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# NATURALLY OCCURRING ARSENIC IN THE UPPER FLORIDAN AQUIFER, SOUTHWEST FLORIDA: IMPLICATIONS FOR AQUIFER STORAGE RECOVERY

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**ABSTRACT**: Aquifer storage and recovery (ASR) facilities have become the storage solution of choice for many communities worldwide. The Southwest Florida Water Management District (SWFWMD) has recently determined that ASR is a critical component for its 20-year strategy to enhance water supply in southwest Florida where, as of January 2002, 26 facilities are in operation and 19 are permitted for construction. The Comprehensive Everglades Restoration Project (CERP) calls for over 330 ASR wells to store over 1.7 billion gallons of water per day. The future of ASR in Florida, however, is unclear because of the discovery of elevated arsenic (As) levels during recovery cycle testing of several ASR facilities throughout southwest Florida. Concentrations are usually highest during the first recharge-recovery cycles. Concentrations of up to 100 ppb were reached in one of four wells recently undergoing testing in the City of Tampa. Here we report our preliminary findings for arsenic concentrations in the Suwannee Limestone, the ASR storage zone for most ASR systems in southwest Florida. This is the first study in a series that address the arsenic issue during ASR

During this study core from 22 wells collected by the Regional Observation Monitor-well Program (ROMP), a division of the SWFWMD, was sampled to gain a better understanding of the arsenic distribution and mineralogy within the Suwannee Limestone. Possible sources for the arsenic include: 1) sulfide minerals, 2) iron oxyhydroxide coatings, 3) organic material, and/or 4) phosphate nodules. Optical microscope descriptions of more than 300 Suwannee Limestone core samples show only little iron oxyhydroxide, while sulfide minerals in the form of framboidal pyrite were abundant. Total arsenic concentrations were determined by hydride generation-atomic fluorescence spectrometry (HG-AFS), which showed much higher values for arsenic in the Suwannee Limestone than previously reported. In addition, the distribution of arsenic throughout the Suwannee Limestone was very heterogeneous. Samples with concentrations in excess of 20 ppm arsenic were chosen for analysis by SEM with the intent to further constrain the mineralogical arsenic association in each sample. We found that framboidal pyrite was again more abundant than expected, being present in more than 50% of the SEM samples. Research is continuing at the University of South Florida to further constrain the mineralogy of the arsenic in question. The next step will be to examine thin sections with apparatus more sensitive than SEM, such as TEM, Microprobe, or SIMS. (Key Words: Arsenic, aquifer storage recovery, Florida, limestone)

## INTRODUCTION

An essential water management tool for geographic areas of great annual rainfall variation is the storage of water during wet periods for later use during dry periods. Storage in surface reservoirs (lakes, ponds, etc.) is often an uneconomic solution because of evaporation and land use considerations. For this reason, aquifer storage and recovery (ASR) facilities have become the storage solution of choice for many communities worldwide. ASR begins with recharge when treated surface waters are pumped underground when an excess of water is available. The water is then stored underground until it is recovered to meet seasonal, long term, or emergency demands (Williams et al., 2002). ASR requires confinement of the storage zone and pumping is typically into brackish areas where ambient groundwater is inadequate for drinking.

ASR already plays a major role in the supply of drinking water to residents in southwest Florida, where, as of January 2002, 26 facilities are in operation and 19 are permitted for construction. This is a large percentage of the approximately 100 ASR facilities in operation worldwide (Arthur, 2002). The Southwest Florida Water Management District (SWFWMD) has recently determined that ASR is a critical component for its 20-year strategy to enhance water supply in southwest Florida, where increasing water consumption has caused drastic lowering of water levels and saltwater upwelling in the Floridan Aquifer System (FAS). Furthermore, ASR will be an integral part in the effort to restore the Florida Everglades (Comprehensive Everglades Restoration Project, South Florida Water Management District). The role of ASR in this unprecedented project will be to capture water normally flowing into Florida Bay and artificially recharging it into the Floridan aquifer in an effort to restore declining water levels. When completed, approximately 330 ASR wells will be storing and recovering water at combined rates of up to 1.7 billion gallons per day. Typically, ASR sites in operation in Florida are

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located in coastal regions of the central and southern peninsula. Water is pumped from a nearby source of surface water (river, pond, etc), treated to meet all primary and secondary drinking water standards, injected through the ASR wells and stored in the Upper Floridan aquifer. Upon recovery, the water is disinfected and added to the potable water supply.

The future of ASR in Florida, however, is unclear because of the discovery of elevated arsenic (As) levels during recovery cycle testing of several ASR facilities throughout southwest Florida (Williams et al, 2000). Concentrations are usually highest during the first recharge-recovery cycles and levels of nearly 100 ppb were reached in one of four wells recently undergoing testing in the City of Tampa (Arthur et al, 2001). Concentrations typically decrease after several recharge-recovery cycles but still have been found to range from 5 to 35 ppb after longer periods of time (Arthur et al, 2001; Figure 1). Background arsenic levels for these facilities were less than 0.2 ppb (Williams et al., 2002). The higher levels of arsenic are particularly alarming when considering that the current maximum contaminant level (MCL) for arsenic has recently been lowered from 50 to 10 ppb. Any solution to the arsenic problem and the safe operation of ASR in Florida is dependant upon a sound understanding of the origin, location, associated mineral phase(s), and mobilization mechanisms of As from the aquifer matrix.

Here we report our preliminary findings for arsenic concentrations in the Suwannee Limestone, the ASR storage zone for most ASR systems in southwest Florida. This is the first study in a series that address the arsenic issue during ASR.

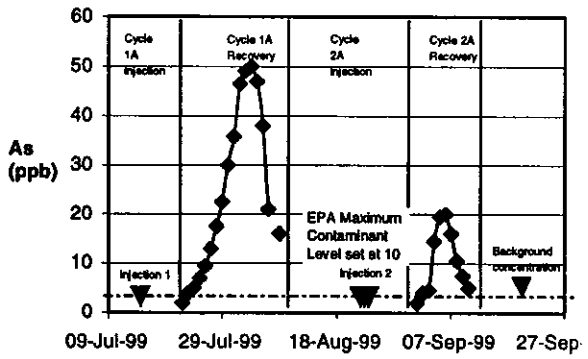


Figure 1: Arsenic concentration through time for two recharge/recovery cycles, Punta Gorda ASR, Charlotte County, Florida (modified from Arthur et al., 2001).

## HEALTH HAZARDS, TOXICITY, AND OCCURRENCE OF ARSENIC

Arsenic in drinking water is considered to be one of the prominent environmental causes of cancer mortality in the world today (Smith et al., 1992; Welch et al., 2000). Acute arsenic poisoning is associated with respiratory, neurological, and cardiovascular disorders, while chronic arsenic exposure has been linked to skin, lung, and bladder cancer (Gorby, 1994; National Research Council, 1999).

In nature arsenic is mostly present in two inorganic and two organic forms, As (III) and As (V), and DMA and MMA, respectively (Jain and Ali, 2000). Trivalent arsenic (As(III)) is about 60 times more toxic than its penta-valent state (As(V)) (Ferguson and Gavis, 1972), and inorganic arsenic compounds are about 100 times more toxic than the organic arsenic compounds DMA and MMA (Nagy and Korom, 1983).

According to a recent study by Welch et al. (2000), natural sources of arsenic in the United States include iron oxyhydroxides, sulfide minerals, organic material, and phosphate. The presence of naturally occurring arsenic in groundwater is due to leaching of arsenic from minerals in the aquifer matrix (Jain and Ali, 2000). Robertson (1989) has further reported that the occurrence and origin of arsenic in groundwater depends on several processes and conditions, such as adsorption-desorption, precipitation-dissolution, oxidation-reduction, ion exchange, grain size, organic contents, biological activity and aquifer characteristics. Furthermore, the geochemical characteristics of the aquifer material and their interactions with the aqueous media, such as artificially recharged water, also play a very important role in controlling retention and/or mobility of arsenic within the subsurface environment (Bhattacharya et al., 1995a).

## HYDROGEOLOGY OF STUDY AREA

The hydrogeology of southwest Florida can be divided into three main lithologic units. From Paleocene to Recent, they are the Floridan Aquifer System (FAS), the Intermediate Aquifer System (IAS) or confining unit, and the Surficial Aquifer System (SAS), respectively (Figure 2). The FAS consists of limestones and dolomites that can be further divided into three sub-units: the Upper Floridan aquifer, the middle confining unit, and the Lower Floridan aquifer. The lithologies are made up of a wide range of sedimentary deposits, including sands, carbonates, clays, and evaporates (Williams et al, 2002). This study focuses on the primary ASR storage zone – the Oligocene Suwannee Limestone – as well as the overlying Arcadia Formation of the Miocene Hawthorn Group (Figure 2).

## Suwannee Limestone

The Lower Oligocene Suwannee Limestone underlies much of west-central Florida, and is the only aquifer storage zone utilized to date in the SWFWMD, although certain areas of the Avon Park Formation in NW Hillsborough County are being considered (Ellison personal communication, 2001; Figure 2). The Suwannee is comprised of light gray to yellowish-gray wackestone and grainstone, contains trace amounts of sand and clay within the upper portions, and some chert and organics throughout (Green et al, 1995). The two main rock types of the Suwannee are a highly vuggy limestone containing prominent gastropod and pelecypod casts and molds, and a fine pelletal limestone with small foraminifers and pellets cemented by micrite. Green et al. (1995) also reports a dolomitic layer, 10 to 20 feet thick that exists in the lower one third of the unit in some areas. The depositional environment of the Suwannee Limestone is considered to be a shallow, warm-water carbonate bank, probably similar to the modern Bahama Banks (Miller, 1986).

| SYSTEM | SERIES | STRATIGRAPHIC UNIT | | HYDROGEOLOGIC UNIT | |
|---|---|---|---|---|---|
| QUATERNARY | HOLOCENE / PLEISTOCENE | UNDIFFERENTIATED SAND AND CLAY DEPOSITS | | SURFICIAL AQUIFER SYSTEM | |
| TERTIARY | PLIOCENE | HAWTHORN GROUP | PEACE RIVER FORMATION | INTERMEDIATE AQUIFER SYSTEM OR CONFINING UNIT | |
| | MIOCENE | HAWTHORN GROUP | ARCADIA FORMATION / TAMPA MEMBER | INTERMEDIATE AQUIFER SYSTEM OR CONFINING UNIT | |
| | OLIGOCENE | SUWANNEE LIMESTONE | | FLORIDAN AQUIFER SYSTEM | UPPER FLORIDAN AQUIFER |
| | EOCENE | OCALA LIMESTONE / AVON PARK FORMATION | | FLORIDAN AQUIFER SYSTEM | MIDDLE CONFINING UNIT |
| | PALEOCENE | OLDSMAR AND CEDDAR KEYS FORMATION | | FLORIDAN AQUIFER SYSTEM | LOWER FLORIDAN AQUIFER |

Figure 2: Simplified stratigraphic column for southwest Florida showing the relationship between the Suwannee Limestone and other units. The Suwannee is the primary storage zone in the area.

### Arcadia Member of the Hawthorn Group

Overlying the Suwannee Limestone in the southern part of the SWFWMD (Figure 3) is the Hawthorn Group. The confining nature of the Hawthorn limits recharge to the Upper Florida aquifer, prompting the SWFWMD to create the Southern Water Use Caution Area (SWUCA) where water shortages are amplified. The Hawthorn Group is comprised of two formations: the Lower Oligocene to Middle Miocene Arcadia Formation and the Middle Miocene to Lower Pliocene Peace River Formation (Williams et al, 2002; Figure 2). The Arcadia Formation is a gray, clayey, fine-grained mudstone to wackestone with highly variable amounts of quartz sand, sand-size to gravel-size phosphate and dolomitized zones throughout. The phosphates in this unit range in size from very fine to coarse, and in color from dark gray, to green-gray, to yellow-orange, and white. Welch et al. (2000) reported that there is a correlation between arsenic and dissolved phosphate in ground water, and that arsenic tends to increase with increasing pH and phosphate. The source of the arsenic in the Suwannee Limestone could have been originally the Hawthorn Group, and subsequent downward leaching secondarily transported it into the Suwannee. Furthermore, there is generally a hydraulic connection between the Upper Floridan aquifer and the lower Arcadia member of the Hawthorn Group (Torres, 2001).

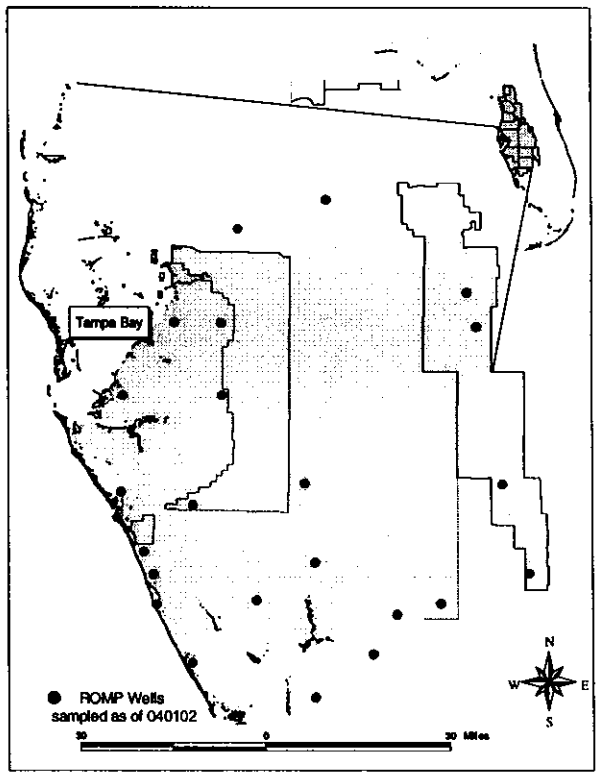


Figure 3: Map showing the location of wells from which core samples were collected. The gray area is the Southern Water Use Caution Area of the SWFWMD.

## METHODS

### Sample Collection and Preparation

During this study core from 22 wells collected by the Regional Observation Monitor-well Program (ROMP), a division of the SWFWMD, was 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. Sampling was carried out with the purpose to sample each core at constant intervals and to collect

samples at locations that may have a higher potential for the presence of arsenic, such as, fractures, organic material, sulfide-rich zones and iron oxyhydroxide-rich zones. For example, if the Suwannee interval was 100 feet thick, then ten constant interval samples were taken by dividing the thickness of the Suwannee into ten equal lengths. "Special interest" samples were taken once the core was examined by using traditional techniques, such as hand lens and stereomicroscope.

A detailed lithological and mineralogical description was performed on each sample using a Leica Zoom 2000 Stereo Microscope with 10.5 to 45 X magnification capabilities. A small portion of each core sample was powdered using a Coors mortar and pestle. Drilling mud was not used during coring, and is therefore not a concern for arsenic contamination, however, the outer edge of each sample was removed prior to powdering, to limit the possibility of contamination by surface water or pieces of the core-bit.

### Analytical Chemistry

Total arsenic concentrations were determined by hydride generation-atomic fluorescence spectrometry (HG-AFS) on a PSA Millennium instrument. This technique allows for the determination of arsenic at levels as low as 20 ppt (parts per trillion). Approximately 0.5 g of powdered sample was placed in Teflon bombs and 10mL (20:1) of a 3:1 mixture of hydrochloric (HCl) and nitric acid ($HNO_3$) was added and allowed to sit at room temperature for 24 hours. After digestion, the acid solution was diluted to 50mL (5:1) and the remaining solids (silicates) were filtered out, leaving a final solution to be archived until analysis. Standard testing of the digestion and detection method showed an average standard deviation of 0.022.

In preparation for the AFS analysis, 10 mL of the sample solution were treated with 30% concentrated HCl, 2% saturated potassium iodide (KI) solution, and deionized water with a final dilution volume of 50 mL (5:1). This sample treatment causes the reduction of As (V) to As (III) prior to the formation of the arsenic hydride ($AsH_3$) via addition of sodium tetraborohydride ($NaBH_4$). The $AsH_3$ is then atomized in a hydrogen flame and concentrations are determined by fluorescence spectrometry. Arsenic in the reagent blank was below detection. Total dilutions throughout the method were 500:1. Instrument conditions were as follows: Filter = 32, Range = 10, Times = 20, 40, 30.

Those samples that showed the highest arsenic concentrations were also examined by scanning electron microscopy (SEM) to constrain the mineralogical associations of the arsenic. Small sample chips were carbon coated and taped onto carbon mounts. Analyses were conducted with a Hitachi S-3500-N (variable pressure) SEM with PGT EDS capabilities and a Robinson backscatter detector for elemental analysis.

## RESULTS

As stated, most naturally occurring arsenic throughout the United States can be found in 1) iron oxyhydroxides, 2) sulfide minerals, 3) organic material, and 4) phosphate. A visual inspection of all limestone core samples from the Suwannee showed the existence of all 4 materials. However, the abundance of sulfide minerals in the form of framboidal pyrite outweighed all other components. Furthermore, in the high porosity zones (moldic) only pyrite could be found.

### AFS Analysis

The following table shows total arsenic content maximum, minimum, and average for the first 5 wells analyzed using AFS-HG. The analysis shows much higher values for arsenic in the Suwannee Limestone than have previously been suggested. Arthur et al. (2001) analyzed arsenic in 36 samples from the Suwannee storage zone and reported an average value of 3 ppm and a maximum of 11 ppm by neutron activation. In addition to higher concentrations, AFS analysis found the distribution of the arsenic in the Suwannee limestone to be very heterogeneous, both vertically in a single core, and laterally from well to well.

| | Average | Min | Max |
|---|---|---|---|
| ROMP TR 8-1 | 4.60 | 0.28 | 26.67 |
| ROMP 14 | 6.48 | 0.50 | 18.39 |
| ROMP 49 | 1.46 | 0.61 | 3.15 |
| ROMP 5 | 5.48 | 1.46 | 27.20 |
| Lemon Bay | 2.48 | 0.11 | 6.21 |

Table 1: Total Arsenic concentrations for 5 wells. Values were obtained using AFS-HG analysis

### SEM Analysis

Samples with concentrations in excess of 20 ppm arsenic were chosen for analysis by SEM with the intent to further constrain the mineralogical arsenic association in each sample. We found that framboidal pyrite was again more abundant than expected, being present in more than 50% of the SEM samples. The following SEM image shows pyrite framboids and pyrite crystals that coexist. Elemental analysis of the framboids, however, showed that if arsenic is present, it is below the detection limit of the EDS detector (1/10% or 1000 ppm).

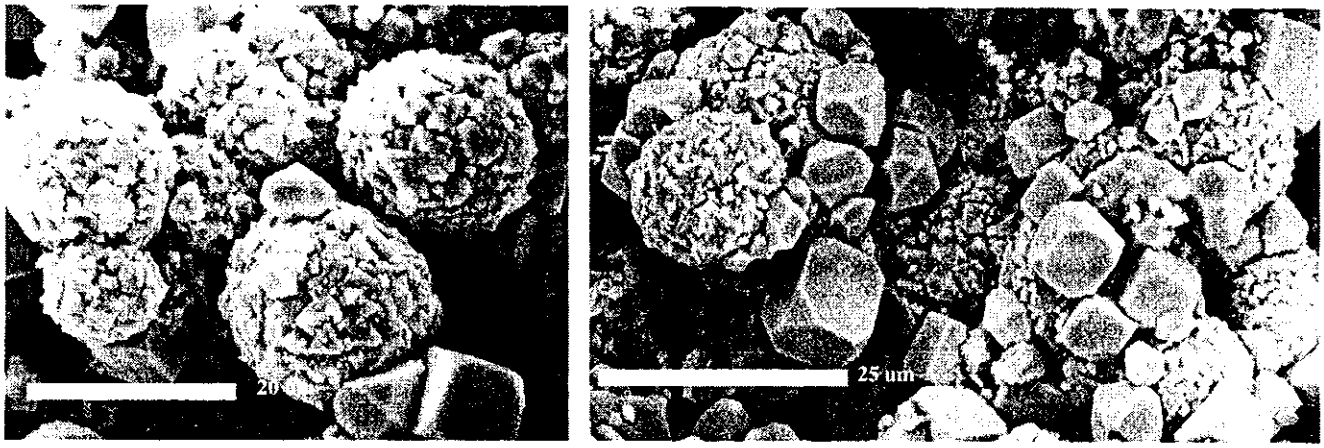


Figure 5: Pyrite framboids and crystals found in the Suwannee Limestone matrix (sample ROMP DV-249).

## DISSCUSSION

Naturally occurring arsenic in the Suwannee Limestone could be associated with sulfide minerals in the limestone matrix such as pyrite ($FeS_2$). Pyrite is found in the Suwannee Limestone in the form of opaque framboids in the calcite crystals (Upchurch, 2001). Pyrite framboids can contain as much as 1000 ppm arsenic as impurities (Thomas and Sanders, 1998). The most common arsenic-bearing minerals in host rocks of the United States include arsenic-rich (arsenian) pyrite and various arsenic sulfides and sulfosalts (Welch et al., 2000). Another suggested location for arsenic could be its incorporation or adsorption to iron or manganese oxyhydroxide coatings on Suwannee Limestone grains. Grain coatings of iron or manganese oxyhydroxide have been shown to contain as much as 500 ppm (Nickson et al, 2000). The ability of Mn and Fe oxides to preconcentrate ions from solution by coprecipitation is well documented (Chao and Theobald, 1976), and the close association between hydrous ferric oxide (HFO) and As has been clearly demonstrated (Pichler et al., 2000). Iron oxyhydroxide coatings on Suwannee sediment particles could be the result of dissolution of pyrite in the overlying Hawthorn formation, followed by downward migration of Fe and As, which then coprecipitated. Iron oxyhydroxide coatings on Suwannee Limestone grains, however, are very infrequent. Arsenic associated with organic material in the limestone matrix is another potential location suggested by Arthur et al (2001). Organic material composed of humic substances has a strong retention for arsenic. Finally, the arsenic could be located within phosphate nodules dispersed throughout the Suwannee Limestone. Lithologic descriptions showed the amount of phosphate seems to increase with increasing amounts of terrigenous clastic material (quartz sand).

The origin of the As in the Suwannee Limestone is unclear. Arsenic could possibly be incorporated into the carbonate shell of marine organisms prior to sedimentation. The arsenic may also have migrated down from the overlying Miocene-aged Hawthorn formation that is known to contain arsenic-bearing minerals. Until the location of the arsenic is known, its origin will remain uncertain.

## CONCLUSIONS

Naturally occurring arsenic becomes mobilized from the primary storage zone in southwest Florida, the Suwannee Limestone, and could be associated with iron sulfides, iron oxyhydroxides, organics, or phosphate nodules. Optical microscope descriptions of more than 300 Suwannee Limestone core samples show very little iron oxyhydroxides present, while sulfide minerals in the form of framboidal pyrite were abundant. AFS analysis of these samples shows much higher concentrations than previously reported, with maximum values as high as 27 ppm. Also, the distribution of arsenic throughout the Suwannee Limestone was very heterogeneous. Samples containing more than 20 ppm arsenic were analyzed with SEM, and show that framboidal pyrite was more abundant than expected, with more than 50% of SEM samples containing framboids. The mobilization of naturally occurring arsenic from the Upper Floridan aquifer-Suwannee Limestone matrix has the potential to become a major problem for future ASR projects in Florida. A better understanding of the origin, mineralogy, and mobilization mechanism is needed before any solution to the problem can be assessed. Research is continuing at the University of South Florida to further constrain the mineralogy of the arsenic in question. The next logical step is to examine thin sections with apparatus more sensitive than SEM, such as TEM, Microprobe, or SIMS.

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