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Drew’s Rock on Section III of the Chattooga River. This erosionally resistant remnant of the Tallulah Falls Formation follows the 40 degree dip of the foliation.
# 10th Annual David S. Snipes/Clemson Hydrogeology Symposium

**April 18th, 2002**

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<td>9:00</td>
<td>Introductory Remarks by David Snipes and the Provost: Dr. Dory Helms (BellSouth Auditorium)</td>
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| 9:20  | **Remediation**  
Chair: Ron Falta | **Groundwater Modeling**  
Chair: Jim Castle | **Fracture Studies**  
Chair: Larry Murdoch |
|       | In-Situ Treatment of a TCE Source Area Using a Jetted Slurry of ZVI and Clay  
Stephen Shoemaker, DuPont Corporate Remediation Group | Uncertainty Analysis for C-Area Groundwater Modeling at the Savannah River Site  
Kevin Brewer, Bechtel Savannah River Inc. | Diffusive Mass Transfer in Fractured, Porous Rock: The Effect of Measurement Scale on Data Interpretation  
Timothy Callahan, College of Charleston |
| 9:45  | Microbial Study on Chlorinated Ethene Biodegradation Within Rottenwood Creek Sediments Hydraulically Connected to Fractured Rock Hydrogeology by Low-Flow Ground-Water Discharge  
Jonathon Waddell, Georgia Tech | Links Between Tectonics, Hydrogeology, and Diagenesis in the San Joaquin Basin, CA: Scientific Discovery Via Mistaken Boundary Conditions  
Alicia Wilson, USC | Characteristics and Design of Hydraulic Fractures in Saprrolite  
Jim Richardson, Shawn Malin, and Qingfeng Tan, Clemson University |
| 10:10 | **Site Characterization using Direct Push**  
Chair: Jim Castle | **Groundwater Modeling**  
Chair: Ron Falta | **Induced Fractures for Remediation**  
Chair: Larry Murdoch |
| 10:30 | Direct Push Electrical Logging and Mapping of Glacial Sequences at Fermilab, Batavia, Illinois  
David Brown, Geoprobe® Systems Inc | What is the benefit of DNAPL source zone remediation?  
Ron Falta, Clemson University | Cost Effective Utilization of Hydraulic Fractures for Remediation of Environmentally Impacted Sites  
Bill Slack, FRx |
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<td>The Hopscotch Method for Fast Simulations of Transient Groundwater Flow</td>
<td>Jim Henley, Clemson University</td>
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<td>Effects of Shallow Induced Fractures on the Performance of Soil Vapor Extraction Wells</td>
<td>Graham Bradner, Clemson University</td>
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<td>11:30</td>
<td>Larry McKay, Groundwater Flow and Contaminant Transport in Sedimentary Rock Saprolite (Main Ballroom)</td>
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<td>12:15</td>
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<td>Simpsonville Uranium Geochemistry Chair: Brian Davies</td>
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<td>General Hydrology Chair: Ming-Kuo Lee, Auburn University</td>
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<td>Residential Tenorm in Upstate SC</td>
<td>Richard Woodruff, Clemson University</td>
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<td>Sediment Source Determination in the Lake Cunningham Watershed, Northern Greenville County, South Carolina</td>
<td>Mark Taylor, Fletcher Group, Inc.</td>
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<td>Time</td>
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| 3:15  | Geostatistically Based Data Interpretation of Surface Geophysical Surveys  
|       | **Thomas Lawrence**, Conestoga-Rovers & Associates          | Fate and Transport of Coal Tar in Saprolite in East Tennessee  
|       |                                                               | **Vijay Vulava**, University of Tennessee                                  | Geomorphic and hydrologic constraints on Cenozoic Tectonism in the Southeast U.S.  
|       |                                                               | **James Knapp**, USC                                                       |
| 3:40  | Better Correlations with Fewer Logs: The Application of Principal Components Analysis to Wireline Log Data  
|       | **Ray Christopher**, Clemson University                       | Evaluation of a Conceptual Model for the Subsurface Transport of Plutonium Involving Surface Mediated Reduction of Pu(V) to Pu(IV)  
|       |                                                               | **Bob Fjeld**, Clemson University                                           | Reservoir Simulation of Heavy Oil Sands in West Coalinga Field, California  
|       |                                                               | **Lekan Fawumi**, Clemson University                                        |
| 4:05  | Development of Three-Dimensional Geological Models for Integration with Seismic Geophysical Data  
|       | **Kristine Mize**, Clemson University                         | Trends in Atmospheric Mercury Deposition in the Southeast  
|       |                                                               | **Dennis Jackson**, Savannah River Technology Center                        |                                                                           |

4:30 - 5:30  **Geoprobe Demonstration at Geology Museum**

5:00  **Mixer at Geology Museum**
Posters (Displayed in the Main Hall)

Treatment of Well Water for Uranium Removal
Birsen Ayaz, Clemson University

Uranium in Well Water in Southern Greenville County and Some Possible Geologic Associations
Bruce Crawford, SC DHEC

Radionuclides in South Carolina Well Water
Pete Stone, SC DHEC

Elevated pH, Alkalinity, Calcium, and Sulfate Associated with High Dissolved Uranium in Ground Water in the Simpsonville Study Area: What Does it Mean?
Pete Stone, SC DHEC

Assessing Migration Pathways of Chlorinated DNAPLs in a Saprolite – Fractured Bedrock Setting
Grant Watkins, ENSR Corporation

Facies-Dependent Permeability Variation and Scale in Shallow-Marine Sandstones, Southern Utah and Central California
Jim Castle, Clemson University
TREATMENT OF WELL WATER FOR URANIUM REMOVAL

AYAZ, BIRSEN, birsena@clemson.edu, and NAVRATIL, JAMES, nav@clemson.edu,
Environmental Engineering and Science, Clemson University-Clemson Research Park,
342 Computer Court, Anderson, South Carolina 29625-6510, 1Institute for Nuclear Energy,
Istanbul Technical University 80626 Maslak, Istanbul, Turkey

High amounts of uranium have been found in drinking water wells near Simpsonville-Greenville,
South Carolina. The purpose of this work was to test the effectiveness of various treatment methods
to remove uranium from actual well water samples. Batch tests were performed with activated
carbon, iron powder, anion exchange resin and cation exchange resin. In the tests, water and the
separation materials were first equilibrated, filtered and then analyzed by alpha spectrometry. The
results of the batch tests showed that it is possible to remove greater than 90% of the uranium in the
drinking water by using any of the sorbants listed above. Simple filtration with 0.1 um had little to
no impact on uranium removal. Results of tests using household treatment devices will also be
presented.

NATURALLY OCCURRING RADIONUCLIDES IN SOUTH CAROLINA GROUNDWATER: AN OVERVIEW

BAIZE, DAVID, Bureau of Water, SC DHEC, Columbia, SC 29201

Recently, additional instances of naturally occurring radionuclides in drinking water wells (both in
public systems and at private homes) have been revealed by wider monitoring of smaller public-
supply wells, fortuitous sampling of private wells, and targeted surveys triggered by such results.
Future sampling on a denser and regional basis will almost certainly reveal other wells and areas
with radionuclide concentrations in excess of drinking-water limits. Uranium, radium, and radon are
chief among the problem constituents. Uranium is problematic in crystalline-rock wells in scattered
parts of the piedmont and Blue Ridge geologic provinces. At least one discrete area of the piedmont
(near Simpsonville / Fountain Inn) has dozens of private wells affected. Radium is a problem in
parts of the innermost coastal plain in sand-aquifer wells, particularly in the Aiken and Lexington
counties area. Radon is presently the least assessed constituent but may very well turn out to be the
most abundant problem, especially in the piedmont. Future sampling based on geologic and
geochemical “targeting” of other suspect areas is planned. In addition to the major task of finding
other wells and areas with radionuclide problems, the overall solution will involve identifying effec-
tive on-site treatment technologies.

Some figures from the piedmont illustrate the uranium problem. Among 322 public-supply
wells serving 279 systems, 7 (ca. 1 out of 50) exceeded the drinking-water limit (not including
several others that failed at initial testing and were never completed as public-supply wells). Among
1001 private wells tested, 93 (ca. 1 in 11) had excessive uranium (though this testing was biased
toward the vicinity of a known problem area).

EFFECTS OF SHALLOW INDUCED FRACTURES ON THE PERFORMANCE OF SOIL VAPOR EXTRACTION WELLS

BRADNER, GRAHAM C., and MURDOCH, LAWRENCE C., lmurdoc@clemson.edu,
Geological Sciences, Clemson University
Induced fractures have been used for more than ten years to enhance the performance of environmental wells in fine-grained formations. Field observations show that the presence of hydraulic or pneumatic fractures can increase the discharge from extraction wells in fine-grained formations by an order of magnitude or more. However, the details of the effects of induced fractures on the performance of wells is poorly known. Two theoretical models were used for this study to evaluate the effects of a sand-filled hydraulic fracture intersecting the screened interval of soil vapor extraction (SVE) well in piedmont saprolite. One model uses an analytical technique similar to that developed by Shan et al [1992] for flow to a single extraction well under steady-state, homogeneous, anisotropic conditions. This solution also incorporates the effects of a low permeability skin around the borehole that has the potential to effect flow to the well. The other model uses a steady-state finite difference solution that considers the fracture as a thin layer in a heterogeneous, anisotropic medium. Theoretical results show that a ratio of at least two orders of magnitude between the permeability of the sand in the fracture and the permeability of the formation is needed to significantly increase the gas specific capacity of the well. Factors related to fracture geometry were also evaluated, and we found that fracture thickness has the greatest influence on well performance, radial extent has some influence, and depth of initiation has the least influence on well performance. A separate analysis that uses the mechanics of fracture propagation to constrain the flow model shows that the volume of injected sand is perhaps the most important variable affecting performance.

Field experiments were conducted where sand-filled hydraulic fractures were created at a depth of 3 m at two sites. One site is underlain by a gneissic granitoid, where the permeability of the overlying saprolite is $k = 0.5 \times 10^{-11}$ m$^2$. The other site is underlain by a muscovite-biotite schist with a permeability of $k = 1.1 \times 10^{-11}$ m$^2$. Gas pump tests were performed on conventional wells, and wells intersecting fractures at both sites. A specialized low-cost, multi-level piezometer, with as many as 14 ports installed along a vertical axis was used to obtain observations of pressure in the subsurface during gas pump tests. Field tests show that a sand-filled hydraulic fracture can increase the gas specific capacity of an extraction well in saprolite from an average value of 28.5 scfm/atm to 289.7 scfm/atm. A total of 15 conventional wells were installed at both sites using different drilling methods. Pump test results show that gas specific capacities vary by an order of magnitude, even though the wells were installed in a relatively small area (1.5 m$^2$). We conclude that the variation is due to low permeability skins around the boreholes. The severity of the skin depends on the drilling and completion methods, and this problem may be more common on SVE wells installed in clay-rich saprolite than previously realized.

**UNCERTAINTY ANALYSIS FOR C-AREA GROUNDWATER MODELING AT THE SAVANNAH RIVER SITE**

BREWER, KEVIN E., kevin.brewer@srs.gov and FOGLE, TAMARA L., tamara.fogle@srs.gov, Bechtel Savannah River Inc., Aiken, SC 29803

This paper presents results from an uncertainty analysis performed for a local groundwater flow and transport model for the C-Area Reactor Groundwater Operable Unit at the Savannah River Site (SRS). The underlying local flow and transport model for this uncertainty analysis is a representation of groundwater flow and contaminant migration through the Upper Three Runs aquifer, southwest to Fourmile Branch and Castor Creek (Bills et al., 2000; and Fogle and Brewer, 2001). The model domain encompasses an area that includes the intermingled southern trichloroethylene (TCE) and southern tritium plumes. Only the TCE plume was considered for this uncertainty analysis, which
focused on the uncertainty of stream TCE contaminant fluxes (Castor Creek and Fourmile Branch), and the stream TCE contaminant flux differences between the basecase and a pump-and-spray phytoremediation scenario.

All groundwater modeling results are subject to uncertainty due to (1) incomplete knowledge of parameter values, (2) incomplete or incorrect knowledge of the physical system, and (3) necessary simplification of the physical system being modeled. The latter two causes are typically considered “modeling uncertainty,” with the first cause as “prediction uncertainty.” For this analysis, only “prediction uncertainty” (i.e., “parameter uncertainty”) was evaluated.

The technical approach used for this uncertainty analysis was based on the classical Monte Carlo method that has been used in many disciplines to evaluate uncertainty and risk. Because the analysis was to quantitatively determine confidence intervals and uncertainty about various groundwater modeling results, other possible uncertainty analysis techniques (such as perturbation and first-order approximation) were determined to be inappropriate. The steady state flow field (simulating the long-term average flow system) was calculated using MODFLOW (McDonald and Harbaugh, 1988). The simulation of 50 years of contaminant transport was calculated using MT3DMS (Zheng and Wang, 1999). The model consisted of 56,682 cells in a total of nine layers.

The Monte Carlo method is relatively straightforward to understand and implement when assessing “prediction/parameter uncertainty.” With the method, random samples from uncertain parameter probability distributions are chosen, the model(s) are run, and the results are extracted and stored. After a significant number of these “realizations” (or “iterations”) are performed, the results are evaluated using standard statistical methods and presentations. The key is to run enough iterations to arrive at stable statistical distributions for the results being evaluated.

For this effort, the Monte Carlo method was implemented as the following algorithm: (a) generate 5000 sets of random parameters, (b) for each iteration (1) Obtain a random parameter value for each of the uncertain modeling parameters, (2) run MODFLOW, (3) if MODFLOW converged, evaluate the closeness of the model results to head and flux calibration targets, (4) if the flow model is within desired calibration ranges, run MT3DMS, and (5) if the MT3DMS final mass balance error is less than 5%, consider the run successful and record desired results. The algorithm was implemented in an Excel spreadsheet using Visual Basic macros and custom programs, with the random parameter values generated using the Crystal Ball add-in for Excel (Decisioneering 2001). The software was constructed to allow distributed processing for blocks of iterations. Up to ten computers were simultaneously used to complete 5000 total iterations for each scenario being analyzed. Total processing time for each 5000 iteration block was approximately one cpu-month (720 cpu-hours).

A total of eight uncertain parameters were used in this analysis, based on the results from the flow and transport model sensitivity analyses. To simplify the software and analysis, parameter layer multipliers were used to vary the uncertain flow and transport parameters in the model input files. Individual parameter layer multiplier distribution types and limits were chosen using professional judgement to achieve an appropriate uncertainty distribution.

The first uncertain parameter/multiplier was recharge, with a normal multiplier distribution and maximum and minimum cutoffs at realistic limits. The next two uncertain parameters were the horizontal hydraulic conductivity zone values in transport model layers 1 and 2 which make up the water table aquifer. The normally distributed multiplier included minimum and maximum cutoffs. Although hydraulic conductivity is generally thought to be lognormally distributed, because the calibrated values were already thought to be on the high-side of possible/likely values, higher probability on the low-end of the distribution was deemed to be realistic, and a normal distribution was chosen to satisfy this assumption. In addition, because of the assumed distribution cutoffs, the
ultimate probability differences between the lognormal and normal distributions would be minor.

The fourth uncertain parameter was the horizontal hydraulic conductivity in the first confined aquifer. The normally distributed multiplier included minimum and maximum cutoffs. As with parameters 2 & 3, the calibrated model values for the Layer 4 Kh zones were believed to be on the high-end. Thus, a normal distribution with a high-end cutoff was assumed to represent the range and likelihood of this uncertain parameter. The fifth and sixth uncertain parameters were the vertical hydraulic conductivities for the upper two confining zones (bottom confining unit for the water table aquifer, and the bottom confining unit for the first confined aquifer zone). Each parameter utilized log-normal distributions with minimum and maximum cutoffs.

The seventh uncertain parameter was longitudinal dispersivity. The calibrated model longitudinal dispersivity was considered a low value compared to typical values reported in the literature, and when compared to the general guidance of longitudinal dispersivity being one-tenth the plume length. Consequently, it was assumed that much higher values would be more probable. Thus, the longitudinal dispersivity multiplier was assumed log-normally distributed and included minimum and maximum cutoffs. The last uncertain parameter was effective porosity. No previously defined probability distributions for porosity at SRS were known, so a triangular distribution was chosen (over a normal distribution) for simplicity.

Forty head targets based on the original flow model head targets (observation points) were used in this analysis. These target values were compared to each iteration’s flow model results. If more than five of the model results were outside the head target range then the iteration was considered “out of calibration;” no uncertainty results were computed and a new iteration was started. Seven flux target arcs from the original calibrated flow model were also used as targets in this analysis. Similar to the process used for the head targets, the flux values were compared. If more than one of the model fluxes were outside the flux target range then the iteration was considered “out of calibration;” no uncertainty results were computed and a new iteration was started.

The assumption of being in calibration with deviation of up to 5 head and one flux targets were considered reasonable, and were selected based on professional judgement to ensure sufficient “successful” iterations. Experience showed that a significantly greater (10-20x) number of iterations would be required if no deviation was allowed, with no significant benefit.

Out of the 5000 realizations (iterations) attempted, only 926 passed the MODFLOW head and flux calibration evaluation and a MT3DMS mass balance check. Of these 926 “successful” iterations, only 13 iterations showed no deviations from calibration targets/ranges. In general, it is believed that enough “successful” Monte-Carlo iterations are performed when there are no further significant changes to the result value’s cumulative mean and standard deviation (so that the ensemble statistics are representative of the overall uncertainty). In this work, the most important result is the total Castor Creek flux – and that value was used to evaluate the adequacy of the number of iterations. Plots of the cumulative mean and standard deviations clearly showed stable cumulative statistics after a few hundred iterations – throughout the forecasted years.

Figures were generated that showed the median, calibrated model, and 5% and 95% confidence levels for TCE mass flux to the two streams for the two scenarios (basecase and phytoremediation). The 95% confidence level, for example, is simply the value, at each time, where 95% of the “successful” iteration results were lower, and does not represent any single iteration. The area between the 5% and 95% confidence levels is considered the 90% confidence interval. Examination of the TCE mass flux reduction between the basecase and phytoremediation scenarios showed that the median of the maximum Castor Creek mass flux reduction (i.e., the largest reduction throughout the 50 year timeframe) is near 5.5 kg/yr. This compares favorably with the previously reported model results of a maximum reduction near 6.5 kg/yr. The uncertainty surrounding
that value is approximately +/- 2.2 kg/yr. The uncertainty surrounding the Fourmile Branch TCE mass flux reduction is even more (when considered as a percentage of total flux), particularly in later years.

Correlation between each parameter and total TCE mass flux to Fourmile Branch and Castor Creek was investigated. Correlation coefficients plots between each parameter and total TCE mass flux to both Castor Creek and Fourmile Branch were constructed and evaluated. Based on the evaluation, there is essentially no correlation between most parameters and Castor Creek TCE mass flux. There appears to be a slight correlation between recharge and Castor Creek TCE mass flux, and a strong positive correlation between Layer 4 Kh and Castor Creek TCE mass flux. It is uncertain whether the correlations of these parameters with the results are masking possible correlations for the other parameters. Overall, it appears that the most important parameter is Layer 4 Kh.

To determine the impact on TCE mass flux results by reducing uncertainty about the Layer 4 Kh value, the basecase scenario was run with the assumption that the Layer 4 Kh value was known (at the calibrated model value). (In a practical sense, the reduction in uncertainty for the Layer 4 Kh value could be achieved by performing aquifer tests throughout the model domain.) The results for this “reduced uncertainty” scenario are shown in Figure 1, which shows that the confidence intervals for the TCE mass flux are slightly reduced (compared to the basecase scenario).

The results of this uncertainty analysis show that the original calibrated model results (for TCE mass flux and discharge location) are within the 90% confidence intervals, assuming uncertainty for eight flow and transport model parameters. The results also indicate that the uncertainty about the TCE mass flux is significant. In particular, at the time of maximum TCE mass flux, the Castor Creek mass flux uncertainty is approximately +/- 50%. Similar results were seen for Fourmile Branch TCE mass flux.

The results showed a strong correlation between Layer 4 Kh and total TCE mass flux, and that the uncertainty about Castor Creek TCE mass flux could be slightly reduced by eliminating the Layer 4 Kh uncertainty. Since correlations between other parameters and total TCE mass flux were insignificant, reductions in those parameter uncertainties would likely not reduce the overall uncertainty of total TCE mass flux.

REFERENCES


Fogle, T.L. and K.E. Brewer, 2001. *Groundwater Transport Modeling for Southern TCE and Tritium Plumes in the C-Area Groundwater Operable Unit (U)*. WSRC-TR-2001-00206 Rev. 0, Savannah River Site, Aiken, South Carolina, June


DIRECT PUSH ELECTRICAL LOGGING AND MAPPING OF GLACIAL SEQUENCES AT FERMLAB, BATAVIA, ILLINOIS

BROWN, DAVID, brownd@geoprobe.com, Geoprobe Systems-Midwest Region Office, Bellevue, KY 41073, KESICH, PAUL, pkesich@fnal.gov, Fermi National Accelerator Laboratory, Batavia, IL 60510, KEMMIS, TIM, tim_Kemmis@earthtech.com, KELLEHER, DAN, dan_Kelleher@earthtech.com, Earth Tech, Inc., Minneapolis, MN 55441, and MCCALL, WESLEY, mccallw@geoprobe.com, Geoprobe Systems, Salina, KS 67401

Understanding groundwater flow through the complex sequence of glacial and glacially related deposits underlying sites in the North American midcontinent requires a detailed characterization of the geometry and properties of the stratigraphic succession at a site. Rapid and economical delineation of stratigraphic unit geometry is possible using direct-push (DP) electrical logging (e-log) obtained with the Geoprobe Systems SC400 Soil Conductivity Probe. The e-logs may be used to supplement information between boreholes characterized by conventional subsurface drilling and sampling techniques or it may be used independently of pre-existing information. The Geoprobe SC400 Soil Conductivity Probe is a direct push Wenner array probe about 15-inches in length and 1.5-inches in diameter while the small dipole array is only 1.5-inches long and 1-inch diameter. Both arrays are effective in defining lithology and locating aquifers and aquitards in alluvial and glacial deposits. The probe is advanced with a direct push machine equipped with a hydraulic hammer to depths exceeding 100 feet under favorable conditions. A two-person team can complete a 60-foot log in about one hour. The portable system is operated from a conventional laptop computer or specialized field computer. The real-time onscreen presentation of the e-log allows for visual interpretation and comparison to other logs and soil cores collected at the site. Logs are printed and saved in ASCII file format that is easily manageable for computer analysis, presentation, and storage. An additional advantage of the system is that no previous borehole or well is required for advancement of the probe and no cuttings are generated while logging. Bottom-up pressure grouting may be conducted to seal the probe holes and prevent potential for contaminant migration.
DIFFUSIVE MASS TRANSFER IN FRACTURED, POROUS ROCK: THE EFFECT OF MEASUREMENT SCALE ON DATA INTERPRETATION

CALLAHAN, TIMOTHY J., callahant@cofc.edu, Department of Geology and Environmental Sciences, College of Charleston, 66 George Street, Charleston, SC 29424

Over the past several years, many forced-gradient tracer tests have been conducted in saturated, fractured volcanic rock at the Nevada Test Site (NTS) and in core samples obtained from the NTS. The main objective was to obtain estimates of solute transport parameters for performance assessment modeling of possible radionuclide migration from the potential high-level radioactive waste repository at Yucca Mountain, Nevada. The laboratory experiments were conducted to determine whether transport parameters obtained from small scale experiments could be extended to field scales.

The laboratory tracer experiments involved two nonreactive anion tracers with different diffusion coefficients, injected at different flow velocities into fractured rock cores obtained from the NTS. The results indicate that the diffusive mass transfer coefficients for the tracers were smaller for tests conducted at slower flow velocities. There are at least two hypotheses that may explain this phenomenon: (1) hydrodynamic dispersion within the fractures dominated over diffusive mass transfer within the porous matrix during the fast-flow tests, or (2) the approximation of the fractured systems as having infinitely-spaced fractures was inaccurate (that is, boundary effects influenced the diffusive mass transfer within the porous matrix). Modeling efforts that test both hypotheses will be presented.

It is uncertain which hypothesis is correct, but it is clear that caution must be exercised when applying laboratory-derived diffusive mass transport parameters in fractured media to larger scales. The results emphasize that contaminant transport should be studied over a range of scales to determine the relative importance of different transport mechanisms and boundary conditions in fractured porous rock.

FACIES-DEPENDENT PERMEABILITY VARIATION AND SCALE IN SHALLOW-MARINE SANDSTONES, SOUTHERN UTAH AND CENTRAL CALIFORNIA

CASTLE, JAMES W., jcastle@clemson.edu, MOLZ, F. J., BRAME, S. E., CURRENT, C. L., FAWUMI, O. K., and FALTA, R W., Departments of Geological Sciences and Environmental Engineering & Science, Clemson University, Clemson, SC 29634-0919
Incorporating sedimentological study of shallow-marine sandstones in Utah and California, analytical property-distribution methods have been conditioned to continuous outcrop control for improved characterization of heterogeneity. A newly designed drill-hole mini-permeameter [Dinwiddie, 2001] was used to obtain data with a sample spacing of 15 cm along horizontal transects and vertical profiles in a portion of the Upper Cretaceous Straight Cliffs Formation near Escalante, Utah. Approximately 500 field permeability measurements on a 6 x 21-m sandstone outcrop demonstrate facies-dependent variations in permeability values and scale. Permeability ranges from 41-1,675 millidarcies in massive-bedded, poorly to well-sorted, very fine to fine-grained, bioturbated sandstone facies. Permeability in this facies shows relatively little variability over a scale of several meters, which is attributed to homogenization due to burrowing. In contrast, permeability ranges from 336 to over 5,500 millidarcies in poorly to moderately sorted, fine- to coarse-grained, cross-bedded sandstone facies. This high degree of variability is caused by small-scale variations in grain size and structure related to the depositional processes. The outcrop permeability data support a new concept for representing natural heterogeneity, which is called the facies-fractal concept [Lu et al., 2001]. This concept, combined with 3D geological models of the stratigraphic architecture, has been applied to understanding the sedimentary structure in the Miocene Temblor Formation at West Coalinga Field in California. Results of incorporating permeability values into the geological models are being used for simulating oil recovery by steam injection.

*Present address (for C.L. Current): RMT, Inc., 100 Verdae Blvd., Greenville, SC 29607-3825*

### BETTER CORRELATIONS WITH FEWER LOGS: THE APPLICATION OF PRINCIPAL COMPONENTS ANALYSIS TO WIRELINE LOG DATA

**CHRISTOPHER, RAYMOND A.,** christ7@clemson.edu, and **HODGES, REX A.**, Department of Geological Sciences, Clemson University, Clemson, SC 29634-0919

An important source of information for interpreting subsurface geology is wireline log data. These logs reflect various geophysical properties of rocks, and although many of them were developed for interpreting porosity and fluid content, their use in interpreting lithology (and hence for correlation) is often of primary importance. When correlating a series of wells, logs that are indicators of lithology (e.g., SP, gamma-ray) are often used in conjunction with overlays or cross plots of other logs (e.g., neutron, sonic, bulk density) to corroborate or refine lithologic interpretations. However, when correlating a large number of wells, each of which is represented by a suite of eight or more logs, the number of overlays and cross plots can become cumbersome, and the resulting interpretations are often ambiguous, confusing, or conflicting.

Principal components analysis is a quantitative method for reducing the number of variables in a data set without sacrificing a significant amount of information, and it is well suited for application to wireline log data. In principal components analysis, each log is treated as a variable. Within this set of variables, some are highly correlated with others, and principal components analysis establishes a weighted linear combination of these correlated variables. As a result, a new, smaller set of uncorrelated variables (or components) is created that contains most of the variability in the original suite of logs, thereby reducing the number of variables without a concomitant reduction in the information contained in the data set. Correlating lithology between wells becomes more efficient when a reduced number of variables (logs) is taken into account. Additionally, the cost of acquiring a suite of logs may be reduced as principal components analysis identifies logs that are not relevant in correlation, and eliminating them from future log runs may be considered.
URANIUM IN WELL WATER IN SOUTHERN GREENVILLE COUNTY AND SOME POSSIBLE GEOLOGIC ASSOCIATIONS

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A distinct area discovered serendipitously by others is substantial in both area (ca. 10 sq-km) and number of private wells (ca. 60) having high concentrations of dissolved uranium (“high” defined here as above the limit for drinking water, 30 μg/L). A few wells show concentrations vastly (>100x) and many wells greatly (>10x) above that limit. The few available analyses for radium and radon show these too can also be greatly to vastly elevated above the recommended or proposed limits (e.g., Ra to >10x the limit and Rd to >10x or >100x the proposed range of limits). A notable characteristic here is the high difference in U concentration that can occur between close by rock wells. This might suggest that simple weathering of the main bedrock is not the immediate source and that localized (laterally or vertically) enriched zones with a soluble source exist. No distinct association between rock-well depth and high U content is apparent.

The exact source (mineral, rock, and structure) is not yet known and seems not to be commonly expressed at the surface, even where bedrock is exposed. Similarly, high U seems restricted to rock wells and is not found in bored wells tapping the saprolite (decomposed rock) regolith above.

This problem area is characterized geologically by a slightly metamorphosed granitoid rock (granodiorite?). Pegmatites are present but exposures were no more radioactive than the host rock itself. Mafic rocks are common at the periphery and can occur as dikes, adding local geochemical diversity. A major geologic thrust-sheet boundary (Reedy River thrust) lies nearby and at some (unknown) depth beneath the area and thus garners suspicion of some involvement.

Gamma logs of rock wells show multiple distinct thin zones of higher gamma activity and groupings of these zones. But these are only about twice the radioactivity of the host bedrock and not as high as one might expect from ore-like enrichment zones of U. Can high U concentrations be weathered or leached from such zones? The vertical groupings of higher-activity zones are marginally correlatable in the sense that an intermediate depth group (<ca. 35 m) and a deeper group (>ca. 50 m) occurs in 3 of the 4 wells logged. Accompanying geophysical logs suggest fractures within higher-gamma zones in two wells, but curiously not with the well of historically highest U concentration in water.

EFFECTS OF VERTICAL HEAD GRADIENTS ON THE INTERPRETATION OF CHEMICAL AND WATER LEVEL MEASUREMENTS IN OBSERVATION WELLS: IGNORED PHENOMENA OF CONSIDERABLE IMPORTANCE

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Much of traditional ground water hydrology is based on horizontal flow concepts. However, it is well known that vertical gradients exist in natural systems, and that such gradients set up spontaneous vertical flows in observation wells, often called ambient flows. [Elci et al., Ground Water, 39, 853-862, 2001] Such gradients may lead also to a water level within a well that does not correspond to local hydraulic head averaged over the screen. The objective of this communication is
to present information showing that vertical hydraulic gradients and the resulting ambient flows may make chemical data from long-screened observation wells highly misleading, and may also provide misleading hydraulic head data. Calculations are based on head, flow-meter, and hydraulic conductivity data obtained at the Savannah River Site (SRS).

Ambient flow and transport simulations for well P26-M1 in the confined Gordon aquifer were performed using the GMS package. Simulated flows agreed well with measurements. Natural flow was upward, so water entered the well through high K layers in the lower portion of the aquifer and exited through similar layers in the upper portion. The maximum upward discharge was about 0.4 m³/day, implying an induced exchange of 12 m³/month from the bottom half of the aquifer to the upper half. Transport simulations illustrate how a contaminant located initially in a lower portion of the aquifer moves continuously into the upper portion and is diluted in the well by in-flowing water. Tracers released in the upper portions of the aquifer may by-pass the observation well entirely, and ambient flow magnitude is sensitive to screen length.

Additional studies at the SRS R-Reactor Seepage Basins indicate that in the presence of the steep vertical hydraulic gradients that exist there, conventional interpretation of well water levels may be grossly inappropriate. More specifically, a well may be screened below the formation water table, and yet exhibit a water level that is below the top of the screen. This phenomenon was inferred at the seepage basins using cone penetration testing with soil moisture and resistivity sensors, and concurrent water level data from wells. Subsequent analytical and numerical analyses demonstrate that the phenomenon is physically possible, and define the necessary hydrogeologic conditions.

WHAT IS THE BENEFIT OF DNAPL SOURCE REMOVAL?

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Recent controlled field experiments performed by Clemson and other universities have demonstrated that about 60% to 90% or more of a DNAPL source may be removed using enhanced remediation techniques. There is currently a major debate over the possible benefits of this magnitude of source removal. One school of thought holds that it is a waste of time to attempt remediation unless Maximum Contaminant Levels (MCLs) can be reached in the source zone. Since this has proven to be essentially impossible, the MCL view leads to a pessimistic view of DNAPL source remediation.

A second school of thought considers the possibility of natural or enhanced attenuation of a plume leaving the source zone. With this view, if the off-site chemical discharge is reduced due to a partial DNAPL source removal, then the resulting plume may be attenuated within an acceptable distance.

Central to this argument is an understanding of the relationship between DNAPL removal and off-site discharge. Because very little quantitative experimental data is available, a series of 3-dimensional numerical simulations were performed to help quantify this relationship. These results show substantial reductions in off-site chemical discharge with partial DNAPL removal. It is shown that the correlation of the DNAPL with permeability is the critical parameter in the relationship. When most of the DNAPL is located in high permeability zones (for example, after a recent spill), most of it must be removed to see a substantial reduction in off-site discharge. Conversely, if most of the DNAPL is present in low permeability zones (for example, at an old site), then only a fraction of it must be removed to see a large reduction in the off-site discharge.

It is hoped that this type of simulation approach, combined with further field testing, and assessment of attenuation capabilities, can lead to a more realistic view of the true benefits of DNAPL source remediation.
A conceptual is proposed to explain the transport behavior of plutonium in laboratory columns packed with a sandy coastal soil from the U. S Department of Energy’s Savannah River Site. In the experiments, a finite step input of plutonium, predominately in the +5 oxidation state, was introduced into the columns and followed by elution with a low-carbonate solution of 0.02 M NaClO₄ at pH 3, 5, and 8. Total plutonium concentrations were measured in the effluent as a function of time. The elution profiles suggest at least two distinct physical/chemical forms of plutonium, each with a different mobility. To explain the observed behavior, a conceptual model is proposed here which includes [1] equilibrium partitioning of plutonium (V) and plutonium (IV) between the aqueous and sorbed phases with pH-dependent, oxidation-state specific distribution coefficients and [2] kinetic reduction of plutonium (V) to plutonium (IV) in the sorbed phase. The conceptual model was applied to the column experiments through a one-dimensional advective/dispersive mathematical model, and predictions of the mathematical model were compared with the experimental data. Overall, the model provided excellent qualitative predictions of the major features observed in the experiments. It also yielded quantitative estimates of the rate constant for surface mediated reduction of plutonium (V) to plutonium (IV) that were of the same order as those calculated from batch data both for this soil and for goethite.

CROATAN WETLAND MITIGATION BANK: GROUND WATER MODELING AS A TOOL FOR HYDROGEOLOGICAL ASSESSMENT IN A LARGE-SCALE ECOSYSTEM STUDY.

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The North Carolina Department of Transportation, in its commitment to provide compensatory wetlands mitigation for unavoidable project related impacts, is pursuing the development of the 1635–hectare Croatan Wetland Mitigation Bank in Craven County, North Carolina. The Bank was previously managed for timber production and has undergone heavy degradation over the past several decades. Approximately 98 percent of the Bank historically may have contained wetland communities on organic and wet mineral soils. More than 41 km of ditches have isolated headwater storage for a pocosin-small coastal plain stream system and extensively altered site hydrology. Data collected for the development of the hydrogeological assessment included subsurface investigation, soil characterization, monitoring of ground water and surface water fluctuations, and monitoring of onsite precipitation. Ground water modeling was conducted using DRAINMOD a numerical model developed to simulate the effectiveness of water table management networks on shallow water table soils. The modeling simulated existing conditions, degree of reduction of potential historical periods of near surface saturation, and a series of future scenarios to forecast the most effective and efficient hydrologic restoration and enhancement alternatives. Hydrologic and hydraulic analyses were used to forecast surface water runoff potential, water budgets, and to assist with jurisdictional wetland delineation. The site is currently under implementation and undergoing monitoring.
THE HOPSCOTCH METHOD FOR FAST SIMULATIONS OF TRANSIENT GROUNDWATER FLOW

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Simulating transient groundwater flow in heterogeneous aquifers can be computationally intensive, with computer run times that try even the most patient investigator. This issue can be particularly severe, for example, where many simulations are required to solve transient inverse problems used to analyze pumping tests. The Hopscotch method (HOP) is an explicit finite difference technique that gets its name from the pattern of nodes used during execution. This method can be faster than many widely used solvers because fewer operations are required per mesh node. For example, 8 FLOPS are required per node at each time step for HOP compared to 14 FLOPS per node for the Crank-Nicolson implicit method using preconditioned conjugate gradient iteration (PCG). HOP is second-order accurate and unconditionally stable for the transient saturated groundwater flow problem. Storage space is used efficiently by overwriting a single array of heads and boundary values during each time step. Transient analyses of a pumping well in 2-D and 3-D randomly heterogeneous, spatially correlated media were conducted using HOP, alternating direction implicit (ADI), and PCG methods. Time steps for the methods were adjusted so that the accuracy of the results was similar. Preliminary results for the 2-D problems indicate that HOP is about 1.5 times faster than the ADI method and 3 to 4 times faster than PCG on an equal accuracy basis. The real payoff appears to come with 3-D problems, however. Results indicate that HOP is between 7 and 10 times faster than PCG for the particular test cases used in the evaluation.

HOP has seen limited application in the groundwater field, in part because it has been omitted from popular groundwater modeling software. We have written a solver for MODFLOW that implements the hopscotch algorithm, which should make this fast solver readily accessible for simulating transient groundwater flow problems. The enhanced speed of HOP promises to be a significant advancement in solving important problems in groundwater flow.

EXPERIMENTAL AND NUMERICAL INVESTIGATION OF UNSATURATED FLOW EFFECTS DURING SURFACTANT FLUSHING OF THE VADOSE ZONE

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Surface-active organic compounds (surfactants) reduce the surface tension of water. Surfactants are commonly used for the in-situ remediation of contaminated groundwater. In addition, many organics of environmental concern, such as TCE and Benzene, can reduce surface tension. Because of the dependence of capillary pressure on surface tension, non-uniform surfactant distributions can result in capillary pressure gradients within the vadose zone. We conducted laboratory experiments and numerical modeling to study unsaturated flow behavior in the presence of surfactant-induced capillary pressure gradients.

The experiments were conducted in a large (2.3m by 1.5m by 0.1m) two-dimensional flowcell packed homogeneously with fine silica sand. Time domain reflectometry probes and tensiometers measured moisture content and soil water pressure, respectively. Flow and transport were also monitored visually through the glass wall of the cell. Ambient groundwater flow through the satu-
rated zone, including the ~55 cm thick capillary fringe, was maintained using constant head devices on the sides of the flowcell. Two laboratory experiments were conducted. In the first experiment, a dyed water solution (no surfactant) was applied at a point source on the soil surface. In the second experiment, surfactant solution (7% n-butanol with dye tracer) was applied at a constant rate at the point source. This scenario was designed to represent either the surface application of surfactant for remediation of the vadose zone, or infiltration of a surface-active contaminant plume.

In the surfactant-free experiment, the dyed water solution was transported horizontally downgradient, entirely within the capillary fringe. This indicates the potential importance of the capillary fringe on transport processes. In the surfactant experiment, however, the lower surface tension of the surfactant solution caused a localized depression of the capillary fringe below the point source and a drainage front that propagated across the box in the downgradient direction. The surfactant-induced drainage of the vadose zone decreased the storage capacity within the capillary fringe and led to more rapid contaminant breakthrough to the watertable. Another unique feature was a stable tension-saturated region, which contained pure water, overlying a drained region containing surfactant solution.

Most conceptual and numerical models do not account for the effect of surfactants on unsaturated flow. We modified the unsaturated flow and transport model HYDRUS-2D (developed by Simunek, et al. of the U.S. Salinity Laboratory) to account for the concentration-dependent effects of dissolved butanol on surface tension and viscosity, and successfully simulated the surfactant infiltration experiment. The results presented here point to the importance of considering transport within the capillary fringe, demonstrate the significant effect that surfactants can have on flow within the vadose zone, and provide a method for modifying standard flow and transport models to account for this effect.

TRENDS IN ATMOSPHERIC MERCURY DEPOSITION IN THE SOUTHEAST

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The US EPA concluded in their Mercury Study Report to Congress that “a plausible link exists between past and present, human-caused, atmospheric emissions of mercury in the U.S. and increased concentrations of mercury that have been found in the environment and freshwater fish.” (EPA 1997) This report, coupled with an increase in mercury advisories for fish, which now include 39 states and five Canadian provinces, has brought concerns about mercury in the environment, and its possible human health risks, to the forefront. The US EPA is currently developing regulatory control strategies for persistent, bioaccumulative chemicals such as mercury. These controls are being implemented through various aspects of environmental regulation such as the Clean Air Act (CAA), the Clean Water Act (CWA), National Pollutant Discharge Elimination System (NPDES), and Total Maximum Daily Loads (TMDL). In this discussion the magnitude of the atmospheric deposition rate of mercury is considered with impacts to water quality in South Carolina and Georgia.

Mercury is an important element due to its complex environmental chemistry, bioaccumulation in the environment, and extreme toxicity. Both the absorption and toxicity of mercury vary depending on the species of the metal and the exposure pathway. In the environment, mercury cycles as a result of natural and anthropogenic activities with the total amount of mercury considered to have increased since the industrial age. In natural water systems mercury can exist in three oxidation states with properties and chemical behavior strongly dependent on this state. In the elemental state, Hg(0), mercury is relatively inert and although reactions with oxygen are thermody-
namically favored, the resulting compound is unstable in sunlight and quickly decomposes. As a result, a significant fraction of the mercury present in the atmosphere is elemental mercury vapor that oxidizes to the mono- and divalent species Hg(I) or Hg(II) rapidly during/after (?) deposition. (EPA 1997)

Of the two oxidized species deposited, the divalent Hg(II) species is more stable and the most common in environmental systems. In natural systems Hg(II) is commonly associated with sulfur in the mineral cinnabar, but it can be associated with inorganic molecules such as chlorine, oxygen and hydroxyl ions, or with organic molecules to form compounds such as methylmercury and dimethylmercury. In addition, Hg(II) readily complexes with humic substances over a wide range of pH with the maximum degree of complexation occurring in slightly acidic conditions. Overall Hg-humic complexes are considered to have a high degree of stability and are minimally effected by the pH of the solution. The compounds most likely to be found under environmental conditions are the mercuric salts HgCl and HgS; mercury hydroxides, the methylmercury compounds, methylmercuric chloride (CH₃HgCl) and methylmercuric hydroxide (CH₃HgOH), and the Hg-humic complexes.

The formation of methyl- and dimethylmercury compounds is important in natural waters as these species are readily bioaccumulated and pose the greatest ecological and health risk. These compounds are produced by the methylation of available Hg(II) by micro-organisms known as methylators. (Gilmour et al. 1992) Numerous methylators have been identified under a wide range of environmental conditions. The process of mercury methylation is complicated and diverse and varies almost on a case by case basis with both methyl- and dimethylmercury species occurring readily in natural waters with ratios dependent upon local environmental conditions.

Mercury deposition rates from numerous measurement stations across the southeast are compared with recent observations from within the Savannah River watershed. Weekly measurements of concentration and deposition of total mercury in precipitation are obtained from the Mercury Deposition Network (MDN) and it’s associated sponsors. The objective of the Mercury Deposition Network (MDN) is to develop a national database of weekly concentrations of total mercury in precipitation to allow researchers to evaluate the seasonal and annual flux of total mercury in wet deposition. The data is used to develop information on spatial and seasonal trends in mercury deposited to surface waters, forested watersheds, and other sensitive receptors. Analysis of precipitation samples for total mercury is performed by Frontier Geosciences, Inc., Seattle WA, USA. Frontier Geosciences provides the environmental sciences community with high-quality contract research, project design and management, and analytical chemistry services concerned with the sources, fate and effects of trace metals. Under this program weekly wet deposition samples are collected and analyzed for total mercury using EPA Methods 1630 and 1631.

The MDN began as a transition network of 13 sites in 1995. Beginning in 1996, MDN became an official network in the National Atmospheric Deposition Program (NADP) with 26 sites in operation. Over 50 sites were in operation during 2000. The MDN is anticipated to operate for a minimum of five years and is managed through the NADP Coordination Office located at the University of Illinois. The MDN provides data for total mercury, but also includes methylmercury if desired by a site sponsor. Historical data are available via the MDN Web page. (http://nadp.sws.uiuc.edu/mdn/) The data collected under this program is expected to regulate industry in the near future. The MDN has been recognized as a critical tool for assessing the effectiveness of Hg controls and lowered emission limits. (National Atmospheric Deposition Program (NRSP-3)/Mercury Deposition Network 2001)

Within the southeastern United States, four (4) MDN stations are active in the states of Georgia and South Carolina. These stations are located at the Congaree Swamp National Monument southeast of Columbia, South Carolina; at the Okefenokee National Wildlife Refuge south of
Waycross, Georgia; Yorkville, Georgia near Rome; and at the Savannah River Site southeast of Aiken, South Carolina. The network uses standardized methods for collection, analyses, and evaluation of total wet mercury deposition. Weekly precipitation samples are collected in a modified Aerochem Metrics model 301 collector that is interfaced with a Belfort universal recording rain gauge. The “wet-side” sampling glassware is removed from the collector every Tuesday and mailed to the Hg Analytical Laboratory (HAL) at Frontier Geosciences in Seattle, WA for analysis by cold vapor atomic fluorescence (Method 1631).

The stations at Congaree Swamp National Monument (SC19) and at the Okefenokee National Wildlife Refuge (GA09) have been in operation for several years. These records (n=315) provide insight on seasonal variations and annual flux of total mercury in wet deposition across the region. Respectively, these stations are funded and operated by the South Carolina Division of Air Quality and the US Fish and Wildlife Service - Air Quality Branch. Using data collected from stations SC19 and GA09 for the period between 1/96 through 12/00, the volume weighted average concentration of total mercury observed in precipitation was determined to be 11.3 ng/l with a median value of 11.2 ng/l. The concentration ranged between 0.3 ng/l and 275.7 ng/l. Variation in the monthly median of concentration is observed, ranging from 29% below the annual median in February to 54% above the annual median in August. The variation of total mercury present in rainfall indicates that total mercury concentrations are below the annual median in the winter and increase through the spring reaching a maximum in late summer and then rapidly decline below the annual median in the early Fall.

Although a significant focus on mercury in the environment is placed on concentration, the most important property associated with the environmental transport is deposition rate, which combines the concentration observed in precipitation with rainfall quantity. This mechanism serves as the primary transport process for mercury to most aquatic systems. (Mason et al. 1994; Mason et al. 1997) In this mechanism deposition to the aquatic system occurs either by direct deposition to the water surface or as runoff from the watershed. (Mason et al. 1999) Recent investigators speculate that mercury provided via direct deposition is more biologically available than that transported via runoff/groundwater. (Mason et al. 2000)

Combining precipitation volume with the measured concentrations reported from the stations at Congaree Swamp National Monument (SC19) and at the Okefenokee National Wildlife Refuge (GA09), seasonal variations and annual flux of total mercury in wet deposition across the region can be determined. For the period between 1/96 through 12/00, the average wet deposition rate of total mercury was 307 ng/m² per week, with a median value of 170 ng/m² per week. The weekly deposition rate ranged between 2.6 ng/m² and 2,625 ng/m². This is consistent with EPA’s estimate that within the Savannah River watershed the average wet deposition of total mercury is 234 ng/m² per week (presented as 12.2 mg/m² per year). (EPA 2001) Variation in the monthly wet deposition rate is observed with the monthly median ranging from 61% below the annual rate in November to 45% above the annual median in July. The general trend indicates nominal weekly deposition at the annual rate in winter that increases slightly through the spring reaching a maximum in late summer and then rapidly declining below the annual median in the Fall. These observations contradict recent statements made suggesting that the highest deposition occurs in winter and spring. (EPA 2001) The seasonal observations from stations SC19 and GA09 are consistent with the observations of wet deposition in the Chesapeake Bay (Mason et al. 2000), in that higher relative concentration and higher rainfall in summer enhances the overall flux in summer months compared to other periods.

In addition to sites SC19 and GA09, two (2) additional stations have gone on-line within the past twelve months. These stations are located in western Georgia near Rome (GA40), and along the
Georgia – South Carolina state line at the Savannah River Site (SC03). Preliminary observations from these stations are consistent with the historical and present observations at Stations SC19 and GA09. Continued monitoring at these stations should provide insight on spatial variations in the wet deposition of mercury as predicted by regional numerical simulations (EPA 1997; EPA 2001). The spatial variation of deposition can be assessed by examining the relationship between weekly flux and rainfall (Mason et al. 2000). Using the limited (6 months) information available, the fluxes observed at stations SC03, SC19, and GA40 are comparable and slightly below those observed at station GA09.

The atmospheric deposition of mercury has been interpreted by the EPA to have impaired the Savannah River because mercury in certain species of fish exceeds consumption guidelines. This impairment led to the development of a Total Maximum Daily Load (TMDL) under the requirements of the Clean Water Act. During the development of the TMDL, estimates of the baseline (1994-1996) and future (2010) loading of mercury to the watershed were made. The proposed TMDL for the Middle and Lower portions of the Savannah River watershed proposes a water quality standard for total mercury of 2.8 ng/l or an allowable load of 32.8 kg/yr. This mercury load has been allocated between atmospheric sources (99%) and wasteload (1%).

Baseline estimates for deposition utilized results from the national RELMAP model that was developed and presented in the 1997 EPA Mercury Report to Congress (EPA 1997). This national scale modeling provides insight on the variation and trends of mercury deposition on a national scale. In the national study, annual wet and dry deposition was examined on a 40 km x 40km (618 mi²) scale across the continental US. During development of the TMDL, EPA concluded that across the watershed, the average wet deposition rate was 12.2 mg/m² per year and the average dry deposition rate was 8.22 mg/m² per year. Using the distribution of wet and dry deposition, an estimate of loading from the watershed to the Savannah River was simulated using a Watershed Characterization System (WCS). This assessment determined that 58.8 kg/yr of mercury was deposited currently being deposited from sources within the “airshed” and that proposed implementations of the Clean Air Act (CAA) would reduce this by 38%-48% by 2010. To validate these proposed reductions, systematic measurements of mercury in precipitation are necessary.

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GEOMORPHIC AND HYDROLOGIC CONSTRAINTS ON CENOZOIC TECTONISM IN THE SOUTHEASTERN U.S.

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Geomorphologic and hydrologic characteristics of the southeastern U.S. in general, and the upstate region of South Carolina in particular, appear to support a history of uplift and tectonism of this “passive” margin during Cenozoic time. Regional topographic anomalies such as the Blue Ridge Escarpment (an ~500 m step in topography, traceable for >1200 km along the Appalachians) and the Eastern U.S. drainage divide (that deviates considerably from the Appalachian topographic divide) likewise suggest a landscape that has been tectonically perturbed in Cenozoic time. The surrounding region is marked today by strong structural control (cataclastic zones) of stream drainage (e.g. South Fork of Saluda), clear evidence for stream capture (e.g. Tugaloo), stranded gravel deposits along river drainages (e.g. Table Rock Reservoir area), and an abundance of natural waterfalls (e.g. Rainbow, Raven Cliff Falls). Such geomorphic features suggest a landscape that is distinctly at topographic disequilibrium. Analysis of drainage patterns and local slopes shows distinct differences between the physiographic regions of the southeastern Atlantic continental margin, apparently without regard to influence of the underlying bedrock. Such relationships may owe their origin to a previously more extensive terrigenous/marine coastal plain cover, extending up-dip of the Fall Line to the Tallapoosa-Rappahannock Lineament, and perhaps marking the pre-erosional location of the Blue Ridge Escarpment. Cenozoic displacement, perhaps as reactivation of Mesozoic faults, appears to be a plausible mechanism for generation of a southern portion of the Blue Ridge Escarpment. Although the exact timing and magnitude of the uplift continues to be questionable, significant activity may have been centered around the major Oligocene and Early Miocene unconformity ending by the time of deposition of the Upland Unit (Mid-Miocene) traceable from New Jersey to Georgia in various stratigraphic units. Estimates for the magnitude of uplift are highly dependent on the former extent of sea level, but are thought to be of approximately 500-1000 m in vertical crustal motion.

FLOOD PLAINS AS SOURCE OF METALS FOR RIVER SEDIMENTS: A CASE STUDY IN LEBANON

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Metals in bed-load sediments derive from local weathered rocks, metals discharged directly into river channel and eroded soils. A contaminated flood plain is a temporary storage system for pollutants and an understanding of soil-sediment interactions is an important prerequisite for modeling fluvial pollutant transport. The objective of this ongoing study is to investigate and partition the sources of metals in bed-load sediments of Nahr-Ibrahim River, Lebanon. The river is largely underlain by of
limestone including dolomite. X-ray diffraction analysis of bed sediment showed peaks corresponding to calcite, dolomite and quartz, and the water column chemistry indicated saturation for Ca and Mg carbonates. The flood plain is mostly terra rossa soils high in iron oxides Bed-load sediments and riparian soils were collected from five sampling sites along a 13 km stretch from the of river mouth, during October, 1999. Sites were chosen after an inventory of possible pollution sources. Total metal contents (Fe, Zn, Mn, Cu, Pb, Cd, As, Cr and Ni) were determined by ICP-MS after an *aqua regia* digestion. Metals are generally higher in soils near industrial zones, busy roads and where susceptible to agricultural contamination. Soils with high Fe amounts also exhibited high content of Mn, Ni, Cr, Cd and As. Site 5 was an exception where sediments contained more Zn, Cu and Cr than adjacent soils. The data have provisionally been interpreted thus:

During dry seasons and low river discharge, water flow is maintained by bed recharge from ground water probably supersaturated with carbonate species. The carbonates are likely to precipitate on any convenient nucleus and one can assume an important nucleus is the “soil-became-sediment” particle lying on the stream bed. Precipitated carbonates will effectively dilute sediment metal concentrations. However, where metals are discharged directly to the river they will be scavenged or co-precipitated with the alkaline earth carbonates and sediment contents may then be higher than soils. The dolomite observed in the sediments is geologically derived.

### GEOSTATISTICALLY-BASED DATA INTERPRETATION OF SURFACE GEOPHYSICAL SURVEYS

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Surface geophysical methods such as electromagnetics (EM) and resistivity have much to offer when facing time or budget constraints. However, most methods of data interpretation cannot produce hard data such as stratum thickness or contaminant concentration directly from survey results. The most common method of data presentation for these methods is a simple contouring of results that allows comparisons of conductivity/resistivity laterally and/or with depth. Another method involves curve-matching techniques relating layer conductivities and cumulative response to apparent conductivity, either by curve matching or analytical modeling. What is needed is an interpretive method that can take geophysical field data and produce quantifiable results in terms of stratigraphy and groundwater quality.

A statistical method of data interpretation for surface geophysical surveys (especially EM) has been developed for use in stratigraphic and groundwater studies. The method (Multivariate Regression Prediction, or MVRP) uses multivariate regression to establish a relationship (expressed in the form of a regression equation) between conductivity readings taken at known (hard) data points and the known stratigraphy or contaminant concentrations (dependent variable) at those points. The assumption is that there is some mathematical relationship between the dependent variable (i.e., depth of stratum, chloride concentration) at a known point and the measured responses for various EM coil spacings/orientations or resistivity readings at various electrode layouts. Once the prediction equations are calibrated for the hard data stations, the dependent variable at other survey data station is calculated directly from the equations. The principal advantage of this method is the quantitative determination at each data station, rather than qualitative interpretation of simple conductivity data plots. The geophysical survey serves as an extension of hard data, rather than a method requiring additional data or another method for correlation.
The accuracy of the predicted values is evaluated through the regression parameters, the Coefficient of Determination (Cd) and Standard Estimate of Error (SEE). The Cd is a measure of the percentage of the total variation in the dependent variable is associated with the variability of the independent variables, and indicates the reliability of the prediction. The SEE is a measure of the scatter of observed data around the predicted regression line. The closer the observed values are to the predicted values, the lower the SEE and greater the precision of the predictions. A quantitative evaluation of the precision of the predictions can be determined using the Two-Sided Tolerance Test (TSTT). A level of confidence can also be quantitatively described using the “t” test.

MVRP analysis has been used with Geonics, Ltd. EM instruments with considerable success, but can be sued with any instrument that can produce multiple readings at each station, like D.C. resistivity. The ultimate objective is to be able to bracket the zone of interest with a number of readings. The Geonics EM34-3, with its ability to produce varied near-surface and depth responses with horizontal and vertical dipoles, as well as different depth responses with coil spacing, has been useful in creating a realistic regression equation. However, when dealing with layers less than one meter in thickness, especially at depth, it may be more prudent to use D.C. resistivity, which allows a greater number of depth readings at various electrode spacings.

Past experience has shown that a general information survey can be performed with five hard data points. However, the level of confidence will be much higher with more hard data points for correlation (higher degrees of freedom). Therefore, for greater precision, it is recommended that at least eight points be used for creating the regression equation.

The MVRP method has been used successfully at a number of landfill sites for determining depth to bedrock, subsurface sand channel delineation, paleokarstic feature locations, and stratigraphic mapping between boreholes. It has also been used to map groundwater chloride concentrations resulting from leaking brine ponds and oilfield wells. Examples follow:

**Stratigraphy - North Florida.** Preliminary borings drilled at a landfill in the panhandle area indicated a possible sand channel along the west side, possible a relict stream channel. Typical stratigraphy consisted of 7 meters of silty/clayey sand underlain by clay, which extended to the top of a limestone stratum at a depth of 12-meters. However, three borings on the west side had encountered 12 to 30 meters of sand. Simple contouring of EM readings taken across the site showed the sand body to actually consist of a series of discontinuous anomalies, most likely old karstic solution features. An MVRP analysis was used to predict the thickness of the sand bodies and also depth to limestone. The depth to limestone regression had a higher Cd and lower SEE versus that of the sand thickness regression. Subsequent confirmatory borings found that actual depth to limestone was within ±2 meters of the predicted depths. Also, the filling material in the paleosinks ranged from clayey sand to clay. Therefore, the lower precision in predicted sand thickness was representing the variation in soil size and conductivity.

**Chloride - North Louisiana.** A plant in North Louisiana that had a regular groundwater monitoring program showed high chloride concentrations in groundwater. There were no plant processes involving chlorides, and the concentration gradient suggested an upgradient source. The plant was located in one of the oldest operating oil fields in Louisiana, and a large number of oil skimmer wells, saltwater injection wells and pipelines, and brine ponds were found surrounding the immediate area. An EM survey with MVRP analysis correlating monitoring well concentrations was used to predict the extent and concentrations of the chloride plume. The EM survey indicated that the upgradient brine ponds and an unknown source south of the investigation area were the sources.

**Stratigraphy - North Arkansas.** An EM survey was conducted at a proposed landfill expansion site in a karstic region of northern Arkansas. The EM survey was used to interpolate between
standard boring locations to characterize the entire expansion site. The MVRP results indicated that a series of bedrock pinnacles were located across the central portion of the property. The general stratigraphic trend appeared to be that of a thick clay overburden overlying dolomite along the ridge tops, thinning to 2 meters or less along draws and at the base of the hills. Areas of greater thickness to dolomite (possible fractures) appeared to be aligned in a north-south trend across the central and western portion of the site. These areas did not have any topographic expressions on the surface. However, a seep observed during the EM survey could have corresponded with one of the possible fractures. No fracture lineaments were observed at the site.

GROUNDWATER GEOCHEMISTRY AND MICROBIOLOGY OF COASTAL PLAIN AQUIFERS, CENTRAL-SOUTH ALABAMA

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We integrate groundwater geochemistry, microbiology, and numerical modeling techniques to study the origin of trace metals and elevated salinity in the coastal plain aquifers in central-south Alabama. Our field data indicate that chemical composition and redox potential of groundwater evolve by biochemical processes as it moves deeper into the subsurface. Significantly higher alkalinity and pH of groundwater correspond to the parallel spikes in Fe and Mn concentrations. These correlations and the presence of the iron-reducing bacteria Pseudomonas mendocina support that elevated Fe and Mn concentrations are derived from bacteria iron and manganese reduction. Reaction path modeling techniques were used to trace the biogeochemical reactions would accompany bacteria Fe (III) and Mn (IV) reduction in the coast plain aquifers. The simulation first equilibrates an oxidized groundwater upstream of the iron reduction zone and then titrates organic substrate acetate into the system. Mn (IV) mineral pyrolusite in the initial system becomes thermodynamically unstable and transforms over time to a sequence of progressively more stable manganese minerals at lower oxidation states. Once reduction of Mn has nearly completed, hematite begins to dissolve to form more stable magnesite at low oxidation states. The modeling results support that Ostwald's Step Rule governs the biotransformation of iron and manganese minerals in coastal plain aquifers. Cl/Br ratios and _D and _18O values are used to determine the source of salinity and chemical evolution of groundwaters. Three water types were identified, including carbonate groundwater, groundwater associated with evaporites, and groundwater of meteoric origin. Groundwater age differences and flow velocities were calculated using the 36Cl/Cl ratios. Calculated groundwater flow velocities within the Eutaw and Tuscaloosa aquifers are about 0.2 m/yr and 0.15 m/yr, respectively. We modeled basin-scale hydrologic and solute transport processes in a cross section extending from the aquifer outcrops to the Gulf Coast. The predicted flow pattern reveals the mixing and interaction between meteoric recharge and groundwater associated with Knox carbonate strata (Ordovician) and Louann Salt. The modeling result shows that the buried Louann salt can significantly increase groundwater salinity in the overlying coastal plain aquifers by advection and diffusion. The modeling results are consistent with Cl/Br ratios and O/H isotope signatures, which indicate that salinity of the groundwater could be derived from seawater that has been evaporated beyond halite saturation.
1. Introduction

The source of salinity and trace elements in sedimentary aquifers remains one of the most controversial problems in basin hydrology. The coastal plain aquifers in central-south Alabama are exploited for large quantities of drinking water at depths, but groundwater is locally contaminated with trace elements of Fe and Mn (> 300 ppb) and its chloride contents increase dramatically (> 100,000 ppm) downdip. Although hydrochemistry and geology of these aquifers have been studied by many investigators (e.g., Scott et al., 1987; Cook, 1993), the source of salinity and the influence of subsurface microorganisms on groundwater chemistry remain poorly understood.

Hydrogeologists have used different tools to construct the hydrologic transport and chemical evolution model for regional groundwater systems. Back and Hanshaw (1970) introduced the hydrochemical facies concept to study the mixing of different groundwaters and water-sediment interaction along a flow path. Geochemists have since increasingly used isotope tracers to study groundwater flow and geochemical processes (e.g., Bentley et al., 1986; Roback et al., 2001). In the past decade, newly developing nucleic-acid technology (e.g., Maden, 2000) allows scientists to investigate how microbial activity create discrete hydrochemical zones in regional aquifer systems (e.g., Lovely and Chapelle, 1995). Since then, the effect of microbial process on chemical evolution of groundwater has been the subject of a large body of research. Because the possible reactions occurring in aquifers are quite complex, scientists have come to rely on numerical modeling techniques to study fluid migration and the nature of biogeochemical processes.

This study emphasizes the integrated approach by applying isotopic tracers, hydrochemistry, microbiology data, and numerical modeling in a regional-scale hydrogeology model. Data including major ions, trace elements, stable isotopes, radioactive isotopes, and microorganisms were collected along two flow paths downgradient from outcrops. Geochemical modeling techniques were used to trace biogeochemical reactions that would accompany bacteria Fe (III) and Mn(IV) reduction in the aquifers. Regional groundwater flow modeling was conducted to provide interpretations of observed salinity distribution in coastal plain aquifers. The results of numerical modeling are integrated with geochemical data to interpret the origin of salinity and chemical evolution of coastal plain aquifers in central-south Alabama.

2. Groundwater Geochemistry and Microbiology

2.1 Major Ions and Trace Elements

Along the western transect, three different hydrochemical facies were identified, including carbonate groundwater, saline groundwater associated with evaporites, and meteoric water. The carbonate facies was related to deep groundwaters that migrated along faults discharge upward into Cretaceous aquifers. Water samples contain significantly higher proportions of sodium and chloride likely derived from evaporated seawater. Groundwaters with low major ion concentrations are largely meteoric water with some influence of the mixing of calcium bicarbonate and sodium chloride type groundwaters.

Significantly higher alkalinity and pH of groundwater in western Alabama correspond to parallel spikes in Fe and Mn concentrations. These correlations suggest that elevated Fe and Mn concentrations are derived from bacterial Fe and Mn reduction reaction such as:

\[
4\text{FeOOH}_{(s)} + \text{CH}_2\text{O} + 7\text{H}^+ \rightarrow 4\text{Fe}^{2+} + \text{HCO}_3^- + 6\text{H}_2\text{O}
\]  
(1)

where \text{CH}_2\text{O} represents organic matter. This dissimilatory iron reduction would release metals and r
raise alkalinity of groundwater at the expense of H⁺, organic carbon, and iron oxides.

2.2 Cl/Br Ratios
Cl/Br ratios were used to determine the source of salinity in groundwater. Different Cl/Br ratios have been observed in various natural waters (Davis et al., 1998) including atmospheric precipitation (50-150), seawater and evaporated seawater (<290), and deep basin brine affected by congruent halite dissolution (>1,000). The Cl/Br ratios of Eutaw samples range from 100 to 200, indicating that the groundwater has been influenced mostly by fresh water incursion and seawater evaporation.

The Cl/Br ratios of Eutaw groundwater show a close correspondence with the seawater dilution and evaporation trajectory (Carpenter, 1978). The Eutaw samples that are considerably more dilute than seawater have Cl/Br ratios slightly lower than seawater, reflecting their meteoric origin. These samples fall slightly to the right or close to the conservative dilution line for seawater and meteoric water. The brine samples that are considerably more saline than seawater plot slightly to the right of the trajectory, indicating that they acquired salinity from remnant evaporite brines, rather than congruent dissolution of evaporite minerals.

2.3 Stable Isotopes (dD/d¹⁸O)
 dD and d¹⁸O values are used to determine the source of groundwaters and their geochemical evolution. Shallow groundwater samples fall close to the local meteoric water line, indicating their common association with atmospheric recharge. The dD-d¹⁸O trend of deep, saline groundwater intersects the evaporation trajectory at a point close to halite saturation, which is consistent with the extent of seawater evaporation inferred from Cl-Br relations. Both dD-d¹⁸O and Cl-Br trends clearly indicate the mixing of remnant evaporated seawater (close to halite saturation) with meteoric water. Groundwaters originated from older Paleozoic carbonate rocks in the Alabama Valley and Ridge display distinctively different dD and d¹⁸O values (Cook, 1997). dD and d¹⁸O values of these samples, again, indicate three possible sources of groundwater. These include meteoric water, evaporated seawater (close to halite saturation), and groundwater from Ordovician/Devonian carbonate rocks.

2.4 Radioactive Isotopes ³⁶Cl
³⁶Cl/Cl ratios of groundwater in the aquifers range from 6×10⁻¹⁵ to 156×10⁻¹⁵. A high ³⁶Cl/Cl ratio near the recharge area corresponds to young groundwater with a strong atmospheric ³⁶Cl signature and gradually decreases moving away from the recharge area. Natural decay of ³⁶Cl with travel time in the aquifers is most likely responsible for the decrease of ³⁶Cl along the flow path. However, progressive mixing with old groundwater with little ³⁶Cl but high Cl concentrations at depths may be responsible for this decline.

Using the equation of Bentley et al. (1986), the calculated ³⁶Cl age difference of groundwater between Moundville and Greensboro is about 110,000 years. Given a flow path of 20 km, groundwater migrates at a rate of about 0.2 m/yr between these two wells in the Eutaw aquifer. The ³⁶Cl age data indicate that groundwater travels at a rate of about 0.15 m/yr in the Tuscaloosa aquifer, close to those in the Eutaw aquifer.
2.5 Microorganisms
Bacteria in Fe- and Mn-rich groundwaters from Marion and Demopolis wells were isolated and identified as to genus and species. The Fe (III)-reducing microorganism Pseudomonas mendocina was identified by DNA sequencing methods. Fe-reducing microorganisms require sources of ferric iron and carbon to grow and metabolize. Fe (III) hydroxides (common in the coastal plain aquifer sediments) such as goethite, hematite, and ferrihydrite can be used as a ferric iron source for these organisms. Pseudomonas Microorganisms mendocina are capable of reducing the most common and insoluble form of iron, Fe (III) hydroxides, which would increase ferrous iron concentrations in groundwater (Hersman et al., 2001).

3. Reaction Paths Modeling

We used the Geochemist’s Workbench (Bethke, 1996) to trace the biogeochemical reactions would accompany bacteria Fe (III) and Mn(IV) reduction in the coast plain aquifers. We begin by equilibrating the Moundville groundwater upstream of the iron reduction zone at 20°C. The calculation assumes the initial concentrations of Fe and Mn reflect equilibrium with hematite (Fe₂O₃) and pyrolusite (MnO₂) in the coastal plain sediments under aerobic conditions. The model then simulates the biogeochemical effects of titration of organic matters acetate (CH₃COO⁻) into the system. The accompanying bacteria growth and metabolism processes were also calculated. We consider biotransformation of hematite by the following metabolic redox reaction

\[
\text{CH}_3\text{COO}^- + 15 \text{H}^+ + 4 \text{Fe}_2\text{O}_3 \rightarrow 8 \text{Fe}^{2+} + 2\text{HCO}_3^- + 8\text{H}_2\text{O}
\]

Here, Fe(III)-reducing bacteria grow by utilizing acetate as the limiting organic substrate to reduce hematite (as electronic acceptor) in the system.

The predicted mineral reactions of manganese and iron oxides follow the well-known Ostwald’s step rule (e.g., Nordeng and Sibley, 1994). Pyrolusite in the initial system first becomes thermodynamically unstable and transforms over time to a sequence of progressively more stable manganese minerals at lower oxidation states:

\[
\text{Pyrolusite (MnO}_2 \rightarrow \text{Bixbyite (Mn}_2\text{O}_3 \rightarrow \text{Hausmannite (MnO}_4 \rightarrow \text{Mn(OH)}_2
\]

Once the reduction of Mn minerals has nearly completed, the iron redox reactions start and hematite (Fe₂O₃) begins to dissolve to form more stable magnesite (Fe₃O₄) at lower oxidation states. This result is consistent with the theoretical redox sequence that Fe reduction will proceed after the Mn reduction reactions are completed. This modeling results support that Ostwald’s step rule governs the biotransformation of iron and manganese minerals in coastal plain aquifers.

4. Basin Hydrology and Solute Transport Modeling

Hydrologic transport processes in the coastal plain aquifers was modeled using the basin-scale groundwater flow model Basin2 (Bethke et al., 1993). The simulations were conducted in a cross section extending from the outcrops in western Alabama southward to the Gulf Coast. The simulations aim at evaluating (1) the dilution of saline connate groundwater (trapped seawater) in the coastal plain aquifers by freshwater incursion and (2) the effects of deep Louann Salt dissolution on groundwater salinity in the coastal plain aquifers.
4.1 Effects of Fresh Water Incursion

The first model simulates the dilution of saline groundwater in aquifers by fresh water incursion. The model assumes that seawater was originally trapped in sediments before the emergence of the coastal plain above sea level. The initial salinity of groundwater in all basin strata, assuming down-to-basin infiltration of seawater during the submergence stage, was set to 0.5 molal. The salinity along the basin surface was then set to 0 molal, to correspond with the emergence of coastal plain. The transient simulation spans a period of 40 m.y. as the coastal plain is exposed to freshwater recharge. The simulation allowed us to evaluate the extent or depth to which the freshwater invades the aquifer since the emergence of the aquifers. The results were compared to observed salinity levels, thereby providing important constraints on the origin of salinity in the aquifer.

The modeling results show that the regional topographic relief provides the drive for the downward recharge of freshwater. The maximum flow velocity predicted by this model is on the order of 1.5 m/yr, with average flow rates <1 m/yr. The calculated velocities are generally consistent with those estimated by $^{36}$Cl method, as discussed earlier. The model shows that freshwater incursion can reduce the salinity of seawater to less than 100 ppm in the coastal plain aquifers within tens of kilometers to the south of the recharge zones. Groundwater salinity quickly increases and approaches that of seawater at distances >100 km to the south of the recharge zone, due to the flat hydraulic gradient in the southern coastal plain.

4.2 Effects of Louann Salt

A solute transport model was developed to examine how the buried Louann Salt might affect groundwater salinity in the coastal plain. Groundwater within the Louann Salt maintains a salinity corresponding to halite saturation (about 6 molal). The result shows that the Louann Salt can significantly increase groundwater salinity in the overlying coastal plain aquifers by advection and diffusion. The large salinity variation creates a density flow, which carries salts toward the relatively shallow strata and results in an increase in fluid salinity. The modeling results suggest very limited downdip infiltration of freshwater to the south of Demopolis due to a very gentle topographic slope, which argues against the potential for freshwater advection to cause larger-scale evaporite dissolution at depth. Therefore, the salinity could not be derived directly from congruent halite dissolution, which would produce much higher Cl/Br ratios (>1000) than those observed in the field (50-200). The elevated salinity in groundwater more likely comes from the deep buried brines reaching halite saturation, in close association with the Louann Salt.

5. Conclusions

This research correlates hydrologic, geologic, geochemical and microbial data to develop an integrated reactive transport model for water, solutes, isotopes, and microbes in coastal plain aquifer systems. Detailed field data and numerical models were used to understand relations between groundwater geochemistry, isotope hydrology and microbiology. The results indicate that chemical composition and redox potential of groundwater evolves by biochemical processes as it moves deeper into the subsurface, which is consistent with the theoretical electrochemical sequence.

Three water types were identified, including carbonate groundwater, groundwater associated with evaporates, and groundwater of meteoric origin. Significantly higher alkalinity and pH of groundwater in western Alabama are correlated with parallel spikes in Fe, Mn, and Sr concentrations. These correlations and the presence of the iron reducing bacteria *Pseudomonas mendocina* suggest that elevated Fe, Mn, and Sr concentrations are derived from bacterial iron and manganese reduction.
Biogeochemical modeling results support that Ostwald’s step rule governs the biotransformation of iron and manganese minerals in coastal plain aquifers.

Cl/Br ratios and ΔD and 18O values were used to determine the source of salinity and the chemical evolution of groundwaters in the coastal plain aquifers. Both dD-d18O and Cl-Br trends indicate the mixing of remnant evaporated seawater (close to halite saturation) with meteoric water. Basin-scale hydrologic transport modeling shows that freshwater incursion can reduce the salinity of seawater to less than 100 ppm in the coastal plain aquifers within tens of kilometers to the south of the recharge outcrops. The solute transport model also shows that the buried Jurassic Louann Salt can significantly increase groundwater salinity in the overlying coastal plain aquifers by advection and diffusion. The modeling results are consistent with Cl/Br ratios and stable isotope signatures, both indicating that salinity of the groundwater could be derived from seawater that has been evaporated beyond halite saturation. The predicted groundwater flow pattern reveals the mixing of meteoric water, carbonate groundwater (from the Ordovician Knox Group), and saline brines associated with Louann Salt. The hydrologic model is consistent with the hydrochemical facies distribution in the Alabama coastal plain.

References


DIRECT PUSH FIELD METHODS FOR CONDUCTING SLUG TESTS

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As risked based corrective actions and the monitored natural attenuation remedial option have grown in use the need to obtain site specific data on formation hydraulic conductivity (K) has dramatically increased. Historically this has required the installation and development of large diameter monitoring wells with traditional drilling equipment at substantial expense. However, smaller diameter direct push tools (DP) and methods eliminate much of the waste generation of conventional drilling and provide cost effective methods for slug testing in unconsolidated materials.

DP ground water sampling tools and small prepacked screen monitoring wells may be used for slug testing. Because of the small diameter of many DP tools it is advantageous to use pneumatic slug testing methods in many situations. A pneumatic slug testing system has been designed for use on DP tools and PVC wells from 0.5-inch up to 2-inches in diameter. In low-K formations the pneumatic method can double the time required for testing and in formations where the water level intersects the screen pneumatic methods are not appropriate. Because of these limitations a new slug test method was developed which uses a mechanical slug with integral transducer. This overcomes the space limitations of the small diameter DP devices and also reduces the effective radius of the well which reduces test duration in low-K formations. A summary of the DP ground water sampling devices and appropriate slug testing methods will provide insight into the application and cost effectiveness of these new slug test procedures.

Geoprobe Systems began development of methods for slug testing in DP ground water sampling devices and cooperative research was undertaken with the Kansas Geological Survey (KGS) to further develop and document the accuracy and limitations of these methods. DP ground water sampling devices were installed adjacent to conventional monitoring wells at a field site that is characterized by an upward fining sequence of alluvial deposits exceeding 70 ft in depth along the Kansas River. Side by side tests were conducted in the DP tools and conventional 2-inch and 4-inch PVC monitoring wells. In general the comparative slug tests revealed very good agreement between the DP methods and conventional well results. However, comparative tests in very high hydraulic conductivity sands and gravels (from 250 ft/day to >750ft/day) revealed that the small diameter DP tool (I.D. 0.625 inch) consistently produced results below those documented in the adjacent 4-inch diameter wells. A simple linear correction has been developed that can be applied to the results in the high-K formations to obtain the correct K-determination from the small diameter DP tool. Additionally, a new larger diameter direct push profiling system (1.5 inch I.D.) was developed that was able to accurately determine the hydraulic conductivity in formations where K exceeded 750 ft/day (2.6 x 10^1 cm/sec) without the need for a correction.

GROUNDWATER FLOW AND CONTAMINANT TRANSPORT IN SEDIMENTARY ROCK SAPROLITE

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Field and laboratory studies in sedimentary rock saprolite in east Tennessee show that groundwater flow is strongly influenced by the distribution of pedogenic clays and Fe/Mn oxides, which occlude
many of the fractures and macropores. These infillings tend to be most common from 60-150 cm depth and form a low hydraulic conductivity layer that impedes vertical infiltration and results in frequent perched water table conditions and rapid downslope flow in the uppermost saprolite. Another zone of rapid downslope flow tends to develop at the saprolite-bedrock interface, because of the hydraulic conductivity contrast between these materials. Transport of contaminants in the saprolite is strongly influenced by these zones and by the dual-porosity nature of the saprolite. Diffusive exchange of solutes between the rapidly flowing water in the fractures or rootholes and the relatively immobile pore water in the fine-grained matrix fractures results in a high degree of retardation and longitudinal spreading of solutes. This was demonstrated in a series of long-term field tracer experiments at ORNL, where breakthrough curves typically had slowly declining “tails” with environmentally significant concentrations still present many years after the initial tracer injection. Colloidal contaminants, or contaminants attached to colloids, are not strongly effected by matrix diffusion because of their larger size, and hence can migrate much faster than conservative solute tracers. This was demonstrated by a field tracer experiment in the weathered shale in which microbial and microsphere tracers migrated at rates of up to 200 m/day over distances of up to 35 m. At this same site solute tracers migrated at rates of 0.1 to 3.2 m/day. Recent investigations of the transport behavior of dense non-aqueous phase liquids (DNAPLs), show that migration of these contaminants are also strongly influenced by the multi-porosity nature (fractures, root holes, dissolution channels and matrix) of the material. Lab experiments show a high degree of variability of pore size and suggest that even small DNAPL spills may migrate to considerable depths.

These studies indicate that many of the conceptual models commonly used for assessing contaminant transport or designing remediation strategies in granular materials or in fractured, low porosity rock, may not be appropriate for saprolite derived from sedimentary rock.
INTEGRATION OF STRATIGRAPHY AND SEISMIC GEOPHYSICS FOR IMPROVED RESOLUTION OF SUBSURFACE HETEROGENEITY

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The objective of this study is to better understand and predict subsurface heterogeneity using an extensive database from the Miocene Temblor Formation, West Coalinga Oil Field, California. The overall approach is to integrate geological work being done at Clemson University with geophysical investigation in progress at Virginia Tech. Cores, borehole geophysical logs, and seismic data, along with outcrop data from a related project, are being used to characterize the heterogeneity.

Within the area of detailed study, three depositional environments are interpreted for the Temblor Formation (in ascending order): estuarine, tide- to wave-dominated shoreline, and subtidal. The nature and scale of heterogeneity differ among the three types of strata. Lateral heterogeneity of the estuarine deposits is interpreted as caused by the elongate geometry of channels and lagoons. The complex character and interbedded nature of sand and clay in the tide- to wave-dominated deposits cause a high degree of vertical heterogeneity. Massive subtidal deposits demonstrate a lower degree of internal heterogeneity because of lithologic mixing by bioturbation.

The construction of three-dimensional geological models based on the borehole geophysical logs and sedimentological interpretations is in progress. During the final stage of the project, investigators from Clemson and Virginia Tech will work together to fully integrate the geological models with the seismic results.

NURE HYDROGEOCHEMICAL AND STREAM SEDIMENT RECONNAISSANCE (HSSR) DATA, DHEC ANALYTICAL DATA, AND IMPLICATIONS FOR DOMESTIC WATER WELL URANIUM-RELATED ISSUES

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Environmental quality is recognized as a cornerstone of a healthy America. Although we tend to focus on anthropogenic pollution, the baseline is that provided by nature. This study addresses that baseline.

Recent discoveries of extreme concentrations of uranium, radon, and radium in domestic water wells near the towns of Simpsonville and Fountain Inn, S.C. (SFI) necessitate the investigation of the nature, extent and source of these anomalous contaminant levels. In addition, a public health threat potentially exists in areas along geologic trends of similar rock type and geologic history. Several of the SFI wells also contain arsenic ranging up to 38 ppb. Concentrations up to three hundred times the drinking water standard (see table), as set forth in the Clean Water Act, have been encountered in over 50 wells in the SFI Area of Greenville County. Health problems have already been diagnosed that can be attributed to these high concentrations.

<table>
<thead>
<tr>
<th>Contaminant</th>
<th>Highest Observed Value Simpsonville/Fountain Inn Area</th>
<th>EPA Maximum Concentration Limit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Uranium</td>
<td>10,100 micrograms/liter</td>
<td>30 micrograms/liter</td>
</tr>
<tr>
<td>Radium-226</td>
<td>42.5 Pico Curies/liter</td>
<td>4 pCi/l</td>
</tr>
<tr>
<td>Radon</td>
<td>49,800 pCi/l (perhaps in error)</td>
<td>300 pCi/l (proposed)</td>
</tr>
<tr>
<td>Arsenic</td>
<td>38 ppb</td>
<td>10 ppb (proposed)</td>
</tr>
</tbody>
</table>

Table: Summary of Contaminant Data
The SFI Area was found by chance – a resident developed health problems leading to analysis of hair and urine that revealed radioactive elements. Some residents of the affected area have been provided public water lines, and others have added filters to their water systems. These and other remedies can be applied once an affected area has been defined. The significance of this study is that it will develop and test tools to systematically and efficiently locate other affected areas so that they can be addressed.

**Background and Preliminary studies**

Uranium prices in this country grew from just over $10 per pound of U3O8 to peak at about $44 per pound in 1979, and it appeared that nuclear power was well on its way to replacing other energy sources for electricity production. In about 1973, DOE’s predecessor agency, the Energy research and Development Administration (ERDA) conducted an assessment of the USA’s potential to produce additional uranium. Part of this assessment involved nationwide geochemical and geophysical surveys. The geochemical surveys involved sampling and analysis of surface and ground water, stream sediment, soil and vegetation, but focused on stream sediment and ground water. The geophysical surveys produced K, U, and Th maps from aerial surveys, but at wide spacings. The objective of the program was regional reconnaissance, not prospect development.

In March of 1979 a safety incident at the Three Mile Island generating plant in Pennsylvania focused national and world attention on the risk associated with nuclear power reactors. In addition, large ore reserves were proven in Australia. These factors combined to stop the development on new nuclear power plants in the US and to drop the price of U3O8 back to the $10 per pound level, where it remained partly because in April of 1986, a disastrous power plant failure occurred at Chernobyl in the USSR. The 1979 events effectively terminated NURE funding, and anomaly verification studies, which had been planned, were not conducted.

**Ground Water Data**

The nominal density for NURE ground water sampling was one sample per 10 square miles. In the Greenville 1X2 degree quadrangle, there were 692 GW samples. Without discounting for cities, lakes and other inaccessible areas, that’s about one per 11.4 square miles. Uranium ranges from a detection limit of about .002 ppb, to over 400 ppb. One hundred forty samples were at or above an anomaly threshold of 0.100 ppb.

Two slightly anomalous NURE samples bracket the SFI area, but there are no samples above the 30 ppb MCL close to the area. A followup sampling program using the NURE data as a starting point would have had a good chance of locating the SFI area.

Once the SFI area was discovered, DHEC reported data from about 150 wells in an area of about 10 square miles, but most were in about a four square mile area. Of these, about one-third had uranium at or above 30 ppb.

**Exploration models**

We plan to use the SFI area to develop an efficient geochemical and geophysical exploration model to locate other areas where ground water supplies are tainted by naturally high levels of uranium and related elements. We will evaluate vegetation and stream pebble sampling as well as car-borne or airborne gamma surveys. Another effort will be to locate families which have had a cradle-to-grave exposure history to high background. Currently we are trying to develop funding to support these activities.

**Summary**

We will review uranium geochemistry, uranium deposits, and the available data from NURE and other sources. NURE data include data on radon and helium which were published in limited distribution documents, but which are worth reviewing as we attempt to explain the SFI Area.
CHARACTERISTICS AND DESIGN OF HYDRAULIC FRACTURES IN SAPROLITE

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There are many potential applications for shallow hydraulic fractures to improve environmental remediation projects, and the geometric form of the fractures is important to all of these applications. Advances in methods for predicting the forms of hydraulic fractures would be an important contribution to the success of their use during remediation. We are in the process of developing design tools through a program that integrates field studies with geotechnical measurements and theoretical analyses of hydraulic fractures. A suite of field implementations of the hydraulic fracturing technique performed at shallow depths in saprolite is central to this effort. Hydraulic fractures have been created at a depth of 1.5 meters by injecting 225 kg (500 pounds) of sand at a site near Pendleton, SC. Monitoring efforts suggest that the fractures are approximately 5 m in maximum dimension, and 1.5 cm in maximum aperture. A borehole extensometer and a pressure transducer are used to give the fracture aperture and injection pressures as functions of time. Preliminary results indicate that the fractures are shaped like asymmetric saucers. Excavation studies planned for the near future will reveal the details of the fracture forms.

The in-situ state of stress is widely recognized as a critical parameter affecting the forms of hydraulic fractures: fractures are expected to be generally flat-lying where the horizontal compression is greater than the vertical compression, whereas they are expected to be steeply dipping where the vertical compression is greatest. The state-of-stress in rock has been measured using several techniques that make use of small hydraulic fractures. The micro-fracturing technique has seen limited application in soils, and important methods that are successful in rock have apparently never been evaluated in soils. We have developed the equipment and techniques to create hydraulic fractures by injecting several ml of liquid at a constant rate and measuring the resulting pressure. Our preliminary results indicate that the lateral stress is greater than the vertical stress at our field site, which is consistent with field observations. Refinements of our technique should provide a method for estimating in-situ stresses in soils for a variety of applications.

It appears to be feasible to predict the forms of hydraulic fractures observed in the field using theoretical analyses and estimates of in-situ stress. A simple 1-D model gives results that are typical of flat-lying, symmetric fractures. We have used a 2-D numerical model to predict fracture traces that curve upward as a saucer-like form, and preliminary results from a 3-D fracture simulator also appear to resemble field observations. We are optimistic that additional investigations will result in a suite of methods for characterizing and predicting the forms of hydraulic fractures at shallow depths.

IN SITU TREATMENT OF A TCE SOURCE AREA USING A JETTED SLURRY OF ZVI AND CLAY

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High jetting was used to emplace a slurry of zero-valent iron (ZVI) and kaolinite throughout a small, well-defined trichloroethene (TCE) impacted source area at DuPont’s Kinston, NC plant. This in situ treatment was completed in conjunction with emplacement of a thin ZVI permeable reactive barrier (PRB) across the plume downgradient of the source area, also using high pressure jetting. The Kinston TCE plume originates from a relatively small source area resulting from past
Hydraulic fracturing has been used across North America and in Europe to optimize various remediation processes. In many cases the use of hydraulic fractures has enabled treatment technologies to be effective where they would otherwise be considered technically and/or economically infeasible. Hydraulic fracturing benefits remediation by either altering in situ flow paths and improving well performance, or by providing a method for delivering reactive or otherwise beneficial compounds to the subsurface. As a consequence of either or both of these mechanisms, remediation processes can be accelerated, inaccessible areas can be reached, and broader areas can be treated from a single point. For instance, at a site in Greenville, South Carolina, air sparging through hydraulic fractures yielded marked reductions in VOCs in offset monitoring wells within a matter of weeks. The results suggest that the site may be closed within the near future. In another case, hydraulic fracturing through inclined wells permitted installation of a dual-phase recovery system within the confines of an old-world house and its tiny garden. Fracturing not only spared the effort of installing undocumented waste handling activity. The impacted zone is limited to a surficial sand 15 to 18 feet deep overlying a thick mudstone confining layer. The water table lies at a depth of four to five feet below ground surface, and average linear groundwater velocity is estimated to be 0.05 to 0.1 feet/day. The plume is 500 feet long and 250 to 300 feet wide at a downgradient distance of 300 feet. TCE concentrations in the source prior to treatment ranged from 50 to 60 mg/l, with plume concentrations of 100 to 150 mg/l at a downgradient distance of 300 feet. Geoprobe sampling was performed to define soil TCE concentrations in the source area. Soil cores were collected from two depth intervals at 16 locations in and around the suspected source. Concentrations ranged from roughly 10 mg/kg to 100 mg/kg (on a wet weight basis) with higher concentrations generally observed at a gradational contact two to three feet above the mudstone interface. No free phase or residual phase DNAPL was observed. From the results of this work it was concluded that the source was limited to a 25 foot diameter area. Treatment was accomplished using high pressure jetting to emplace ZVI in the defined source soils. The treatment slurry consisted of 95% kaolinite and 5% Peerless ZVI (-50 mesh) on a dry weight basis. A total of 11 treatment columns were emplaced to depths ranging from 15 to 18 feet. The estimated treatment column diameters ranged from 5 to 6 feet and columns were placed at centerline distances of 4 to 5 feet. In addition, a low hydraulic conductivity cofferdam of jetted clay/ZVI slurry was placed completely around the source area perimeter. As part of the same project, jetting was used to emplace a 400-foot long PRB across the plume about 300 feet downgradient of the source area. The slurry design for the PRB was changed to consist of –50 mesh Peerless ZVI in a guar gum slurry. The resulting PRB has an effective thickness of 2 to 3 inches of ZVI. The source area was resampled by Geoprobe coring about 11 months after treatment. The resampling effort consisted of taking duplicate cores at the same source area locations sampled in 1998 prior to treatment. Only two out of 16 previously contaminated locations contained detectable TCE and/or breakdown products in the post-treatment cores. Periodic sampling of monitoring wells downgradient of the source has been on-going since 1999. While TCE concentrations have declined, concentrations remain elevated. Monitoring will continue to evaluate the long-term effectiveness of treatment.
Elevated up-to-greatly elevated concentrations of several naturally occurring radionuclides have been encountered in water from widely scattered individual wells and some very distinct clusters of drinking-water wells in South Carolina. Uranium, radium, and radon are particularly troublesome in terms of local commonness in certain areas and their degrees of exceeding acceptable levels in drinking water. This knowledge of distribution is still based merely upon routine monitoring results from public water-supply systems, some accelerated monitoring of smaller public systems, and a very few local-area investigations of private wells triggered by nearby problems discovered fortuitously. Denser and especially geologically targeted monitoring in the (hopefully) near future is likely to reveal many other occurrences especially among home wells, which are not yet subject to any routine monitoring (even at a broad survey level).

Uranium problems are revealed mainly in the piedmont (and Blue Ridge) region where they occur in isolated wells and in at least one large cluster. This singular-vs-clustering difference may relate as much to densities of sampled wells (at present) as to actual local uranium distribution. The occurrence of other clusters is feared and needs concerted investigation.

Radium problems occur rather widely and within very broad clusters in parts of the innermost coastal plain sandhills (mainly found to date in that portion to the southwest, toward Georgia). One multi-well town system has been abandoned (Leesville). Growing circumstantial evidence from public wells is raising concern that many home wells might be affected in this wide region of abundant home-well use. Radium at high levels can also occur along with uranium in rock wells of the piedmont (but only a few high U wells have been tested for both).

Radon measurements in survey examinations of public-supply wells and some home-well testing in the piedmont indicate that this is a widespread problem in that region.

ELEVATED PH, ALKALINITY, CALCIUM, AND SULFATE ASSOCIATED WITH HIGH DISSOLVED URANIUM IN GROUND WATER IN THE SIMPSONVILLE STUDY AREA: WHAT DOES IT MEAN?

High uranium concentrations in ground water are associated here with a broad area of granitoid uppermost rock (seen frequently exposed at the surface but generally lying below a sandy saprolite). Regionally in the piedmont much more-visibly metamorphosed felsic schists and gneisses predominate. In either case, generally one would expect slightly acidic to circumneutral, fairly low alkalinity, fairly low TDS ground waters from such felsic and granitoid rocks. However, more basic and perhaps more reactive mafic rocks (e.g., amphibolite) are also found at the periphery and as dikes...
within the study area. Of 25 geochemical investigation wells (both high and low U, with a few mafic-rock and bored wells included) the higher U concentrations (say, >100 mg/L) are associated conspicuously with higher pH, alkalinity, and calcium and sulfate contents in the water. The mineral(s), rock(s), and reaction(s) causing this associated geochemical signature are yet unknown and are undetected or unimplied in surface exposures (where weathering likely tends to obscure them). Some simple geochemical evidence or tests, however, based on pumped ground water help to evaluate plausible alternatives.

High elevated pH, alkalinity, Ca, and depleted $^{14}$C (see below) seem to suggest some mineral carbonate involvement, while abundant dissolved silica (avg. ca 28 mg/L) shows considerable weathering of silicate rock too. Does the elevated sulfate suggest weathering of sulfide minerals, conceivably even induced by better oxygenation under a pumped regime, or does it (like the appreciable detected nitrate) merely reflect human additions (e.g., via fertilizer or septic tanks)?

Ground water is generally of a Ca-Na-HCO$_3$ (bicarbonate) character. Cl is insufficient to explain Na from NaCl (e.g., septic tank effects) and a source from rock weathering is thus indicated. Alkalinity (as bicarbonate) vs Ca molar ratios are mostly around the 2:1 ratio that suggests dissolution of mineral carbonate (e.g., possible marble veins in underlying metamorphic rock, hydrothermal calcite in fracture fill, even much younger precipitate in fractures). But the highest Ca concentrations are closer to a 1:1 relationship that at lower concentrations might have suggested direct reaction of recharge CO$_2$ with Ca-bearing silicate rock.

Carbon isotopic ratios in dissolved bicarbonate show that one of the carbon sources involved in its formation is depleted in $^{14}$C and enriched in $^{13}$C relative to soil-derived CO$_2$ dissolved in recharge. This would be generally consistent with dissolution of ancient carbonate. But even possible upwelling of ancient mineralized ground water from deeper geologic zones is not yet entirely out of the question, though not favored on topographic grounds.

SEDIMENT SOURCE DETERMINATION IN THE LAKE CUNNINGHAM WATERSHED, NORTHERN GREENVILLE COUNTY, SOUTH CAROLINA

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Faced with proving that sediment from its quarrying operations was not adversely affecting surface water quality, Hanson Aggregates East conducted a study of the Lake Cunningham watershed in northern Greenville County. The Greer Commission of Public Works (CPW) operates a public water supply system that draws water from Lake Cunningham. Protection of the public water supply was a significant concern.

Traditional methods of evaluating the sediment load in surface waters would be inconclusive because they provide no information about material source. A methodology that conclusively identified sources of sediment from a manageable number of samples was required. A study plan based on specific sediment characteristics to determine the sources and distribution of sediment in the watershed was developed. The study premise was that sediment from the quarry operation would be composed of minerals found in crushed stone, the product from the quarry.

The study integrated the hydrology, surface water chemistry, sediment characteristics and mineralogy of sediment samples from the watershed. Mineralogy was determined using X-ray diffraction. Using this “fingerprinting” technique, the Fletcher Group demonstrated that sediment from the quarry does not have a material adverse impact on surface water in the watershed. The fact that this study was specific and conclusive was beneficial to both Hanson and the public. The focused scope of the study resulted in prompt conclusions based on a reasonable amount of sample collection and analysis.

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Recent discoveries of extreme concentrations of uranium (U), radon (Rn), and radium (Ra) in the ground water near the town of Fountain Inn, SC necessitate the investigation of the nature, extent and source of these anomalous readings. In addition, a public health threat potentially exists in areas along trend that contain a similar rock type and geologic history throughout EPA Region 4.

The focus of this study will be to understand the distribution and cause of the uranium occurrence and then to develop methods to predict the occurrence of additional anomalous zones initially in South Carolina and later within EPA Region 4. The primary method of modeling will be through the use of existing GIS spatial analysis tools developed by ESRI-USC.

Phase I of the study will focus on examining and determining the cause and local distribution of uranium, radium and radon in the immediate area. Items to be determined are the nature and extent of the mineralization, the origin of the mineralization, and methods of detection and prediction in the local area. These techniques will then be used to extrapolate along trend other areas that should be examined for potential occurrence of the same mineralization. Phase II will take information developed in the Simpsonville area and project along trend to identify any other area of examination for a similar occurrence of minerals that could potentially be a health hazard from the consumption of drinking water or from indoor radon, a known carcinogen.

Data from the Department of Energy’s (DOE) National Uranium Resource Evaluation (NURE) program, a regional geochemical reconnaissance for uranium and associated elements, strongly suggest there is every reason to believe that scores of additional high radioactivity wells serving hundreds of persons exist in an area between New York and Alabama that are geologically similar to the Fountain Inn area. Neither the public health nor the energy resource implications of the NURE data have ever been systematically investigated.

Techniques will be evaluated for the ability to detect the anomalous zone in the subsurface. Techniques such as radiometrics, magnetics, geochemistry (including stream sediment analysis, pebble coatings, and analysis of indigenous plants that send roots into the ground water) and other common and established exploration methods will be utilized to define this local area.

The reason for this is to develop a model that can be used to help key in on other areas with similar geologic features. This is the tried and proven approach used in all mineral/petroleum exploration. Fountain Inn serves as a pilot study area in which the salient features of the target are identified. From this a rational exploration program can be developed that searches the largest possible area with the least effort by comparing Fountain Inn key features to known regional geologic features. Field investigations in Fountain Inn should include, but not be limited to, gamma radiation surveys, geologic mapping, vegetation, soil and water geochemistry and so forth. The most useful of these then become part of the tool kit to identify other hazardous areas.

Phase II

At the same time as the Fountain Inn Study, available regional data, including but not limited to data from the NURE program, should be examined to estimate the probability and likely locations of other High-U ground water. The NURE data include high quality analyses for U and associated elements in ground water, stream water, and associated sediments. All available geologic, hydrologic and chemical data will be collected and analyzed to identify potential areas for examination.
A significant number of the anomalies identified will be followed up. The objective is to establish with some certainty whether the approach selected can identify or rule out problem areas. There will be over 100 potential anomalies in a few Southeastern States. If this phase indicates that a significant number of citizens are at risk from high U in ground water, then decisions will have to be made about protecting public health.

SPECIATION AND SORPTION CHARACTERISTICS OF CD AND ZN IN BAXITIC SOILS OF JAMAICA

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Cadmium and Zinc are strongly associated in many environmental materials; in rocks the Zn/Cd ratio is typically 100/1. Soils in Manchester Parish, Jamaica have been shown to contain unusually high contents of Cd (mean=52 mg/kg and maximum=931 mg/kg compared with world mean=roughly 0.5 mg/kg). In addition, the Zn/Cd ratio is unusually small at about 20/1. The soils are bauxitic, deep profiles are formed in commercial bauxite deposits, shallow soils have been described as Terra Rossa. They are generally of near neutral pH as a consequence of unconformably overlying pure Miocene limestones.

Since cadmium is potentially highly toxic to humans, a better understanding of its soil chemistry is needed. The soils are Oxisols rich in hydrous oxides of Fe and Mn which are known to sorb Cd and Zn strongly. The sorption characteristics of the high Cd soils have been investigated to find an explanation for the unusual Zn/Cd ratios and the ability of these soils to retain Cd under the high leaching regime of humid tropical conditions. A chemical fractionation procedure was used in order to identify the chemical pools in which Cd and Zn are held in these soils. The experimental approaches comprise: 1) batch equilibration of soil with solutions of Cd and Zn at low concentration and constant temperature. Metal sorption was modelled using the Langmuir isotherm. This was preferred over other models since the resulting concentration plots provide sorption maxima for each element and each soil. 2) a sequential chemical extraction procedure designed to investigate the relative amounts of Cd and Zn in the freely exchangeable pool, the carbonate-bound pool, the Fe oxide-bound pool, the Mn oxide-bound pool and in the residue.

The paper will report results from these experiments and will show that soils with the highest Cd contents appear to be nearly saturated with respect to Cd. Zinc contents exceed the measured sorption maxima. Much of the soil Cd is easily removed during the fractionation procedure. Both Zn and Cd are relatively easily leached from soil profiles and deposits of bauxite require one or more million years to form. The experimental data are therefore interpreted to suggest the soil Cd is unlikely to have originated from the bauxite parent rock and some active geological process must be sought in which Cd is still being supplied to the soils.

FATE AND TRANSPORT OF COAL TAR IN SAPROLITE (HIGHLY WEATHERED BEDROCK) IN EAST TENNESSEE

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Soil and groundwater contamination from various organic compounds (PAHs, VOCs, heterocyclic NSOs, etc.) can be found at 1000s of former manufactured gas plants (FMGPs) all over the United
States as a result of coal coking operations (http://www.hatheway.net/). Coking operations at an
industrial site (Tennessee Products Site or TP Site) in south Chattanooga, TN resulted in the release
of large volumes of coal tar, creosote, and other dense non-aqueous phase liquids (DNAPLs) be-
tween 1918 and 1987. This has led to extensive contamination in the subsurface and in nearby
Chattanooga Creek. This site is underlain by up to 12 m of fill and clay-rich saprolite derived from
in-situ weathering of the underlying limestone bedrock. The saprolite soils at the site contain numer-
ous fractures and macropores formed by dissolution and by root action, which are potential pathways
for DNAPL migration. The bedrock at this site is also fractured and contains solution-enlarged
fractures or conduits.

The extent of subsurface contamination is poorly defined at the site, but there is evidence of
immiscible coal tar in both the saprolite and the underlying bedrock to depths of approximately 30
m. Previous and planned remediation programs at the site focus mainly on excavation of coal tar
residue or near-surface highly contaminated soils/sediments from the surrounding area and from the
bottom of nearby Chattanooga Creek. Although these programs may be successful at removing the
most visible contamination problems, they do not address the very substantial contamination in the
deeper residual soils and the underlying karstic bedrock.

Our study focuses on the influence of macropores and fractures in the residual soils and
highly weathered portion of the bedrock on fate and transport of organic contaminants at the TP site.
The long-term objectives are to develop a better understanding of the processes governing migration
and dissolution of coal tar in fractured sub-soils. Field investigations in the saprolite are planned to
examine the distribution of immiscible coal tar and dissolved compounds, to determine what fracture
or macropore types are susceptible to invasion, and also determine the nature and extent of migration
into the fine-grained matrix. In conjunction with the field investigations, a laboratory investigation is
underway using a column of undisturbed saprolite in which “fresh” coal tar was introduced. Ground-
water is being flushed through the column for the past 6 months to examine leaching of coal tar
compounds. At the end of the experiment the column will be dismantled and sampled using a micro-
coring technique to evaluate diffusion of these compounds into the fine pore structure of the sapro-
lite, which is expected to play a major role in controlling leaching of these compounds.

MICROBIAL STUDY ON CHLORINATED ETHENE BIODEGRADATION WITHIN
ROTENWOOD CREEK SEDIMENTS AFFECTED BY LOW-FLOW GROUND-WATER
DISCHARGE

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INTRODUCTION

Site History

Air Force Plant 6 (AFP6), located northwest of Atlanta (GA) in Cobb County, was constructed in
1942 in order to support the increasing industrial needs of the Air Force in World War II. AFP6
initially produced B-29 Aircraft, until production stalled in 1946. In 1951, under pressure from the
Korean War, the largest contractor, Lockheed Martin Aeronautics Company, commenced repair of B-
29 aircraft, along with production of the B-47. Presently, Lockheed Martin Aeronautics Company is
the principal contractor on AFP6. As a result of aircraft production and repair, many cleaning sol-
vents, acids, lubricants, oils, paints, hydrocarbons, and various other chemicals have been used at the
plant. (History derived from IT Corp. (1999), PES Inc. (1995), Stewart (2000), and ASC (2001))
Site Contamination

The B-4 industrial area of AFP6 is heavily contaminated with organic compounds including chlorinated ethenes (tetrachloroethene, trichloroethene, and biodegradation products 1,2-dichloroethene, and vinyl chloride), chlorinated ethanes (1,1,1-trichloroethane and degradation products 1,1-dichloroethene and 1,1-dichloroethane), and petroleum hydrocarbons (benzene, toluene, ethyl benzene, and xylenes [BTEX]) (unpublished U.S. Geological Survey study, 2001). Of these contaminants, trichloroethene (TCE) is the most widespread and prevalent, as it is found both inside and outside AFP6 boundaries (Stewart, 2000; Gonthier and Waddell, 2001).

In the subsurface, TCE may be biodegraded under both aerobic and anaerobic conditions. In the presence of oxygen and a suitable primary substrate (such as toluene), certain aerobic bacterial populations cometabolize TCE (Wackett, 1995; Newman and Wackett, 1997; McCarty, 1997). Under anaerobic conditions, TCE (along with other chlorinated ethenes) may be utilized by specialized microbial populations as metabolic electron acceptors (McCarty, 1997; Löfler, 1999). Specifically, these microorganisms couple chloroethene reduction with simultaneous oxidation of an available electron donor. As a result, TCE is stepwise reductively dechlorinated to dichloroethene (both cis and trans isomers), vinyl chloride (VC), and ethene and innocuous inorganic chloride ions are released. Of the dichloroethene isomers, cis 1,2-dichloroethene (cis-DCE) is typically the major intermediate (Bradley, 2000). Unfortunately, the stepwise reductive dechlorination of TCE is not often complete. The only pure microbial culture observed to completely reduce trichloroethene to ethene is Dehalococcoides ethenogenes, isolated by researchers at Cornell University (Maymó-Gatell and Chien, 1997; Gossett and Zinder, 1997; Maymó-Gatell et al., 1999). Lower chlorinated ethenes may be biodegraded by other mechanisms, such as aerobic and anaerobic oxidation (Bradley and Chapelle, 1996, 1997, 1998, 1999 a & b, 2000 a & b; Bradley et al., 1998 a, b, & c; Bradley, 2000; Verce et al., 2000; Chapelle, 2001).

Site Hydrogeology

AFP6 is situated within the Powers Ferry Formation of the Sandy Springs group, composed of biotite-plagioclase gneisses, garnet schists, and amphibolites (Higgins, 1988), in the Southern Piedmont geologic province. Three hydrogeological zones generally characterize the Piedmont: fractured crystalline metamorphic and/or igneous bedrock, an overlying variable thickness regolith (composed of soil and saprolite), and a transition zone separating the two (Champion, 1989). The overlying regolith and transition zone are generally hydraulically connected with the underlying fractured crystalline rock (Champion, 1989), with the regolith serving as a ground-water reservoir (storage capacity depending on thickness) and the fractures in the bedrock transmitting ground water from recharge areas to discharge areas (Heath, 1989; LeGrand, 1989; Stone et al., 1988). The three idealized Piedmont hydrogeological zones, shown in Figure 1, are discussed below with increasing depth.
Saprolite within the regolith is defined as significantly weathered and decomposed bedrock (Fleck and White, 1989; Donn et al., 1989), and is characterized by low permeability, relict (preserved after mineral replacement) fractures and rock structure, and inherent heterogeneity and anisotropy (Donn et al., 1989; Stone et al., 1988). The composition of saprolite, controlled by the type of parent bedrock, is variable within the Piedmont geologic province (Donn et al., 1989), as well as the thickness (LeGrand, 1967). At AFP6, thickness of the saprolitic regolith varies within small distances (Gonthier and Waddell, 2001; SME Inc., 2001) and compositionally is related to the underlying crystalline rock.

Transition zones within the Piedmont, generally, are composed of weathered and highly fractured crystalline bedrock with residual boulders and saprolitic zones, grade into regolith with decreasing depth, and grade into competent fractured bedrock with increasing depth (Donn et al., 1989; Heath, 1989; Harned and Daniel, 1989). The transition zone is believed to be the most permeable of the three zones as a result of intense, minute bedrock fracturing due to mineral planes of weakness, expansion during preliminary chemical weathering, and little transformation to clay that induces sagging and impedes ground-water flow in open fractures (Harned and Daniel, 1989). At AFP6, thickness of the transition zones varies within small distances (Gonthier and Waddell, 2001; SME Inc., 2001).

Crystalline rock basalms of the Piedmont, in comparison to the overlying low permeability saprolitic regolith, is composed of high permeability, secondary porosity, low storativity fractures that promote ground-water transport (Donn et al., 1989), and are also characterized by high anisotropy and heterogeneity (Heath, 1989; McKibben and Spigner, 1989). These fractures may have originated from exfoliation, jointing, faulting, and/or intrusive events (Donn et al., 1989). The orientation of fractures within the bedrock, along with fracture widths, will affect the extent and rate of ground water and contaminant flow (Donn et al., 1989). Within the crystalline rock basement beneath AFP6, the strike of bedrock foliation is N45E with a dip of 60∞ to the southeast (Thomas J. Crawford, U.S. Geological Survey, written commun., 1996; Gonthier and Waddell, 2001). The major joint set beneath AFP6 strikes around N26W with a nearly vertical dip (Thomas J. Crawford, U.S. Geological Survey, written commun., 1996; Gonthier and Waddell, 2001). Other fracture orientations are observed, and under study by the U.S. Geological Survey. Contacts between various rock types in proximity to AFP6 parallel the strike of bedrock foliation (SME Inc., 2001).
Rottenwood Creek

AFP6 is located on a topographic high and is flanked by Rottenwood Creek, at a lower topographic elevation, to the northeast. Thus, ground-water flow and contaminant transport are believed to flow north easterly into the creek, a suspected ground-water sink (Gonthier and Waddell, 2001). Rottenwood Creek, shown in Figure 2, is perennial, characterized by nearly constant low flow with flashy periods during and after rainfall events, and follows a trellis pattern controlled by subsurface geologic features: southeasterly flowing creek reaches are believed to parallel the primary joint set and northeasterly flowing creek reaches are believed to parallel prominent foliation planes (Gonthier and Waddell, 2001).

Figure 2: Locations where USGS diffusion sampler and grab sample samples were taken (from Gonthier and Waddell, 2001)

In the idealized Piedmont, it has been assumed that due to observed regolith discharge into streams, ground water in the underlying fractured rock also discharges into the streams (Nelson, 1989). However, it is also possible that flow in the fractured rock may subvert the stream or creek and be transported to another watershed (Nelson, 1989). However, the Piedmont province is believed to be composed of small, individual, and localized watersheds with little regional flow or hydraulic connection between watersheds (Field and Dowd, 2001). A Piedmont study revealed that, in general, hydraulic heads in individual, packer isolated fractures (in proximity to a stream) were greater than the local stream water levels, greater than hydraulic heads measured in the overlying regolith, and increased with fracture depth within the bedrock; thus suggesting that ground water within the fractured rock discharged into the stream and that underflow to a neighboring watershed was unlikely (Nelson, 1989). It is unknown whether fractures in proximity to AFP6 are transmitting ground water entirely into Rottenwood Creek (in a fashion similar to that described in Nelson, 1989) or bypassing the creek underneath.

A U.S. Geological Survey contaminant transport study was carried out in the upper length of Rottenwood Creek, in proximity to the TCE-contaminated B-4 area of AFP6. Surface water and limited ground-water samples were taken along this creek stretch using diffusion samplers as described by Vroblesky and Hyde (1997). TCE was detected in 22 of 36 surface-water sites along the approximately 2-mile stretch of creek. The TCE concentrations in proximity to the locations where sediment sample were collected were below 1 part per billion (ppb) (Gonthier and Waddell, 2001). cis 1,2-Dichloroethene was detected at 8 out of 36 sites, and in proximity to sediment sampling sites.
described below (Gonthier and Waddell, 2001). No TCE or biodegradation products were detected in surface-water samples at site 25 (location where the first sediment sample was collected, see below) (Gonthier and Waddell, 2001), but TCE was detected at 0.28 ppb in a ground-water sample at the same site (Gonthier, unpublished results). No surface-water or ground-water samples were collected at site 35 (location where the second sediment sample was collected, see below) (Gonthier and Waddell, 2001). US Geological Survey study results suggest hydraulic connection between ground-water contamination within the B-4 area subsurface and Rottenwood Creek.

The objective of this study is to evaluate the potential of indigenous microorganisms, derived from Rottenwood Creek, to degrade the target contaminants: tetrachloroethene (PCE), TCE, cis-DCE, and VC, and to support or refute potential for intrinsic bioremediation (natural attenuation) at AFP6. Microcosms and sediment-free enrichment cultures, derived from creek sediment samples and established as described below, were utilized to aid in isolation and identification of chloroethene reductively dechlorinating microbial populations and to quantify rates of PCE, TCE, cis-DCE, and VC biotransformation to ethene.

**METHODOLOGY**

**Rottenwood Creek Sediment Sampling**

Sediment samples were removed from USGS sites 25 and 35 in Rottenwood Creek (see figure 2 above), placed in air-tight jars, immediately transported to the laboratory, and stored at 4∞C. The creek was in a period of low-flow conditions at the time of sediment sampling. Low-flow conditions, observed in the summer of 2000, were due to drought conditions and suggest total creek discharge from infiltrating ground water. Thus any aqueous or sediment sample taken from the creek is likely in connection with ground-water discharge derived from the hydraulically connected fractured rock and/or saprolitic hydrogeology.

**Microcosm Preparation**

Sediment material (1 gram per microcosm) from both sites was transferred to 20-milliliter (ml) serum bottles inside an anoxic chamber. An artificial mineral salts medium was added to a total volume of 10-ml as described (Löffler et al. 1996, 1997; Fennell et al., 2001). A total of 40 microcosms were established: 20 per sediment sample (see Table 1 below). Duplicate microcosms received either a spike of PCE, TCE, cis-DCE, or VC along with an electron donor (either pyruvate or acetate). Control microcosms were autoclaved for 30 minutes on two consecutive days, then spiked with either PCE, TCE, cis-DCE, or VC, and incubated with acetate as the electron donor. PCE, TCE, and cis-DCE were added from concentrated stock solutions in hexadecane to initial concentrations of 0.13 millimolar (mM), 0.22 mM, and 0.21 mM, respectively. Gaseous undiluted VC was injected by syringe into microcosms to a final aqueous concentration of 0.3 mM. All microcosms were capped with butyl rubber stoppers, and incubated in an inverted position in the dark. Chloroethenes, ethene, ethane, and methane were quantified by gas chromatography as described (Löffler et al. 1999).

<table>
<thead>
<tr>
<th>Sediment Sample #</th>
<th>Chloroethene Amended</th>
<th>Electron Donor Added</th>
<th>Quantity</th>
</tr>
</thead>
<tbody>
<tr>
<td>1, 2</td>
<td>PCE</td>
<td>Acetate</td>
<td>2 live, 1 killed</td>
</tr>
<tr>
<td>1, 2</td>
<td>PCE</td>
<td>Pyruvate</td>
<td>2 live</td>
</tr>
<tr>
<td>1, 2</td>
<td>TCE</td>
<td>Acetate</td>
<td>2 live, 1 killed</td>
</tr>
<tr>
<td>1, 2</td>
<td>TCE</td>
<td>Pyruvate</td>
<td>2 live</td>
</tr>
<tr>
<td>1, 2</td>
<td>cis 1,2-DCE</td>
<td>Acetate</td>
<td>2 live, 1 killed</td>
</tr>
<tr>
<td>1, 2</td>
<td>cis 1,2-DCE</td>
<td>Pyruvate</td>
<td>2 live</td>
</tr>
<tr>
<td>1, 2</td>
<td>VC</td>
<td>Acetate</td>
<td>2 live, 1 killed</td>
</tr>
<tr>
<td>1, 2</td>
<td>VC</td>
<td>Pyruvate</td>
<td>2 live</td>
</tr>
</tbody>
</table>
Transfer of Reductively Dechlorinating Cultures

Sediment-free enrichment cultures, used to enhance isolation of chloroethene transforming microorganisms, were obtained from dechlorinating microcosms after three consecutive transfers of inoculate (1% [vol/vol]) to 160-ml serum bottles containing 100-ml of mineral salts medium and approximately 60-ml of headspace. PCE, TCE, and cis-DCE were dissolved in hexadecane, and 0.2-ml were added to give to give initial aqueous chloroethene concentrations of 0.166 mM, 0.253 mM, and 0.32 mM, respectively. VC was added by syringe to give an initial aqueous concentration of 0.3 mM. Pyruvate (5 mM) or acetate (5 mM) was added as an electron donor for the duplicate cultures during the first transfer, pyruvate (5 mM) was added for the second transfer, and pyruvate (5 mM) or lactate (5 mM) was added for the third transfer.

Chloroethenes, ethene, ethane, and methane were quantified by gas chromatography as described by Löffler et al. (1999). The third transfer was also being used to quantify chloroethene biotransformation rates with small time-scale gas chromatograph sampling (every 14 days) in order to better observe the accumulation and depletion of amended target contaminants and biodegradation products.

RESULTS

Microcosm Studies

Complete transformation of the added chloroethenes to ethene was observed in twenty out of twenty-five live microcosms sampled, suggesting the presence of an anaerobic reductively dechlorinating (chlororespiring) microbial population(s). No dechlorination products were found in autoclaved killed microcosms indicating that the transformation reactions observed in the live microcosms were due to biological activity. A summary of chloroethene amended microcosm end product formation is included in Table 2 below.

<table>
<thead>
<tr>
<th>Sediment Sample # / Electron Donor Added</th>
<th>PCE Amended</th>
<th>TCE Amended</th>
<th>cis-DCE Amended</th>
<th>VC Amended</th>
<th>Methane detected?</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sediment 1 / pyruvate</td>
<td>Ethene</td>
<td>VC</td>
<td>Ethene, Ethane</td>
<td>Ethene</td>
<td>Yes, in cis-DCE amended microcosms</td>
</tr>
<tr>
<td>Sediment 2 / pyruvate</td>
<td>Ethene</td>
<td>Ethene</td>
<td>Ethane</td>
<td>Ethene</td>
<td>Yes, in cis-DCE amended microcosms</td>
</tr>
<tr>
<td>Sediment 2 / acetate</td>
<td>Ethene</td>
<td>Ethene</td>
<td>Ethane</td>
<td>Ethene</td>
<td>Yes, in cis-DCE amended microcosms</td>
</tr>
</tbody>
</table>
More rapid production of biotransformation end products was observed in microcosms derived from site 25 sediment, in comparison to production observed in microcosms derived from site 35 sediment. Consequently, aqueous samples were removed from sediment 1 microcosms for inoculation of sediment-free enrichment cultures. Microcosms (labeled by sediment sample #, chloroethene added, and electron donor added) used for transfer to sediment-free medium were Sed1/PCE/pyruvate, Sed1/TCE/pyruvate, Sed1/cis-DCE/pyruvate, and Sed1/VC/pyruvate.

**Sediment Free Enrichment Cultures**

Complete contaminant biotransformation to ethene was observed in five of the eight sediment-free enrichment cultures inoculated from sediment 1 microcosms in the first transfer as described above. A summary of end products produced by chloroethene amended and microcosm inoculated sediment-free enrichment cultures is contained in Table 3. Transfer of PCE dechlorinating microorganisms from the microcosm Sed1/PCE/pyruvate to sediment-free enrichment cultures was not successful. Transfers from microcosms Sed1/TCE/pyruvate, Sed1/cis-DCE/pyruvate and Sed1/VC/pyruvate to enrichment cultures were successful, resulting in degradation of the amended chlorinated ethene to ethene. Transfers made using pyruvate as electron donor possessed more efficient and rapid biotransformations than those with acetate.

The second transfer as described above, from the first sediment-free enrichment cultures to the second group of sediment-free enrichment cultures, was successful (complete reductive dechlorination to ethene) for those enrichment cultures amended with PCE, TCE, cis-DCE, and VC. Due to the lack of activity in PCE amended enrichment cultures in the first transfer, microcosm Sed1/PCE/Pyruvate was used for the second transfer to PCE amended, sediment-free enrichment cultures. Use of pyruvate for all sediment-free enrichment cultures during the second transfer was chosen based on biotransformation results obtained from the first transfer sediment-free enrichment cultures.

Results from the third transfer, currently within the incubation stage, are pending.

<table>
<thead>
<tr>
<th>Table 3. Results for First and Second Transfers</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Transfer #/Electron Donor Added</strong></td>
</tr>
<tr>
<td>-----------------------------------------------</td>
</tr>
<tr>
<td>Transfer 1/Pyruvate</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Electron Donor Added</th>
<th>Activity</th>
<th>amended cultures</th>
</tr>
</thead>
<tbody>
<tr>
<td>Transfer 1 / Acetate</td>
<td>No activity</td>
<td>VC VC Ethene No</td>
</tr>
<tr>
<td>Transfer 2 / Pyruvate</td>
<td>Ethene Ethene</td>
<td>Ethene Yes, in PCE and cis-DCE amended cultures</td>
</tr>
</tbody>
</table>
DISCUSSION

Microbial reductive dechlorination of chloroethenes completely to ethene and ethane was observed in microcosms established with Rottenwood Creek sediments, as well as sediment-free enrichment cultures inoculated from microcosms. Ethane formation was only observed in the presence of methanogenic activity. These findings suggest that a microbial population or community, derived from and indigenous to Rottenwood Creek sediments, exists within prepared microcosms and sediment-free enrichment cultures capable of reductively dechlorinating chloroethenes (PCE, TCE, cis-DCE, and VC) to harmless end products and indicate the potential of indigenous microorganisms to degrade target contaminants discharging into Rottenwood Creek from the fractured rock and/or saprolite hydrogeology suggested to be hydraulically connected (as described in Gonthier and Waddell (2001)).

Future research includes further enrichment and characterization of the chloroethene degrading population(s). 16S rRNA gene-based probes targeting known reductively dechlorinating populations will be used to identify the dechlorinating microorganisms in the sediment-free enrichment cultures as described (Löffler, 2000)

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Bradley, P.M., and Chapelle, F.M., 1999a, Methane as a product of chloroethene biodegradation under methanogenic conditions: Environmental Science & Technology, v. 33, no. 4, p. 653-656.


Chlorinated aliphatic hydrocarbons (CAHs) present unique investigative and remediation challenges, especially when the CAHs have impacted fractured rock. These challenges can be significant if sufficient volumes of CAHs were released to create a dense non-aqueous phase liquid (DNAPL) source zone within the aquifer. Chlorinated DNAPLs are persistent and because they are denser than water, their vertical and lateral migration within a saprolite-fractured rock terrain is influenced by numerous lithologic and structural heterogeneities that are difficult to quantify.

Successful techniques for assessing DNAPL and dissolved phase plumes that originate from these sources are illustrated at a manufacturing facility in the Piedmont of South Carolina. Soil and groundwater are impacted by trichloroethene and its degradation compounds. The facility is located on a topographic upland that forms a drainage divide between two surface watersheds. Groundwater from the saprolite and the transition (partially weathered rock) zones discharge to nearby tributaries. Deeper fractured bedrock exhibits regional flow behavior and does not have direct hydraulic communication with surface water bodies near the site. Migration of residual DNAPL and dissolved CAHs...
in the aquifer are simultaneously controlled by soil lithology, groundwater potentiometric gradients, fractures and secondary porosity features, and bedrock surface contours.

Surface and borehole geophysics were used to characterize subsurface lithologic and structural features that control plume migration. Surface geophysics included seismic refraction surveys, azimuthal resistivity soundings, and electromagnetic (EM) induction profiling and very low frequency EM profiling. Borehole techniques employed to characterize fractures zones and preferential flow pathways included caliper logging, gamma logging, borehole video logging, packer testing, and heat pulse flow meter tests. These techniques were combined with a program of well installations and direct-push sampling to characterize subsurface conditions and to develop a conceptual site model (CSM).

The CSM illustrates multi-directional plume migration based on hydrogeologic characteristics unique to three distinct aquifer zones (i.e., regolith/saprolite, transitional/shallow bedrock, and deep bedrock). Residual DNAPL is immobile in the upper saprolite unit but contaminant matrix diffusion in this source zone creates a dissolved plume that migrates in multiple directions toward both watersheds under the influence of hydraulic gradients. Characterizing the transition zone where saprolite grades to competent bedrock was critical for delineating DNAPL impacts. This highly weathered zone contains secondary porosity features and is more permeable than the overlying saprolite. DNAPL mass in this unit has migrated along fractures and weathered zones in directions oblique to regional groundwater flow. Similarly, DNAPL migration in shallow bedrock is controlled by the bedrock surface dip and fracture orientations that were identified using seismic refraction and the conductivity and resistivity geophysical surveys, respectively. Although deeper bedrock zones with lower fracture density are less impacted by DNAPL, a dissolved CAH plume exists in this zone and it migrates in the direction of regional potentiometric flow. Geophysics was an invaluable tool to identify subsurface anomalies that control migration of DNAPL and dissolved plumes at this site.

**EFFECTS OF PRESCRIBED FIRE AND THINNING ON NUTRIENT FATE AND TRANSPORT AND EROSION POTENTIAL IN HIGHLY ERODED PIEDMONT FORESTS OF SOUTH CAROLINA**

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Early U.S. agricultural and grazing practices altered much of the southeastern forestland and exposed soils, leading to increased erosion and nutrient runoff. Through the early 1900s, large tracts of land in the upper piedmont of South Carolina were in agriculture. Most areas were logged out and overfarmed (i.e., eroded and nutrient depleted) to the extent that productivity was severely impaired and the geomorphology of the land was completely altered. The resultant landscape was mostly barren, consisting of depleted soils dissected by deep (3-20 m) gullies that cut almost to the parent material (saprolite). In the early 1930s, nearly 400,000 acres were reserved as the Sumter National Forest (SNF) to improve land and water resources. These lands were subsequently afforested to stabilize the soil, improve water quality and provide forest cover for habitat and forest products.

Planned management regimes for the restored areas include thinning and prescribed fire. The effects of these practices are uncertain and controversial; they may have long-term implications for hillslope processes on this landscape. The principal concern is that fire may destroy the protective
organic layer and underlying vegetative root mat, thereby increasing the soil’s susceptibility to erosion and nutrient depletion. Since the nutrient capital of these highly eroded soils is contained in the upper 5-20 cm of soil, oxidation of the forest floor and erosion of mineral soils is likely to have significant ramifications for site productivity and potential nutrient runoff. Additionally, maintaining the integrity of the slopes is of paramount importance, as erosion would cause increased sedimentation in the streams and adjoining rivers.

This study, addressing the effects of thinning and prescribed fire on the surface soil properties and erosion potential, is a full factorial on the Enoree Ranger District adjacent to the Broad River in the SNF. Resin disks and soil chemistry analysis will provide assessment tools for nutrient movement and erosion fences will collect sediment washed from slopes to gauge erosion on 24 test plots over a variety of geomorphologic conditions. This experiment will measure the effect and degree of such land management practices on eroded landscapes; such analyses could provide inferences for watershed-wide plant, wildlife and water quality estimates for managed areas.

LINKS BETWEEN TECTONICS, HYDROGEOLOGY, AND DIAGENESIS IN THE SAN JOAQUIN BASIN, CA: SCIENTIFIC DISCOVERY VIA MISTAKEN BOUNDARY CONDITIONS

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Tectonic evolution of sedimentary basins has the potential to greatly alter fluid flow systems. In turn, fluid flow can play an important role in driving chemical reactions in the subsurface (diagenesis). This study was designed to determine links between the evolution of the tectonically-active San Joaquin basin and the diagenetic history of the Miocene Stevens Sandstone. Coupled numerical models were used to solve equations describing variable-density fluid flow, heat transport, solute transport, tectonic uplift, sediment compaction, and clay dehydration reactions. Simulations show the development of compaction-driven flow at depth and two opposing topography-driven flow systems on the basin margins. The distribution of salinity in the basin is shown to be controlled by freshwater influx and clay dehydration, and compaction-driven flow is focused through the Stevens Sandstone, which forms a permeable conduit through the basin.

Simulations also show a striking change in flow direction in the Stevens Sandstone at 5 Ma. This change corresponds to a transition from dolomite to calcite precipitation in the rock record, which is quite reasonable because the flow reversal signals a change in fluid source from magnesium-rich seawater to calcium-enriched pore fluids from depth. The change in flow direction, however, probably did not occur in the real basin. Simulated flow in the Stevens Sandstone prior to 5 Ma was driven by boundary conditions that failed to account for the density difference between seawater and fresh water. Corrected boundary conditions would eliminate the change in flow direction, thereby obscuring the onset of compaction-driven flow. The benefits of correcting the boundary conditions can certainly be argued, but the most urgent remaining questions probably relate to the density of the researcher.
High concentrations of uranium (30 to 10,100 µg/L) were found in 80 private drinking water wells near Simpsonville, SC. The elevated uranium concentration is most likely the result of pegmatite veins running east of Greenville and southwest of Simpsonville. The water is relatively soft to moderately hard (43 - 68 mg/L as CaCO₃) with a pH range of 7.5 – 8.1 and alkalinity of 47 – 68 mg/L as CaCO₃. Using these parameters, MINTEQA2 and Geochemist Workbench computer models were used to determine the speciation of uranium in the well water and determine what effect, if any, heating of the water will have with regard to the solubility of the uranium. The models predicted that uranium would precipitate as a di- or tri-carbonate uranyl complex. Gamma-ray spectroscopic analysis of hot water tanks in 4 homes with well water concentration between 575 and 9083 µg/L revealed an estimated 5 to 65 g of uranium in each hot water tank. Spectroscopy was performed using an HPGe transportable detector (ORTEC PoPTop, model 6MX-25190-P-A) in conjunction with a Canberra Inspector 2000 (model IN2K). The accumulation of uranium in the hot water tanks is consistent with model predictions. The presence of ²³⁵U was indicated by its 143.8 and 185.7 keV gamma rays and corroborated with the 63.3, 92.3, and 92.8 keV ²³⁴Th gamma rays. This precipitation results in the creation of TENORM (technologically enhanced naturally occurring radioactive materials) in the hot water heaters.