# FINAL REPORT

# Environmental Consequences of Nutrients and Organic Matter Injection into Carbonate Aquifers; Implications for Water Quality in Aquifer Storage and Recovery (ASR) Technology

A WATER INSTITUTE 2007 PROGRAM INITIATION FUND PROJECT

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## Summary

The research funds provided by the Program Initiation Fund has resulted in preliminary data the will serve as the basis of a research proposal to the South Florida Water Management District and perhaps other State of Florida Water Management Districts. In addition, the funds have supported research by graduate and undergraduate students that has resulted in two scientific presentations and will result in a research publication. The Program Initiation Fund has provided a venue for the formation of a new research collaboration between the three PIs and other UF scientists.

## Accomplishments

1) Contact was made with Dr. Jonathon Arthur, an assistant state geologist and acting Director at the Florida Department of Environmental Protection/Florida Geological Survey in Tallahassee. Dr. Arthur has served on the ASR Issue Team of the South Florida Ecosystem Restoration Task Force, Comprehensive Everglades Restoration Plan (CERP) committees and workgroups and the National Academy of Sciences Committee on Sustainable Underground Storage of Recoverable Water. He agreed to collaborate on the project and provided us with materials from ASR sites from each of Florida's four major aquifer formations (Ocala and Avon Park: Eocene, Suwannee: Oligocene, Hawthorn: Miocene).

2) Analysis of the chemical properties of the four aquifer materials was spearheaded by Dr. Harris. X-ray diffraction confirmed a range in mineralogical composition, from calcite dominance (Ocala) to dolomite dominance (Avon Park) and with appreciable apatite in the Hawthorn limestone. Residues following carbonate dissolution in a pH-5 buffer contained quartz, cristobolite, palygorskite, and apatite. Scanning electron microscopy in conjunction with energy-dispersive x-ray fluorescence elemental spectroscopy revealed the presence of S and K which were not accounted for by XRD, but otherwise elemental spectra were consistent with mineralogical data. Total As concentrations were low (0.53-1.07 mg $kg^{-1}$), but in the range reported for Florida aquifer material. The As released to pH-5 buffer extraction ranged from 20-79%. Results from solid-state and chemical assessments confirmed that specimens were appropriate for use in pilot experiments.

3) Dr. Zimmerman and Jin Jin, a graduate student, conducted dissolved organic matter (DOM)-mineral adsorption experiments on each of the four aquifer rock types using a variety of DOM sources. These experiments entailed measurement of aquifer material surface areas, DOM concentration measurements before and after adsorption, and use pf fluorometry and liquid chromatograph to examine the chemical character of the DOM before and after contact periods. They found a number of interesting contrasts between aquifer types and preferential adsorption of OM types. For example, Ocala Formation carbonate had greater DOM-adsorption affinity as well as adsorption capacity than that of the Suwannee Formation. A reduction in the fulvic-like peak intensity occurred following carbonate adsorption while the protein-like peaks remain almost unchanged indicating the preferential adsorption of fulvic acids. These findings indicate that more work is needed to examine the influence of DOM on subsurface biogeochemical reactions during ASR. Jin presented his findings both at national meetings and the 2008 UF Water Institute Symposium and is preparing to submit these finding for publication.

4) The four aquifer samples were analyzed in Dr. Bonzongo's laboratory for total arsenic, iron, and aluminum concentrations (via digestion in concentrated HCl-$HNO_3$-HF for 12 hours at $105^0$C and analysis by induced coupled plasma - atomic emission spectrometry: ICP-AES). Arsenic concentrations were greatest in in Hawthorn (~4.9 ppm) aquifer material, and similar in

Avon, Suwannee, and Ocala aquifer materials were similar (~3 ppm). As was directly related to Fe concentration, possibly indicating an association with Fe sulfides.

5) Dr. Bonzongo also studied the release of As in static batch experiments as well as the influence of DOM on this process. Aquifer materials were equilibrated with either tap water or tap water containing sodium-acetate at a final concentration of 1.1 mg C/ml. After the initial mixing and de-aeration with $N_2$, the slurries were incubated for 20 days. At the end of the incubation period, the mixtures were centrifuged and supernatants were filtered, acid digested, and analyzed for total As by ICP-AES. Results are presented below:

| **Sample ID** | **Arsenic ( g/L)** |
|---|---|
| Avon | 2.31 |
| Avon + organic carbon | <10* |
| | |
| Suwannee | <10 |
| Suwannee + organic carbon | 4.25 |
| | |
| Ocala | 80.01 |
| Ocala + organic carbon | 155.85 |
| | |
| Hawthorn | 41.84 |
| Hawthorn + organic carbon | 10.05 |

***Below the instrument analytical detection limit of 10□g/L***

These results suggest that As is released from solid minerals to the aqueous phase at different rates, with Avon and Suwannee materials releasing significantly less As than Ocala and Hawthorn samples. The addition of organic carbon resulted in either increased As dissolution (Suwannee and Ocala) or decreased levels of As released (Avon and Hawthorn).

6) An incubation experiment is currently underway to generate data on the influence of DOM and microbes on As release from the aquifer materials. These data should provide further justification for the proposed larger research project with external support.

**<u>Proposal</u>**

The PIs have been meeting with other UF scientists to develop a research proposal to the South Florida Water Management District and perhaps other State of Florida Water Management

Districts that will be submitted through the Water Institute. This proposal effort is being led by Stuart Norton, a doctoral student in the UF - Environmental Engineering Sciences Department with nine years of experience as a consulting engineer with Jones Edmunds & Associates, Inc. Drs. Mike Annable, Kirk Hatfield, and Mark Newman are also a part of this proposed research team.

The goals of the proposed project will be to identify the physiochemical and microbiological processes that contribute to the mobilization of arsenic during ASR and determine the mechanisms controlling the fate and transport of arsenic during ASR and AR. This information will be used to develop and run more ‘realistic’ reactive-transport models. As part of this proposal, the Zimmerman-Bonzongo-Harris team propose a series of experiments to quantitatively evaluate the possible role of microbes and DOM on As release in subsurface carbonate aquifers. In addition to the water-mineral-As-release column experiments proposed, we would like to run parallel column studies in which water with DOM, mineral with added native groundwater microbes, and DOM + microbes treatments. Released As will be measured in each of these systems and compared to that of water + mineral only systems. In addition to mineralogical analysis of column fills before and after reaction, influent and effluent of the columns will we analyzed for:

- DOM quality and chemical composition to gauge the extent of reaction (adsorption) with mineral or microbes (respiration).
- Microbial cells to gauge the extent of microbial attachment or flow through
- Inorganic carbon and major elements to quantity mineral dissolution and or microbial respiration
- As ($As^{+4}$ and $As^{+5}$) to measure released As and its oxidation state

These experiments will provide input parameters for the proposed reactive transport modeling that will make the results of these models more ‘realistic’. That is, by including the effects of DOM and microbes, we will be able to establish a range of conditions that can be fed into model for model sensitivity analyses. The experiments may also point toward novel water pre-treatment or field treatment approaches that can reduce the risk of As release in the future.