Arkansas Water Resources Center

Submitted to the U.S. Geological Survey

ANNUAL TECHNICAL REPORT

FISCAL YEAR 2006

For the Period

03/01/06-02/28/07

Publication No. MSC-102.2006

Arkansas Water Resources Center
112 Ozark Hall
University of Arkansas
Fayetteville, Arkansas 72701

Arkansas Water Resources Center
Annual Technical Report
FY 2006

Introduction

State Wide Mission: The Arkansas Water Resources Center (AWRC) has a statewide mission to plan and conduct water resource research. AWRC cooperates closely with colleges, universities and other organizations in Arkansas to address the state's water and land-related problems, promote the dissemination and application of research results and provide for the training of scientists in water resources. Through the years, projects have included irrigation, ground water modeling, non-point source pollution, quality of ground water and surface water, efficient septic tank design and ecosystem assessment. These projects have been funded by a variety of federal, state, local and tribal sources.

Support Provided: The Center acts as a liaison between funding groups and the scientists and then coordinates and administers grants once they are funded. Accounting, reporting and water analyses are major areas of support offered to principal investigators.

Technology Transfer: AWRC sponsors an annual water conference held in Fayetteville, Arkansas each spring, drawing an average 100 researchers, students, agency personnel and interested citizens to hear about results of current research and hot topics in water resources throughout the state. AWRC also co-sponsors short courses and other water-related conferences in the state and region. In addition, AWRC maintains a technical library containing over 900 titles, many of which are on-line. This valuable resource is utilized by a variety of user groups including researchers, regulators, planners, lawyers and citizens.

AWRC Water Quality Laboratory: The Center maintains a modern water quality laboratory that provides water analyses for researchers, farmers and others who submit samples through the Cooperative Extension Service and the Department of Housing and Urban Development.

Research Program

AWRC has contributed substantially to Arkansas water resources via research and training of students. In 2006, 32 projects passed through the Center which included funding from a variety of organizations including 1)USGS 104B program, 2)U.S.G.S., 3)U.S.D.A., 4) NSF, 5) NASA, 6) NRCS, 7)Arkansas Natural Resources Commission, 8)Arkansas Department of Environmental Quality, 9)Rogers Water Utilities, 10)Upper White River Basin Foundation, 11)Walton Family Foundation, 12)Beaver Water District, 13)Environmental Protection Agency, 14) Washington County, 15)Santee Sioux Nation. These projects involved training of 23 students made up of 5 undergraduates, 12 master's and 6 Ph.D. candidates.

Sediment Characterization in Three Coves - Beaver Reservoir, Arkansas

Basic Information

Title:	Sediment Characterization in Three Coves - Beaver Reservoir, Arkansas
Project Number:	2006AR122B
Start Date:	3/1/2006
End Date:	2/28/2007
Funding Source:	104B
Congressional District:	3
Research Category:	Climate and Hydrologic Processes
Focus Category:	Geomorphological Processes, Geochemical Processes, Sediments
Descriptors:	Sedimentation, Land Use Change, Watershed Processes, Environmental Chemistry, Coring
Principal Investigators:	Stephen K. Boss, Brian E. Haggard

Publication

1. Patton, J.A., in progress, Comparative Sedimentation in Three Coves, Beaver Reservoir, Northwest Arkansas, Ph.D. Dissertation, Environmental Dynamics Program, Univesity of Arkansas, Fayetteville, AR, expected completion, May 2008.
2. Patton, J.A. and S.K. Boss, 2007, Selected Trace and Major Element Concentrations of Beaver Lake Sediment Cores: Arkansas Water Resources Center Annual Conference, 24-25 April 2007, Fayetteville, Arkansas (CD).
3. Boss, S.K. and J.A. Patton, 2006, Sedimentation in Beaver Lake: An Ozark Mystery?, Arkansas Water Resources Center Annual Conference, 18-19 April 2006, University of Arkansas, Fayetteville, Arkansas (CD).
4. Kurz, M.J., J.A. Patton and S.K. Boss, 2006, Comparative geomorphic analysis of three sub-watersheds of Beaver Reservoir, northwest Arkansas, Geological Society of America Annual Meeting Abstracts with Programs, v. 38, No. 7, p. 353.
5. Patton, J.A. and S.K. Boss, 2006, Fusion of disparate data sets in quantifying reservoir sedimentation, Geological Society of America Annual Meeting Abstracts with Programs, v. 38, No. 7, p. 137.
6. Patton, J.A. and S.K. Boss, 2005, Influence of land use change on reservoir sedimentation: A comparative study, Geological Society of America annual Meeting Abstracts with Programs, v. 37, No. 7, p. 354.

Problem and Research Objectives

Sediment has been identified by the USEPA as a primary non-point source of water quality impairment in United States lakes and streams and is currently responsible for the listing of more than 30% of all impaired freshwater streams in the United States. Excessive sedimentation is considered a dangerous pollutant and can threaten the viability of aquatic biota by acting not only as a direct pollutant, but as both a sink and a source for other contaminants including heavy metals and nutrients. In recent years, impacts to the quality of water from Beaver Reservoir of northwest Arkansas resulting from rapid area development have been recognized. Preliminary studies of sediment loading identified multiple potential sedimentation 'hot spots' in upper Beaver Reservoir and the watershed of a major tributary (West Fork of the White River). Degradation of water quality due to nutrient loading (agricultural, septic, and suburban sources) and sediment loading (non-point sources), contamination from urban and storm-water runoff (point and non-point sources), and pollution due to lakeshore residential development (point-source) and recreational boating (non-point source) are of paramount concern. Public complaints of excessive sedimentation resulting from the filter backwash of a local water authority have also resulted in at least one citizens' lawsuit against the authority and investigation by the Arkansas Department of Environmental Quality. However, systematic studies to compare effects of watershed activities on sediment loading or to characterize the chemistry of sediment deposited within Beaver Reservoir since impoundment have not been conducted.

The objectives of the study were:

1) Characterize major and trace element chemistry of sediment deposited in three coves of Beaver Reservoir, northwest Arkansas. Two coves are at the terminus of watersheds where different land use changes have occurred since impoundment of Beaver Reservoir 40 years ago. One cove is at the terminus of a relatively pristine watershed protected by the Hobbs Wildlife Management Area and serves as a control site documenting natural background sedimentation in Beaver Reservoir;
2) From chemical analyses of sediments, estimate the masses of major and trace elements in each core and attempt to determine major or trace element signatures related to urbanization, industrialization, or sub-urbanization within each watershed;
3) From estimated masses of major and trace elements, estimate mass fluxes within the watershed based on known lake age, watershed area, and sediment volume within each cove;
4) Use patterns of chemical constituents in cores to elucidate watershed-scale chemical signatures that may be related to specific land use changes over time.

Methodology

Coring of sediments in coves of Beaver Reservoir (northwest Arkansas) was performed in order to characterize the chemistry of sediments accumulating within the reservoir at the terminus of three sub-watersheds in which different land use histories have occurred. Monte Ne Cove lies at the mouth of a sub-watershed in which land use changed from largely agriculture to industrial and (increasingly) residential development during the last 40 years. Prairie Creek Cove lies at the mouth of a sub-watershed in which land use changed from largely agricultural to urban and residential development during the last 40 years. Blackburn Creek Cove lies at the mouth of a nearly pristine, forested watershed protected by the Hobbs Wildlife Management Area during the last 40 years, and serves as a control site to characterize natural background sedimentation. Cores were analyzed for ten metals using a sequential extraction technique (described below) and included Al, Fe, Mn, Pb, Hg, Cu, Ni, Cd, Cr, and Zn.

Sediment coring was performed in Monte Ne and Prairie Creek Coves using a 0.05 m diameter aluminum piston corer with an internal polycarbonate sleeve. The corer was driven by gravity into the sediments until refusal. Eight cores were collected from the coves. Upon removal of the piston core from the sediments, the inner polycarbonate sleeve containing the intact sediment cores was removed. Upon return to the lab, each core was processed and sampled at 0.1 m intervals providing a total of 58 sediment samples to be analyzed.

Each sample was processed in a five-stage sequential extraction technique to better understand how the metals are bound to the sediments. The sequential extraction has five steps and uses the following procedures:

1) Exchangeable fraction (TF1) – agitate 1 g of sediment at room temperature for 1 hour with 8 ml of 1M NaOAc (sodium acetate) at pH = 8.2
2) Carbonate fraction (TF2) – solid residue from TF1 agitated for 4 hours with 8 ml of 1M NaOAc to pH 5.
3) Amorphous Fe + Mn oxides fraction (using Chao reagent) (TF3) – solid residue from TF2 is added to 20ml of NH_2-OH-HCl (hydroxylamine hydrochloride) in 0.25M HCl. Heat to 50°C for 30 minutes.
4) Organic fraction (TF4) – solid residue from TF3 is added to 3 ml of 0.02M HNO_3 and 5 ml of 30% H_2O_2 to pH 2 and heated to 85°C for 2 hours. Then another 3 ml of 30% H_2O_2 is added and then heated to 85°C for 3 hours.
5) Total extraction – solid residue from TF4 is added to 7.5 ml of 7M HNO_3 for 2.5 hours on a water bath at 70°C for 30 minutes, then heated to 100°C for 2 hours.

After each extraction step, the suspensions were centrifuged at 4000 rpm for 30 minutes. The supernatant was decanted into 50 ml collecting centrifuge tube and 8 ml of DI water was added to the extraction tubes. The extraction tube was centrifuged at 4000 rpm for 30 more minutes and the resulting supernatant was decanted into the previous collecting

centrifuge tube. It was then filtered using a 0.45 μm syringe filter into a 50 ml centrifuge tube and diluted up to the 50 ml mark on the centrifuge tube using DI water. The next extraction step started with the same extraction tube and resulting residue.

The samples were then processed using an ICP-OES for the ten metals at the USEPA certified New Mexico Bureau of Geology and Mineral Resources Laboratory using USEPA approved lab methods.

Principal Findings and Significance

Analysis of complete lab results are currently ongoing with preliminary results indicating elevated levels of several elements in Monte Ne and Prairie Creek coves with extreme variability in the range of metal concentrations within each core. Mercury results are not available due to an equipment malfunction at the New Mexico State laboratory. The total concentrations for the metals Cd, Cu, Fe, Ni, and Zn were significantly above background levels in all cores from both coves with Al, Cr, and Mn also being well above background levels in the Monte Ne cores and Pb being elevated in the Prairie Creek cores. Extremely elevated Al values (20 times higher than background) were found in the Monte Ne cores and are assumed to be a result of the filter backwash from the local water authority (Beaver Water District) where alum has been used as the principal coagulant at the plant since its inception. The sequential extraction procedure showed positive results in that the majority of the metals in all cores were released during the final extraction stage, indicating an overall low probability of future release into the water column. The only metal in the Monte Ne cores that appear to be in a more available form that were above the USEPA Threshold Effect Concentration (TEC) was Cr, while the Prairie Creek cores had Ni, Cd, and Zn all above this threshold concentration. In both instances, the TEC's were exceeded during the third step, indicating a strong association with amorphous iron and manganese that are known to be unstable under anoxic conditions.

The sources of the contaminants are currently being investigated. Several urbanization studies have identified Cd, Cr, Cu, Ni, and Zn as all being strongly correlated with urbanization and land use alteration. The results of this analysis are also being utilized in a larger USEPA funded study that compares the land use histories and geomorphic properties of the three identified coves with reservoir sediment quantity and quality to provide insights into the development effects on reservoir water quality.

The significance of this research are the results are now 1) providing needed baseline data to be used for future monitoring of sediment chemistry and water quality, 2) assisting in developing models for sediment yield from watersheds as a consequence of land use change, 3) aiding in defining sediment budgets and contaminant mass balances, 4) aiding development of models of mobilization and transport of contaminants resulting from different land use practices, and 5) providing data for understanding effects of sediment/sediment contaminants on surface water quality.

Metal Mobilization, Especially Arsenic, Related to Ground-water Level Fluctuation in the Alluvial Aquifer

Basic Information

Title:	Metal Mobilization, Especially Arsenic, Related to Ground-water Level Fluctuation in the Alluvial Aquifer
Project Number:	2006AR125B
Start Date:	3/1/2006
End Date:	2/28/2007
Funding Source:	104B
Congressional District:	Third
Research Category:	Ground-water Flow and Transport
Focus Category:	Geochemical Processes, Groundwater, Hydrogeochemistry
Descriptors:	Evolution of Ground Water, Arsenic, Alluvial Aquifer, Arkansas
Principal Investigators:	Kenneth F. Steele, Ralph K. K Davis

Publication

1. Sharif, M.U., R.K. Davis, K.F. Steele, B. Kim, T.M. Kresse and J.A. Fazio, 2007, Distribution and variability of redox zones as control of spatial variability of arsenic in the Mississippi River Valley alluvial aquifer, southeastern Arkansas, USA (submitted to Contaminant Hydrology).
2. Sharif, M.U., B. Kim, R.K. Davis, K.F. Steele, T.M. Kresse, J.A. Fazio, 2006, Lithologic and recharge controls on the spatial variability of arsenic in the Mississippi River Valley Alluvial aquifer, southeastern, Arkansas. Proceedings of the Geological Society of America, Annual Meeting, Philadelphia, PA, October 2006 (poster).
3. Kim, B., M.U. Sharif, T.M. Kresse, J.A. Fazio, J. Cothren, R.K. Davis, K.F. Steele, 2006, Comparision of potentiometric maps produced by densely spaced measurement points and USGS 7.5' manual elevation picks for the alluvial aquifer of eastern Arkansas, Proceedings of the Geological Society of America Annual Meeting, Philadelphia, PA, October 2006 (poster).
4. Sharif, M.U., R.K. Davis, K.F. Steele, B. Kim, T.M. Kresse, J.A. Fazio, 2007, Distribution and variability of redox zones controlling spatial variability of arsenic in the Mississippi River Valley alluvial aquifer, southeastern Arkansas, Arkansas Water Resources Center Annual Conference., April 24-25, 2007 (oral presentation)[CD].
5. Kim,B. In Preparation (expected completion December 2007) Hydrogeochemical Evolution of Ground Water in an Intensively Pumped Alluvial Aquifer. Ph.D Dissertation, University of Arkansas, Fayetteville
6. Sharif, M.U., In Preparation (expected completion December 2007) Flow and Hyrogeochemical Evolution of Arsenic in Groundwater: Tracking Sources and Sinks in the Mississippi River Alluvial Aquifer Southeastern Arkansas, USA. Ph.D. Dissertation, University of Arkansas
7. Sharif, M.U., R.K. Davis, K.F. Steele, B. Kim, T.M. Kresse and J.A. Fazio, 2007, Surface complexation modeling using PHREEQC for predicting solid-phase arsenic concentrations in the sediments of the Mississippi River Valley alluvial aquifer, Arkansas, USA(submitted to Aqueous Geochemistry
8. Sharif, M.U., R.K. Davis, K.F. Steele, B. Kim, T.M. Kresse and J.A. Fazio, 2007, Inverse geochemical modeling of groundwater evolution with emphasis on arsenic in the Mississippi River Valley alluvial aquifer, Arkansas (submitted to Journal of Hydrology)

This project had two main components: a laboratory simulation and a field component. This report is designed to allow either component to be read. Thus there is duplication between the two portions of this report.

Field Component

Problem and Research Objectives

Following the accumulation of evidence for the chronic toxicological health effects of As in drinking water, including cancer, the US Environmental Protection Agency (U.S. EPA) reduced the MCL for As from 50 to 10 µg/L (U.S. EPA, 2001). Most municipal-supply water systems in eastern Arkansas draw water from deeper tertiary aquifers where As is generally <0.5 µg/L. Impacts from As to municipal-supply water systems in Arkansas are low. However, the potential health impact of As to drinking water supply systems in Arkansas is still significant. Approximately 200 public water supply wells completed in the shallow Mississippi River Valley alluvial aquifer (herein referred to as the alluvial aquifer) serve about 450,000 people. These public water supply wells include commercial hunting camps, gasoline stations, trailer parks, and restaurants, as well as most private domestic wells. Recent publications documenting water quality in the Bayou Bartholomew watershed of southeastern Arkansas (Kresse and Fazio, 2002) revealed that 21 out of 118 irrigation water wells completed in the shallow alluvial aquifer (25-30 m) had As concentrations >10 µg/L. Kresse and Fazio (2003) provide evidence for reductive dissolution of hydrous Fe oxide (HFO), and release of sorbed and/or co-precipitated trace metals as the source of soluble As in the alluvial aquifer. Their evidence is mainly based on observed statistical correlations between As and various redox-sensitive parameters (NO_3^--N, NH_4-N, and Fe) favorable for reductive dissolution of HFO. These results are similar to alluvial environments in other parts of USA and abroad. The data of Kresse and Fazio (2002) indicate that domestic wells completed in alluvial aquifer may present risks to 18% of the private well owners not protected by the Safe Drinking Water Act (SDWA), and increased treatment costs for those public water supplies completed in this aquifer. The major objectives of the research are as follows:

1) determine the geochemistry of soils, sediments, and ground water, spatial and vertical distribution, mobilization, speciation (Fe and As) and advective transport of As in different geochemical environments (soils, sediments, and ground water).
2) identify important mineral phases in the aquifer by XRD, SEM, and chemical analysis, and assess the solubility or saturation indices of these minerals by geochemical tools Phreeqc (Parkhurst and Appelo,1999) and Minteq (U.S. EPA, 1991), and their relations to As partitioning and solubilities in the environment
3) Identify redox environments in the aquifer on the basis of redox-sensitive parameters (As and Fe speciation, ORP, DO, NO_3-N, NH_3-N, SO_4^{2-}, S^{2-}), and their relations to As distribution among the phases below:
   a) water soluble,
   b) exchange sites,
   c) carbonate minerals,
   d) amorphous Fe (HFO) and Mn oxides (HMO),
   e) organic, and

f) residual.

4) apply and evaluate geochemical modeling tools (surface complexation and inverse modeling options) as an aid in predicting the behavior, distribution , temporary and permanent sources and sinks (mineral phases) for As in the aquifer and evaluate the model sensitivity and ability to portray true field conditions.

Materials and Methods

Site Selection

Within the 225 km^2 study area three contrasting sites for nested monitoring wells were selected as a high As (>50 μg/L) area in the northwest (DRL1), a medium As (10-50 μg/L) area in the south (DRL2), and a low As (<10 μg/L) area in the northeast (DRL6). These locations for monitoring wells were selected based on As background data (Kresse and Fazio, 2002), geologic cross sections prepared from borehole logs of Arkansas Geologic Commission (AGC), groundwater flow maps, distribution of surface aquitard, and primary recharge areas. Three pairs of nested monitoring wells were drilled, installed, developed, and sampled at the selected sites in February 2006. The capital letter "D" and "S" are used after the site designation letters (DRL1, DRL2 or DRL6) to describe deep and shallow monitoring wells, respectively.

Collection of Cuttings

A hollow stem auger drill rig equipped with a 152 cm long and 7.62 cm outside diameter (O.D.) CME® sampler (steel) was used to extract continuous sediment cores to a depth of 12 m. The same rig equipped with a 46 cm, split-spoon sampler accepting a 5 cm O.D. steel liner was used to collect cores at approximately150 cm intervals to a depth of 36.5 m. No drilling fluid was used to minimize borehole contamination. Core recovery using the CME® sampler was 80% or greater, while a varying rate of 30% to 90% core recovery was achieved with the split-spoon sampler. The lower-volume core recovery was due to the increase of fine-sand fractions which flowed from the core barrel even with the use of sediment traps. The extracted cores were collected, wrapped in aluminum foil, labeled, and transported to the laboratory for physical and chemical analysis. A sub-sample (about 200 g) of each core was also separated in the field into plastic Ziploc® bags, and preserved below 4°C to provide fresh sample for Fe speciation, and comparison between extraction procedures using dry and fresh wet sediments. Sediment samples were labeled numerically after the monitoring well ID (e.g. DRL1S1, DRL1S2).

Monitoring Wells

At each site two monitoring wells with 5 cm O.D. PVC pipe were installed at a depth of 10.6 m and 36.6 m, respectively. The shallow wells were screened from 4.5 to 10.6 m, and the deep wells were screened from 33.5 to 36.6 m. Each aspect of monitoring well installation was completed by standard procedures (Wayne et. al., 1997) and complied with federal, state, and local regulations. The depth to groundwater was measured with a Solinst® Model 101 meter. Accurate groundwater elevation was calculated from post-

processed land-surface elevation data. The land surface data, with an estimated precision of ±2 cm, were generated by survey-grade Trimble® 4000SSE GPS units using the Fast Static method of data collection. The same GPS units were used to acquire land-surface elevation data used in the preparation of a detailed groundwater flow map, which was based on measurement of depth to groundwater at 174 water wells in the study area. The monitoring wells were initially developed using a PVC bailer attached to the wire-line on the drill rig, and secondarily using a Redi-Flo® VFD GRUNDFOS pump.

Groundwater Sampling, Field and Laboratory Analyses

All chemical analyses were performed on groundwater samples collected from the monitoring wells with a generator-driven submersible pump (Redi-Flo® VFD GRUNDFOS) in June 2006. Sample collection, handling, and preservation procedures of United States Geological Survey (Shelton et al., 1994) were followed when appropriate to ensure data quality and consistency. Prior to sample collection, the well was pumped continuously for 30-45 minutes until the temperature, electrical conductance (EC), pH, oxidation reduction potential (ORP), and dissolved oxygen (DO) readings stabilized within the accepted guidelines of NAWQA. After stabilization of the monitoring parameters, the following steps (**Table 1**) were performed in the field:

Table 1. Groundwater parameters measured in the field.

Parameters	*Units*	*Instrument and Model*	*Methods*
Temperature	°C	YSI® Model 30 handheld Salinity, Conductance, and Temperature Meter	
EC	µS/cm		
pH		Multi Probe Orion® 3-Star portable pH/ ORP meter	
ORP	RmV		
DO	mg/L	YSI® 550A Dissolved Oxygen meter	
Alkalinity	mg/L as CaCO3	HACH® Digital Titrator	HACH Method 8203
Dissolved S^{2-}	µg/L	HACH® spectrophotometer (DR 2800)	HACH 8131 (Methylene Blue)
Fe^{2+}	mg/L		HACH 8146 (1, 10 Phenanthroline)
Fe (total)	mg/L		HACH 8008 (FerroVer)
Mn^{2+}	mg/L		HACH 8148 (Periodate Oxidation)
Inorganic As Speciation	µg/L	Separated using Anion exchange columns and measured by ICP-MS	Edwards et al. (1998)
Inorganic and Organic As Speciation	µg/L	Separated using Anion and Cation exchange columns and measured by ICP-MS	Grabinski (1981)

Volatile Organic and Inorganic C	ppm	Thermo® TVA-100B Toxic Vapor Analyzer, which uses both Flame Ionization Detector (FID) and Photo Ionization Detector (PID)	

Collection of Groundwater Samples for Total Analysis

A set of four groundwater samples were collected in 100 ml HDPE bottles, that were (1) filtered (0.45µm) and acidified (2) not-filtered and acidified (3) filtered (0.20µm) and acidified, and (4) filtered (0.45µm) and not-acidified. Acidification was achieved by adding concentrated HNO_3 (VWR® Omni trace grade) until pH reached 2 or less standard units. Dissolved SiO_2 and cations including Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, Mn^{2+}, Fe^{2+}, Al^{3+}, Ag, B, Ba, Be, Cd, Cr, Cu, Li, Ni, Mo, Pb, Se, Sb, Sr, Ti, Zn, V, and As were measured on the acidified samples by Inductively Coupled Plasma Mass Spectrometer (ICP-MS) following EPA method 200.8. Dissolved NH_3-N and anions including Cl^{-}, Br^{-}, F^{-}, SO_4^{2-}, NO_3^{-}-N, PO_4^{3-}-P were measured on the non-acidified samples by Ion Chromatograph following standard EPA method Anion 300.0. Total organic carbon (TOC) was measured by a TOC analyzer using the liquid sample module. Filtering was done using two disposable syringes with filters (0.45µm and 0.20µm). Both filtered and non-filtered samples were analyzed by ICP-MS to identify the significance of particulate trace metals (e.g. As, Fe) in groundwater. All groundwater samples were analyzed in the Arkansas Department of Environmental Quality (ADEQ) laboratory, Little Rock, AR. Standard calibrations were based on standard addition for all dissolved ions analyzed in the laboratory.

Preparation of Sediment Samples and Laboratory Analysis

Sealed sections of the stored core samples were opened and sub-sampled in February 2006 for grain-size, porosity, and geochemical analyses. About 100 g of stored sediment from each core were separated and dried below 40° C in an oven. The sediments were crushed by a conventional porcelain pestle and mortar, and passed through a 1 mm nylon screen. These screened sediment samples were used for a sequential extraction procedure for major cations and trace metals, including As. Grain size analysis was done with little or no crushing on dried pre-screened samples by using a micro pipette method (Miller and Miller, 1987). Porosity was measured by weighing 50 ml hand-packed sediments in a graduated cylinder. Water was slowly added to the 50 ml mark and the sample was shaken to remove air bubbles and saturate evenly with water. Gravimetric porosity [$(1-(\rho_b/\rho_s)$] was calculated by mean particle density (ρ_s =mass of solids/volume of solids) and dry bulk density (ρ_b =mass of dry solids/volume of dry solids). The five-step sequential extraction (modified from Tessier et al., 1979 and Chao and Zhou, 1983) was conducted using 2 g dry sediment. The steps of the extraction procedures are as follows:

1. Exchangeable: 16 ml of 1 M sodium acetate to pH 8.2 for 1 hour.
2. Carbonates: 16 ml of 1 M sodium acetate to pH 5 for 4 hours.
3. Amorphous Fe and Mn oxides: 40 ml of 0.25 M NH_2-OH-HCl (hydroxylamine hydrochloride) in 0.25 M HCl; heat to 50 °C for 30 minutes.

4. Organic matter: 6 ml of 0.02 M HNO_3 and 10 ml of 30% H_2O_2 to pH 2 with HNO_3; heat to 85 °C for 2 hours, and later 6 ml of 30% H_2O_2; heat to 85 °C for 3 hours.
5. Hot HNO_3 leachable As: 15 ml of 7 M HNO_3 for 2.5 hours at 70 °C for the first 30 minutes and later at 100 °C for the next 2 hours.

The last step of the sequential extraction (hot HNO_3 extraction) was used to represent the least environmentally-available As. A separate rigorous HNO_3-H_2SO_4 acid extraction (9 ml concentrated HNO_3, 4 ml concentrated H_2SO_4, and 5 ml distilled deionized water was added in the digestion tube with 2 g dry sediment and heated at 90 °C for 30 minutes) (Adeloju et al., 1994) was also completed. A total of 60 sediment samples were extracted. Five duplicates, one gravel-pack sample, a bentonite grout sample, eight wet sediment samples preserved in the freezer, and two coarse (>1mm) sediment samples were also extracted for quality control and

XRD and SEM Analysis

Dried sediment samples were powdered using a grinding mill (RockLabs®) for X-ray Diffractometry (XRD) and Scanning Electron Microscopy (SEM) analysis. XRD measurements used Cu Kα radiation and a graphite monochrometer on a Philips® vertical diffractometer, stepped at 0.5 s/0.02°, from 2 to 100° 2θ. Iterative identification of minerals in the samples used PC-APD® Diffraction software of Philips Analytical with search/match of the reference mineral database and generated powder patterns. Five sediment samples were magnetically separated by a Frantz® Isodynamic Separator Model L-1, and were analyzed by XRD. A subset of the magnetically separated minerals was analyzed by a Hitachi® S-2300 SEM to identify the nature of crystallinity of magnetic minerals.

Organic Carbon and Inorganic Sediment Sulfur Analysis

Thirty sediment samples from three monitoring well sites were analyzed for total organic carbon (TOC) and inorganic sediment sulfur**.** TOC was analyzed using a Shimadzu® TOC 5050 analyzer equipped with the solid sample module (SSM 5000A). Reduced inorganic sulfur compounds (pyrite + elemental sulfur + acid volatile monosulfides) were measured by chromium reduction method or Canfield method (Canfield et al., 1986). Chromium reduction does not reduce or liberate either organic sulfur or sulfate sulfur, which makes the method specific only to reduced inorganic sulfur phases. The detection limits for TOC and inorganic sediment sulfur were 0.1% and 0.01% of sediment, respectively.

Geochemical Modeling

The surface complexation modeling (SCM) of PHREEQC (Parkhurst and Appelo, 1999) was used to predict the differences between the sorbed As in HFO derived from sequentially extracted chemical data and model simulations. The Diffuse Layer model (DLM) of Dzombak and Morel (1990) was used to simulate surface complexation reactions. The model sorbents were selected as ferrihydrite and goethite.

The PHREEQC was also used for inverse geochemical modeling. Groundwater analyses from Kresse and Fazio (2002) were used in the model, rather than from the nested wells, as the larger data set facilitated the selection of optimal initial and final endpoints along the dominant flow path direction (NW-SE) on the high-precision water level contour map in the area. Potential phases were included into the model from XRD and SEM analysis of sediment samples.

Principal Findings and Significance

Twenty one of 118 irrigation water wells completed in the shallow (25-30 m thick) Mississippi River Valley alluvial aquifer in the Bayou Bartholomew watershed, southeastern Arkansas had arsenic (As) concentrations (<0.5 to 77 µg/L) exceeding 10 µg/L. Two nested monitoring wells (10 m and 36 m deep) were installed in the vicinity of the highest, median, and lowest concentrations of As at three sites in Jefferson County, Arkansas. Sediment and groundwater samples were collected to characterize the mobilization, transport, and distribution of As in aquifers. A traditional five-step sequential extraction was performed to differentiate the exchangeable, carbonate, amorphous Fe and Mn oxide, organic, and hot HNO_3-leachable fraction of As and other compounds in sediments. The Chao extraction removes amorphous Fe and Mn oxides by reductive dissolution and is a measure of reducible Fe and Mn in sediments. The hot HNO_3 extraction removes mostly crystalline metal oxides. Significant total As (20%) is sorbed to amorphous Fe and Mn oxides in sediments. Arsenic abundance is not significant in carbonate minerals or organic matter. Significant (40-70 µg/Kg) exchangeable As is only present at shallow depth (0-1 m). Arsenic is positively correlated with Fe extracted by Chao reagent (r=0.83) and HNO_3 (r=0.85) (Fig. 1). Increasing depth has a positive relationship (r=0.56) with Fe (II)/Fe (the ratio of Fe concentration in the extracts of Chao reagent and hot HNO_3), but it has a negative relationship (r=-0.45) with As extracted by Chao reagent (Fig. 2). The ratio of Fe (II)/Fe is positively correlated (r=0.76) with As extracted from Chao reagent (Fig. 3). Although the ratio of Fe (II)/Fe increases with depth, the amount of reducible Fe decreases noticeably with depth. The amount of reducible hydrous Fe oxides (HFO), as well as the As sorbed decreases with depth. Possible explanations for the decrease in reducible HFO and its sorbed As with depth include historic flushing of As and Fe derived from reductive dissolution of HFO and aging of HFO to crystalline phases having less sorptive capacity. As^{+5}, the dominant As-species in groundwater, has positive relations (r=0.84) to decreasing redox (RmV).

The capacity of the surface complexation model to predict As in sediments using selected sorbents (ferrihydrite, goethite) was assessed by comparing As concentration derived from the same extraction methods from which the selected sorbents were quantified. The model results using ferrihydrite and goethite as sorbents are unsatisfactory for sediments in the deep alluvial aquifer (21-36.5 m), where the model over predicts 4 to 24-fold of extracted As in sediments. The model results using the same sorbents are relatively satisfactory for sediments in the shallow alluvial aquifer (0-17 m). At 0-10 m, the model using ferrihydrite predicts 57% of extracted As by Chao reagent. At 10-17 m, the model using ferrihydrite provides the best overall prediction of 92% of extracted As by Chao reagent. At 0-17 m, the model using goethite predicts 82% of extracted As by hot HNO_3

acid. The model is very sensitive to the concentration of As^{3+}, As^{5+} and the presence of competitive ions as HCO_3^-, H_4SiO_4, CO_3^{2-}, PO_4^{3-}, Fe^{2+}, etc. in groundwater.

According to the inverse modeling calculation, the major processes affecting groundwater composition along the flow path are the dissolution of calcite, gypsum, barite, fluorite, HFO, exchange reactions of Ca^{2+} for Na^+ on exchange sites, and precipitation of sulfide. X-ray crystallographic (XRD) analysis detects quartz, orthoclase feldspar, calcite, dolomite, gypsum, fluorite, goethite, hematite, magnetite, kaolinite, smectite, illite and chlorite as crystalline phases in the sediment samples. In an attempt to identify the nature of crystallinity of magnetic minerals, a subset of magnetically separated minerals were analyzed by scanning electron microscopy (SEM) that revealed both crystalline and amorphous phases. The amorphous magnetic phases are assumed to be ferrihydrite, the most common Fe oxyhydroxide in sedimentary environments. Amorphous Fe oxyhydroxide phases were also confirmed by chemical extraction procedures using Chao reagent (Chao and Zhou, 1983), which dissolves amorphous phases of Fe and Mn oxyhydroxides.

Interpretation of hydrogeochemical data, ambient redox environment, and geochemical modeling results in the area suggests reductive dissolution of HFO as the

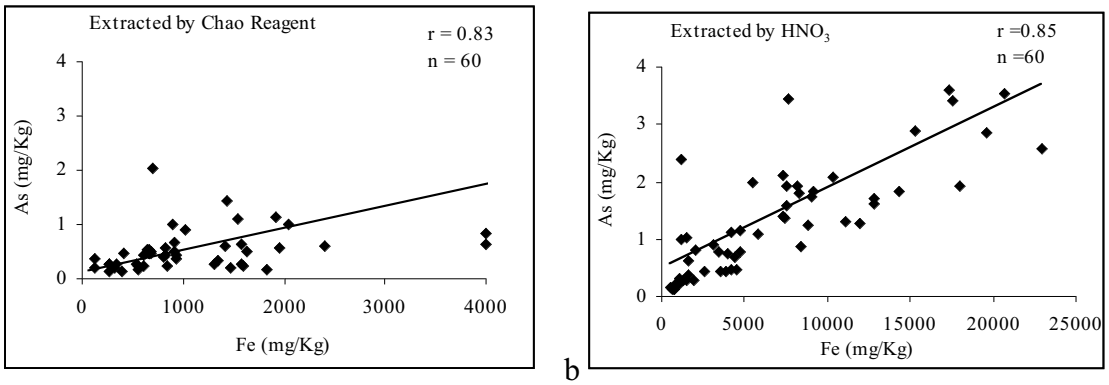

Fig. 1 Relationship between As and Fe in sediments.

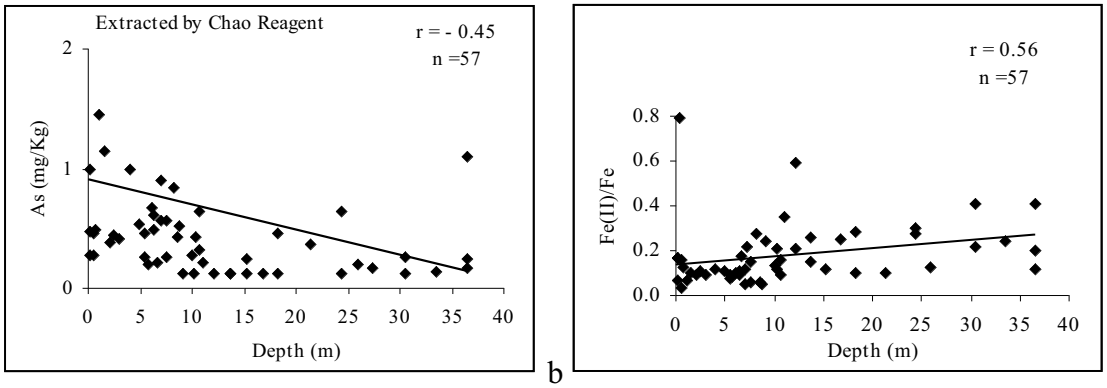

Fig. 2 Vertical distribution of As and Fe (II)/Fe in sediments.

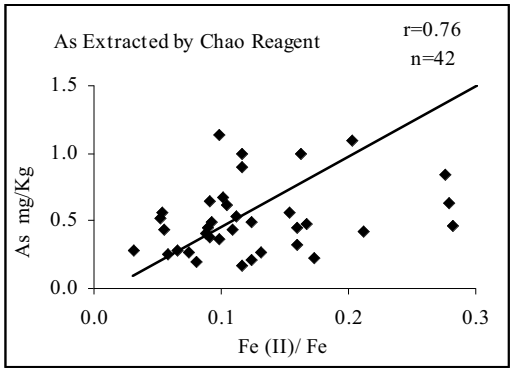

Fig. 7 Relationship between the ratio of Fe (II)/Fe and As in sediments.
dominant As release mechanism.

Gypsum solubility and SO_4^{2-} reduction with co-precipitation of As and sulfide is an important limiting process controlling the concentration of dissolved As in groundwater. Spatial and temporal variability of As is controlled by spatial distribution and redox status of different redox zones at various depths in the aquifer. The redox state is the primary control on the rate of HFO reduction and the amount of As in groundwater.

This work expands that of Kresse and Fazio (2003) by focusing on As mobilization and transport in a specific area of the alluvial aquifer within the Bayou Bartholomew watershed with the highest known concentrations of As. This study is unique in that it is the first detailed study of the transport and fate of As in a large alluvial aquifer that has relatively low to moderate As concentrations (<0.5-77 µg/L; Kresse and Fazio, 2003) in comparison with other better known alluvial aquifers with As pollution, such as Bangladesh (2.5-846 µg/L; Ahmed et al., 2004). The results of this research project are applicable to the remainder of the Mississippi River Valley alluvial aquifer, especially in Louisiana, Mississippi, Tennessee, and Missouri.

References

Adeloju, S.B., Dhindsa, H.S., and Tandon, R. K., 1994. Evaluation of some wet decomposition methods for mercury determination in biological and environmental materials by cold vapor atomic absorption spectroscopy. Anal. Chim. Acta. 285, 359-364.

Ahmed, K.M., Bhattacharya, P., Hasan, M.A., Akhter, S.H., Alam, S.M.M., Bhuiyan, M.A.H., Imam, M.B., Khan, A.A., Sracek, O., 2004. Arsenic enrichment in groundwater of the alluvial aquifers in Bangladesh: an overview. Appl. Geochem.19, 181-200.

Canfield, D.E., Raiswell, R., Westrich, J.T., Reaves, C.M., and Berner, R.A., 1986. The use of chromium reduction in the analysis of reduced inorganic sulfur in sediments and shales. Chem. Geol. 54, 144-159.

Chao, T. T., and Zhou, L., 1983. Extraction techniques for selective dissolution of amorphous iron oxides from soils and sediments. Soil Sci. Soc. Am. J. 47, 225-232.

Dzombak, D.A., Morel, F.M.M., 1990. Surface complexation modeling: Hydrous ferric oxide. John Willey and Sons, Toronto.

Edwards, M., Patel, S., McNeill, L., Hsiao-wen Chen, Frey, M., Eaton, A.D., Antweiler, R.C., and Taylor, H.E., 1998. Considerations in As analysis and speciation: A modified field technique can quantify particulate As, soluble As (III), and soluble As (V) in drinking water. J. AWWA 90 (3), 103-113.

Grabinski, A.A., 1981. Determination of arsenic (III), arsenic (V), monomethylarsonate, and dimethylarsinate by ion-exchange chromatography with flameless atomic absorption spectrometric detection. Anal. Chem. 53, 966-968.

Kresse, T.M., and Fazio, J.A., 2002. Pesticides, water quality and geochemical evolution of groundwater in the alluvial aquifer, Bayou Bartholomew Watershed, Arkansas. Arkansas Department of Environmental Quality. Water Quality Report WQ02-05-1, Little Rock, AR.

Kresse, T.M. and Fazio, J.A., 2003. Occurrence of arsenic in groundwaters of Arkansas and implications for source and release mechanisms. Arkansas Dept. of Environmental Quality, Water Quality Report WQ03-03-01, Little Rock, AR.

Miller, W. P. and Miller D. M., 1987. A micro-pipette method for soil mechanical analysis. Commun. In Soil Sci. Plant Anal. 18 (1), 1-15.

Parkhurst, D.L., and Appelo, C.A.J., 1999. User's guide to PHREEQC (ver.2) - A computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations. U.S. Geol. Survey Water Resources Inv. Report 99-4259.

Shelton, L.R. and Chapel P.D., 1994. Guidelines for collecting and processing samples of stream bed sediment for analysis of trace elements and organic contaminants for the National Water-Quality Assessment (NAWQA) Program. USGS Open File Report 94-458.

Tessier, A., Campbell, P. G. C., Bisson, M., 1979. Sequential extraction procedure for the speciation of particulate trace metals. Anal. Chem. 51 (7), 844-851.

U.S. EPA, 1991. MINTEQA2, A geochemical assessment data base and test cases for environmental systems: Ver. 3.0 user's manual. EPA/600/3-91/-21. Athens, GA. Allison, J.D., Brown, D.S., and Novo-Gradac, K.J.

U.S. EPA, 2001. 40 CFR Parts 9, 141, and 142, National Primary Drinking Water Regulations; Arsenic and clarification to compliance and new source contaminants monitoring; Final rule, in Federal register, 66 (14), January 22, 2001.

Wayne, W.L., Franceska, D.W., Michael T.K., 1997. Guidelines and standard procedures for studies of ground-water quality: Selection and installation of wells, and supporting documentation. U.S. Geological Survey Water Resources Investigation Report 96-4233.

Laboratory Simulation Component

Problem and Research Objectives

Statement of the Problem

It is reported that the total withdrawals of ground water in the State of Arkansas has increased from 2600 Mgal/day in 1975 to 6950 Mgal/day in 2000 (Bryant et al., 1985; Holland, 2004). Most ground-water withdrawals are in eastern Arkansas, where ground water is used for aquaculture and irrigation of crops, e.g., rice and soybeans. Agricultural usage of ground water exhibits significant seasonal variations. During the growing season there is intensive ground water pumping which results in a declining water table. Significant water level decline and/or water level fluctuation have been regarded as one of the most critical issues in eastern Arkansas (Bryant et al., 1985; Cooper, 2002; Holland, 2004; Joseph, 1999). The ground-water level has declined more than 10 ft since the 1960s in some parts of the Mississippi River Valley region including Cross, Jackson, Jefferson, Lee, Lonoke, Monroe, Prairie, and Woodruff counties (Joseph, 1999). Ground water level monitoring associated with this project showed that from July, 2006 to September, 2006 temporal ground-water level fluctuation was more than 20 ft (Figure 8.1.). The temporal ground-water level fluctuation caused by intensive daily or weekly scheduled pumping (about 1600 to 2500 gal/min pumping per square mile) can affect hydrogeochemical evolution. Twenty one out of 118 irrigation wells in a study of Bayou Bartholomew watershed (Kresse and Fazio, 2003) had arsenic concentrations exceeding the US EPA maximum contaminant level (10 μg/L) with high iron concentrations (median 10 mg/L and maximum of 43 mg/L). These wells were completed in shallow Quaternary alluvial deposits (alluvial aquifer) with depths of 25-30 m. Heavy metal (arsenic will be included with the heavy metals in the report) mobilization mechanisms are complex. Previous research reveals that the mechanisms are related with mineral oxidation-reduction, sorption-desorption, and/or ion exchange-substitution processes depending on the hydrogeochemical environment of the aquifer (Acharyya, 1997; Acharyya et al., 2000; Appelo and Postma, 2005; Fiedler and Sommer, 2004; Moral and Hering, 1993; Stumm, 1992). In summary, these observations indicate that fluctuating ground-water level causes redox environment fluctuation which is one of the major factors affecting heavy metals (e.g. arsenic) mobilization mechanism in the aquifer.

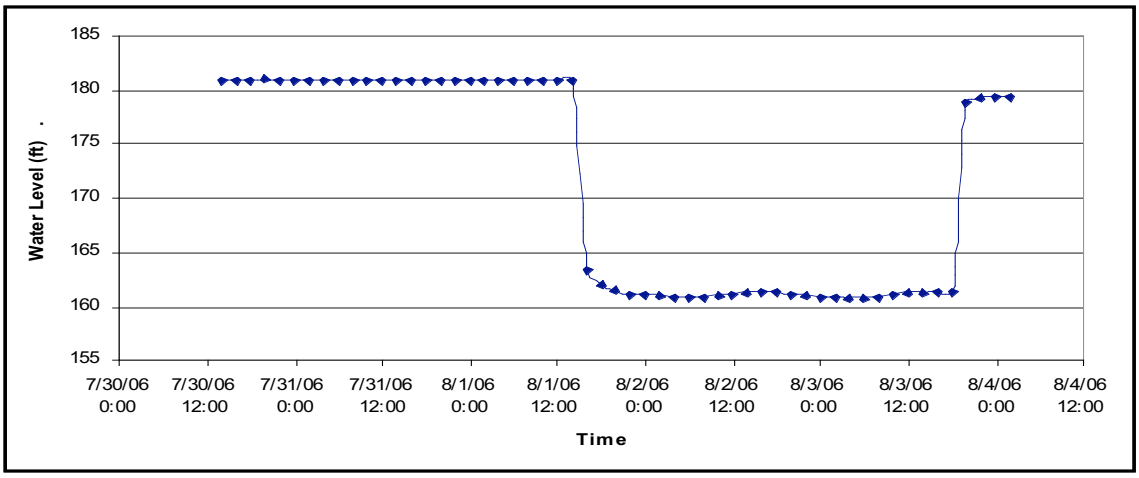

Figure 8.1.Ground-water levels for five days near Pine Bluff, Arkansas. The measurements were made with a data logger during the irrigation season in August of 2006.

There is little research on the impact of intensive ground-water withdrawals and the relationship of the withdrawals with ground-water level fluctuation on water quality and on geochemical processes (e.g. development of a reducing environment that can mobilize metals). The effect of seasonal and daily ground-water level fluctuation caused by intensive ground-water withdrawals is difficult to examine because of the difficulty of controlling subsurface parameters in the field. For example, water level fluctuation, recharge rate, redox potential, and other parameters, which can control geochemical processes, cannot be easily adjusted and observed in the field. Also, it is difficult to collect data representing the characteristics of a site and its geochemical processes because of the heterogeneity of the aquifer materials. Laboratory scale column experiments allow examination of water level fluctuation and oxidation-reduction potential of a specific layer of sediment. The results from the experiments can provide essential information for elucidating the effect of intense pumping of ground water on water level fluctuation and the associated change in redox environments.

Research Objectives

The objectives for the research are as follows;

(1) The first objective is to determine the impact of ground-water level fluctuation on metal concentrations for the intensively pumped alluvial aquifer. This objective requires laboratory column tests comparing physicochemical parameters in water from two columns with fluctuating water level (one oxic and one anoxic) and a column with stable water level environments.

(2) The second objective is to determine the metal mobilization mechanisms e.g. sorption – desorption, cation exchange, reduction of metal hydroxides for eastern Arkansas alluvial aquifer. This objective will be achieved utilizing geochemical modeling

(e.g. PHREEQC) with column tests results, and field collected data, including literature data and data from a dissertation project at the same site (Sharif, 2007).

Methodology

Monitoring Well Drilling and Sediment Preparation

Column tests have been conducted with the sediments collected from drilled monitoring wells. Monitoring wells were drilled at three sites along a flow path of ground water near Pine Bluff, southeastern Arkansas. There are shallow and deep wells at each site. In order to collect representative sediment and water samples no drilling fluids were used. Optimum depth of the wells was to the base of the alluvial aquifer (about 36 m). The flow path selected was based on points of high, medium and low arsenic concentrations of ground water in the Bayou Bartholomew watershed (Kresse and Fazio, 2002). Sediment samples were collected from each well as it was drilled. The length of the sample collected was based on the sample barrel length (5 ft length and 4 in diameter), and the homogeneity of the sediments for unsaturated zone (about up to 30 ft). Sediments from the greater deeps were collected using a split spoon sampler (18 in length and 2 in diameter). Below about 70 ft, core samples were collected every 10 to 20 ft based on homogeneity of the sediments.

Laboratory columns were packed with sediments in the same sequence as in the field and the amount based on the approximate ratio of collection depth in the field to a scaled stratigraphic column and lithological characteristics. For each laboratory column, the three deep well cores were subsampled 10 times, i.e., each layer represents a sample from each of the three deep wells. Each sediment layer was sieved with mesh No.10 sieve (2 mm opening) to remove gravel and homogenize each stacked layer before filling the column. Three columns with same sediment constituents were prepared. Each column was well packed with sediments by vibrating it and gently pressing on it. Two other columns with different sediments were built.

Column and Simulation Design

Design Factors and Considerations

Although laboratory column tests can not simulate all the field conditions perfectly, column tests are the best method to investigate the relation between ground-water fluctuation and geochemical evolution (i.e. metal release). Some parameters affecting metal mobilization include CO_2 partial pressure, horizontal ground water flow rate and direction, temperature, microbiological activities, and light (i.e. ultra-violet (UV) to catalyze redox change) can not be perfectly matched with field conditions. However, several assumptions can be made: 1) Temperature is constant under the sub-surface environment. If the laboratory temperature is constant and the difference between field temperature and laboratory temperature is not significant (less than 5 °C, which results in less than 5 % difference in solubility), the effect of temperature difference can be ignored. 2) Comparison of laboratory parameter measurement data (e.g. temperature, Eh,

pH) with field measurement data does not have significant difference (less than 10 %, which means general acceptable error range for 90 % confidence level, differences from the maximum or minimum field measurement). This means that laboratory test data compare well with the field data which means that the laboratory data can be used to represent field data. 3) Oxidation or oxidation catalysis by UV light can be ignored because the column test is not under direct sunlight and the test time is not very long relatively. 4) Gaseous constituent of the column including CO_2 partial pressure is similar with field condition.

Another factor for columns tests was how to obtain feed water for the tests. The available feed water sources are:

1) artificial ground water with composition based on chemical analysis of field collected ground water,
2) rain water or surface water collected at the research site,
3) deionized water,
4) field collected ground water.

Artificial ground-water constituents (e.g., chelated metals, and ionic strength) can not perfectly represent field conditions in part because of heterogeneity. Rain water or surface water at the research site could simulate vertical and horizontal recharge but as previously noted representative recharge water does not exist because of heterogenic hydrogeology. Dionized water can be used as recharge water without any pre-treatment, but the dissolution capacity of the sediments is changed and it is not valid to compare the column test results with field conditions. Field collected ground water is the most appropriate water to simulate actual fluctuation condition and sediment - water interactions in the aquifer. The most negative aspect for using field collected ground water is that it will be oxidized during transporting to laboratory. However, this problem can be avoided by using a pre-treatment column to develop a reducing environment in field collected ground water.

Column Test Setup

Feed water for the water level fluctuation column studies was collected from a monitoring well (DRL1), which has the highest arsenic and iron concentration among the three monitoring wells. Field collected water was passed through a pre-treatment column to develop a reducing environment that mimics actual aquifer ground water at the study site. The pretreated, reduced ground water was distributed to two test columns (one to be oxic and the other to be anoxic) to simulate water level fluctuation and a continuous flow column to remain fully water saturated for comparison to water level fluctuation columns. The two water level fluctuation columns periodically received feed water to maintain saturation, and pumping for de-watering and sample collection. Sample collection dates were based on the fluctuation simulation schedule (Table 9.1.). The continuous flow column remained fully saturated and water passed through the column continuously without de-watering. For the continuous flow column, water samples were collect from the effluent water container.

One of the most important parameters for the column tests is oxygen. Field measurement of alluvial aquifer ground water revealed that dissolved oxygen in ground water was less than 0.1 mg/L. This means the environment is anoxic. To simulate this field environment, oxygen was controlled for the column test. A nitrogen shielding box was installed for isolating the system from the air (Figure 9.1.). Also, all columns packed with sediments were purged with nitrogen gas before adding feed water, in order to remove oxygen in the pore spaces in the sediment. In order to see the effect of oxygen intrusion into the alluvial aquifer caused by intensive pumping, the air hole for one column was connected to air (oxic column) directly, and the air hole of the other column connected to oxygen absorbent solution (anoxic column). The two columns were tested for water level fluctuation simulation.

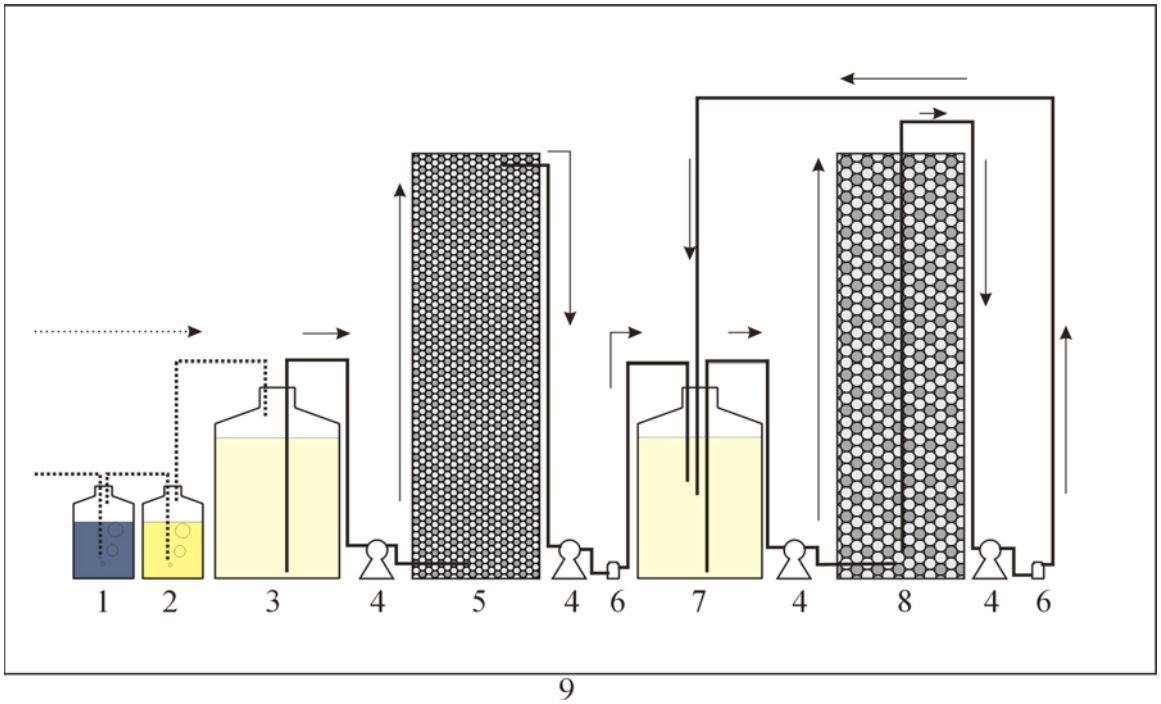

Figure 9.1. Water flow diagram for column studies. Arcrilic tubing was used to make the columns. (1) Pyrogallol 6 % under KOH 30 % alkaline solution medium for absorbing oxygen, (2) 15 % ascorbic acid solution for absorbing oxidants, (3) Raw ground water tank, (4) Peristaltic pump, (5) Pre-treatment column, (6) Effluent bottle for sampling and measuring, (7) Storage container, (8) Main test columns comprised of two water level fluctuation simulation columns and one continuous flow column, Two types of flow direction were tested (see Figure 9.2.) for main columns. (9) Outside nitrogen shielding box to keep air out. The inner diameter of column is about 5 in. Dotted arrow line indicates air flow, and solid arrow lines indicate water flow.

Flow direction is another essential factor in determining geochemical evolution. The alluvial aquifer is recharged mainly by horizontal flow from the recharge source and to a lesser degree by vertical infiltration. The first experiment was conducted utilizing inverse flow to avoid trapping air in the sediment column, as well as simulating recharge (Direction 1 for oxic, anoxic and continuous flow, and Direction 3 for pre-treatment column on Figure 9.2). For the fluctuation simulation, water from the pre-treatment

column was fed into the oxic and anoxic columns until there was sufficient saturation from the bottom of the column for a sample to be pumped for collection. For simulating vertical infiltration, as well as to allow sufficient interaction between water and silt layer, a second experiment was conducted by utilizing Direction 2 (for oxic, and anoxic columns) and Direction 3 (for continuous flow and pre-treatment columns) flow direction.

Table 9.1. Water level fluctuation in the columns and sampling plan schedules.

Test Set	Column Type	Feeding (Recharge)	Saturation	Effluent (Pumping)	De-watering	Repeat	Sampling
1	Oxic	48 hours	5 days	48 hours	5 days	5 cycles	Every effluent
	Anoxic	48 hours	5 days	48 hours	5 days	5 cycles	
	Continuous Flow	Continuously saturated and periodically circulation of water in the system. Flow direction was Direction 1 and Direction 3 (Figure 9.2).					Same with oxic/anoxic
2	Oxic	48 hours	12 days	48 hours	5 days	3 cycles	Every effluent
	Anoxic	48 hours	12 days	48 hours	5 days	3 cycles	
	Continuous Flow	Continuously saturated and periodically circulation of water in the system. Flow direction was Direction 1 and Direction 3 (Figure 9.2).					Same with oxic/anoxic

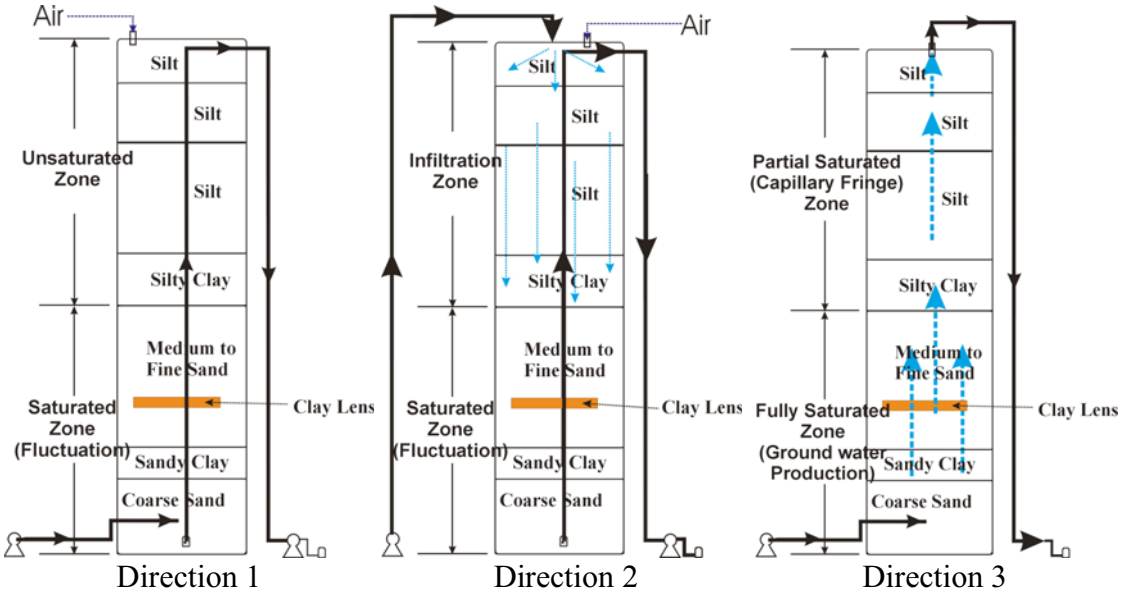

Figure 9.2. Water flow directions for anoxic, oxic and continuous flow columns. Direction 1 was the flow direction for oxic column, anoxic column, and continuous flow column test set number 1. Direction 2 was the flow direction for oxic column and anoxic column test set number 2. Direction 3 was the flow direction for continuous flow column test set number 2, and pre-treatment column.

9.3. Parameters, Sampling and Analysis

The parameters studied in the column experiments and field samples were (1) major metal mobilization factors (pH, oxidation-reduction potential (ORP), Fe (total, ferric, ferrous), Mn, As, Cd, Cr, Pb), (2) redox parameters (dissolved oxygen (DO) , total organic carbon (TOC), dissolved organic carbon (DOC), NO_3-N, NH_3-N, SO_4), (3) overall water quality monitoring parameters (total dissolved solids (TDS), conductance (EC), temperature), (4) cations and anions for determining water quality and geochemical evolution e.g., cation exchange (Ca, Mg, Na, K, HCO_3, Cl, PO_4). Column test samples were collected using a flow cell to avoid air contacting with water samples. In order to confirm column test results, field data were compared with column test results.

Sequential acid extractions for investigating sediment characteristics and potential metal mobilization capacity were conducted. The extractions for chemical forms and leaching agents were; a) acid soluble form (mainly fixed in carbonate minerals), which was leached using 0.1 M acetic acid; b) reducible form (fixed in Fe-and/or Mn-oxides), which was leached using 0.1 M hydroxylamine hydrochloride solution, adjusting pH to 2 using HNO_3 acid; c) organic form, which was first decomposed by 0.1 M sodium pyrophosphate solution heated on a hot plate and dissolved into 1 M ammonium acetate solution; and d) insoluble form (fixed mainly in sulfide and rarely in silicate minerals), which was dissolved in concentrated HNO_3 (Tessier et al., 1979). Some hydrogeologic parameters including porosity and hydraulic conductivity were determined to characterize alluvial aquifer hydrogeology.

Fe^{3+} / Fe^{2+} speciation and Mn concentrations were determined immediately after collection by colorimetric methods. ORP, pH, DO, temperature, conductivity of water were measured by utilizing *in-situ* meters on the column effluent. (Figure 9.1). Water samples were collected from the effluent bottle (about 200 mL per collection) by the fluctuation schedule. Water samples were analyzed following EPA Analytical Methods (EPA, 2000) or Standard Methods for Water and Wastewater Examination (Clesceri et al., 2005). General methods are listed here: 1) metals were analyzed by inductively coupled plasma mass spectrometry (ICP-MS), and 2) anions were analyzed by ion exchange chromatography (IC). 3) Organic carbon (TOC, DOC) were analyzed by combustion and then CO_2 analyzing instrumental system. 4) Alkalinity was determined by the sulfuric acid titration method, and 5) TDS was analyzed by the drying and weighing method.

Data Acquisition and Analysis

Quality Assurance / Quality Control

Quality assurance and quality-control measures were followed at every step to ensure data quality. Methods, sampling, and analytical protocols of USGS National Water-Quality Assessment (NAWQA) programs were generally followed (http://water.usgs.gov/nawqa/).

Analytical precision was monitored by replicate analysis at a minimum of 10% of the samples. Corrective action was indicated if the relative percent difference between the two sub-samples is greater than 20%.

Bias was assessed through transportation of spiked and blank media to and from the field as well as matrix spiking of split sub-samples prior to analysis. The QC accuracy range was defined through control charts (3 standard deviations from mean recovery) constructed from previous data. If the QC accuracy criterion was violated, no further samples were analyzed until the problem was resolved by demonstrating, with spiked blanks, that the analytical system was in control again

Data Analysis

The acquired data were 1) field collected, available literature, other sources such as (e.g. real-time USGS or US EPA physicochemical monitoring data on-line for sediment and ground water, 2) physicochemical parameters in the feed water (after passing through the pre-treatment column), 3) physicochemical parameters after fluctuation simulation by column tests, 4) physicochemical parameters from continuous circulation column by scheduled , periodical sampling (Table 9.1), and 5) sediment sequential extraction analyses data. Comparison of data 1) with data 2), 3), and 4) can confirm the adequacy of column tests and its adaptability and limits to field conditions. Paired Student-T test results of data 2) and 3) indicates the sediment water interaction change under the various fluctuation conditions. Paired Student-T test results of data 3) and 4) can determine the impact of water level fluctuation on metal mobilization.

Speciation modeling by utilizing the PHREEQC geochemical model can estimate the equilibrium state of the system. That is, the concentrations and activities of the various ionic species are calculated by the model with the chemical composition of a ground-water sample. The result can be used to indicate if some metals can precipitate and exchange. Saturation indices for minerals from the modeling can be used to determine sink/source for dissolved iron which is the highly suspected sink for heavy metals e.g.,. As.

Surface Complexation Models (Parkhurst, 1995) can simulate sorption – desorption in sediment water interaction and provide interpretation of the physical and chemical processes. Iron oxyhydroxides are probably the most important adsorbents in sandy aquifers because of their abundance and strong binding affinity. The surface complexation model of PHREEQC considers hydrous ferrous oxide to be an important adsorbent of arsenic in sediment water interaction.

The data 3), 4) and 5) are used as input into the speciation module and surface complexation module of the PHREEQC program to achieve speciation and solubility of mineral phase, sorption – desorption processes, exchangeable ions, and their relation to heavy metal mobility in the water. The comparison of each result can provide the influence of water level fluctuation on metal mobilization mechanism.

Principal Findings and Significance

Considering Redox Environment

In-situ water quality monitoring data indicate that no oxygen penetrated the silt layer in the columns, though the air hole of the oxic column was connected to the air. However, black nodules were formed on the top part of the oxic column, which are thought to be metal. Compared to the anoxic column, the oxic column had higher ORP values, which meant it was under more oxidizing environment, whereas dissolved oxygen concentration was 0.01 to 0.2 mg/L for all columns.

Aerobic (also known as aeration) limit depth is the depth to which aeration occurs in top soil due to relatively high concentrations of oxygen from biological and physical activities, e.g., from plant roots. Advection of oxygen into the soil is positively correlated with depth of the water table, but the aerobic limit depth is less than 4 ft from the surface (Silins and Rothwell, 1999). Plant root growth and the presence of organic material control the aerobic limit depth (Armstrong, 1971). In the vadose zone, capillary fringe induces ground water upwelling and the force is controlled by grain size (Berkowitz et al., 2004; Keeling, 2004; Klenk and Grathwohl, 2001). Capillary fringe might reduce aerobic limit depth by causing reverse force vertical infiltration and diffusion

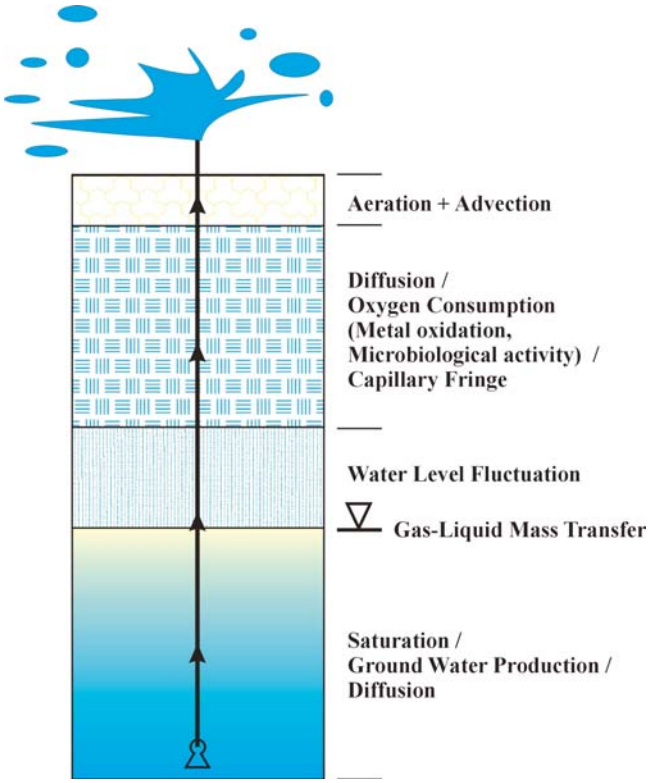

Figure 10.1. Simplified conceptual model for oxidation of ground water by water level fluctuation.

Oxygen transfer process from the air into ground water can be conceptualized based on advection, diffusion, and gas absorption (Callebaut et al., 1982; Holder et al., 1999; Lewis and Whitman, 1924). If ground water level declines by pumping, oxygen advection into soil increases. Compared with diffusion, advection is more effective in transferring gas due to its higher flux. However, advection is very limited by capillary fringe and porosity, and the limited depth can be defined as the "aeration limit depth." From the aeration limit depth, diffusion occurs from the surface to the ground water level. Considering geochemical processes including metal oxidation, sorption-desorption; and microbiological activities, the amount of oxygen which can reach the ground-water level is very limited. Gas absorption processes occur on the surface of the ground water. At a certain depth, oxygen concentration becomes equilibrated between the amount of gas absorption, and diffusion limited advection. If water level declines because of pumping, the advection depth (which means aeration depth) increases. Then the amount of oxygen transport at a certain depth could increase because of the driving force of diffusion. The concentration gradient would increase due to the increase of aeration depth. After recharge, the ground water level increases again, then more oxygen can be dissolved into ground water at a certain depth. There is already more oxygen during the declining water level by advection and diffusion. This amount of oxygen might not increase the dissolved oxygen concentration in the ground water because the oxygen might be consumed by metals or be consumed converting a reducing environment in the ground water to an oxidizing one (Figure 10.1). This simplified conceptual model can be used to explain the relationship between ground-water fluctuation and development of redox environments.

Arsenic Concentration

The first experiment results show that the oxic column water has about 18 % (range 11 to 31 %) higher arsenic concentration, than the anoxic column. However, more elaborate investigation is necessary to varify the difference of the metal release mechanism between the oxic column and the anoxic column.

Metal Mobilization Mechanism

Many research results indicate that arsenic adsorption-desorption on iron oxyhydroxide is critical in determining the arsenic concentration in the ground water (Bowell, 1994; Kneebone et al., 2002; Pierce and Moore, 1982). Figure 10.2 and 10.3 show that there are significant differences between higher arsenic concentration (greater than 25 µg/L) and lower arsenic concentration (less than 25 µg/L) release mechanism associated with iron oxyhydroxides. It is likely that arsenic desorption and iron oxyhydroxides dissolution are the major processes in continuous flow and pre-treatment columns. In contrast adsorption-desorption might occur repeatedly in oxic and anoxic (water level fluctuation) columns.

The Piper diagram (Figure 10.4) shows that pre-treatment water has calcium – bicarbonate water type, and it coincides with field conditions. Kim, et al. (2004) explained cation exchange by utilizing major cation and anion equivalent ratio for eastern Arkansas ground water. (Na+K)/Cl ratio increases; whereas, (Ca+Mg-SO4)/HCO3 ratio decreases (less than 1), which indicates Ca-Na cation exchange on clay surface. Oxic and anoxic column data show that Ca-Na cation exchange has occurred (Figure 10.4 and 10.5).

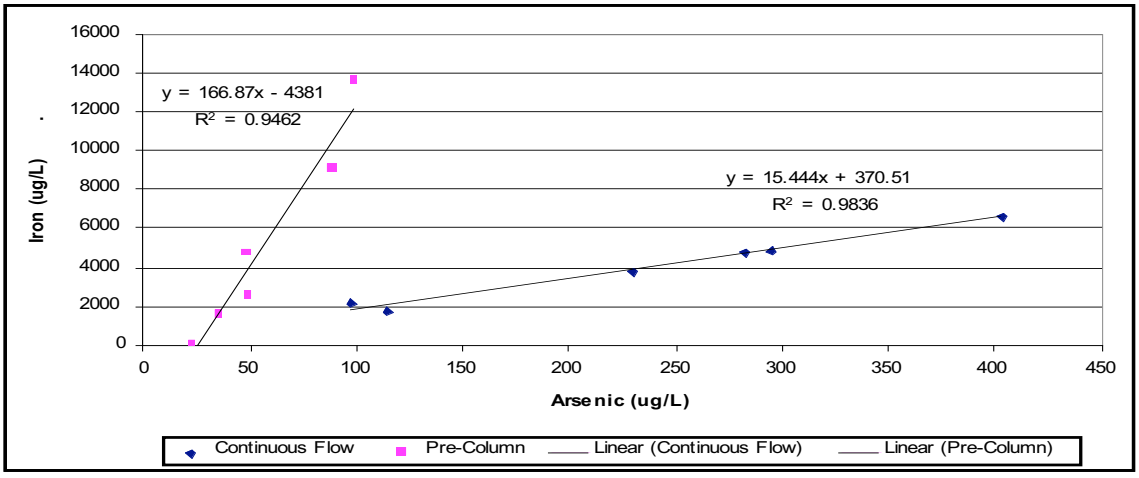

Figure 10.2. Iron concentration in µg/L versus arsenic concentration in µg/L for continuous flow column and pre-treatment column.

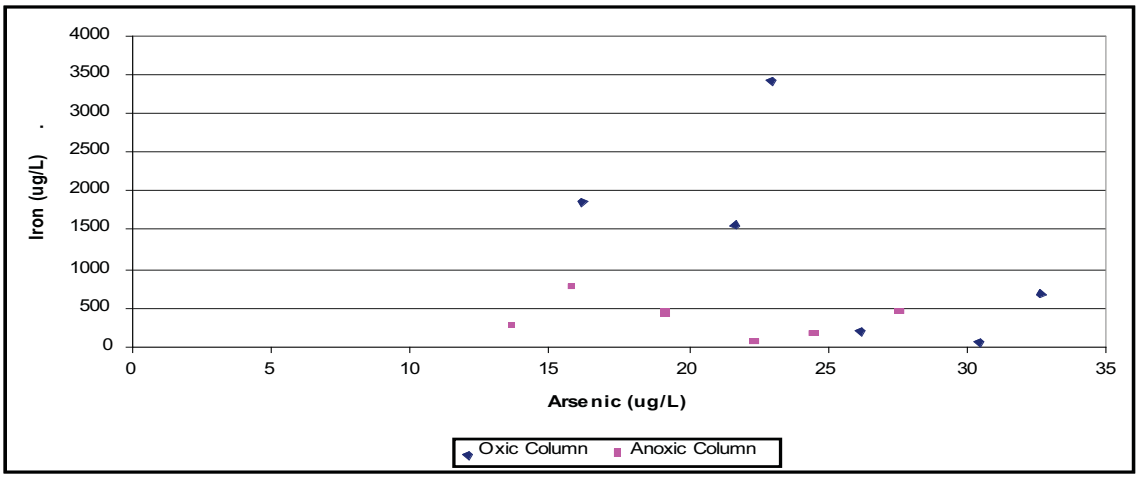

Figure 10.3. Iron concentration in µg/L versus arsenic concentration in µg/L for oxic column and anoxic column.

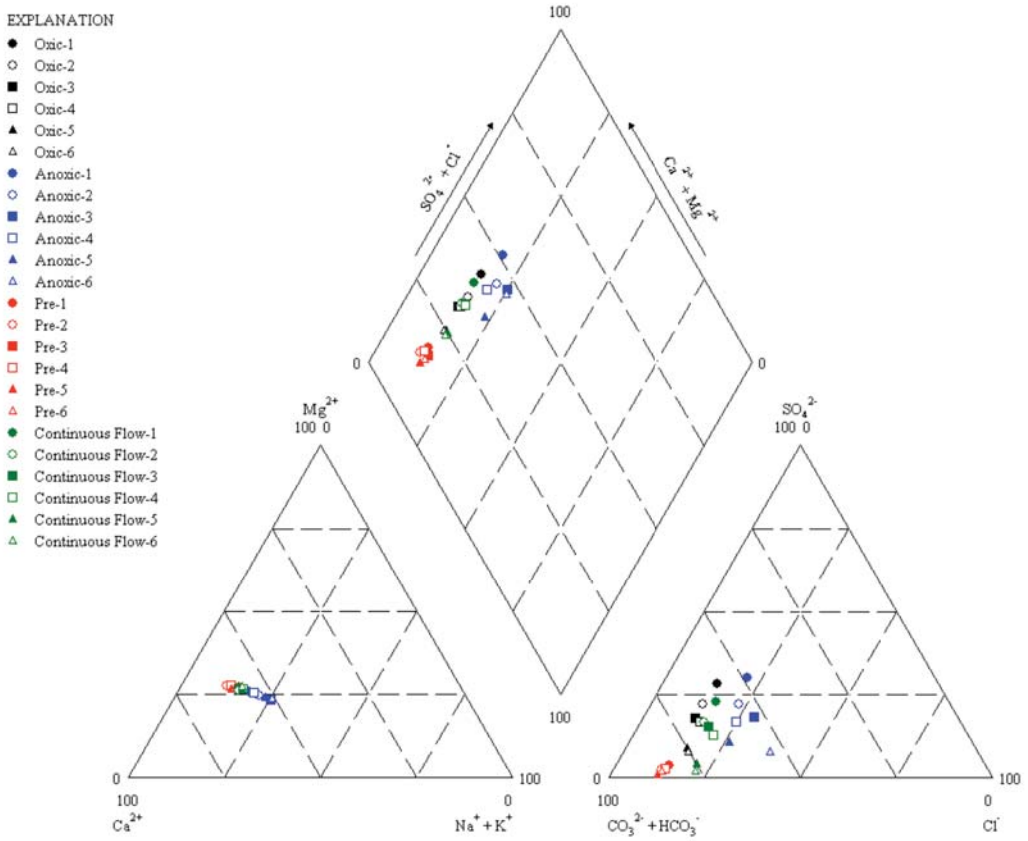

Figure 10.4. Piper diagram of the sampled water from column test.

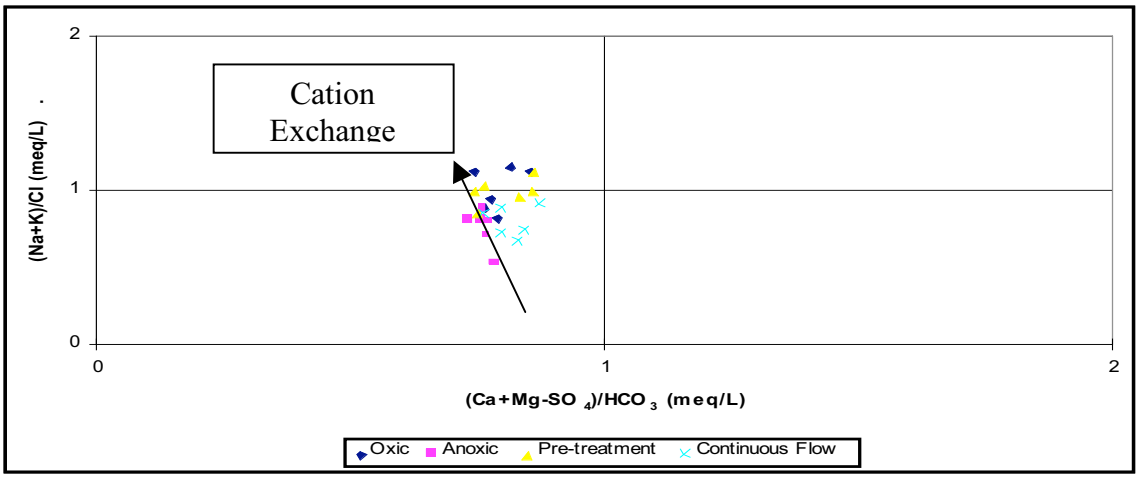

Figure 10.5. Major cation and anion milli equivalent ratio.

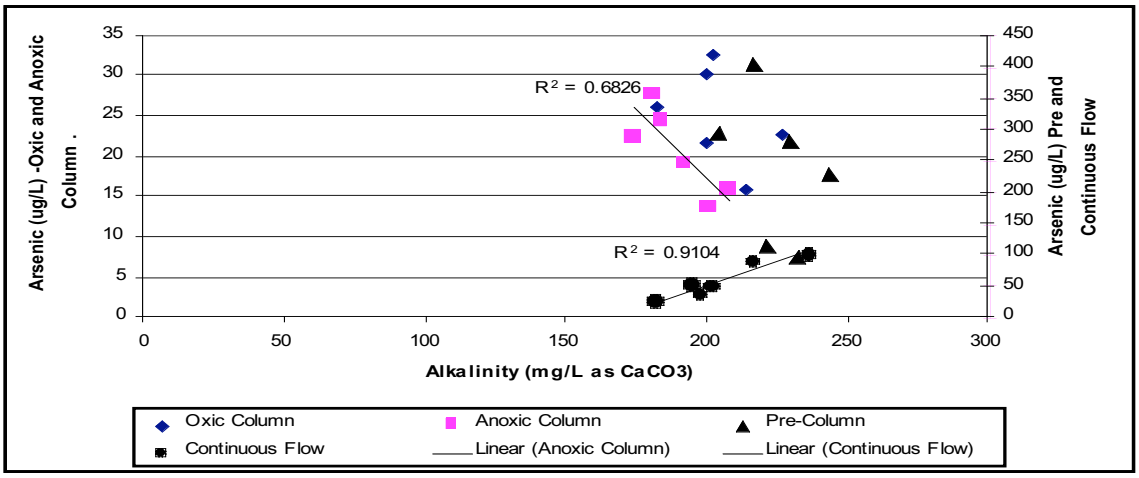

Figure 10.6. Arsenic concentration in µg/L versus alkalinity (in mg/L as $CaCO_3$)

There are significant differences in metal concentrations between continuous flow and oxic / anoxic columns. The arsenic concentration from the continuous flow column has positive correlation with alkalinity (bicarbonate) and negative correlation with calcium and sulfate, whereas the arsenic concentration from the anoxic water column has negative correlation with alkalinity (bicarbonate) and positive correlation with calcium and sulfate (Figure 10.6, 10.7, and 10.8). pH of the solutions ranged from 6.49 to 6.89 and the difference between each solution was not significant. Minor cation exchange is shown on the Piper diagram. It is estimated that calcite precipitation – arsenic desorption – iron oxyhydroxide dissolution are the main mechanism of metal mobilization in continuous flow / pre-treatment columns, whereas Ca-Na cation exchange, sorption-desorption of arsenic on calcareous precipitations (Goldberg and Glaubic, 1988), pyrite oxidation and

dissolution of iron oxyhydroxide are the main mechanisms of metal mobilization in oxic / anoxic water level fluctuated columns.

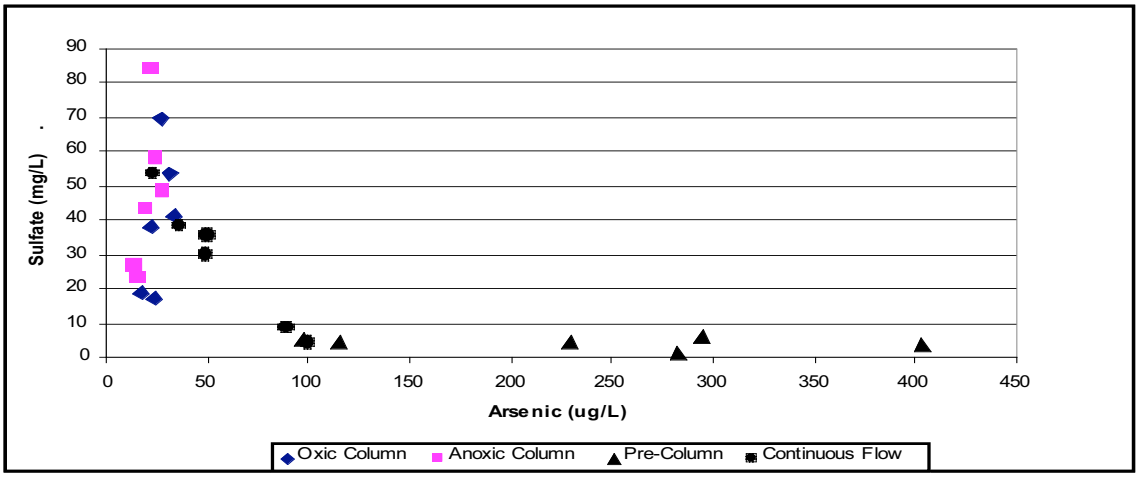

Figure 10.7. Sulfate in mg/L versus arsenic in µg/L.

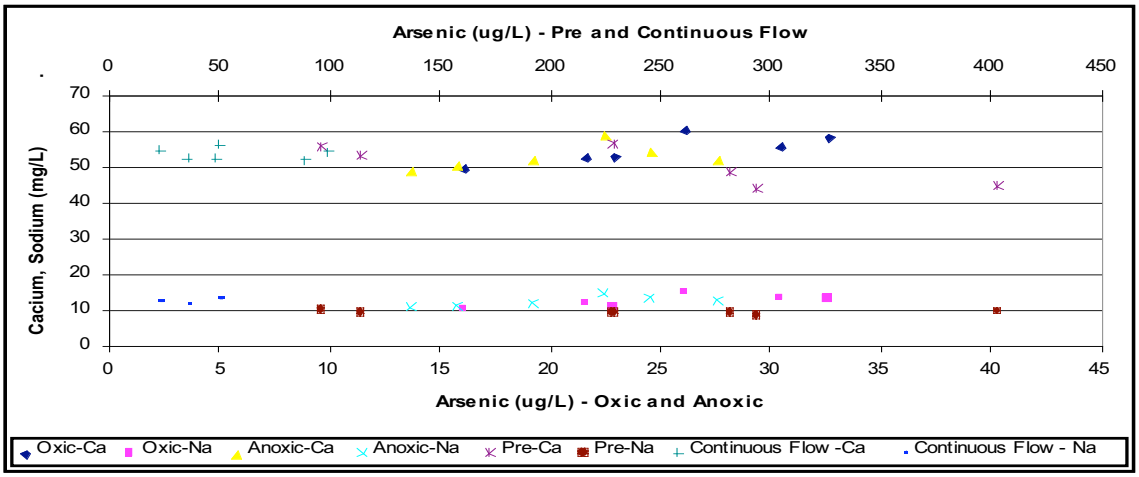

Figure 10.8. Calcium (upper data points) and sodium (lower data points) in mg/L versus arsenic in µg/L.

Future Research

Vertical infiltration through the silt layer may provide more detailed information for investigating metal mobilization mechanism and oxygen transport. More elaborate numerical geochemical modeling with the collected data is required to validate the conceptual model.

References

Acharyya, S.K., 1997, Arsenic in ground water-Geological overview: Consultation on Arsenic in Drinking Water. New Delhi, India: World Health Organization.

Acharyya, S.K., Lahiri, S., Raymahashay, B.C. and Bhowmic, A., 2000, Arsenic toxicity of ground water in parts of the Bengal Basin of India and Bangladesh: the role of Quaternary stratigraphy and Holocene sea level fluctuation. Environmental Geology, vol. 39, 1127-1137.

Appelo, C.A.J., and Postma, D., 2005, Geochemistry, groundwater and pollution (2nd Ed.). A.A. Balkema Publishers. London. 649p.

Armstrong, W., 1971, Oxygen Diffusion from the Roots of Rice Grown under Non-waterlogged Conditions, Physiol. Plant., 24, 242-247pp.

Berkowitz, B., Silliman, S.E., and Dunn, A.M., 2004, Impact of the Capillary Fringe on Locan Flow, Chemical Migration, and Microbiology, Vadose Zone Journal, 3, 534-548pp.

Bowell, R.J., 1994, Sorption of Arsenic by Iron Oxides and Oxyhydroxides in Soils, Applied Geochemistry, 9, 279-286pp.

Bryant, C.T., A.H. Ludwig, and E.E. Moris, 1985, Ground-water problems in Arkansas, USGS Water-Resources Investigation Report 85-4010, Little Rock, AR.

Callebaut, F., Gabriels, D., Minjauw, W., and De BoodT, M., 1982, Redox Potential, Oxygen Diffusion Rate, and Soil Gas Composition in Relation to Water Table Level in Two Soils, Soil Science, 134 (3), 149-156pp.

Clesceri, L.S., Greenberg, A.E., and Eaton, A.D., 1999, Standard Methods for Examination of Water and Wastewater, 20th edition. American Public Heath Association, Washington D.C., 1325 pp.

Cooper, C.D., 2002, Spatial Characterization of Hydrochemistry for the Alluvial and Sparta aquifers of the Grand Prairie Region, Eastern Arkansas. Master's thesis, University of Arkansas, Fayetteville. Arkansas.

Fiedler, S., and Sommer, M., 2004, Water and Redox Conditions in Wetland Soils - Their Influence on Pedogenic Oxides and Morphology, Soil Science Society of America Journal, vol. 68(1), 326-335.

Goldberg, S. and Glaubig, R.A., 1988, Anion Sorption on a Calcareous, Montmorillonitic Soil-Arsenic, Soil Sci. Soc.Am. J., 52, 1297-1300pp.

Holder, A.W., Bedient, P.B., and Hughes, J.B., 1999, Modeling the Impact of Oxygen Reaeration on Natural Attenuation, Bioremediation Journal, 3 (2), 137-149pp.

Holland, T.W., 2004, Estimated Water Use in Arkansas, 2000, USGS Scientific Investigations Report 2004-5230, Denver, CO.

Joseph, R., 1999, Status of water levels and selected water quality conditions in the Mississippi River Valley alluvial aquifer in eastern Arkansas, USGS Water-Resources Investigation Report 99-4035, Little Rock, AR.

Keeling, J., 2004, Metal Ion Dispersion Through Transported Cover at Moonta, South Australia, In: Roach I.C. ed. Regolith, 161-165pp.

Kim, B., Steele, K.F., and Fugitt, T., 2004, Comparison of dissolved and acid-extractable metal concentrations of ground water, eastern Arkansas, USA, Environmental Informatics Archives, Vol. 2, p. 272-284.

Klenk, I.D. and Grathwohl, P., 2002, Transverse Vertical Dispersion in Groundwater and the Capillary Fringe, J. of Contaminant Hydrology, 58, 111-128pp.

Kneebone, P.E., O'Day, P.A., Jones, N., and Hering, J.G., 2002, Deposition and Fate of Arsenic in Iron- and Arsenic- Enriched Reservoir Sediments, Environ. Sci. Technol., 36, 381-386pp.

Kresse, T.M., and Fazio, J.A., 2002, Pesticides, Water Quality and Geochemical Evolution of Ground water in the Alluvial Aquifer, Bayou Bartholomew Watershed, Arkansas. Arkansas Department of Environmental Quality. Water Quality Report WQ02-05-1, Little Rock, AR, 111.

Kresse, T.M., and Fazio, J.A., 2003, Occurrence of Arsenic in Ground waters of Arkansas and Implications for Source and Release Mechanisms. Arkansas Department of Environmental Quality. Water Quality Report WQ03-03-01, March 2003.

Lewis, W.K. and Whitman, W.G., 1924, Principles of Gas Absorption, Ind. and Eng. Chem., 16 (12), 1215-1220pp.

Morel, F.M.M., and Hering, J.G., 1993, Principles and Applications of Aquatic Chemistry. John Wiley & Sons, Inc., NY. 588p.

Parkhurst, D.L., 1995, Users guide to PHREEQC- A computer program for speciation, reactionpath, advective-transport, and inverse geochemical calculations. USGS Water Resour. Invest. Rep. 95-4227.

Pierce, M.L. and Moore, C.B., 1982, Adsorption of Arsenite and Arsenate on Amorphous Iron Hydroxide, Water Res., 16, 1247-1253pp.

Sharif, M., 2007. Written communication.

Silins, U. and Rothwell, R.L., 1999, Spatial Patterns of Aerobic Limit Depth and Oxygen Diffusion Rate at Two Peatlands Drained for Forestry in Alberta, Can. J. For. Res., 29, 53-61pp.

Stumm, W., 1992, Chemistry of the Solid-Water Interface. John Wiley & Sons, Inc., New York, NY, 428p.

Tessier, A., Campbell, P. G. C., and Bisson, M., 1979, Sequential extraction procedure for the speciation of particulate trace metals. Anal. Chem. 51(7), 844–851.

U.S. Environmental Protection Agency., 1994, Analytical Methods Manuals - Methods for the Determination of Metals in Environmental Samples -- Supplement I. EPA 600 R-94/111. EPA, Cincinnati, OH. ix + 281 pp.

Occurrence and antibiotic resistance in fecal indicator bacteria upstream and downstream of wastewater treatment plants in northwest Arkansas

Basic Information

Title:	Occurrence and antibiotic resistance in fecal indicator bacteria upstream and downstream of wastewater treatment plants in northwest Arkansas
Project Number:	2006AR131B
Start Date:	3/1/2006
End Date:	2/28/2007
Funding Source:	104B
Congressional District:	3rd
Research Category:	Biological Sciences
Focus Category:	Ecology, Surface Water, Treatment
Descriptors:	antibiotic resistance, E. coli, indicator bacteria, wastewater treatment effluent, stream water, surface water, microorganisms
Principal Investigators:	Mary Cathleen Savin, Brian E. Haggard

Publication

1. In progress: Akiyama, Tatsuya, expected 2008, "Occurrence and antibiotic resistance in fecal indicator bacteria upstream and downstream of wastewater treatment plants in northwest Arkansas," MS Thesis, Department of Crop, Soil and Environmental Sciences, University of Arkansas, Fayetteville, Arkansas 72701.
2. Savin, M., 2007, Antibiotic resistance in aquatic bacteria downstream from effluent discharge, 2007 Arkansas Water Resources Center Conference, University of Arkansas, Fayetteville, Arkansas, April 24-25, 2007[CD].

Problem and Research Objectives

Removal of antibiotics and genetic elements encoding antibiotic resistance may be incomplete in wastewater treatment plants. The addition of low levels of antibiotics, antibiotic residues, and/or genetic elements to aquatic ecosystems can create both ecological and health concerns due to the potential development of antibiotic resistance in microbial populations. To screen for the presence of pathogens it is accepted protocol to use bacterial indicators. Ideally, indicators of fecal contamination should be organisms that are easily detected and useful in all water types. Indicators should not grow in water, but should be abundant in direct proportion to fecal contamination and should be present whenever a pathogen is present. Both fecal coliforms and fecal enterococci are members of intestinal microflora of warm-blooded animals. A recent United States Geological Survey (USGS) study revealed the presence of low levels of antibiotics in northwest Arkansas streams, including Mud Creek in Fayetteville and Spring Creek in Springdale. We are screening for the presence of E. coli and Enterococcus sp. in Mud Creek and Spring Creek and detecting levels of antibiotic resistance to antibiotics in Mud Creek.

Objective 1: To determine numbers of *E. coli* and *Ent. faecalis* in two Arkansas streams upstream and downstream of wastewater treatment plants.
Objective 2: To determine antibiotic resistance of *E. coli* in the water and sediment for five different antibiotics.

Methodology

To determine the occurrence and distribution of indicator bacteria, each creek is being sampled upstream from the wastewater treatment plant, as the effluent enters the stream, and at two sites downstream from the wastewater treatment plant. Most probable numbers (MPN) are calculated for total coliforms and *E. coli* using the Colilert® reagent and for fecal enterococci using Enterolert™ Systems (IDEXX Laboratories, Westbrook, ME). In addition, the MPN of *E. coli* are determined both with and without the addition of an antibiotic (for a total of five antibiotics). MPN are “confirmed” by isolating the contents of positive (fluorescing) Quanti-tray wells and testing for the presence of E. coli and fecal enterococci.

To determine antibiotic resistance, each sample is placed in three to five more sets of Colilert® trays as described above; however, tubes also contain one of five antibiotics. Selected antibiotics include a representative of a class of antibiotics: quinolone (ofloxacin), sulfonamide (sulfamethoxazole), β-lactam (ampicillin), trimethorpim, or tetracycline (tetracycline). Three of the antibiotics, the macrolide, quinolone, and sulfonamide, have been detected previously in Mud Creek, one of the streams being tested in this study. National Committee for Clinical Laboratory Standards (NCCLS) breakpoints, where available, are used to guide concentrations of antibiotics. Bacteria are isolated for future identification of bacterial strains and diversity and for testing against multiple antibiotics.

Principal Findings and Significance

Government regulatory agencies need scientific data to make appropriate and sound decisions to protect water quality and human health. Understanding the occurrence and distribution of indicators of fecal contamination as recommended by U. S. EPA is essential to microbial source tracking and identification of public health risk. Additionally, to identify if streams receiving effluent from a point source are increasing in antibiotic resistance downstream from that point source will enable regulators to develop preventive strategies to protect water quality in streams receiving wastewater discharge.

Mud Creek (Fayetteville, AR) was sampled on June 25, September 14, and December 6, 2006 and Spring Creek (Springdale, AR) was sampled on August 16, with a third stream Columbia Hollow (Decatur, AR) sampled on August 30, 2006. In the first year of data collection, we focused on ofloxacin, ampicillin, and tetracycline. Low levels (<1 ppb) of ofloxacin were detected downstream but not upstream of effluent inputs to Mud Creek and Spring Creek, but no ofloxacin was detected in Columbia Hollow. Tetracycline was detected in Mud Creek in December only. Ampicillin was not detected in any of the samples. Most probable numbers of bacteria varied by sampling site, stream, and sampling time. In 2006, MPN in the presence of antibiotics were measured across antibiotic concentrations. Ampicillin and tetracycline resistance bacteria have been detected at all sampling locations, despite a lack of ampicillin detection and tetracycline being detected on only one sampling date. Data are very preliminary and the trends suggest an increase in levels of antibiotic resistance at the first downstream site, but not the second downstream locations in Mud Creek and Spring Creeks. Ofloxacin resistant bacteria have been detected in the effluent and first downstream location, but not in the upstream location. Sampling is being followed up by a second year of testing in 2007. In 2007, MPN of antibiotic resistant bacteria are being measured in sediment and water at one antibiotic concentration and also in the presence of trimethoprim or sulfamethoxazole in addition to the other three antibiotics previously tested.

. C. Savin. 2003. Microbial dynamics in long-term research plots receiving alum-treated and untreated poultry litter. *In* Annual Meetings Abstracts [CD-ROM]. ASA, CSSA, and SSSA, Madison, WI.

A hydrogeological investigation of nitrate processing within a karst watershed

Basic Information

Title:	A hydrogeological investigation of nitrate processing within a karst watershed
Project Number:	2006AR137B
Start Date:	3/1/2006
End Date:	2/28/2007
Funding Source:	104B
Congressional District:	3rd
Research Category:	Ground-water Flow and Transport
Focus Category:	Water Quality, Water Quality, Water Quality
Descriptors:	karst, interflow, nutrients, nitrogen, microbial processing, nitrate isotopes
Principal Investigators:	Susan Ziegler, John Van Brahana

Publication

1. Winston, Byron, 2006, "MS Thesis," Department of Biological Sciences, Fulbright College of Arts and Sciences, University of Arkansas, Fayetteville, Arkansas, 88p.
2. Brahana, John V., Tiong Ee Ting, Mohammed Al-Qinna, John F. Murdoch, Ralph K. Davis, Jozef Laincz, Jonathan J. Killingbeck, Eva Szilvagyi, Margaret Doheny-Skubic, Indrajeet Chaubey, Phillip D. Hays, Greg Thoma, 2005, Quanitfication of Hydrologic Budget Parameters for the Vadose Zoane and Epikarst in Mantled Karst, "in" U.S. Geological Survey Karst Interest Group Proceedings, Rapid City, South Dakota, p. 144-152.
3. Hays, Phillip, Jozef Laincz, Byron Winston, Susan Ziegler, Indrajeet Chaubey, Tim Kresse, Van Brahana, 2005, Elucidation of N-Processing within a Mantled Karst Watershed, "in" U.S. Geological Survey Karst Interest Group Proceedings, Rapid City, South Dakota
4. Laincz, Jozef, Byron Winston, Susan Ziegler, Phillip Hays, 2004, A coupled beigeochemical/hydrological approach for elucidating transport and cycling of nitrogen within mantled karst watersheds, Geological Society of America Abstracts with Programs, Vol. 36, No. 5, p. 258.
5. Laincz, Jozef, Byron Winston, Susan Ziegler, Phillip Hays, Tim Kresse, John Fazio, 2005, A Biogeochemical/hydrological approach to characterize transport and cycling of nitrogen in mantled karst watersheds, Geological Society of America Abstracts with Programs, Vol. 37, No. 7, p. 28.
6. Hays, Phillip, Susan Ziegler, Jozef Laincz, Byron Winston, 2006, Nitrogen Transport and cycling in the interflow zone of a mantled karst watershed in Northwest Arkansas, Geological Society of America Abstracts with Programs, Vol. 38, No. 7, p. 195.
7. Winston, Byron, Jozef Laincz, Susan Ziegler, Phillip Hays, 2005, Biogeochemical Processing of N in a Mantled Karst Watershed, Eos Trans. AGU, 86(18), Jt. Assem. Suppl., Abstract H43D-04.
8. Ziegler, Susan, Byron Winston, Jozef Laincz, Phillip Hays, Tim Kresse, John Fazio, 2005, The extent and variability of biogeochemical processing within a mantled karst watershed, AWRC Conference Proceedings [CD].
9. Laincz, Jozef, 2005, A biogeochemical/hydrological approach to characterize transport and cycling of nitrogen in mantled karst watershed: AWRC Conference Proceedings [CD].
10. Hays, Phillip, Jozef Laincz, Byron Winston, Susan Ziegler, Indrajeet Chaubey, Tim Kresse, Van Brahana, 2006, Elucidation of N-Procedding within a Mantled Karst Watershed, AWRC Conference Proceedings [CD].
11. Laincz, Jozef, Phillip Hays, Byron Winston, Susan Ziegler, 2004, A coupled biogeochemical/hydrological approach for elucidating transport and cycling of nitrogen within mantled karst watersheds, Arkansas Watershed Advisory Group Conference Proceedings, Little Rock, Arkansas.

Problem and Research Objectives

Animal production and associated on-land application of animal manures in karst watersheds pose a substantial threat to water quality because of thin soils, rapid infiltration, a predominance of conduit flow, and minimal opportunity for processing of nutrients such as nitrate. Balanced nutrient application presupposes an understanding of biogeochemical processes and controls on nitrate transport and cycling in karst. This research focused on investigation of these processes and controls in the interflow zone - an intermediate zone between the focused-flow and diffuse-flow soil zones in karst with an increased residence time and a potential for microbial remediation of nitrate.

Methodology

A hydrologic conceptual model was established through a dye tracer experiment of a study site situated in mantled karst of the Ozark Highlands at the University of Arkansas Savoy Experimental Watershed. Chicken litter was applied to the study area. Dissolved organic carbon concentrations and bioavailability, concentrations of reactive (nitrate) versus conservative (chloride) constituents, and nitrate isotopic composition were determined for soil (diffuse), interflow, and focused flow zones under low flow and high flow conditions.

Principal Findings and Significance

Data indicate considerable short-circuiting or bypass of dissolved species past the soil zone, but that a majority of flow spends some residence time in the interflow zone. Data also indicate that nearly 40 percent of nitrate moving through the interflow zone may have been microbially processed. The level of processing was highly variable and dependent upon flow-path and hydrologic conditions. Bioavailability of dissolved organic carbon in the interflow zone was elevated relative to the focused-flow zone under high-flow conditions, providing a needed substrate for nitrate processing in this zone. Results suggest the interflow zone appears to be a potentially important zone for nitrate attenuation in karst settings.

Information Transfer Program

AWRC sponsors an annual water conference held in Fayetteville each spring, drawing in about 100 researchers, students, agency personnel and interested citizens to hear about results of current research and hot topics in water resources throughout the state. AWRC also co-sponsors short courses and other water-related conferences in the state and region. The 2006 Conference featured 20 oral presentations and 11 posters during the one and one-half day conference.

In addition, AWRC maintains a technical library containing over 900 titles, many of which are on-line. This valuable resource is utilized by a variety of user groups including researchers, regulators, planners, lawyers and citizens. Many AWRC publications have been converted to electronic pdf format which can be accessed via our web site at http://www.uark.edu/depts/awrc. Click the "Publications" link on the left-hand side of the page to view these publications.

2006 Arkansas Water Resources Center Conference

Basic Information

Title:	2006 Arkansas Water Resources Center Conference
Project Number:	2006AR183B
Start Date:	4/18/2006
End Date:	4/19/2006
Funding Source:	104B
Congressional District:	Third
Research Category:	Water Quality
Focus Category:	Water Quality, Water Supply, Non Point Pollution
Descriptors:	
Principal Investigators:	Ralph K. Davis

Publication

1. Davis, R.K., 2006, 2006 Annual Arkansas Water Resources Center Conference, April 18, April 19, 2006, University of Arkansas Center for Continuing Education, Fayetteville, AR, Conference Agenda and Abstracts on-line at http://www.uark.edu/depts/awrc/Publications/2006AWRCConference/TrifoldLF.pdf

2006 Arkansas Water Resources Center Conference

TUESDAY, April 18
8:00am to 7:00pm

Registration and Continental Breakfast.....7:30 am

Ralph K. Davis, Director , Arkansas Water Resources Center
Welcome and Introductions.....8:10 am

PRESENTATIONS
***Denotes Speaker**

Factors Affecting Phosphorus Runoff

Session Moderator: J. Van Brahana, Professor, Geosciences, University of Arkansas, Fayetteville

Effects of grazing practices on pasture hydrology and nutrient runoff. *John Pennington[1], Philip Moore [2], Dave Brauer[1], Barbara Bellows[1], Dan Pote[3], Kris Brye[1], and Mary Savin[1]. 1. Crop, Soil and Environmental Sciences, UA; 2. USDA/ARS, UA; 3. USDA/ARS, Booneville, AR ...**8:15 am**

Incorporating poultry litter into perennial grassland to improve water quality. * Dan Pote, USDA/ARS, Booneville, Arkansas.....**8:40 am**

Effect of soluble P applications on P runoff from pastures. *Paul DeLaune, Division of Agriculture, UA .....**9:05 am**

Revising the Arkansas phosphorus index. *Philip Moore, USDA/ARS, UA.....**9:30 am**

Break..... 9:55 – 10:25 am

Surface and soil water chemistry during the first year following poultry litter application to pastures and a pine plantation. * Hal O. Liechty[1], Joshua Richardson[2], Stacy Wilson[3], and Robert Colvin[4] 1. Associate Professor, 2. Graduate Research Assistant, 3. Program Technician I, School of Forest Resources, University of Arkansas, Monticello; 4. Research Associate, Southwest Research and Extension Center, Division of Agriculture.....**10:25 am**

Savoy Experimental Watershed: Subbasin Delineation and Runoff

Where does the runoff come from – Experimental and modeling results from Savoy watershed. I. Chaubey[1], M. Leh[1], J.V. Brahana[2], J. Murdock[1], and B. Haggard[1]. 1. Biological and Agricultural Engineering, UA; 2. Geosciences, UA.....**10:50 am**

Delineation of three contiguous karst spring basins and their daily evapotranspiration at the Savoy Experimental Watershed in Northwest Arkansas. * J. Van Brahana and Jon Killingbeck, Geosciences, UA.....**11:15 am**

USGS Water Science Center: What's New?

Current activities of the USGS Arkansas Water Science Center. *Dave Freiwald, USGS, Little Rock, AR.....**11:40 am**

Lunch (Lunch on your own: list of restaurants in conference packet).....**12:05-1:30 pm**

Hydrogeologic Investigation Near Dardanelle, AR

Session Moderator: Tim Kresse, Professional Geologist, Water Division, Arkansas Department of Environmental Quality

The Arkansas River's alluvial aquifer in central Arkansas: Physical hydrogeology of the aquifer at Dardanelle. *Stephen W. Kline[1], Timothy M. Kresse[2], John A. Fazio[2], William L. Prior[3], William D. Hanson[3], Tyler M. Treece[1], and Roger Miller[4]. 1. Arkansas Tech University; 2. Arkansas Department of Environmental Quality; 3. Arkansas Geological Commission; 4. Arkansas Department of Health.....**1:30 pm**

The Arkansas River's alluvial aquifer in central Arkansas: Geochemistry of the aquifer at Dardanelle. *Timothy M. Kresse[1], John A. Fazio[1], Roger A. Miller[2], and Stephen W. Kline[3]. 1. Arkansas Department of Environmental Quality; 2. Arkansas Department of Health; 3. Arkansas Tech University .....**1:55 pm**

Hot Springs Hydrogeology and Hydrochemistry

Influence of locally derived recharge on springs in Hot Springs Nationa Park. * Phillip D. Hays[1] and Richard W. Bell [2] and Stephen Rudd[3]. 1. USGS and Department of Geosciences, UA; 2. USGS, Albequerque, NM; 3. U.S. National Park.....**2:20 pm**

Characteristics of thermal springs and the shallow ground-water system at Hot Springs National Park, Arkansas. *Daniel S. Yeatts, USGS, Little Rock, AR .....**2:45 pm**

Break..... 3**:10-3:40 pm**

Wetlands to Lake Modeling

Constructed wetlands as a component of optimal ground-water management. * John B. Czarnecki and David A. Freiwald, USGS, Little Rock, AR.....**3:40 pm**

Evaluating the impacts of changes in the quality of inflow water to Beaver Lake using a calibrated two-dimensional water-quality model, 2001-2003. Joel Galloway and *Reed Green, USGS, Little Rock, AR .....**4:05 pm**

Sedimentation in Beaver Lake: An Ozark Mystery? *Stephen K. Boss and J.A. Patton, Environmental Dynamics Program, 113 Ozark Hall, University of Arkansas, Fayetteville, Arkansas .....**4:30 pm**

***RECEPTION AND POSTER SESSION,**
Tuesday, April 18.....5:00-7:00 pm
***See back page for poster titles**

WEDNESDAY, April 19
8:00am to 12:05pm
Registration and Continental Breakfast..... 7:30 am

WORKSHOP
Using Bio-Indicators for Developing Nutrient Criteria in Rivers and Streams

Moderator: Marty D. Matlock, PhD, PE, CSE, Associate Professor of Ecological Engineering, UA

The challenge of nutrient criteria development. *Marty Matlock, Biological and Agricultural Engineering, UA .....**8:00 am**

Additional Presentations and Posters on Back Page

Biological data tell a complex story – an overview of the NAWQA results. *Jim Petersen, NAWQA Study Unit Chief, Ozark Plateau, USGS, Little Rock, AR ..... **8:30 am**

Application of a nutrient diffusing substrate bio-assay for stream assessment. *Andrea Ludwig, Biological and Agricultural Engineering, UA..... **9:00 am**

Break..... .9:30-10:00 am

Using a nutrient diffusing substrate bio-assay to develop stream nutrient thresholds. *Richard Kiesling, Stream Ecologist, USGS, Austin, TX ..... **10:00 am**

Other applications of the nutrient diffusing substrate bio-assay – reservoirs, toxicity testing, etc. *Brian Haggard, Biological and Agricultural Engineering, UA..... **10:30 am**

Working Session – Finding the Right Number. This session will be a moderated discussion with the participants. Each table will be given a scenario to consider, and will provide a summary of that scenario with their recommended criteria ..... **11:00 am**

RECEPTION AND POSTER SESSION
TUESDAY, APRIL 18……..**5:00-7:00 pm**

POSTERS

Arkansas' nutrient criteria development plan, Arkansas Department of Environmental Quality, Little Rock, AR.

A tool for estimating best management practice effects in Arkansas. K. Merriman, Research Assistant, M. Gitau, Program Associate, I. Chaubey, Associate Professor, Biological and Agricultural Engineering Department, UA.

Identification and evaluation of limiting factors on algal growth in headwater Ozark streams. Andrea Ludwig, Marty Matlock, and Brian Haggard, Ecological Engineering Group, Department of Biological and Agricultural Engineering, University of Arkansas, Fayetteville, AR 72701.

Investigation of historic "cattle dipping vat", Lake Fort Smith expansion project. Paul R. Easley, Environmental Manager, Environmental Services Department, City of Fort Smith, 3900 Kelley Highway, Fort Smith, AR.

A hydrogeologic and water quality evaluation of the Springfield aquifer in the vicinity of north-central Washington County, Arkansas, Laubhan, Aaron, Davis, Ralph K., Brahana, J.V. Geosciences, UA.

The Arkansas River's alluvial aquifer in central Arkansas:Physical hydrogeology of the aquifer at Dardanelle. Kline, S.W. [1], Kresse, T.M.[2], Fazio, J.A.[2], Prior, W.L.[3], Hanson, W.D.[3], Miller, R.A.[4], Treece, T.M.[1], (1) Center for Energy, Natural Resources, and Environmental Studies, Arkansas Tech University, 1815 Coliseum Dr, Russellville, AR 72801, stephen.kline@atu.edu, (2) Water Division, Arkansas Department of Environmental Quality, P.O. Box 8913, Little Rock, AR 72219, (3) Arkansas Geological Commission, 3815 West Roosevelt Rd, Little Rock, AR 72204, (4) Department of Engineering, Arkansas Department of Health and Human Services, 4815 W. Markham St, Little Rock, AR 72205

Field investigations of rainfall-runoff processes in a Karst watershed. M. Leh[1], I. Chaubey[1], J.V. Brahana[2], J. Murdoch[1] and B.E. Haggard[1] [1]Department of Biological & Agricultural Engineering UA, [2]Department of Geosciences, UA

Comparison of artificial neural network models for hydrologic prediction in agricultural watersheds. E. Mutlu, Chaubey, I., Hexmoore, H., and Bajwa, S.

Public supply water-use trends for Benton and Washington Counties in Arkansas, 1960 thorugh 2004. Terrance W. Holland[1], Mike Guess[2], and Rusty McAllister[2] [1]U.S. Geological Survey Arkansas Water Science Center, 401 Hardin Road, Little Rock, AR 72211, [2]Arkansas Natural Resources Commission, 101 East Capitol, Suite 350, Little Rock, AR 72201

Estimating surface runoff in the Illinois River basin for the management of nonpoint source phosphorus loads. Adam T. McClymont[1], Mary C. Savin[2], and Brian E. Haggard[3] [1]Adam T. McClymont, senior in the Department of Crop, Soil, and Environmental Sciences, Dale Bumpers College of Agricultural, Food and Life Sciences; [2]Mary C. Savin, Assistant Professor, Crop, Soil and Environmental Sciences, Dale Bumpers College of Agricultural, Food and Life Sciences; [3]Brian E. Haggard, Associate Professor, Biological and Agricultural Engineering, Dale Bumpers College of Agricultural, Food and Life Sciences

Delineation of point and nonpoint sources within the Kings River and Longs Creek watersheds, Northwest Arkansas. Ty Johnson and R.K. Davis, Department of Geosciences, University of Arkansas, Fayetteville, Arkansas.

WELCOME TO THE

AWRC

2006 ARKANSAS WATER RESOURCES CONFERENCE

April 18 & 19, 2006
at the

Center for Continuing Education
and the
Fayetteville Radisson
70 North East Avenue
Fayetteville, Arkansas

Student Support

Student Support					
Category	**Section 104 Base Grant**	**Section 104 NCGP Award**	**NIWR-USGS Internship**	**Supplemental Awards**	**Total**
Undergraduate	2	0	0	3	5
Masters	5	0	0	7	12
Ph.D.	3	0	0	3	6
Post-Doc.	0	0	0	0	0
Total	10	0	0	13	23

Notable Awards and Achievements

Establishing Effective Partnerships: A partnership between the Upper White River Basin Foundation and the Arkansas Water Resources Center is a bi-state dual University partnership with a goal of minimizing cross boarder conflicts and resolving water quality concerns within the Upper White River watershed. AWRC is working closely with a regional watershed group (Upper White River Basin Foundation, Branson, Missouri), and Missouri State University to provide basic geographic spatial data and water quality data for the watershed on which sound environmental management decisions can be based. Our close relationship with this group has led to additional interaction with another newly formed Watershed Advisory group for the Illinois River Basin in Northwest Arkansas. We have been selected as one of the primary entities to collect, compile, interpret, and report on water quality in the Illinois River basin. This is significant because it shows that the data provided through the AWRC research teams is considered to be sound, reliable, and unbiased. Maintaining this type of independent credibility provides a valuable asset in terms of dispute resolution on both water quantity and water quality concerns in these trans-boundary waters.

USGS 104 B funds were leveraged through a partnership with the Arkansas Department of Environmental Quality and additional University resources to investigate arsenic release and mobilization mechanisms in the Mississippi River Valley alluvial aquifer in eastern Arkansas. This is important because a high percentage of small public water systems and most of the domestic users in the region rely on this aquifer as a source of potable water. The research supported two Ph.D. students at the University of Arkansas and has resulted in the submission of three papers to refereed journals with an additional two papers in preparation, as well as presentation at the Geological Society of America Annual meeting in 2006.

Collaborative Multidisciplinary Interagency Research Programs

The Arkansas Water Resource Center in conjunction with a multidisciplinary team have leveraged funding provided by the USGS 104 B program over several years to supplement infrastructure and provide basic and applied research at the Savoy Experimental Watershed, Northwest Arkansas. The Savoy Experimental Watershed (SEW) is an approximately 1,250 hectare University of Arkansas property managed by the UA Department of Animal Sciences. Cooperation between the Colleges of Agriculture, Engineering and Arts

and Sciences has provided access to this valuable site for basic and applied research related to assessing methods to minimize environmental impacts from animal agriculture and other sources of nutrient and bacterial loading to the environment. The facility is located about 24 km west of the University of Arkansas campus in northwest Arkansas. It was selected because it is representative of mantled-karst aquifers throughout northwest Arkansas, the Ozarks and much of the remaining 20% of the United States dominated by karst topography. Ongoing research at the site has facilitated development of a fully instrumented site that allows investigation of the integrated transport of surface applied nutrients and bacteria through primary pathways to their ultimate discharge into major streams. USGS 104 B funds have been provided through AWRC to several researchers utilizing SEW over the last several years with a goal of providing seed data, creating the basis for preparation of proposals to other entities. This includes investigation of transport and storage of E. coli bacteria in streams and aquifers of Northwest Arkansas. Results of this project were recently published in the Journal of the American Water Resources Association (Davis et al. 2005). The initial state and Federal funds provided via the Arkansas Science and Technology Authority and the USGS 104 B program provided initial data sets which were then used as the basis for a proposal to the National Science Foundation which was awarded for continued research in this area.

Dr. Phil Hays who holds a joint appointment with the USGS and the University of Arkansas, and Dr. Susan Ziegler, UA Department of Biological Sciences are conducting an interdisciplinary study with USGS, USDA, and the UA Departments of Geosciences and Biological Sciences to define biogeochemical processes occurring in karst, and how nitrogen transport and utilization is controlled by the interplay of biological and hydrological inputs to the complex systems. Additional funds provided by the USGS 104 B program have augmented this project providing resources to investigate nitrogen processing in a Karst Soil Catena. Results of their work were recently published by Defaw et al. (2005), and presented at the Geological Society of America and American Geophysical Union annual meetings.

Dr. Indrajeet Chaubey, Biological and Agricultural Engineering at UA, and Dr. J. Van Brahana, Geosciences at UA, utilized seed funds provided under the USGS 104 B program in conjunction with funding from US EPA, USDA, Arkansas Department of Environmental Quality, and others to establish a fully instrumented facility at SEW with a main goal of understanding nutrient (nitrogen and phosphorus) fate in strongly linked surface–subsurface karst agricultural watersheds, which is critical to development of effective management strategies to protect human health and minimize adverse effects of phosphorus on river and lake systems. Their team has published several papers related to the site including several papers in the proceedings of the USGS Karst Interest Group (Brahana et al, 2005; and Laincz et al, 2005).

Leaders in Non-Point Source Water-Quality Monitoring

The Arkansas Water Resource Center continues to be a leader in non-point source water-quality monitoring related to nutrient loading of surface waters in the Ozark Plateaus Province. Dr. Marc Nelson, who heads up the AWRC Water Quality Laboratory, leads the monitoring program for five sites throughout the area. High quality nutrient loading data collected by Dr. Nelson and his team are regarded as the best available data for calculation of Total Maximum Daily Loads. These data are also routinely used by other researchers involved with development of non-point source pollution decision support systems. The decision support systems which are being developed for the ten high priority watersheds in the state by Dr. Indrajeet Chaubey will be used to prioritize resource allocation to minimize non-point source nutrient and sediment loading to the surface waters of the state. Dr. Chaubey is leading a team that models and assesses impacts of Best Management Practices on non-point source loading at the watershed

scale using the Soil Water Assessment Tool (SWAT) model. The base data sets provided by Nelson et al are used as calibration data for the modeling effort. Chaubey has published numerous recent articles including one dealing with DEM resolution affects on SWAT model results which was recently published in the Journal of Hydrologic Processes (Chaubey et al 2005).

Dr. Brian Haggard, UA Biological and Agricultural Engineering (2006) published an article on the Effect of Reduced Effluent Phosphorus Concentrations at the Illinois River, Northwest Arkansas in the Journal of Environmental Quality and a second paper along with Dr. Thomas Soerens, UA Civil Engineering (2006) on Sediment Phosphorus Release at a Small impoundment on the Illinois River, Arkansas and Oklahoma, USA as a direct result of funding provided through the USGS 104 B program. The research conducted by Dr. Haggard supports and extends ongoing efforts by Nelson and Chaubey by looking more closely at the impacts of point sources of contamination at the watershed scale.

Cutting Edge Research

Dr. Mary Savin, UA Crops, Soils and Environmental Sciences used 104 B funds to investigate antibiotic resistance in fecal indicator bacteria in the vicinity of municipal waste water discharge to streams. Understanding the occurrence and distribution of indicators of fecal contamination as recommended by U. S. EPA is essential to microbial source tracking and identification of public health risk. Additionally, to identify if streams receiving effluent from a point source are increasing in antibiotic resistance downstream from that point source will enable regulators to develop preventive strategies to protect water quality in streams receiving wastewater discharge. Their initial findings indicate that a portion of bacteria in the effluent were resistant to select antibiotics. The data provided by the seed grant provided through the USGS 104 B program will provide the basis for development of a larger research proposal to continue this critical area of research. Dr. Brian Haggard conducted separate but related research on the occurrence of antibiotics in select Ozark streams, looking specifically at the transport, degradation, and residence time of antibiotics below waster water treatment discharge points. Both areas of research will help us better understand anthropogenic impacts to aquatic ecosystems, and long-term sustainability under our current waste water treatment and discharge policies.

Publications from Prior Projects

1. 2005AR158B ("The Vadose-Zone Losses of Soluble Heavy Metals from Pasture Soil Amended with Varying Rates of Poultry Litter") - Articles in Refereed Scientific Journals - Pirani, A.L., K.R. Brye, T.C. Daniel, B.E. Haggard, E.E. Gbur and J.D. Mattice. 2006. Soluble metal leaching from a poultry-litter-amended Udult under pasture vegetation. Vadose Zone J., 5:1017-1034.
2. 2005AR158B ("The Vadose-Zone Losses of Soluble Heavy Metals from Pasture Soil Amended with Varying Rates of Poultry Litter") - Articles in Refereed Scientific Journals - Pirani, A.L., K.R. Brye, B.E. Haggard, T.C. Daniel and J.D. Mattice. Poultry litter rate effects on nutrient leaching from a Udult under pasture vegetation. Soil Sci. Soc. Am. J. (In review).
3. 2001AR3661B ("Economics of Water Management to Sustain Irrigated Agriculture in Eastern Arkansas Watersheds") - Articles in Refereed Scientific Journals - Hill, J.E. Wailes, M. Popp, J. Popp, K. Young and B. Watkins. 2006. "Surface Water Diversion Impacts on Farm Income and Sources of Irrigation Water: The Case of the Grand Prairie in Arkansas. J. Soil and Water Conservation 61(4): 185-191.
4. 2001AR3661B ("Economics of Water Management to Sustain Irrigated Agriculture in Eastern

Arkansas Watersheds") - Other Publications - Hignight, J., E.J. Wailes, J. Popp, and J. Smartt. 2006. Investing in On-Farm Reservoirs Under Alternative Land Tenure Arrangements. B.R. Wells Rice Research Studies 2005. Arkansas Agricultural Experiment Station Research Series 540, pp. 413-419.

5. 2002AR5B ("Phosphorus Concentrations and Sediment Phosphorus Flux in Streams and Reservoirs: Effect of Chemical Amendments") - Articles in Refereed Scientific Journals - Ekka, S.A., B.e. Haggard, M.D. Matlock, I. Chaubey. 2006. Dissolved phosphorus concentrations and sediment reactions in effluent-dominated Ozark streams. Ecological Engineering 26, 375-391.
6. 2005AR90B ("Effect of Reduced Effluent Phosphorus Concentrations at the Illinois River, Northwest Arkansas") - Articles in Refereed Scientific Journals - Haggard, B.E. and T.S. Soerens. 2006. Sediment phosphorus release at a small impoundment on the Illinois River,Arkansas and Oklahoma, USA. Ecological Engineering 28, 280-287.
7. 2002AR13B ("Processes And Controls Affecting Water/Rock Interaction in Abandoned Underground Coal Mines, Including Feasibility and Risk Assessment of Using Mine Water for Public Drinking Water Sources") - Conference Proceedings - Varnell, C.J. and J.V. Brahana. 2006. Establishing hydraulic connnections between flooded underground coal mines using continuous monitoring of surface flood pulses: Geological Society of America Abstracts with Programs, v. 38, no. 6.
8. 2005AR82B ("The distribution of roxarsone and its byproducts in soils, soil pore-water, groundwater, and stream water") - Other Publications - Young, H., C.B. Dowling and T. McKay. 2006. The effects of poultry litter application on the metal body burden of ground-dwelling arthropods (poster), ACS Midwest Regional Conference, Quincy, IL.
9. 2005AR82B ("The distribution of roxarsone and its byproducts in soils, soil pore-water, groundwater, and stream water") - Other Publications - McKay, T. and C.B. Dowling. 2006. The effects of metal-rich poultry litter on ground beetles (oral), 80th Annual Meeting of the Southeastern Branch Entomological Society of America, Wilmington, NC.
10. 2001AR15B ("Linkages Between Watershed Dynamics and Habitat Contraction of an Endemic Species in Little Red River Headwaters (LRRH)") - Articles in Refereed Scientific Journals - Abanda, P.A. and R. Hannigan. 2006. Diagenetic controls of trace element partitioning in shales. Chemical Geology, 230: 42-59.
11. 2001AR15B ("Linkages Between Watershed Dynamics and Habitat Contraction of an Endemic Species in Little Red River Headwaters (LRRH)") - Other Publications - Cox, L. and R. Hannigan. 2006. Organomercury Speciation in Black Shale Bedrock Streams. Society of Environmental Toxicology and Chemistry North American Meeting, Montreal Quebec Canada, Nov 5-9.
12. 2001AR15B ("Linkages Between Watershed Dynamics and Habitat Contraction of an Endemic Species in Little Red River Headwaters (LRRH)") - Other Publications - Medlin, E., S. Coghlan Jr., R. Hannigan. 2006. Discrimination Among Walleye Stocks of Three Tributaries of the Upper Little Red River Using Otolith Microchemistry. 136th Annual Meeting of the American Fisheries Society, Lake Placid NY, Sept 10-14.
13. 2001AR15B ("Linkages Between Watershed Dynamics and Habitat Contraction of an Endemic Species in Little Red River Headwaters (LRRH)") - Other Publications - Lyerly, M.S., S. Coghlan, Jr., T. Bly, J. Williams, D. Bowman and R. Hannigan. 2006. Otolith microchemistry discriminates between hatchery and wild salmonines in the Little Red River, AR, tailwater system. 136th Annual Meeting of the American Fisheries Society, Lake Placid NY, Sep 10-14.
14. 2001AR15B ("Linkages Between Watershed Dynamics and Habitat Contraction of an Endemic Species in Little Red River Headwaters (LRRH)") - Other Publications - Hannigan, R., Invited, 2006. Reconstruction of Environmental Life Histories of Fish Using Otolith Chemistry. National Science Foundation - Biological Sciences Seminar Series, June 8.

15. 2001AR15B ("Linkages Between Watershed Dynamics and Habitat Contraction of an Endemic Species in Little Red River Headwaters (LRRH)") - Other Publications - Cox, L. and R. Hannigan. 2006. GC-ICP-MS. Applied to Organometal Sepciation in Black Shale Bedrock. Pittcon 2006, Orlando FL, March 16, (oral).
16. 2001AR15B ("Linkages Between Watershed Dynamics and Habitat Contraction of an Endemic Species in Little Red River Headwaters (LRRH)") - Other Publications - Poku, E., Y. Chai and R. Hannigan. 2006. Trace Metal Speciation by Chromatography-Inductively Coupled Plasma Mass Spectrometry. Pittcon 2006, Orlando FL, March 16 (oral).
17. 2005AR77B ("Flow and hydrochemical evolution of arsenic in ground water: tracking sources and sinks in the alluvial aquifer of southeastern Arkansas, USA") - Articles in Refereed Scientific Journals - Kim, B., K.F. Steele and T. Fugitt. 2006. Comparison of Dissolved and Acid-Extractable Metal Concentrations of Ground Water, Eastern Arkansas, USA, Journal of Environmental Informatics, Vol. 7, p. 56-65.
18. 2005AR77B ("Flow and hydrochemical evolution of arsenic in ground water: tracking sources and sinks in the alluvial aquifer of southeastern Arkansas, USA") - Other Publications - Kim, B. and K.F. Steele. 2005. Application of geologic information for ground-water quality management. Proceedings of the XXXI International Hydrologic Resources Congress, Seoul, Korea, p. 5577-5585.