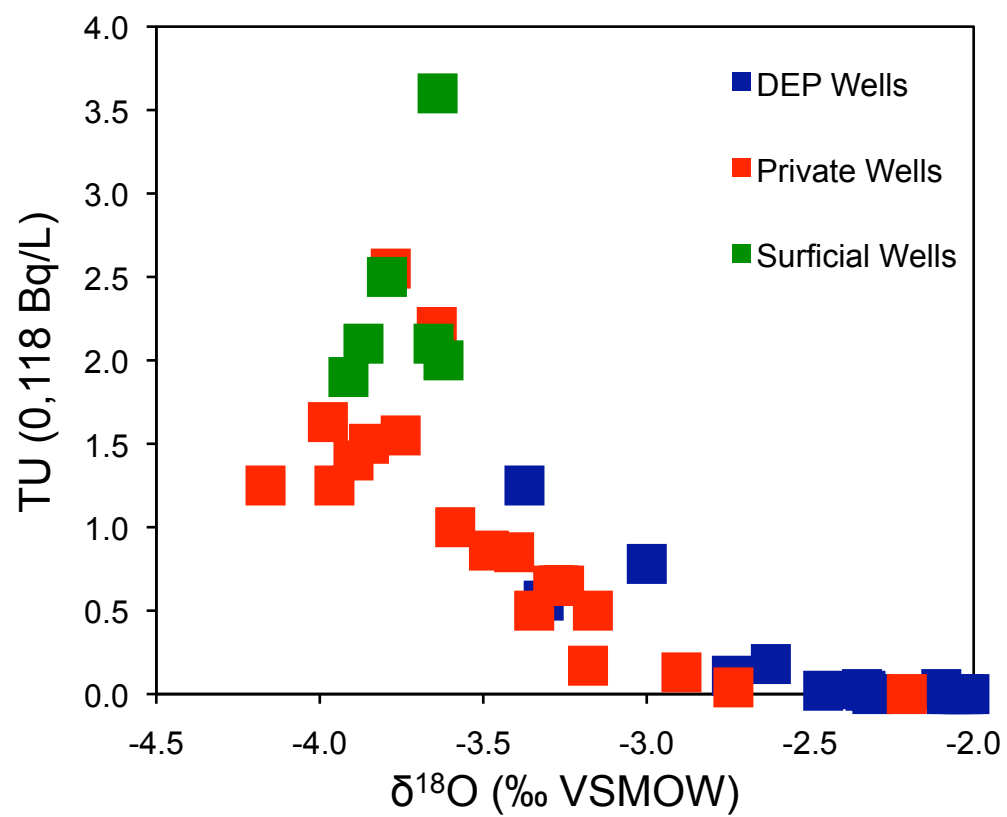


Fig. 21 $\delta^{18}\text{O}$ vs TU plot of private supply wells, DEP monitoring wells and surficial monitoring wells.

8. Tables

Table 1 Field and laboratory measurements of groundwater samples collected from the 5 DEP monitoring well clusters in the Lithia area, Central Florida

[illegible]

Table 2 Field and laboratory measurements of groundwater samples collected from the 8 shallow observation wells installed in April 2009 in the Lithia area, Central Florida

Field ID	Sample ID	Date	Turbidity	pH	Conductivity	DO	ORP	S	HCO ₃	Al	Si	As	Ca	Co	Cr	Cu	F	Fe	K	N	Pb	Mg	Mn	Mo	Ni	N	K	Se	Sr	SO ₄	S	P	V	Zn	A ¹⁰	BO	As ¹⁰	As ¹⁰	Y	As	As (AFS)	SS (AFS)		
					µS/cm	%	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
SURFICIAL MW-1	MW-1	Apr-09	2.0	7.1	209	10.6	0.9	192	24	106	60	0.25	1.5	1	26	12	0.3	0.5	0.3	7680	0.31	0.2	81.6	614	3.3	13.9	0.0	2.4	0.2	27.8	108	157	750	0.05	0.27	2	5	0.6	54	0.0	0.1	0.5	1.7	2.6
SURFICIAL MW-2	MW-2	Apr-09	1.1	6.5	1625	15.3	1.3	159	7	189	60	0.25	1.4	1	153	12	0.3	0.5	0.3	7680	0.31	0.2	81.6	614	3.3	13.9	0.0	2.4	0.2	27.8	108	157	750	0.05	0.27	2	5	0.6	54	0.0	0.1	0.5	1.7	2.6
SURFICIAL MW-3	MW-3	Apr-09	8.4	6.4	3405	12.5	1.0	2	20	38	60	0.25	0.4	1	339	22	0.3	0.7	0.4	79100	0.74	0.2	44.8	320	0.3	32.8	0.0	1.7	0.3	21.4	442	381	2020	0.05	2.5	2	66	2.2	10.9	0.0	0.0	0.6	1.6	2.5
SURFICIAL MW-4	MW-4	Apr-09	10.6	6.8	235	8.0	0.7	48	65	105	480	0.25	0.3	1	28	11	2.1	0.5	0.4	1350	0.08	0.3	11.3	36	3.7	1.0	0.0	0.5	0.2	16	4.6	51.2	16	0.05	0.89	2	5	3.6	21.3	0.0	2.0	2.0	0.4	3.0
SURFICIAL MW-5	MW-5	Apr-09	7.6	6.6	163	60.9	5.1	9.5	13	39	110	0.25	0.5	1	16	17	0.8	0.5	0.4	71	0.08	0.2	5.6	44.9	4.6	3.6	3.6	0.4	9.82	14.6	4.8	31.3	1.2	0.05	1.1	4.5	9	3.9	23.5	0.0	0.0	0.0	0.9	2.8
SURFICIAL MW-6	MW-6	Apr-09	7.4	6.3	346	86.7	7.2	72	33	24	220	0.25	1.3	1	36	32	1.3	0.5	0.3	81	0.16	0.4	10.6	17.9	3.9	5.5	17.0	2.6	0.58	17.2	7.5	43.6	20	0.05	0.76	12	5	3.8	23.1	0.2	0.0	0.3	1.2	2.7
SURFICIAL MW-7	MW-7	Apr-09	5.4	6.6	231	14.7	1.2	144	83	78	160	0.25	0.3	1	25	19	1.3	0.5	0.8	3300	0.13	0.2	8.3	63.7	1.2	0.5	0.0	0.7	0.2	14.2	4.1	33	11	0.12	1.6	2.2	5	3.6	22.1	0.0	0.0	0.3	0.2	2.4
SURFICIAL MW-8	MW-8	Apr-09	2.8	7.1	157	69.0	5.7	17.0	11	79	60	0.25	1.0	1	17	7	0.3	0.3	0.3	66	0.08	0.2	7.8	29	4.1	1.0	0.7	0.4	0.46	10.9	3.3	36.2	2.6	0.11	0.12	3.8	5	3.8	23.6	4.0	0.0	4.0	6.5	3.8

Table 3 Field and laboratory measurements of groundwater samples collected from selected private supply wells in the Lithia area, Central Florida

WELL ID	Date	Time	Lat	Long	Depth	Flow	EC	Temp	pH	Ca	Mg	Na	K	Fe	Mn	Cu	Zn	Al	As	Se	NO ₃	NO ₂	PO ₄	SO ₄	CO ₃	Si	Cl	Br	I	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P	Q	R	S	T	U	V	W	X	Y	Z	AA	AB	AC	AD	AE	AF	AG	AH	AI	AJ	AK	AL	AM	AN	AO	AP	AQ	AR	AS	AT	AU	AV	AW	AX	AY	AZ	BA	BB	BC	BD	BE	BF	BG	BH	BI	BJ	BK	BL	BM	BN	BO	BP	BQ	BR	BS	BT	BU	BV	BW	BX	BY	BZ	CA	CB	CC	CD	CE	CF	CG	CH	CI	CJ	CK	CL	CM	CN	CO	CP	CQ	CR	CS	CT	CU	CV	CW	CX	CY	CZ	DA	DB	DC	DD	DE	DF	DG	DH	DI	DJ	DK	DL	DM	DN	DO	DP	DQ	DR	DS	DT	DU	DV	DW	DX	DY	DZ	EA	EB	EC	ED	EE	EF	EG	EH	EI	EJ	EK	EL	EM	EN	EO	EP	EQ	ER	ES	ET	EU	EV	EW	EX	EY	EZ	FA	FB	FC	FD	FE	FF	FG	FH	FI	FJ	FK	FL	FM	FN	FO	FP	FQ	FR	FS	FT	FU	FV	FW	FX	FY	FZ	GA	GB	GC	GD	GE	GF	GG	GH	GI	GJ	GK	GL	GM	GN	GO	GP	GQ	GR	GS	GT	GU	GV	GW	GX	GY	GZ	HA	HB	HC	HD	HE	HF	HG	HH	HI	HJ	HK	HL	HM	HN	HO	HP	HQ	HR	HS	HT	HU	HV	HW	HX	HY	HZ	IA	IB	IC	ID	IE	IF	IG	IH	II	IJ	IK	IL	IM	IN	IO	IP	IQ	IR	IS	IT	IU	IV	IW	IX	IY	IZ	JA	JB	JC	JD	JE	JF	JG	JH	JI	IJ	JK	JL	JM	JN	JO	JP	JQ	JR	JS	JT	JU	JV	JW	JX	JY	JZ	KA	KB	KC	KD	KE	KF	KG	KH	KI	KJ	KK	KL	KM	KN	KO	KP	KQ	KR	KS	KT	KU	KV	KW	KX	KY	KZ	LA	LB	LC	LD	LE	LF	LG	LH	LI	LJ	LK	LL	LM	LN	LO	LP	LQ	LR	LS	LT	LU	LV	LV	LW	LX	LY	LZ	MA	MB	MC	MD	ME	MF	MG	MH	MI	MJ	MK	ML	MM	MN	MO	MP	MQ	MR	MS	MT	MU	MV	MW	MX	MY	MZ	NA	NB	NC	ND	NE	NF	NG	NH	NI	NJ	NK	NL	NM	NO	NP	NQ	NR	NS	NT	NU	NV	NW	NX	NY	NZ	OA	OB	OC	OD	OE	OF	OG	OH	OI	OJ	OK	OL	OM	ON	OO	OP	OQ	OR	OS	OT	OU	OV	OW	OX	OY	OZ	PA	PB	PC	PD	PE	PF	PG	PH	PI	PJ	PK	PL	PM	PN	PO	PP	PQ	PR	PS	PT	PU	PV	PW	PX	PY	PZ	QA	QB	QC	QD	QE	QF	QG	QH	QI	QJ	QK	QL	QM	QN	QO	QP	QQ	QR	QS	QT	QU	QV	QW	QX	QY	QZ	RA	RB	RC	RD	RE	RF	RG	RH	RI	RJ	RK	RL	RM	RN	RO	RP	RQ	RR	RS	RT	RU	RV	RW	RX	RY	RZ	SA	SB	SC	SD	SE	SF	SG	SH	SI	SJ	SK	SL	SM	SN	SO	SP	SQ	SR	SS	ST	SU	SV	SW	SX	SY	SZ	TA	TB	TC	TD	TE	TF	TG	TH	TI	TJ	TK	TL	TM	TN	TO	TP	TQ	TR	TS	TU	TV	TW	TX	TY	TZ	UA	UB	UC	UD	UE	UF	UG	UH	UI	UJ	UK	UL	UM	UN	UO	UP	UQ	UR	US	UT	UU	UV	UW	UX	UY	UZ	VA	VB	VC	VD	VE	VF	VG	VH	VI	VJ	VK	VL	VM	VN	VO	VP	VQ	VR	VS	VT	VU	VV	VW	VX	VY	VZ	WA	WB	WC	WD	WE	WF	WG	WH	WI	WJ	WK	WL	WM	WN	WO	WP	WQ	WR	WS	WT	WU	WV	WX	WY	WZ	XA	XB	XC	XD	XE	XF	YG	YH	YI	YJ	YK	YL	YM	YN	YO	YP	YQ	YR	YS	YT	YU	YV	YW	YX	YY	YZ	ZA	ZB	ZC	ZD	ZE	ZF	ZG	ZH	ZI	ZJ	ZK	ZL	ZM	ZN	ZO	ZP	ZQ	ZR	ZS	ZT	ZU	ZV	ZW	ZX	ZY	ZZ	AA	AB	AC	AD	AE	AF	AG	AH	AI	AJ	AK	AL	AM	AN	AO	AP	AQ	AR	AS	AT	AU	AV	AW	AX	AY	AZ	BA	BB	BC	BD	BE	BF	BG	BH	BI	BJ	BK	BL	BM	BN	BO	BP	BQ	BR	BS	BT	BU	BV	BW	BX	BY	BZ	CA	CB	CC	CD	CE	CF	CG	CH	CI	CJ	CK	CL	CM	CN	CO	CP	CQ	CR	CS	CT	CU	CV	CW	CX	CY	CZ	DA	DB	DC	DD	DE	DF	DG	DH	DI	DJ	DK	DL	DM	DN	DO	DP	DQ	DR	DS	DT	DU	DV	DW	DX	DY	DZ	EA	EB	EC	ED	EE	EF	EG	EH	EI	EJ	EK	EL	EM	EN	EO	EP	EQ	ER	ES	ET	EU	EV	EW	EX	EY	EZ	FA	FB	FC	FD	FE	FF	FG	FH	FI	FJ	FK	FL	FM	FN	FO	FP	FQ	FR	FS	FT	FU	FV	FW	FX	FY	FZ	GA	GB	GC	GD	GE	GF	GG	GH	GI	GJ	GK	GL	GM	GN	GO	GP	GQ	GR	GS	GT	GU	GV	GW	GX	GY	GZ	HA	HB	HC	HD	HE	HF	HG	HH	HI	HJ	HK	HL	HM	HN	HO	HP	HQ	HR	HS	HT	HU	HV	HW	HX	HY	HZ	IA	IB	IC	ID	IE	IF	IG	IH	II	IJ	IK	IL	IM	IN	IO	IP	IQ	IR	IS	IT	IU	IV	IW	IX	IY	IZ	JA	JB	JC	JD	JE	JF	JG	JH	JI	IJ	JK	JL	JM	JN	JO	JP	JQ	JR	JS	JT	JU	JV	JW	JX	JY	JZ	KA	KB	KC	KD	KE	KF	KG	KH	KI	KJ	KK	KL	KM	KN	KO	KP	KQ	KR	KS	KT	KU	KV	KW	KX	KY	KZ	LA	LB	LC	LD	LE	LF	LG	LH	LI	LJ	LK	LM	LN	LO	LP	LQ	LR	LS	LT	LU	LV	LV	LW	LX	LY	LZ	MA	MB	MC	MD	ME	MF	MG	MH	MI	MJ	MK	ML	MM	MN	MO	MP	MQ	MR	MS	MT	MU	MV	MW	MX	MY	MZ	NA	NB	NC	ND	NE	NF	NG	NH	NI	NJ	NK	NL	NM	NO	NP	NQ	NR	NS	NT	NU	NV	NW	NX	NY	NZ	OA	OB	OC	OD	OE	OF	OG	OH	OI	OJ	OK	OL	OM	ON	OO	OP	OQ	OR	OS	OT	OU	OV	OW	OX	OY	OZ	PA	PB	PC	PD	PE	PF	PG	PH	PI	PJ	PK	PL	PM	PN	PO	PP	PQ	PR	PS	PT	PU	PV	PW	PX	PY	PZ	QA	QB	QC	QD	QE	QF	QG	QH	QI	QJ	QK	QL	QM	QN	QO	QP	QQ	QR	QS	QT	QU	QV	QW	QX	QY	QZ	RA	RB	RC	RD	RE	RF	RG	RH	RI	RJ	RK	RL	RM	RN	RO	RP	RQ	RR	RS	RT	RU	RV	RW	RX	RY	RZ	SA	SB	SC	SD	SE	SF	SG	SH	SI	SJ	SK	SL	SM	SN	SO	SP	SQ	SR	SS	ST	SU	SV	SW	SX	SY	SZ	TA	TB	TC	TD	TE	TF	TG	TH	TI	TJ	TK	TL	TM	TN	TO	TP	TQ	TR	TS	TU	TV	TW	TX	TY	TZ	UA	UB	UC	UD	UE	UF	UG	UH	UI	UJ	UK	UL	UM	UN	UO	UP	UQ	UR	US	UT	UU	UV	UW	UX	UY	UZ	VA	VB	VC	VD	VE	VF	VG	VH	VI	VJ	VK	VL	VM	VN	VO	VP	VQ	VR	VS	VT	VU	VV	VW	VX	VY	VZ	WA	WB	WC	WD	WE	WF	WG	WH	WI	WJ	WK	WL	WM	WN	WO	WP	WQ	WR	WS	WT	WU	WV	WX	WY	WZ	XA	XB	XC	XD	XE	XF	YG	YH	YI	YJ	YK	YL	YM	YN	YO	YP	YQ	YR	YS	YT	YU	YV	YW	YX	YY	YZ	ZA	ZB	ZC	ZD	ZE	ZF	ZG	ZH	ZI	ZJ	ZK	ZL	ZM	ZN	ZO	ZP	ZQ	ZR	ZS	ZT	ZU	ZV	ZW	ZX	ZY	ZZ	AA	AB	AC	AD	AE	AF	AG	AH	AI	AJ	AK	AL	AM	AN	AO	AP	AQ	AR	AS	AT	AU	AV	AW	AX	AY	AZ	BA	BB	BC	BD	BE	BF	BG	BH	BI	BJ	BK	BL	BM	BN	BO	BP	BQ	BR	BS	BT	BU	BV	BW	BX	BY	BZ	CA	CB	CC	CD	CE	CF	CG	CH	CI	CJ	CK	CL	CM	CN	CO	CP	CQ	CR	CS	CT	CU	CV	CW	CX	CY	CZ	DA	DB	DC	DD	DE	DF	DG	DH	DI	DJ	DK	DL	DM	DN	DO	DP	DQ	DR	DS	DT	DU	DV	DW	DX	DY	DZ	EA	EB	EC	ED	EE	EF	EG	EH	EI	EJ	EK	EL	EM	EN	EO	EP	EQ	ER	ES	ET	EU	EV	EW	EX	EY	EZ	FA	FB	FC	FD	FE	FF	FG	FH	FI	FJ	FK	FL	FM	FN	FO	FP	FQ	FR	FS	FT	FU	FV	FW	FX	FY	FZ	GA	GB	GC	GD	GE	GF	GG	GH	GI	GJ	GK	GL	GM	GN	GO	GP	GQ	GR	GS	GT	GU	GV	GW	GX	GY	GZ	HA	HB	HC	HD	HE	HF	HG	HH	HI	HJ	HK	HL	HM	HN	HO	HP	HQ	HR	HS	HT	HU	HV	HW	HX	HY	HZ	IA	IB	IC	ID	IE	IF	IG	IH	II	IJ	IK	IL	IM	IN	IO	IP	IQ	IR	IS	IT	IU	IV	IW	IX	IY	IZ	JA	JB	JC	JD	JE	JF	JG	JH	JI	IJ	JK	JL	JM	JN	JO	JP	JQ	JR	JS	JT	JU	JV	JW	JX	JY	JZ	KA	KB	KC	KD	KE	KF	KG	KH	KI	KJ	KK	KL	KM	KN	KO	KP	KQ	KR	KS	KT	KU	KV	KW	KX	KY	KZ	LA	LB	LC	LD	LE	LF	LG	LH	LI	LJ	LK	LM	LN	LO	LP	LQ	LR	LS	LT	LU	LV	LV	LW	LX	LY	LZ	MA	MB	MC	MD	ME	MF	MG	MH	MI	MJ	MK	ML	MM	MN	MO	MP	MQ	MR	MS	MT	MU	MV	MW	MX	MY	MZ	NA	NB	NC	ND	NE	NF	NG	NH	NI	NJ	NK	NL	NM	NO	NP	NQ	NR	NS	NT	NU	NV	NW	NX	NY	NZ	OA	OB	OC	OD	OE	OF	OG	OH	OI	OJ	OK	OL	OM	ON	OO	OP	OQ	OR	OS	OT	OU	OV	OW	OX	OY	OZ	PA	PB	PC	PD	PE	PF	PG	PH	PI	PJ	PK	PL	PM	PN	PO	PP	PQ	PR	PS	PT	PU	PV	PW	PX	PY	PZ	QA	QB	QC	QD	QE	QF	QG	QH	QI	QJ	QK	QL	QM	QN	QO	QP	QQ	QR	QS	QT	QU	QV	QW	QX	QY	QZ	RA	RB	RC	RD	RE	RF	RG	RH	RI	RJ	RK	RL	RM	RN	RO	RP	RQ	RR	RS	RT	RU	RV	RW	RX	RY	RZ	SA	SB	SC	SD	SE	SF	SG	SH	SI	SJ	SK	SL	SM	SN	SO	SP	SQ	SR	SS	ST	SU	SV	SW	SX	SY	SZ	TA	TB	TC	TD	TE	TF	TG	TH	TI	TJ	TK	TL	TM	TN	TO	TP	TQ	TR	TS	TU	TV	TW	TX	TY	TZ	UA	UB	UC	UD	UE	UF	UG	UH	UI	UJ	UK	UL	UM	UN	UO	UP	UQ	UR	US	UT	UU	UV	UW	UX	UY	UZ	VA	VB	VC	VD	VE	VF	VG	VH	VI	VJ	VK	VL	VM	VN	VO	VP	VQ	VR	VS	VT	VU	VV	VW	VX	VY	VZ	WA	WB	WC	WD	WE	WF	WG	WH	WI	WJ	WK	WL	WM	WN	WO	WP	WQ	WR	WS	WT	WU	WV	WX	WY	WZ	XA	XB	XC	XD	XE	XF	YG	YH	YI	YJ	YK	YL	YM	YN	YO	YP	YQ	YR	YS	YT	YU	YV	YW	YX	YY	YZ	ZA	ZB	ZC	ZD	ZE	ZF	ZG	ZH	ZI	ZJ	ZK	ZL	ZM	ZN	ZO	ZP	ZQ	ZR	ZS	ZT	ZU	ZV	ZW	ZX	ZY	ZZ	AA	AB	AC	AD	AE	AF	AG	AH	AI	AJ	AK	AL	AM	AN	AO	AP	AQ	AR	AS	AT	AU	AV	AW	AX	AY	AZ	BA	BB	BC	BD	BE	BF	BG	BH	BI
---------	------	------	-----	------	-------	------	----	------	----	----	----	----	---	----	----	----	----	----	----	----	-----------------	-----------------	-----------------	-----------------	-----------------	----	----	----	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----

Table 4 Average chemical compositions of pyrite in thin sections from cores DEP-1 and DEP-2

Mineral	Sample	Core	Fe wt %	S wt %	As ppm	Sb ppm	Zn ppm	Mo ppm	Ca wt%	Total wt %
pyrite	152-149	DEP-1	42	52	8788	730	320	0	0,19	95
pyrite	152-149b	DEP-1	47	52	2113	0	48	0	0,53	99
pyrite	190-187	DEP-1	47	52	1281	18	40	0	0,04	99
pyrite	190-187	DEP-1	48	53	360	0	15	0	0,03	101
pyrite	213-209b	DEP-1	47	53	451	9	68	0	0,15	100
pyrite	213-209	DEP-1	46	52	1412	16	54	0	0,24	98
pyrite	60-57a	DEP-2	47	53	794	9	59	0	0,22	99
pyrite	60-57b	DEP-2	46	52	1164	11	806	0	0,39	98
pyrite	137-136	DEP-2	38	51	6597	57	19	0	0,52	90
pyrite	206-203d	DEP-2	47	53	1846	32	28	0	0,03	100
pyrite	207-206b	DEP-2	47	52	1713	25	98	0	0,11	99
pyrite	222-219	DEP-2	46	54	681	66	21	0	0,76	101
pyrite	226-222	DEP-2	48	53	285	13	6	0	0,06	101

Table 5 Average chemical compositions of powellite in thin sections from core DEP-1

Mineral	Sample	Core	Fe ppm	S ppm	As ppm	Sb ppm	Zn ppm	Mo wt%	Ca wt%	Total wt %
powellite	152-149	DEP-1	5935	4690	15050	0	755	23	15	41
powellite	156-152	DEP-1	472	3216	17640	34	1312	42	21	66

Dr. Pichler reported that during the analysis of pyrite crystals found in cores DEP-1 and 2, the MDL for molybdenum was 30 ppm.

Table 6 Tritium (^3H) and Helium (^3He) Ages

Field ID	^3H [TU]	^3H - ^3He [TU]	Alter [Jahre]
DEP-1 (145-165')	0.56	5	40
DEP-1 (205-225')	0	0.5	>50
DEP-1 (250-270')	0	0	>50
DEP-1 (300-320')	0	0.5	>50
DEP-2 (143-163')	1.25	3.7	30
DEP-2 (197-217')	0.18	0.5	20
DEP-2 (256-276')	0	0	>50
DEP-2 (300-320')	0	0	>50
DEP-3 (147-167')	0.78	3.7	30
DEP-3 (195-215')	0	0	>50
DEP-3 (245-265')	0	0	>50
DEP-3 (300-320')	0	0	>50
DEP-4 (143-163')	0.03	0	>50
DEP-4 (208-228')	0	0	>50
DEP-4 (255-275')	0.03	0	>50
DEP-4 (300-320')	0.02	0	>50
DEP-5 (153-173')	0.11	0.6	32
DEP-5 (200-220')	0.02	0	>50
DEP-5 (250-270')	0	0	>50
DEP-5 (300-320')	0	0	>50
2802 PRITCHER MANOR COURT	1.25	16.5	46
2815 HARTLEY LANE	1.55		
3010 TOOLE ROAD	1	5.6	33
5364 WOOD ROAD	1.63	9	33
7911 CAREY ROAD	0.17	1	32
7935 CAREY ROAD	1.4	10.5	38
8010 EDSON ROAD	0.65	13	54
8133 EDISON ROAD	0.5		
8312 BOB WIGGS AVENUE	2.2		
8408 BOB WIGGS AVENUE	2.55		
8410 PRITCHER ROAD	0.13		
8438 BOB WIGGS AVENUE	0.65		
8506 PRITCHER ROAD	0.5	2.6	30
8601 PRITCHER ROAD	1.25	2.7	20
8602 ROCKN T RANCH	0.86		
8710 COUNTY LINE ROAD	0.04	0	
8721 COUNTY LINE ROAD	0.85	5	35
8834 CAREY ROAD	1.5	11.5	38
SCHOOL IRRIGATION WELL	0	0	>50
SCHOOL VOLLEYBALL COURT	0.65	2.25	27
SURFICIAL MW-1	2.1	9.2	30
SURFICIAL MW-2	2.22	7.4	26
SURFICIAL MW-3	1.85		
SURFICIAL MW-4	3.6	23.3	38
SURFICIAL MW-5	1.9	4.2	21
SURFICIAL MW-6	2.5	10.4	30
SURFICIAL MW-7	2		
SURFICIAL MW-8	2.1	6.4	25

Appendix: Enchem Tasks

To date EnChem Consulting has performed the following tasks:

December 2007

We analyzed 40 supply well samples for total arsenic and antimony as well as arsenic speciation (arsenite and arsenate) and field measurements for sulfide (HS^-). Compilation and interpretation of oxygen and hydrogen isotope data.

February 2008

Carried out a detailed stratigraphic description of two cores (DEP-1 and DEP-2) to delineate the presence of arsenic in the aquifer matrix, which included (a) the chemical analyses of 144 core samples (arsenic, antimony, iron, sulfur, silica, calcium, magnesium, strontium, molybdenum and phosphorous).

April 2008

Completed the detailed description of samples taken from cores DEP-1 and DEP-2 by stereo microscope. Preparation of 18 thin sections for electron microprobe analyses of mineral phases to determine arsenic, antimony, calcium, molybdenum, zinc and sulfur concentrations. These samples were chosen based on their bulk chemical composition. Electron microprobe analyses of those samples.

May 2008

We analyzed 20 samples from well clusters DEP-1, DEP-2, DEP-3, DEP-4, and DEP-5 (4 per cluster) for total arsenic, arsenic speciation (arsenite and arsenate), antimony and molybdenum.

June 2008

We analyzed 20 samples from well clusters DEP-1, DEP-2, DEP-3, DEP-4, and DEP-5 (4 per cluster) for total arsenic, arsenic speciation (arsenite and arsenate), antimony and molybdenum.

October 2008

We analyzed 20 samples from well clusters DEP-1, DEP-2, DEP-3, DEP-4, and DEP-5 (4 per cluster) for total arsenic, arsenic speciation (arsenite and arsenate), antimony and molybdenum.

April 2009

We analyzed 40 samples from well clusters DEP-1, DEP-2, DEP-3, DEP-4, and DEP-5 (4 per cluster), as well as 20 samples from private supply wells which were chosen based on As and Mo concentrations for total arsenic, arsenic speciation (arsenite and arsenate), antimony and molybdenum.

These 40 wells were also sampled for groundwater dating using the tritium-helium method (T-He). Data for the T-He samples will be available late 2009 or early 2010 since this type of analysis takes about 6 months to complete. Oxygen and hydrogen isotopes for these 40 samples are also in the process of being analyzed.

Appendix: Water Levels in DEP-1 to DEP-5

Well I.D.	Top-of-Casing Elevation (NGVD) ¹	Date	Time	Water Level Below Top-of-Casing	Water Level (NGVD)
DEP-1 (145-165')	110.35	04/18/08	923	53.65	56.70
		05.05.08	1544	59.36	50.99
		06.09.08	1419	66.13	44.22
		10/13/08	1714	52.25	58.10
		04/22/09	1029	66.07	44.28
DEP-1 (205-225')	110.40	04/18/08	921	57.71	52.69
		05.05.08	1541	63.25	47.15
		06.09.08	1417	71.54	38.86
		10/13/08	1716	55.61	54.79
		04/22/09	1027	71.00	39.40
DEP-1 (250-270')	110.21	04/18/08	920	57.63	52.58
		05.05.08	1539	63.19	47.02
		06.09.08	1416	71.48	38.73
		10/13/08	1718	55.54	54.67
		04/22/09	1023	70.95	39.26
DEP-1 (300-320')	110.25	04/18/08	918	57.76	52.49
		05.05.08	1537	63.32	46.93
		06.09.08	1415	71.61	38.64
		10/13/08	1719	55.65	54.60
		04/22/09	1020	71.07	39.18
DEP-2 (143-163')	91.11	04/18/08	853	38.73	52.38
		05.05.08	1524	45.08	46.03
		06.09.08	1436	51.66	39.45
		10/13/08	1645	37.15	53.96
		04/22/09	1013	51.47	39.64
DEP-2 (197-217')	92.33	04/18/08	849	42.21	50.12
		05.05.08	1526	48.05	44.28
		06.09.08	1435	56.37	35.96
		10/13/08	1648	40.24	52.09
		04/22/09	1009	55.43	36.90
DEP-2 (256-276')	91.43	04/18/08	846	42.73	48.70
		05.05.08	1528	48.51	42.92
		06.09.08	1433	56.98	34.45
		10/13/08	1643	40.70	50.73
		04/22/09	1005	56.50	34.93
DEP-2 (300-320')	91.48	04/18/08	844	42.77	48.71
		05.05.08	1529	48.51	42.97
		06.09.08	1431	57.02	34.46
		10/13/08	1647	40.75	50.73
		04/22/09	1007	56.52	34.96
DEP-3 (147-167')	84.45	04/18/08	907	32.40	52.05

		05.05.08	1517	38.59	45.86
		06.09.08	1447	45.55	38.90
		10/13/08	1703	30.63	53.82
		04/22/09	929	45.00	39.45
DEP-3 (195-215')	84.42	04/18/08	905	35.57	48.85
		05.05.08	1516	41.32	43.10
		06.09.08	1446	49.78	34.64
		10/13/08	1701	33.58	50.84
		04/22/09	934	49.21	35.21
DEP-3 (245-265')	84.08	04/18/08	902	35.17	48.91
		05.05.08	1514	40.92	43.16
		06.09.08	1445	49.36	34.72
		10/13/08	1659	33.17	50.91
		04/22/09	937	48.80	35.28
DEP-3 (300-320')	83.25	04/18/08	859	34.31	48.94
		05.05.08	1510	40.06	43.19
		06.09.08	1444	48.49	34.76
		10/13/08	1658	32.36	50.89
		04/22/09	944	47.97	35.28
DEP-4 (143-163')	99.82	04/18/08	939	40.89	58.93
		05.05.08	1559	45.21	54.61
		06.09.08	1402	52.96	46.86
		10/13/08	1729	38.41	61.41
		04/22/09	1037	53.02	46.80
DEP-4 (208-228')	99.53	04/18/08	938	45.57	53.96
		05.05.08	1557	50.90	48.63
		06.09.08	1401	59.21	40.32
		10/13/08	1731	42.68	56.85
		04/22/09	1035	58.85	40.68
DEP-4 (255-275')	99.51	04/18/08	941	45.55	53.96
		05.05.08	1556	50.88	48.63
		06.09.08	1400	59.19	40.32
		10/13/08	1733	42.66	56.85
		04/22/09	1032	58.93	40.58
DEP-4 (300-320')	99.11	04/18/08	934	45.13	53.98
		05.05.08	1550	50.46	48.65
		06.09.08	1359	58.76	40.35
		10/13/08	1735	42.25	56.86
		04/22/09	1030	58.37	40.74
DEP-5 (153-173')	86.87	04/18/08	1051	38.67	48.20
		05.05.08	1449	44.48	42.39
		06.09.08	1326	52.83	34.04
		10/13/08	1604	37.36	49.51
		04/22/09	1236	52.27	34.60
DEP-5 (200-220')	86.97	04/18/08	1050	38.91	48.06
		05.05.08	1447	44.78	42.19
		06.09.08	1325	53.17	33.80

		10/13/08	1606	37.61	49.36
		04/22/09	1233	52.58	34.39
DEP-5 (250-270')	87.12	04/18/08	1047	40.28	46.84
		05.05.08	1446	46.10	41.02
		06.09.08	1323	54.86	32.26
		10/13/08	1607	38.49	48.63
		04/22/09	1228	54.52	32.60
DEP-5 (300-320')	87.16	04/18/08	1045	40.31	46.85
		05.05.08	1445	46.13	41.03
		06.09.08	1320	54.91	32.25
		10/13/08	1609	38.54	48.62
		04/22/09	1225	54.56	32.60

Appendix: Core Description DEP-1

[illegible]

Appendix: Core Description DEP-2

[illegible]

Appendix: Core Chemistry DEP-1

Sample ID	Sample Interval	Sample Depth (ft)	Al ICP* mg/kg	Si ICP mg/kg	Fe ICP mg/kg	Mg ICP mg/kg	Ca ICP mg/kg	P ICP mg/kg	Sr ICP mg/kg	S ICP mg/kg	Mo ICP mg/kg	As AFS* mg/kg	Sb AFS mg/kg	Stratigraphy
DEP-1-136-132	136-132	134	575	357	337	4482	402709	85	1516	959	43	2.0	3.14	Hawthorn
DEP-1-141-136	141-136	138	489	316	1102	3276	317728	113	664	732	53	7.7	9.50	
DEP-1-144-141	144-141	142	173	294	1960	1620	119487	3215	304	764	53	10.5	0.81	
DEP-1-149-144	149-144	146	-14	174	151	2202	413831	73	919	1147	81	2.1	9.54	
DEP-1-152-149	152-149	150	1235	1028	467	1423	215257	775	423	1540	880	11.1	5.23	
DEP-1-156-152	156-152	154	168	434	225	1319	316397	63	478	728	158	31.0	9.32	
DEP-1-160-156	160-156	158	297	402	160	1280	300095	63	356	277	5	1.6	0.06	
DEP-1-164-160	164-160	162	574	507	316	1876	302281	109	408	359	15	3.2	0.13	
DEP-1-168-164	168-164	166	618	501	263	1664	259601	1199	377	401	5	1.5	0.06	
DEP-1-172-168	172-168	170	408	464	976	1220	255371	802	302	1310	30	4.7	0.34	
DEP-1-176-172	176-172	174	616	500	390	1601	213118	1502	427	428	1	1.2	0.05	Tampa
DEP-1-180-176	180-176	178	7040	1052	6580	9405	227519	4709	617	3798	<0.5	14.1	0.23	
DEP-1-184-180	184-180	182	7490	841	10000	8285	46863	3967	176	7339	<0.5	25.3	0.20	
DEP-1-187-184	187-184	185	6940	886	7545	7695	23284	3903	156	5705	<0.5	3.9	0.12	
DEP-1-190-187	190-187	188	5460	759	42210	6185	118489	3069	238	44609	<0.5	101.9	0.33	
DEP-1-193-190	193-190	191	7345	836	7660	6900	172719	5140	498	4813	<0.5	18.2	8.22	
DEP-1-196-193	196-193	194	2236	848	2511	3956	281702	217	508	2580	<0.5	7.3	0.32	
DEP-1-199-196	199-196	197	3274	834	1517	6505	289829	132	845	972	<0.5	2.1	0.09	
DEP-1-205-199	205-199	202	1982	723	1047	7285	290922	69	639	915	16	2.1	0.05	
DEP-1-209-205	209-205	207	1002	933	1143	7325	282129	47	1025	719	<0.5	0.4	0.03	
DEP-1-213-209	213-209	211	4038	955	4573	26055	264306	94	827	4605	56	22.7	1.06	
DEP-1-216-213	216-213	214	409	548	730	3460	295437	24	716	551	4	1.9	3.84	
DEP-1-222-216	222-216	219	239	420	304	2292	405086	26	902	310	15	1.9	0.23	
DEP-1-228-222	228-222	225	283	386	588	2121	398479	39	592	679	8	3.1	0.21	
DEP-1-232-228	232-228	230	886	736	688	3123	377804	223	1253	1086	51	10.7	1.40	
DEP-1-236-232	236-232	234	45	239	155	2853	409886	34	768	407	1	0.6	0.07	
DEP-1-236-232SP	236-232	235	41	190	223	2668	391207	36	775	510	1	0.9	8.59	
DEP-1-238-236	238-236	237	133	378	143	2555	417490	30	704	440	2	0.8	0.08	
DEP-1-244-238	244-238	241	103	318	173	2422	377567	43	660	419	<0.5	0.4	0.03	
DEP-1-248-244	248-244	246	647	630	974	2380	338118	34	626	1330	8	5.6	6.27	
DEP-1-253-248	253-248	250	33	199	159	2807	414211	41	807	357	5	0.9	0.09	
DEP-1-256-253	256-253	254	10	149	137	2687	397291	42	651	310	5	0.8	0.08	
DEP-1-261-256	261-256	258	33	187	173	2357	401521	51	523	536	8	1.2	0.20	
DEP-1-266-261	266-261	263	-2	123	128	2316	400713	54	500	510	4	1.9	5.26	
DEP-1-271-266	271-266	268	-10	119	130	2686	419534	41	474	363	2	0.3	0.01	
DEP-1-276-271	276-271	273	2	42	114	2199	394011	63	528	449	1	0.6	0.02	
DEP-1-280-276	280-276	278	58	130	200	2494	413165	70	581	328	3	1.9	2.60	
DEP-1-284-280	284-280	282	9	134	116	1954	386312	102	574	226	<0.5	0.3	0.01	
DEP-1-288-284	288-284	286	10	156	113	2095	383935	91	488	263	1	0.3	9.42	
DEP-1-292-288	292-288	290	-5	124	117	2136	376046	90	583	233	1	0.5	0.04	
DEP-1-296-292	296-292	294	13	123	158	2194	407985	100	620	221	<0.5	0.3	0.03	
DEP-1-297-296	297-296	296	-10	107	154	2292	414163	116	674	276	<0.5	0.5	0.01	
DEP-1-300-297	300-297	298	5	148	180	2139	396055	197	636	267	2	2.1	3.12	
DEP-1-303-300	303-300	301	116	307	277	2732	419677	116	628	356	1	2.1	2.49	
DEP-1-308-303	308-303	305	121	355	180	2682	405513	125	534	273	1	0.5	0.07	
DEP-1-312-308	312-308	310	62	253	188	2735	404943	181	572	286	1	0.9	0.13	
DEP-1-316-312	316-312	314	48	208	1154	2377	370913	155	568	1358	<0.5	7.1	0.18	
DEP-1-321-316	321-316	318	49	246	405	2389	368203	150	654	529	3	3.1	0.18	
DEP-1-321-316SP	321-316	319	46	206	421	2525	366920	150	629	537	4	3.2	8.45	
DEP-1-326-321	326-321	323	100	306	545	2147	383650	107	617	619	3	2.9	0.06	
DEP-1-332-326	332-326	329	42	215	322	2659	402899	119	526	454	3	1.0	7.53	
DEP-1-336-332	336-332	334	185	220	406	2696	391160	202	525	510	2	1.2	0.05	
DEP-1-339-336	339-336	337	111	204	391	2321	402139	83	557	346	4	1.6	0.06	
DEP-1-343-339	343-339	341	-38	47	199	2676	402662	68	627	351	1	1.0	0.04	
DEP-1-346-343	346-343	344	-31	66	263	2508	422861	75	866	341	3	1.3	0.07	
DEP-1-351-346	351-346	348	-17	96	260	2524	422766	104	528	295	<0.5	1.1	0.06	
Note: * ICP indicates elements analyzed by inductively coupled plasma-optical emission spectrometry and AFS indicates elements determined by atomic fluorescence spectrometry, yellow highlighted cell indicate the four depth intervals which are monitored														

Appendix: Core Chemistry DEP-2

Sample ID	Sample Interval	Sample Depth (ft)	Al	Si	Fe	Mg	Ca	P	Sr	S	Mo	As	Sb	Stratigraphy
			ICP* mg/kg	ICP mg/kg	ICP mg/kg	ICP mg/kg	ICP mg/kg	ICP mg/kg	ICP mg/kg	ICP mg/kg	ICP mg/kg	ICP mg/kg	AFS* mg/kg	
DEP-2-16-6	16-6	11	4906	331	1131	-384	3554	2878	126	104	<0.5	0.7	0.03	Surficial
DEP-2-19-16	19-16	17	9965	766	973	1726	18902	13105	644	155	<0.5	0.5	0.07	
DEP-2-22-19	22-19	20	7390	4680	5370	693	195817	70600	788	2281	<0.5	6.2	0.83	
DEP-2-26-22	26-22	24	7590	3125	4803	3054	140589	51000	319	1376	<0.5	10.6	0.90	
DEP-2-29-26	29-26	27	4711	1770	7450	63500	196530	29810	425	1579	7	25.3	0.93	
DEP-2-32-29	32-29	30	3653	1570	5115	71100	190779	23520	357	1235	15	18.8	0.66	
DEP-2-35-32	35-32	33	9030	1468	12410	62450	161407	22775	330	1069	16	47.5	2.06	
DEP-2-39-35	39-35	37	3239	1247	4241	68650	150285	9040	198	554	19	12.7	0.50	
DEP-2-43-39	43-39	41	2607	1537	4179	87950	193584	8840	273	1413	6	7.9	0.41	
DEP-2-46-43	46-43	44	4627	1458	4828	78550	167823	12340	261	3373	9	10.1	0.43	
DEP-2-47-46	47-46	46	6970	1290	6490	45050	123574	19815	319	4006	6	9.6	0.36	
DEP-2-50-47	50-47	48	2510	891	2555	96150	187643	3621	214	1722	6	3.2	0.20	
DEP-2-53-50	53-50	51	6145	1339	3597	21605	65637	17380	225	2953	2	5.0	0.35	
DEP-2-56-53	56-53	54	7165	1317	3780	27570	89924	17755	263	2854	2	5.3	0.82	
DEP-2-60-57	60-57	58	5360	1655	5535	73200	212405	32360	469	6100	63	25.5	1.61	Hawthorn
DEP-2-63-60	63-60	61	2280	1363	1865	108450	210171	8045	200	1520	7	4.2	0.29	
DEP-2-66-63	66-63	64	4662	1097	2520	85700	205656	24845	376	2413	4	5.0	0.19	
DEP-2-67-66	67-66	66	3988	1641	2952	99050	210551	15560	294	2297	6	7.7	0.35	
DEP-2-70-67	70-67	68	3118	1408	2237	88750	235504	25275	442	2406	8	6.1	0.55	
DEP-2-73-70	73-70	71	2735	1413	1982	98050	226854	18415	352	2296	33	7.9	0.87	
DEP-2-76-73	76-73	74	2843	1172	1525	98850	209553	9745	269	1617	13	5.2	0.57	
DEP-2-80-76	80-76	78	3443	1410	2448	92700	200856	15265	303	1523	5	5.1	0.73	
DEP-2-84-80	84-80	82	2638	1325	2258	94200	189544	9595	215	1304	3	3.1	0.29	
DEP-2-88-84	88-84	86	3376	1192	2003	83550	164591	7630	172	913	<0.5	2.2	0.20	
DEP-2-92-88	92-88	90	2533	909	1453	85550	173432	7235	170	1065	7	4.5	0.36	
DEP-2-96-92	96-92	94	2132	1216	1873	4275	182510	4144	93	1689	11	9.1	1.03	
DEP-2-97-96SP	97-96	95	1864	578	910	4198	327804	1246	320	699	4	10.6	1.55	
DEP-2-97-96	97-96	96	2354	1321	1009	3315	146483	1193	102	674	21	4.7	0.63	
DEP-2-101-97	101-97	99	1884	228	952	3556	312120	760	353	690	3	4.1	0.31	
DEP-2-105-101	105-101	103	794	837	387	3201	271483	931	323	463	48	7.0	0.85	
DEP-2-108-105	108-105	106	724	794	305	1662	192205	649	240	307	25	4.8	0.50	
DEP-2-112-108	112-108	110	1624	289	527	2567	329468	991	314	607	42	6.7	0.92	
DEP-2-116-112	116-112	114	2154	129	608	3218	279563	611	490	451	7	2.0	0.09	
DEP-2-118-116	118-116	117	832	579	315	2777	303755	550	811	491	5	1.5	0.06	
DEP-2-125-118	125-118	121	970	165	268	2979	349002	289	612	444	3	1.3	0.06	
DEP-2-129-125	129-125	127	801	241	429	2492	364829	358	739	820	<0.5	1.1	0.01	
DEP-2-132-129	132-129	130	899	434	1018	4801	379800	87	1086	836	1	1.9	0.05	
DEP-2-136-132	136-132	134	292	152	135	3846	401141	79	1371	838	0	1.0	0.00	
DEP-2-137-136	137-136	136	4564	189	2391	12280	251141	317	1167	1128	123	25.0	1.65	
DEP-2-142-137	142-137	139	158	81	155	898	223241	252	529	513	0	1.0	0.01	
DEP-2-146-142	146-142	144	391	567	1161	2323	226378	1249	533	525	3	1.9	0.04	
DEP-2-148-146	148-146	147	55	600	5825	686	100285	65	249	393	11	2.5	0.14	
DEP-2-152-148	152-148	150	98	565	2368	2620	325048	90	909	917	6	2.7	0.10	
DEP-2-152-148SP	152-148	151	267	603	4931	2403	254515	92	684	670	7	3.2	0.04	
DEP-2-156-152	156-152	154	384	232	325	4072	418061	63	1276	907	10	3.8	0.05	
DEP-2-161-156	161-156	158	-1	172	113	1214	392871	25	795	1041	6	5.9	0.06	
DEP-2-165-161	165-161	163	856	154	436	713	40504	14	53	433	2	1.2	0.03	
DEP-2-169-165	169-165	167	1022	386	363	1384	176996	51	296	669	1	0.8	0.02	
DEP-2-172-169	172-169	170	313	729	304	959	243061	50	387	789	1	0.8	0.01	
DEP-2-176-172	176-172	174	320	282	214	1072	224572	52	496	470	1	1.2	0.05	
DEP-2-179-176	179-176	177	1313	365	489	3470	276046	1298	927	431	<0.5	0.9	0.02	
DEP-2-183-179	183-179	181	1521	349	577	3694	256179	466	614	357	<0.5	0.9	0.01	
DEP-2-186-183	186-183	184	1683	286	677	3378	229468	825	618	358	<0.5	0.6	0.02	
DEP-2-188-186	188-186	187	988	120	892	1745	213783	388	283	963	4	4.8	0.21	
DEP-2-193-188	193-188	190	990	426	447	1960	243489	2608	637	651	3	3.4	0.13	
DEP-2-196-193	196-193	194	674	149	451	1630	256654	1271	359	751	3	3.8	0.22	
DEP-2-199-196	199-196	197	2322	1196	2523	5520	234743	2331	415	2123	5	8.4	0.17	
DEP-2-203-199	203-199	201	13640	325	14935	13345	168631	6135	429	9970	<0.5	24.2	0.58	
DEP-2-206-203	206-203	204	14680	723	20115	14070	30770	5235	197	14791	<0.5	32.7	0.67	
DEP-2-207-206	207-206	206	12430	368	16670	12135	30917	5445	213	10978	<0.5	36.8	0.62	
DEP-2-211-207	211-207	209	647	526	1561	4435	209553	24	452	1159	1	6.7	0.13	
DEP-2-215-211	215-211	213	3402	575	3511	4925	320010	1299	662	2550	<0.5	10.4	0.30	
DEP-2-215-211	215-211	214	89	158	186	3366	400523	30	1223	624	<0.5	1.5	0.01	
DEP-2-219-215	219-215	217	399	186	579	4337	365589	27	1036	514	0	2.0	0.09	
DEP-2-222-219	222-219	220	1097	440	1008	2699	362262	38	702	1295	30	11.2	1.19	
DEP-2-226-222	226-222	224	1325	1348	1906	3991	299762	308	532	2280	10	8.5	0.52	
DEP-2-231-226	231-226	228	181	283	194	2529	391778	33	613	364	0	0.7	0.02	
DEP-2-236-231	236-231	233	279	234	371	1791	386074	15	515	576	1	6.4	0.44	
DEP-2-241-236	241-236	238	2	160	139	2251	406749	24	564	329	0	0.5	0.07	
DEP-2-246-241	246-241	243	145	335	512	1421	395247	88	453	558	1	1.7	0.14	
DEP-2-249-246	249-246	247	43	188	121	2601	407082	37	490	311	1	0.5	0.06	
DEP-2-253-249	253-249	251	610	299	313	2302	380323	55	478	473	1	3.5	0.12	
DEP-2-257-253	257-253	255	-25	93	162	2432	406084	27	549	315	1	0.4	0.04	
DEP-2-262-257	262-257	259	-10	130	146	2293	414734	61	502	233	<0.5	0.3	0.01	
DEP-2-266-262	266-262	264	1	135	143	2406	400238	63	469	253	<0.5	0.1	0.02	
DEP-2-269-266	269-266	267	44	208	129	3839	407985	119	492	367	1	0.4	0.02	
DEP-2-274-269	274-269	271	25	176	122	3931	394297	161	467	444	0	0.7	0.03	
DEP-2-278-274	278-274	276	62	196	144	4185	396625	148	562	428	0	0.8	0.04	
DEP-2-282-278	282-278	280	26	170	220	3001	397576	206	448	345	<0.5	0.4	0.01	
DEP-2-286-282	286-282	284	80	222	881	2877	396958	119	713	987	3	6.1	0.11	
DEP-2-290-286	290-286	288	102	19										

Appendix: Core Chemistry DEP-5

Sample ID	Al ICP mg/kg	Si ICP mg/kg	Fe ICP mg/kg	Mg ICP mg/kg	Ca ICP mg/kg	P ICP mg/kg	Sr ICP mg/kg	S ICP mg/kg	Mo ICP mg/kg	As ICP mg/kg	As AFS mg/kg
84-80	4317	394	2953	95250	204950	13120	297	1653	-1	-2	1,52
87-84	10910	946	9475	30520	156200	53900	651	5210	-4	-10	4,43
88-87	5915	580	3473	60650	164700	22995	366	1956	-2	-3	1,38
92-88	3987	777	2157	45365	131450	18930	262	1833	3	-1	2,17
95-92	2687	310	4100	2171	13685	2878	65	3781	-2	-3	1,79
97-95	2242	313	573	2327	83000	1964	96	367	-1	-1	0,60
98-97	3307	529	3268	2639	18415	5870	99	3210	-2	-4	1,50
105-98A	2713	467	2308	2573	20730	3673	93	2321	22	14	7,32
109-105	1936	482	1803	2329	143100	3030	123	1205	6	1	1,73
111-109	2612	478	3080	2135	42360	5935	106	3178	3	2	4,27
114-111	7655	501	3431	6715	41350	14395	191	1411	0	-6	3,60
117-114	2861	246	1220	4953	224250	1244	466	817	9	17	9,17
121-117	1642	205	459	2907	188650	1067	372	408	5	2	1,04
124-121	1967	267	659	4536	321500	1567	926	532	4	2	1,37
127-124	1213	171	479	4076	357550	606	975	602	4	3	1,05
129-127	2130	169	749	5645	296400	316	677	475	5	0	0,90
132-129	2397	181	722	6030	254150	354	796	435	6	2	1,43
135-132	629	131	197	2619	309000	377	859	461	5	4	0,51
137-135	1206	81	386	3824	254250	552	610	490	6	2	0,91
141-137	1117	140	306	3475	273100	702	384	520	10	5	1,08
144-141A	1374	158	417	3923	320900	450	455	617	7	3	1,03
147-144	976	188	591	3103	318550	680	548	958	44	16	5,38
150-147	539	48	387	4496	284850	146	895	667	7	4	2,25
154-150	716	76	355	5580	293850	88	794	901	31	15	6,74
157	-1	-36	150	3174	410150	56	1195	944	-1	5	0,89
157-154	97	14	334	2213	325550	53	1035	637	2	4	0,84
162-157A	4624	364	5490	20205	196050	238	835	5490	225	77	41,29
167-162	1933	151	2328	10280	304600	130	994	2549	32	22	12,62
171-167	-28	190	370	1683	282500	26	946	449	1	4	0,91
177-174	132	207	1298	256	65700	88	264	384	3	3	0,77
180-177	84	-5	167	4208	388250	103	1707	770	2	7	1,25
185-180	1964	675	817	8795	143200	152	768	1027	94	10	5,81
188-185	200	76	161	4246	372900	89	1405	1661	4	5	1,86
191-188	639	46	243	1219	182550	51	294	539	3	3	0,97
194-191	356	270	146	3001	339200	388	585	508	0	3	0,44
197-194	268	212	147	2068	369500	100	554	739	6	3	0,92
199-197	377	146	211	2258	323500	132	486	412	4	5	0,35
202-199A	482	148	315	2486	327850	130	497	502	3	4	0,49
205-202	642	192	382	3430	340100	152	572	957	2	1	0,83
208-205	1567	159	720	6025	150150	831	423	547	4	-1	0,74
211-208A	415	71	242	2045	328350	377	438	738	2	4	0,56
214-211	1048	85	456	2469	210250	1438	329	563	4	2	0,78
219-217	865	185	342	3270	159000	1952	237	400	2	3	0,70
221-219 A	10455	383	10970	11650	113400	7085	271	7950	3	1	13,32
221-219 B	2544	285	2058	4025	149200	1379	298	800	4	-1	12,69
224-221	8910	411	70100	10185	42605	5555	216	80950	-56	-4	56,24
227-224A	10035	297	17200	10040	53650	6730	236	15235	20	37	33,85
231-227	1668	220	2179	1158	85350	2252	405	717	1	-4	1,10
234-231A	363	156	1123	2269	390600	58	708	1493	-1	8	3,40
237-234	368	226	328	2725	396600	53	1015	756	8	7	2,85
241-237	3234	278	820	5445	290650	31	563	880	111	19	11,58
244-241	947	429	319	1577	294200	23	296	429	32	18	8,06
247-244	3899	329	14255	3886	40375	11	114	15175	224	31	24,41
251-247	666	311	202	2405	375900	28	490	319	2	4	1,16
255-251	54	-44	260	2665	410100	34	506	543	3	2	0,08
259-255	296	299	146	1918	389450	56	325	250	-1	2	0,28
263-259A	-29	-119	101	3245	433950	18	523	270	5	3	0,08
269-263	79	139	150	2220	419700	27	471	318	-1	5	0,25
270-267	-27	-122	67	2004	406150	39	440	325	0	4	0,12
275-270	-32	-119	100	2118	418500	39	393	307	1	5	0,12
278-275	-35	-131	90	2363	417750	39	467	489	-1	4	0,13
281-278	17	-68	103	2622	415150	46	437	298	-1	3	0,14
284-281	2	-97	66	2206	408300	83	405	312	-1	1	0,09
287-284	-12	-96	100	2111	413950	75	410	252	-1	2	0,09
289-287	19	-44	118	2364	410350	105	403	278	1	2	0,12
291-289	14	-41	87	2451	397800	91	406	286	0	2	0,14
295-291	25	-60	242	2789	414950	105	404	465	7	5	0,32
299-295	4	-91	124	2369	407150	159	409	297	-1	3	0,21
303-299	41	-24	124	2336	421950	106	464	292	0	3	0,13
307-303	7	-47	202	2493	430500	122	530	347	0	4	0,28
309-307	37	-47	303	2493	404550	186	496	363	-1	3	3,66
312-309	23	-14	352	2378	400100	461	531	378	5	6	0,75
315-312	63	44	272	2669	415700	110	522	312	0	4	0,28
317-315	82	108	215	2427	393800	134	413	357	-1	5	0,42
320-317	79	123	455	3156	369250	165	408	731	-1	3	0,70