Arsenic and ASR in Southwest Florida: Source, Abundance, and Mobilization Mechanism
Suwannee Limestone, Upper Floridan Aquifer

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Abstract:

Recent analyses of recovered water from two ASR facilities in west-central Florida showed arsenic concentration in excess of 100 µg/L, more than 10-times the current EPA drinking water standard. Detailed mineralogical and chemical analyses of the Suwannee Limestone, the primary storage zone for ASR in Central Florida, indicates that, while arsenic is ubiquitous throughout the Suwannee Limestone, it is highly concentrated in framboidal pyrite. Elevated levels of arsenic in pyrite were documented by SEM and Electron Probe Microanalysis with EDX and WDX capabilities, respectively, showing greater than 1000 ppm arsenic. The pyrite containing the arsenic is normally stable in the reducing environment of the aquifer, but the artificial recharge of oxidized surface water during ASR changes the redox conditions and is believed to cause the framboidal pyrite to become unstable, thus releasing the arsenic.

Statement of Problem

During recharge and recovery cycle testing of two ASR facilities in the Southwest Florida Water Management District (SWFWMD, Figure 1), it was determined that high levels of naturally occurring arsenic were present in recovered water (Arthur et al. 2001).

Concentrations were highest in the first recharge-recovery cycle and reached levels of nearly 100 ug/l (ppb) in one of the four wells undergoing testing (Figure 2). Although arsenic concentrations decreased in subsequent cycle tests, in the first well to complete three full cycle tests, concentrations still ranged from 5 to 35 ug/l. The analyses not only show elevated arsenic levels, but also show an increase in concentrations of uranium, strontium, and other potentially harmful elements (Arthur et al., 2000).

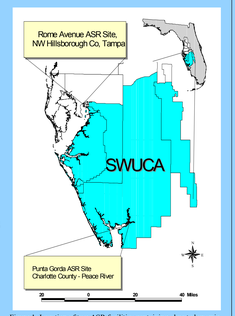


Figure 1: Location of two ASR facilities containing elevated arsenic concentrations (modified from Arthur et al. 2001). The Southern Water-use Caution Area is the most likely area for future ASR projects.

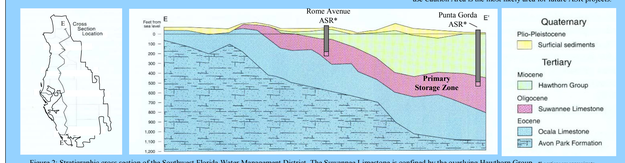


Figure 2: Stratigraphic cross section of the Southwest Florida Water Management District. The Suwannee Limestone is confined by the overlying Hawthorn Group. *Locations are approximate.

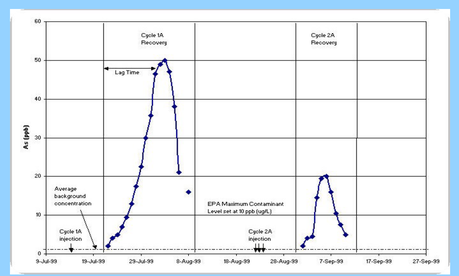


Figure 3: Arsenic concentration through time for two recharge/recovery cycles, Punta Gorda ASR, Charlotte County, Florida (modified from Arthur et al, 2001). The Rome Avenue ASR site also showed increased As concentrations.

Arthur and others (2001), have proposed three potential sources for naturally occurring arsenic being mobilized from the Suwannee Limestone:

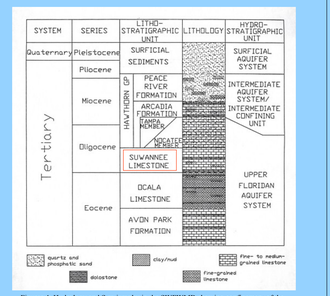
1) In sulfide minerals such as pyrite (FeS_2) within the limestone matrix,
2) Adsorbed to iron and manganese oxyhydroxide coatings on the limestone grains,
3) Or in organic material in the limestone matrix.

Natural arsenic in groundwater of the United States has also been shown to source from these minerals, with the sulfides and iron oxides being the most common association (Welch et al., 2000). Arsenic can be mobilized either by oxidation of pyrite or reduction of iron hydroxides.

Hydrology and Stratigraphy

The Suwannee Limestone is confined by the Hawthorn Group (Figures 2 and 4) and contains abundant mollusk molds and casts in some areas, creating moldic porosity. These conditions are ideal for ASR.

The lithology of the Suwannee Limestone throughout the study area consists primarily of limestone, which has been described as a wackestone mud to pelletal, foraminiferal grainstone. It contains minor amounts of phosphatic quartz sand and clay, some dolomite, chert nodules, and organic material (Green et al, 1995). Framboidal pyrite has also been documented in trace amounts.



Figures 4: Hydrology and Stratigraphy in the SWFWMD showing confinement of the primary ASR storage zone in the area, the Oligocene Suwannee Limestone. The cross section below also shows this confinement, as well as the distribution of the Suwannee in the SWFWMD.

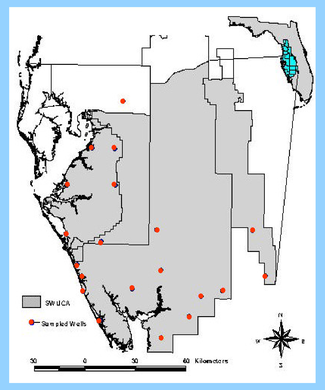


Figure 5: Map showing the location of SWFWMD wells where core samples were collected. Future ASR facilities will likely be near the west coast where saltwater upconing limits the supply of groundwater. Core samples were supplied by the Regional Observation Monitor Well Program (ROMP) of the SWFWMD and the Florida Geological Survey.

Sample Collection

During this study, cores from 22 wells were sampled to gain a better understanding of the arsenic distribution and mineralogy within the Suwannee Limestone (Figure 3). Core selection was limited to wells with discrete monitor intervals in the Suwannee Limestone to allow for future correlation of core data and water quality data with the certainty that no mixing with other formation water has occurred.

Each core was sampled at an even spacing to ensure representation of the entire Suwannee Limestone interval. "Special Interest" samples were also taken. These areas contained visible pyrite, organic material or iron oxyhydroxides.

Analytical Methods

To determine the exact location of the arsenic, the following steps were used:

1) Well Selection based on core availability and open-casing interval
2) Core collection – samples were taken with depth and suspected areas of arsenic occurrence (ie. observable FeOH, FeS_2, $CaPO_4$, or organic material).
3) Acid digestion of powdered sample using Aqua Regia (3:1 HCl to HNO_3) after removing all drill bit surfaces.
4) Analyze aliquot using Hydride Generation-Atomic Fluorescence Spectrometry (HG-AFS) to determine total As concentration in Rock (PSA Millennium)
5) Analyze aliquot using Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES) to determine other elements such as Fe, S, P, etc. and compare with As concentrations (PE Optima 2000 DV)
6) Analyze thin sections of the highest 25 As samples using Scanning Electron Microscopy with Energy Dispersive X-Ray (SEM-EDX) capabilities and a Robinson backscatter detector for elemental analysis.(JSM-5900-LV)
7) Analyze thin sections using Electron Probe Microanalyzer (EPMA) with Wave Dispersive X-Ray (EM-WDX) capabilities (JXA-8900-R)

Results

Lithologic Descriptions

Visual and microscopic inspection of the Suwannee Limestone mineralogy showed all previously suggested sources of arsenic were present in trace amounts throughout. Samples were largely composed of pure limestone. Primary and secondary trace minerals, including framboidal pyrite or marcasite, apatite, and quartz sand occurred throughout. Pyrite was the most abundant and often occurred along with secondary calcite in fossil molds.

Scanning Electron Microscope

The following SEM images show well developed framboidal pyrite distributed throughout the entire thickness of the Suwannee Limestone. Each framboid is about 10 to 20 µm in diameter and is composed of many equant, equidimensional pyrite microcrystals. Single euhedral pyrite crystals were also observed (circled). Energy Dispersive Spectroscopy (Figure 6) shows a well defined arsenic peak (Figure 6), proving for the first time that the framboids contain As greater than 1000 ppm.

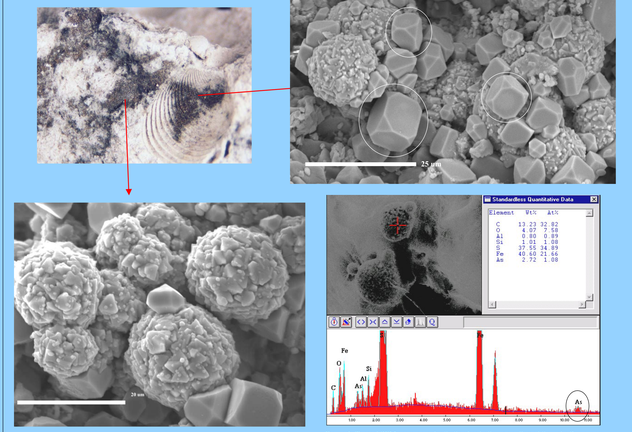


Figure 6: Typical SEM spectrograph of a framboid of pyrite collected from the Suwannee Limestone. Note two As peaks. The As peak on the left can sometimes be confused with Mg. The As peak on the right proves the pyrite contains arsenic.

Whole Rock Chemistry

Chemical analyses of digested samples were carried out using HG-AFS to detect total arsenic concentrations, and ICP–OES for other important elements including Fe, S, P, Ca, Si, Sr, Mn, and Mg. Iron and sulfur have very good correlation, suggestion that all of the iron and sulfur in the rock is bound together as pyrite (Figure 7). Lack of correlation with arsenic may suggest another source, but probably indicates the varying percentage of arsenic in pyrite (Figures 8 and 9). Microprobe data (Table 1) supports this interpretation.

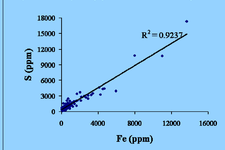


Figure 7: XY plot of Sulfur vs. Iron in the Suwannee Limestone. Very good correlation exists between Fe and S.

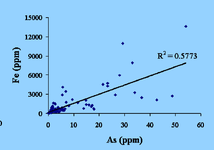


Figure 8: XY plot of Fe vs. As.

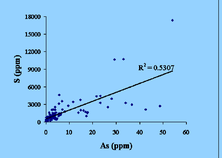


Figure 9: XY plot of Sulfur vs. Arsenic.

Electron Probe Microanalysis

Electron Microprobe with Wave Dispersive X-ray analyzer was used to analyze pyrites, iron hydroxides, organics, and phosphate for arsenic. Both arsenic peaks are present only in framboidal pyrite and supports SEM data. Table 1 shows the variability of arsenic within each framboid.

Sample	Fe	S	As
DV249-1	43.93	49.08	1.23
LB-764-1	39.65	48.94	0.1819
H-281-1	41.76	48.55	0.1711
14-730G-1	38.24	47.16	0.2287
5-875-1	42.81	49.32	1.28
P-2-58-1	44.04	51.81	0.3147
8-1-544-1	39.83	33.32	0.2521
8-1-544-2	42.24	33.02	0.2935

Table 1: Wt % Fe, S, and As in selected pyrite framboids from Electron Probe Microanalysis. Note variability in As concentrations vs. Fe and S.

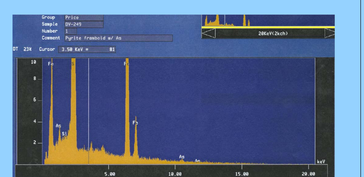


Figure 10: Spectrograph from Microprobe analysis of pyrite framboids showing both arsenic peaks.

Discussion

The Fe-S-As-O-H system in groundwater is primarily controlled by redox conditions. Groundwater of the Suwannee LS is, in most cases, reducing, and pyrite is believed to be the dominant mineral phase following the Eh pH diagram below (Figure 11).

The following images show oxidized framboids of pyrite with a ring of iron hydroxide. This ring is typical of oxidized framboids (Evangelou, 1995). Based on the Eh-pH stability diagram given as an example, the iron hydroxides are not believed to be stable in subsurface reducing environment and are only a result of oxidation of pyrite after exposure to the atmosphere. This is, however, the same oxidation process that would take place during aquifer storage and recovery. ASR recharge water is treated to potable drinking water standards prior to injection and thus has much higher DO content than typical groundwater. Oxidation of pyrite takes place by the following reactions:

Initial oxidation by O_2:

$$FeS_2 + 7/2\ O_2 + H_2O \Rightarrow Fe^{2+} + 2\ SO_4^{2-} + 2\ H^+$$

The Fe^{2+} produced can be further oxidized to Fe^{3+}, which in turn hydrolyzes into iron hydroxide.

$$Fe^{2+} + 0.5\ O_2 + H^+ \Rightarrow Fe^{3+} + H_2O \quad \text{and}$$

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

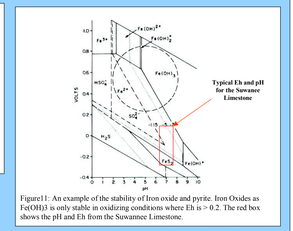
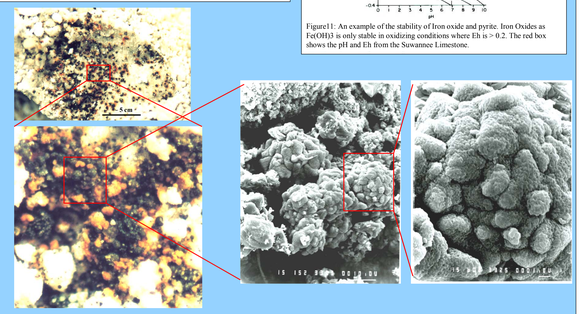


Figure11: An example of the stability of Iron oxide and pyrite. Iron Oxides as Fe(OH)3 is only stable in oxidizing conditions where Eh is > 0.2. The red box shows the pH and Eh from the Suwannee Limestone.



Conclusions

Our detailed lithological, mineralogical, and geochemical study of arsenic in the Upper Floridan aquifer, Suwannee Limestone shows:

1) All previously suggested sources for the arsenic can be found in trace amounts throughout the Suwannee Limestone.
2) Framboidal pyrite was the most abundant and was unevenly distributed throughout, occurring most often with secondary calcite in moldic porosity zones used during ASR.
3) Nodular phosphate, quartz, clay, and organics were also present in trace amounts, while iron hydroxides were very rarely observed.
4) Framboidal pyrite contains arsenic at concentrations in excess of 1000 ppm, although arsenic concentrations vary from pyrite crystal to pyrite crystal. Other trace minerals contain arsenic in much lower amounts when compared to framboidal pyrite.

ASR recharge water in Florida is treated with O_3 prior to injection, which causes the water to be highly oxidized relative to the low-oxygen conditions of the Suwannee Limestone water. This change in redox conditions will cause the dissolution of framboidal pyrite, thus releasing high concentrations of arsenic. This study indicates that, if the pyrite hypothesis is accepted, the current injection practices in Florida should be revised to prevent the release of arsenic during ASR.

Acknowledgements

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Selected References

Arthur J. D., Cowart J. B., and Dabous, A.A., 2001. Florida Aquifer Storage and Recovery Geochemical Study. 1999 Progress Report. Tallahassee, Florida Geological Survey, pp 1-69

Arthur J. D., Cowart J. B., and Dabous, A.A., 2002. Mobilization of arsenic and other trace elements during aquifer storage and recovery, southwest Florida. Submitted for publication in a USGS report on proceedings of the USGS Artificial Recharge Workshop, Sacramento, California, April 2002

Green, R., Arthur, J. D., and DeWitt, D., 1995, Lithostratigraphic and hydrostratigraphic cross sections through Pinellas and Hillsborough Counties, southwest Florida: Florida Geological Survey Open File Report 61, pp 26

Pichler, T., Hendry, M. J., Hall, G. E. M., 2000 The mineralogy of arsenic in uranium mine tailings at the Rabbit Lake In-pit Facility, northern Saskatchewan, Canada. Journal of Environmental Geology. vol 40, pp 495-506

Ruiter K.H. and Stuyfzand P.J., 1998. An experiment on well recharge of oxic water into an anoxic aquifer. in Peters, J.H., et al. (eds.), Artificial Recharge of Groundwater, A.A. Balkema, Rotterdam, Netherlands, pp 474-479

Welch A.H., Westjohn D.B., Helsel D.R., and Wanty, R.B., 2000. Arsenic in Ground Water of the United States: Occurrence and Geochemistry. USGS Circular.

Williams H., Cowart J. B., Arthur J. D., 2002. Florida Aquifer Storage and Recovery Geochemical Study, Southwest Florida: year one and year two progress report. FGS Report #100