**Columbia University Superfund Basic Research Program**
**Annual Project and Core Updates – 2007**

# *Health Effects and Geochemistry of Arsenic and Manganese*

**P.I. -- Joseph H. Graziano, Ph.D.**

**Highlight #1: Better remediation through chemistry: Increasing the efficacy of pump and treat remediation strategies for arsenic contaminated sites.**

**Background:** Arsenic is a prevalent contaminant at US Superfund sites, present at more than 500 sites. "Pump and treat" remediation is commonly used at contaminated groundwater sites, with more than 900 such sites nationwide. However, arsenic remediation by pump and treat systems is often complicated by relatively slow release of arsenic from iron and aluminum (hydr)oxides on the surface of aquifer solids. As such, sites utilizing pump and treat are expected to require many decades to reach desired clean up levels and have high annual costs.

The Vineland Chemical Company located in southern NJ improperly stored and disposed of their arsenic chemicals for several decades as a biocide manufacturing facility. This led to extensive arsenic contamination of subsurface soils and groundwater in addition to offsite arsenic transport. At the Vineland Superfund Site, a large pump and treat remediation facility (~ 2 million gallons/day) began operation in 2000, and has significantly reduced offsite arsenic transport. It also led to an initial decrease in groundwater total arsenic concentrations in the pumping wells by as much as 10x. Several more years of pump and treat as well as remediation efforts focused on excavation, cleaning, and replacing contaminated vadose zone soils has led to only relatively minor additional improvements in groundwater arsenic levels, which can still have more than 1000 ppb As, depending on the well. The aquifer sediments are still elevated in arsenic and represent a reservoir of approximately 100,000 kilograms of arsenic at the Vineland site, causing continued groundwater contamination.

**Advances:** Columbia University scientists hypothesized that the time frame for remediating arsenic contaminated aquifers via pump and treat could be substantially reduced by subsurface additions of chemical amendments. The goal is to increase the mobilization of arsenic from aquifer solids and therefore increase the amount of arsenic being removed from the aquifer with each volume of water pumped out of the ground and treated. To date, the scientists have primarily focused on laboratory experiments designed to evaluate the efficacy of chemical amendments for mobilizing arsenic from aquifer solids. The most promising chemical amendments have been sodium phosphate and oxalic acid. Phosphate has a similar chemical structure to arsenate and can replace arsenic sorbed to the surfaces of aquifer minerals. Oxalic acid is a natural soil acid often responsible for dissolving and transporting iron and aluminum oxides in vadose zone soils, and these phases are also important on aquifer mineral surfaces.

Column experiments using arsenic-contaminated aquifer sediment (~80 ppm arsenic) from Vineland suggest that both phosphate and oxalic acid can be effective at significantly increasing arsenic mobility compared to groundwater alone. The effluent water arsenic concentrations in these column experiments reached 100,000 ppb and 70,000 ppb for 10 mM oxalic acid and 100 mM phosphate experiments, respectively, whereas the influent arsenic concentration was only ~10 ppb. More importantly, extrapolations for site clean up progress using data from these column experiments suggest that chemical treatments could lower the site's clean up time-scale from ~600 years with ambient groundwater alone to only 4 years with 10 mM oxalic acid, based on the clean up goal of lowering the concentration of arsenic on aquifer solids to less than 20 ppm.

The Columbia scientists are now planning *in situ* field experiments using subsurface chemical amendments to build on these laboratory results. Modeling groundwater flow and transport at the site has helped design optimal locations for injection and monitoring wells within the cone of depression of a site recovery well. Furthermore it has helped constrain amendment concentrations, injection rates and pumping rates needed for these experiments. Before carrying out the injection of chemical amendments, the investigators will first perform inert tracer experiments to confirm the conclusions from numerical modeling efforts and to build confidence that any chemicals added will be recovered at the existing large-volume recovery well.

The Columbia scientists also plan to investigate several basic science questions directed towards both the mechanisms by which the oxalic acid mobilizes arsenic as well as the eventual rates of microbial degradation and sorption of oxalic acid.

**Significance:** Chemical amendments appear to show great promise in dramatically reducing the time required to use pump and treat intervention to remediate the Vineland megasite and potentially many other sites with arsenic contaminated aquifers. This would be an important innovation since pump and treat options can be quite an expensive technique. A 2003 survey of annual operation and maintenance costs using pump and treat reported a mean annual cost of ~$0.6M, with the Vineland Superfund pump and treatment costs being the highest surveyed at $4M/yr.

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To learn more about this research, please refer to the following sources:

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**Project 1: *Genotoxic and Cell Signaling Pathways of Arsenic in Mammalian Cells***
**PI: Tom Hei**

1) The overall goals of this project remain unchanged.

2) During the current funding period, we examined the effects of arsenic treatment on mitochondrial morphology in mammalian cells. Arsenite-treated cultures (1 µg/ml for 60 days) exhibited a dramatically elongated or filamentous morphology. This extended mitochondrial morphology was also evident in cells stained histochemically for cytochrome c oxidase (COX) after only 15 days of arsenic exposure. This change in mitochondrial morphology correlated with depletion in mtDNA copy number and increase in large heteroplasmic mtDNA deletions.

Using quantitative RT-PCR and primers for the hamster 12S and 18S rRNA genes, we found that arsenic treatment (1 µg/ml for 60 days) reduced the mtDNA copy number to <65% of control levels. The effect was dose dependent and could be detected at a lower dose of 0.25µg/ml. Furthermore, using nested PCR analyses, we showed that arsenic treatment induced large heteroplasmic mutations in mtDNA of hamster cells. Similarly, we detected an increase in mtDNA deletions after arsenic exposure in two normal human cell lines: small airway epithelial cells and normal lung fibroblasts, both derived from tissues that are known to have high incidences of cancer in arsenic exposed humans.

In our previous studies, we have shown sodium arsenite to be an inducer of apoptosis for malignant human melanoma. While many melanomas express the death receptors TRAIL-R2/DR5 or TRAIL-R1/DR4 on their cell surfaces, they often exhibit resistance to exogenous TRAIL. One of the main contributors to TRAIL-resistance of melanomas is an up-regulation of the transcription factors STAT3 and NF-κB that control the expression of antiapoptotic genes, including *cFLIP, XIAP* and *Bcl-xL*. On the other hand, JNK is involved in the negative regulation of *cFLIP* expression. During the current funding period, we showed that resveratrol (a polyphenolic phytoalexin) down-regulated STAT3 activation, while activating JNK that suppressed expression of the antiapoptotic cFLIP (an inhibitor of caspase-8) and Bcl-xL proteins and increased the sensitivity of DR5-positive melanomas to exogenous TRAIL. Interestingly, sodium arsenite treatment or γ-irradiation substantially up-regulated surface expression of DR5 in human melanomas. This approach and the subsequent down regulation of antiapoptotic cFLIP and Bcl-xL (by resveratrol), appear to constitute an efficient way to reactivate apoptotic death pathways in TRAIL-resistant human melanomas. Taken together, these results suggest that resveratrol in combination with TRAIL may have a significant efficacy in the treatment of human melanomas.

3) Arsenic is an important environmental carcinogen that affects millions of people worldwide through contaminated water supplies. A better understanding of the

mutagenic/carcinogenic mechanism of arsenic should provide a basis for better interventional approach in both treatment and prevention of arsenic induced cancer.

4) In the coming year, we will use multiplex PCR and DNA sequencing to identify the incidence and types of mitochondrial DNA mutations in arsenic-induced skin lesions with or without concurrent UV exposure based on the Bangladeshi cohort. Furthermore, we will determine the effects of reseveratrol on the general signaling pathways regulating cell survival and apoptosis in normal and melanoma cells.

**Publications:**

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Ivanov, V., Partridge, M.A., Johnson, J.E., Huang, S.X.L., Zhou, H., and Hei, T.K., Resveratrol sensitizes human melanomas to TRAIL through modulation of anti-apoptotic gene expression in conditions of partial suppression of mitochondrial function. ***Exp. Cell Research*** (In press, 2007).

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**Project 2: *A Cohort Study of Health Effects of Arsenic Exposure in Bangladesh***
**PI: Habibul Ahsan**

This prospective cohort study recruited 11,746 men and women in Araihazar, Bangladesh, during 2000-2002 to investigate the health effects of arsenic exposure, with an initial focus on skin lesions and skin cancers. The design of this multidisciplinary project and cohort description has been published [Ahsan et al., 2005]. We have numerous publications utilizing the baseline cross-sectional data on arsenic exposure and prevalent skin lesion cases [Ahsan et al., 2006; Argos et al., 2007; Chen et al., 2006].

An in-person interview and clinical examination are conducted every 2 years. In our previous progress report, we summarized the two- and four-year follow-up visits. The six-year follow-up visit of the cohort is currently underway. To date, approximately 3,000 participants have been contacted and interviewed.

The objectives of our current analyses and the follow-up interviews underway are to specifically examine the aims stated in the renewal of this project:

1). To examine the full dose-response relationship between arsenic exposure from drinking water and incidence of skin lesions and, in particular, skin cancer in the HEALS cohort with enhanced statistical power.

2). To determine the full dose-response relationship between arsenic exposure from drinking water, incidence, mortality from chronic lung disorders, and mortality of lung cancer in the HEALS cohort.

3). To determine the full dose-response relationship between arsenic exposure from drinking water, incidence, and mortality from CVD (ischemic heart disease and stroke) in the HEALS cohort.

4). To further evaluate the role of arsenic in skin and lung disorders, we plan to examine the effects of As exposure and metabolism on serum levels of EGFR and CC16, respectively, along with the roles of these biological markers in arsenic-related skin and lung disorders.

5). To further evaluate the role of As in CVD, we plan to examine the effects of arsenic exposure on ultrasonic measures of carotid artery IMT, a preclinical marker of CVD.

Based on the data collected from the first two follow-up visits (two-year and four-year visits) of the cohort, we see that the incidence of cancer within the study population is lower than what we expected based on extrapolation from other studies of arsenic health effects in other countries and also WHO cancer incidence data for Bangladesh (based on incidence in India). We are currently working to enhancing our detection of the cancer cases that do occur within our study cohort, however, the lower cancer incidence may pose a challenge for us to currently evaluate the cancer incidence components of our specific aims due to decreased statistical power. We are confident in our assessments of skin lesions, mortality, CVD, and chronic lung disorders. However, to enhance our ability to successfully implement all of our specific aims we decided to expand our cohort size. Currently, new participants are being enrolled into the cohort as part of a planned expansion for a total sample size of 20,000 participants. To date, approximately 6,000 additional individuals have been newly enrolled. Interview data and biological specimens are being collected from the newly enrolled participants in the identical manner as the original cohort.

**Project 2-supported 2007 publications:**

Ahsan H, Chen Y, Kibriya MG, Slavkovich V, Parvez F, Jasmine F, et al. “Arsenic metabolism, genetic susceptibility, and risk of premalignant skin lesions in Bangladesh.” Cancer Epidemiol Biomarkers Prev 2007;16(6):1270-8.

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Parvez F, Brnadt-Rauf PW, et al. (In press). "Non-malignant Respiratory Effects of Chronic Arsenic Exposure from Dinking Water in Bangladesh: A Molecular Epidemiological Study." EHP.

**Project 3: *Consequences of Arsenic and Manganese Exposure on Childhood Intelligence***
**PI: Joseph Graziano**

This project builds upon our discovery that arsenic and manganese exposure from drinking water have adverse effects on intelligence in children. Our past work has occurred in Bangladesh, where water used for drinking and cooking contains naturally elevated concentrations of both arsenic and manganese.

In the past year we launched a new study of elementary school children in New Hampshire to determine whether exposure to arsenic impairs intellectual functioning in a U.S. population. The study seeks to recruit a total of 500 children. The work has not gone well and has encountered many problems that have had to be addressed. A year ago, our University of New Hampshire (UNH) project director – who had extensive experience working in NH elementary schools - was fired by UNH "for cause." The University of New Hampshire Dean also left UNH. Consequently, it took a few months to replace our staff, and the first recruitment letters were not sent to parents until January, 2007. In addition, despite the approval *a priori* of the School District Superintendents, many School Principals refused to participate. Many parents did not respond to our invitation letter, and many of those that did eventually refused to participate because they objected to the collection of a urine sample. Thus, despite our efforts, between Jan-June, 2007, only 18 children were recruited. During the summer we modified our approach based on these experiences. We let one staff member go, and are using that money to provide $25 to the participating families. Now, the parental response letters will not be mailed to UNH staff, but returned directly to the child's teacher. The urine sample is now optional, since toenail As has always been the primary biomarker of exposure. In addition, we are now studying 3rd, 4th and 5th graders, not just 4th graders. We have also expanded the study into Maine, and have two districts (and five school principals) on board. The IRB protocols have been modified to reflect these changes, and have been approved by the Columbia University and UNH IRBs. We are cautiously optimistic that these changes will improve our progress.

Simultaneously, our work with children in Bangladesh continues. We have expanded our research to determine whether exposure to arsenic and manganese has an adverse effect on motor function. In addition, by providing deep, low arsenic and low manganese wells after assessments of motor and cognitive functioning, we will determine whether the adverse effects of arsenic and manganese are reversible. We have completed a pilot study of motor function – a new outcome for us – in 90 children and those results are being analyzed. The Columbia University IRB has approved minor modifications to our protocol, and approval of those changes are under review by the Bangladesh Medical Research Council (i.e., IRB). We expect to launch the main study of 300 children in January, 2008, when a large group of Columbia scientists will travel to Bangladesh.

Finally, we published a study concerning the transfer of arsenic and its metabolites to the fetus during pregnancy (Hall et al, 2007).

**Students whose research is supported at least in part by Project 3**:

At the Mailman School of Public Health:

Marni Hall, Ph.D. student in Environmental Health Sciences
Khalid Khan, Dr.PH student in Environmental Health Sciences

At the University of New Hampshire:

Patricia Jarema, Ph.D. student in Research Administration and Management

**Reference:**

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**Project 4: *One-Carbon Metabolism, Oxidative Stress and Arsenic Toxicity in Bangladesh***
**PI: Mary V. Gamble**

There is considerable variability in progression from arsenic (As) exposure to clinical manifestations of disease, and nutritional status may account for some of this variability. Methylation of ingested inorganic arsenic (InAs) to methylarsonic- (MMA) and dimethylarsinic acids (DMA) relies on folate-dependent one carbon metabolism and facilitates urinary As elimination. As a new member of this SBRP, we wish to expand our RO1 supported studies (Nutritional Influences on Arsenic Toxicity or NIAT) which demonstrated that folic acid supplementation increases As methylation[1,2] and lowers total blood As and blood MMA concentrations[3].

The first aim of this proposal utilizes the repository of biological samples established by the Cohort Study (Project #2) to conduct a nested case-control study. We here test the hypothesis that at the time of enrollment, participants who subsequently went on to develop As-induced skin lesions (SLs) had lower indices of one-carbon metabolism (e.g. low plasma folate and/or high homocysteine) as compared to non-skin lesion controls. This study includes 274 incident SL cases (i.e. cases were free of SLs at baseline, but developed SLs by 2 years after recruitment), and 274 control subjects individually matched to cases for gender, age (within 5 years) and frequency matched for water arsenic (within 100 µg/L). As preliminary data for a new R21 application, we also analyzed genomic methylation of peripheral blood leukocyte DNA (PBL DNA) using a [3H]-methyl incorporation assay.

Conditional logistic regression analyses revealed that the odds ratios (95% C.I.s) for subsequent development of SLs for participants who, at baseline, had marginal folate status (plasma folate < 9 nmol/L), high Hcys (> 10.4 µmol/L), or hypomethylated PBL-DNA (below the median) were 1.6 (1.05 – 2.5; $p = 0.005$), 1.7 (1.1 - 2.6; $p = 0.01$), and 1.7 (1.1 – 2.7; $p = 0.008$), respectively. These studies indicate that folate deficiency, hyperhomocysteinemia, and hypomethylation of genomic PBL-DNA are independent risk factors for arsenic-induced skin lesions (manuscript in preparation).

For the second aim, we proposed to address a fundamental question: To what extent do urinary As metabolites reflect As metabolites in the circulation? We calculated Spearman correlation coefficients for total arsenic and arsenic metabolites between blood (µg/L) and urine (µg/g cr) in 130 Bangladeshi adults. In each case, the correlations were very high, ranging from 0.68 to 0.81 ($p < 0.0001$ for all metabolites). However, when the arsenic metabolites were expressed as a percentage of total arsenic, the correlations between blood and urine, although still highly significant, were somewhat less strong (Spearman correlations: 0.32 – 0.44; $p < 0.001$). Most striking were the differences in distributions of %MMA (13% in urine vs. 40% in blood) and %DMA (72% in urine vs. 34% in blood)[3], consistent with a short circulating half-life of DMA which is rapidly excreted in urine. To date, the general belief has been that we can assess As methylation capacity in urine; however, these findings suggest that studies analyzing As metabolites in urine have more limitations than previously believed.

Fieldwork for aim's 3 & 4 is now scheduled to begin in January 2008.

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2. Gamble MV, Liu X, Ahsan H et al. Folate and Arsenic Metabolism: A double-blind placebo controlled folic acid supplementation trial in Bangladesh. Am J Clin Nutr 2006;84:1093-101.
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**Project 5:** ***Mobilization of Natural Arsenic in Groundwater***
**PI: Yan Zheng**
Co-Investigators: Martin Stute, and Alexander van Geen

The past year was characterized by intensive field campaigns in Bangladesh and New England that not only established new locations for further field and laboratory experiments but also resulted in exciting new findings:

**Groundwater Arsenic Along a Flow Path: Testing Hydrological Control Hypothesis**

The geochemical and hydrogeological characteristics of Site K in Araihazar established through field campaigns in Dec. 2006, Mar., May and Nov 2007, combined with observations over time, have indicated that it is an ideal location to study As mobilization along a flow path. Graduate student Karrie Radloff is to ascertain whether the relationship between dissolved As concentrations and ($^3H/^3He$) ages will hold in a single aquifer (Stute, et al., 2007), and to determine the rate of As mobilization through direct comparison of As concentration vs. $^3H/^3He$ ages and field manipulation.

**Mineralogy and Mobility of Fe and As in Meghna River Sediments in Bangladesh**

Building on our discovery that arsenic discharged from groundwater is trapped in the sediment of the Meghna River bank, and represents a source of As to groundwater on the time scale of thousands of years (Datta, et al., 2007), graduate student Hun Bok Jung is conducting a study of the mechanism causing enrichment of As along the Meghna River. High spatial density piezometers deployed in Nov. 2007 show that groundwater Fe, As, and $PO_4$ showed systematic attenuation from well water to riverbank porewater, indicating trapping of As in a reactive barrier consisted of ferrihydrite. Laboratory experiments conducted determined the capacity of As sorption by the natural reactive barrier and simulated the conditions of As re-mobilization during seasonal cycles.

**Bedrock Geology Control As, U, Rn Spatial Distribution in Greater Augusta, Maine**

Two sets of private well samples were collected in 2006 (n=787) in 13 towns encompassing 1000 $km^2$ area of Greater Augusta, Maine and in 2007 (n=343) in 4 cluster areas that are chosen to represent low, intermediate and high As occurrence. Graduate student Qiang Yang conducted a geostatistical analysis that demonstrates for the first time the bedrock geology controls the spatial pattern of As distribution at local scale ($10^0$-$10^1$ km) relevant to community planning applicable to New England. The detailed hydrogeochemical study has revealed mechanisms of As mobilization (Jung, et al., in prep.) that can be traced to As containing pyrite prevalent in the Silurian meta-sedimentary rock, for which samples have been collected in Aug., 2007. Column experiments of these rocks by post-doc Beth O'Shea will illustrate the reactions responsible for As release.

**Preparation for Push Pull Experiment in Deep Aquifer**

A set of sorption experiments were conducted by Zheng in Nov. 2007 on sediment cuttings obtained at Site I, the proposed push pull experiment site, to determine the sorption capacity and kinetics of the deep aquifer sediment. The orange sand to which the As will be injected to in the field is found to sorb up to several mg/kg As at a rate that is reasonably fast, with a half time of < 1 day.

Students and Post-docs whose research is supported at least in part by Project 5:

Bethany O'Shea, Post-doc fellow, Columbia University Science Fellow
Hun Bok Jung, $4^{th}$ yr PhD candidate, Earth and Environmental Sciences, City University of New York (CUNY)
Kathleen A Radloff, $4^{th}$ yr PhD candidate, Environmental Engineering, Columbia

Qiang Yang, 2nd yr candidate, Earth and Environmental Sciences, CUNY
Margaret Bounds, Undergraduate, Environmental Science, Barnard College

**Publications:**

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**Project 6: *Mobilization of anthropogenic arsenic in groundwater***
**PI: Steven Chillrud**
Co-investigators: Martin Stute, H. James Simpson, Brian Mailloux, John Stolz

Project 6 focuses on investigations of arsenic behavior at the Vineland Superfund site, a former arsenic biocide manufacturing plant in Vineland, NJ. Groundwaters and sandy subsurface soils beneath the site in southern New Jersey have become extremely contaminated with arsenic as a result of decades of improper chemical storage and disposal. In addition, groundwater discharge to an adjacent stream resulted in significant arsenic transport offsite. Despite extensive remediation, including excavating, washing and replacing vadose zone soils as well as operating a large groundwater P&T facility, groundwater arsenic can still be >1000 ppb.

During this past year, we have primarily focused on laboratory experiments evaluating the efficacy of chemical amendments for mobilizing As from aquifer solids, which represent a reservoir of As for continued groundwater contamination. The ultimate goal of this work is to accelerate As pump and treatment remediation at Vineland and potentially other sites. In addition, groundwater modeling efforts using MODFLOW and MT3D are helping us plan *in situ* forced gradient field experiments using subsurface chemical amendments. Experiments were also carried out to investigate the relative sorption behaviors of inorganic and organic arsenic species to uncontaminated site soils.

Column experiments using arsenic contaminated aquifer sediment (~80 ppm As) from the Vineland site suggest that both phosphate and oxalic acid can be effective at increasing As mobility, with effluent water As concentrations reaching 70,000 ppb and 100,000 ppb for 100 mM phosphate and 10 mM oxalic acid experiments, respectively. Furthermore, extrapolations for site clean-up progress using data from these column experiments suggest that chemical treatments could lower the site's clean-up timescale from ~600 years with ambient groundwater alone to as little as 4 years with 10 mM oxalic acid.

We have also been performing molecular studies to understand the effect of elevated arsenic concentrations on the microbial ecology of the subsurface. Interestingly, we have found that the arsenic reductase gene, *arrA*, is present in only small concentrations and is non-detectable at many locations. This is in direct contrast to other environments such as Mono Lake where arrA is thought to be the driver of arsenic cycling. Instead, we observe a diverse population of microbes with the arsenical compound resistance *acr3*, gene. This gene is at best poorly studied in the environment yet our results indicate it may be important in arsenic cycling.

Finally, we have also begun to investigate the geochemistry and microbiology at Union Lake, situated downstream of the Vineland Chemical site. Seasonal changes in lake chemistry, including incomplete eutrophication, may result in arsenic mobilization from sediments into the water column in the summer, as previously described (Ficklin et al). Preliminary observations indicate that eutrophication in the summer of 2007 did not occur to an extent permitting As mobilization, although Mn was released to some degree in lake bottom waters. Lake sediments at a depth of ~5 cm have been shown to contain As porewater concentrations of >3000 ppb. Investigations are ongoing to determine if As cycling genes are present in these environments.

**Students and Postdocs involved in studies in 2007:**

Alison Keimowitz, PhD 2005, Earth and Environmental Science, currently postdoctoral fellow at Columbia University

Rachel Foster, post-doctoral fellow at Columbia University

Karen Wovkulich, 3rd year graduate student, Earth and Environmental Science, Columbia University

Ekaterina Alexandrova, Undergdraduate, Barnard College

Allison Lacko, undergraduate student, Columbia University

Peter Wagner, undergraduate student, Columbia University

Jared Fox, Frederick Douglass Academy III in the south Bronx. This past summer as a part of Columbia University's Science Teacher Research Program

Sasha Harbajan, George Washington Carver High School Harlem Children Society. www.harlemchildrensociety.org.

**2007 Publications and meetings:**

Keimowitz, A.R., B. J. Mailloux, P. Cole, M. Stute, H. J. Simpson, S.N. Chillrud. Laboratory investigations of sulfate reduction as a groundwater arsenic remediation strategy. Environ. Sci. Tech. 2007, 41, 6718-6724.

Wovkulich, K., M. Stute, H.J. Simpson, B. Mailloux, A. Lacko, A. Keimowitz, Z. Cheng, S. Chillrud. Mobilization of Arsenic from Contaminated Sediments for Improved Remediation. Poster at the annual Superfund Basic Research Program Meeting. Durham, N.C., 2007.

Wovkulich, K., H.J. Simpson, M. Stute, B. Mailloux, A. Keimowitz, Z. Cheng, S. Chillrud. Improving Arsenic Remediation Through Chemistry: Laboratory and Modeling Data for a Superfund Site Highly Contaminated with Arsenic (Vineland, NJ). Oral presentation at the annual Superfund Basic Research Program Meeting. Durham, N.C., 2007.

**Project 7: *Mitigation of Arsenic Mobilization in Groundwater***
**PI: Alexander van Geen**
Co-Investigators: Yan Zheng, Martin Stute, Zhongqi Cheng, Peter Schlosser, Andrew Gelman, and Alex Pfaff

This year's contributions of 15 published papers/manuscripts in press and 5 submissions under review can be divided under 3 headings (1) exploration of the mechanisms of As mobilization, (2) As mitigation and policy, and (3) collaborations with public health scientists. The following paragraphs highlight studies under (1) and (2) where Project 7 played a leading role.

Considerable attention continues to be devoted to establishing the consequences of a high-degree of spatial variability of As concentrations in Bangladesh groundwater that has been documented using a simple device, coined the needle-sampler, that simultaneously collects groundwater and aquifer particles. This work has resulted in three papers of a descriptive nature from Bangladesh but also other affected countries such as West Bengal, India, Vietnam, and Nepal (Metral et al. *Geochemical Transactions*, in press; van Geen et al., submitted to *Applied Geochemistry*; van Geen et al., in revision for *Env. Sci. Technol.*). The last two of these papers also includes a simple model that explores the time scale over which shallow aquifers are likely to be flushed at various flow rates on the basis of distribution coefficient that appears to be remarkably constant over a wide range of conditions. The needle-sampler has also been used to conduct incubation experiments in novel ways and to test the impact of various amendments to probe the mechanisms underlying As mobilization in reducing aquifers (Radloff et al., Env. Sci. Technol., 2007; Radloff et al., submitted to *Applied Geochemistry)*

Contributions from Project 7 under the heading of arsenic mitigation in Bangladesh included an encouraging response of the study population of Araihazar to well-labeling and the installation of community wells was documented in the survey conducted by Opar et al. (2007), which was independently confirmed by a marked drop in urinary As concentrations documented by the biomedical team (Chen et al., 2007). The paper by van Geen et al. that appeared in *J. Environmental Science and Health* showed with detailed time-series that deep community wells are, by and large, reliable and low-maintenance sources of safe drinking water but also that they can occasionally fail and therefore must be periodically monitored.

**Submitted Manuscripts:**

Radloff, KA, AR Manning, B. Mailloux, Y. Zheng, MM Rahman, MR. Huq, KM Ahmed, M Stute, A van Geen, Considerations for conducting incubations to study the mechanisms of As release in reducing groundwater aquifers, submitted to *Applied Geochemistry*, December 2007.

van Geen, A, K Radloff, Z Aziz, Z Cheng, MR Huq, KM Ahmed, B Weinman, S. Goodbred, M. Berg, PTK Trang, L Charlet, J Metral, D Tisserand, S Guillot, S Chakraborty, AP Gajurel, BN Upreti, Comparison of arsenic concentrations in simultaneously-collected groundwater and

aquifer particles from Bangladesh, India, Vietnam, and Nepal, submitted to *Applied Geochemistry*, December 2007.

van Geen, A., Y. Zheng, S. Goodbred Jr., A. Horneman, Z. Aziz, Z. Cheng, M. Stute, B. Mailloux, B. Weinman, M.A. Hoque, A.A. Seddique, M.S. Hossain, S.H. Chowdhury, and K. M. Ahmed, Flushing history as a hydrogeological control on the regional distribution of arsenic in shallow groundwater of the Bengal Basin, submitted to *Environmental Science and Technology*, revision requested November 2007.

Dhar, R.K., Y. Zheng, M. Stute, A. van Geen, Z. Cheng, M. Shanewaz, M. Shamsudduha, M.A. Hoque, M.W. Rahman, and K.M. Ahmed, Temporal variability of groundwater chemistry in shallow and deep aquifers of Araihazar, Bangladesh, submitted to *Journal of Contaminant Hydrology*, revision requested October 2007.

Aziz, Z., A. van Geen, R. Versteeg, A. Horneman, Y. Zheng, S. Goodbred, M. Steckler, M. Stute, B. Weinman, I. Gavrieli, M.A. Hoque, M. Shamsudduha, and K.M. Ahmed, Impact of local recharge on arsenic concentrations in shallow aquifers inferred from the electromagnetic conductivity of soils in Araihazar, Bangladesh, submitted to *Water Resources Research*, minor revision requested October 2007.

**Peer-reviewed publications in 2007:**

Auffan, M., J. Rose, O. Proux, D. Borschneck, A. Masion, P. Chaurand, J.L. Hazemann, C. Chaneac, J.P. Jolivet, M. Wiesner, A. van Geen, J.Y. Bottero, Enhanced adsorption of arsenic onto maghemites nanoparticles: As(III) as a probe of the surface structure and heterogeneity, Langmuir, in press December 2007.

Horneman, A., M. Stute, P. Schlosser, W. Smethie Jr, N. Santella, B. Mailloux, E. Gorman, Y. Zheng, and A. van Geen, Degradation of CFC-11, CFC-12 and CFC-113 in anoxic shallow aquifers of Araihazar, Bangladesh, submitted to *Journal of Contaminant Hydrology*, in press November 2007.

Métral, J., L. Charlet, S. Bureau, S. B. Mallik, S. Chakraborty, K.M. Ahmed, M.W. Rahman, Z. Cheng, and A.van Geen, Comparison of dissolved and particulate arsenic distributions in shallow aquifers of Chakdaha, India, and Araihazar, Bangladesh, *Geochemical Transactions*, in press November 2007.

Weinman, B, SL Goodbred Jr., Y. Zheng, Z. Aziz, AK Singhvi, YC Nagar, M. Steckler, A. van Geen, Contributions of floodplain stratigraphy and evolution to the spatial patterns of groundwater arsenic in Araihazar, Bangladesh. *Geological Society of America Bulletin*, in press October 2007.

van Geen, A., Z. Cheng, Q. Jia, A. A. Seddique, M. W. Rahman, M. M. Rahman, and K. M. Ahmed, Monitoring 51 deep community wells in Araihazar, Bangladesh, for up to 5 years: Implications for arsenic mitigation, *Journal of Environmental Science and Health*, 42, 1729-1740, 2007.

Hafeman, D., P. Factor-Litvak, Z. Cheng, A. van Geen, H. Ahsan, Association between manganese exposure through drinking water and infant mortality in Bangladesh, *Environmental Health Perspectives*, in press March 2007.

Radloff, K.A., Z. Cheng, M.W. Rahman, K.M. Ahmed, B.J. Mailloux, A.R. Juhl, P. Schlosser, and A. van Geen. Mobilization of arsenic during one-year incubations of grey aquifer sands from Araihazar, Bangladesh, *Environmental Science and Technology*, 41, 3639-3645, 2007.

Chen, Y., A. van Geen , J. Graziano , A. Pfaff, M. Madajewicz, F. Parvez , I. Hussain, Z. Cheng, V. Slavkovich, T. Islam, and H. Ahsan, Reduction in urinary arsenic levels in response to arsenic mitigation in Araihazar, Bangladesh, *Environmental Health Perspectives*, 115, 917-923, 2007.

Stute, M., Y. Zheng, P. Schlosser, A. Horneman, R.K. Dhar, M. A. Hoque, A. A. Seddique, M. Shamsudduha, K. M. Ahmed, and A. van Geen, Hydrological control of As concentrations in

Bangladesh groundwater, *Water Resources Research*, 43, W09417, doi:10.1029/2005WR004499, 2007
Chen, Y., P. Factor-Litvak, G.R. Howe, J.H. Graziano, P. Brandt-Rauf, F. Parvez, A. van Geen, and H. Ahsan, Arsenic exposure from drinking water, dietary intakes of B vitamins and folate, and risk of high blood pressure in Bangladesh: A population-based, cross-sectional study, *American Journal of Epidemiology* 165, 541-552, 2007.
Wasserman,G.A., Liu, X., Parvez, F., Ahsan, H., Factor-Litvak, P., Kline, J., van Geen, A., Slavkovich, V., LoIacono, N.J., Levy, D., Cheng Z., Graziano, J.H., Water arsenic exposure and intellectual function in 6-year-old children in Araihazar, Bangladesh, *Environmental Health Perspectives*, 115, 285-289, 2007.
Madajewicz, M., A. Pfaff, A. van Geen, J. Graziano, I. Hussein, H. Momotaj, R. Sylvi, and H. Ahsan, Can information alone both improve awareness and change behavior? Response to arsenic contamination of groundwater in Bangladesh, *Journal of Development Economics*, 84, 731–754, 2007.
Cheng, Z., B.M. Buckley, B. Katz, W. Wright, R. Bailey, K.T. Smith, A. van Geen, Arsenic in tree rings at a highly contaminated site, *Science of the Total Environment*, 376, 324-334, 2007.
Opar, A., A. Pfaff, A. A. Seddique, K. M. Ahmed, J. H. Graziano, and A. van Geen, Responses of 6500 households to arsenic mitigation in Araihazar, Bangladesh, *Health & Place* 13, 164-172, 2007.
Chen Y, Hall M, Graziano JH, Slavkovich V, van Geen A, Parvez F, Ahsan H. A prospective study of blood selenium levels and the risk of arsenic-related premalignant skin lesions. *Cancer Epidemiol Biomarkers Prev*, 16:207-13, 2007.

**Students supported at least in part under Project 7 over the past year**

Kathleen Radloff, Earth & Environmental Engineering, Columbia, PhD candidate.
Zahid Aziz, Earth & Environmental Science, Columbia, PhD candidate.
Jessica Leber, Earth & Environ. Sci. and Journalism, Columbia MS 2007.
Christine George, Mailman School of Public Health, Columbia, PhD candidate.
Sajaa Ahmed, sophomore, Columbia College.

**Administrative Core**

Director: Joseph Graziano
Deputy Director: Alexander van Geen

**General Activities**: The Administrative Core continues to function smoothly. Dr. Graziano, the Program Director, and Dr. van Geen, the Associate Director, communicate virtually every working day with regard to the integration of our biomedical and non-biomedical research programs. This communication is evidenced by the number of truly multi-disciplinary publications that have come from our program, involving close collaboration between biomedical, earth, and social scientists. Our monthly two-hour seminars (one hour biomedical and one hour non-biomedical) are exceptionally well attended. We believe that our SBRP is unique with regard to the extent that these two dimensions of the program are highly integrated. Our seminar program can be viewed at http://superfund.ciesin.columbia.edu/niehsWeb/.

In November, 2007. our External Advisory Committee convened for one day at Columbia University's Lamont-Doherty Earth Observatory to review our progress. The composition of the committee includes: a) Chien-Jen Chen, Committee Chair, and Chairman of the Graduate Institute of Taiwan; b) Andrew Gelman, Professor of Statistics at Columbia University; c) Zoltan Szabo, Research Hydrologist, USGS; d) Margaret Karagas, Chair, Section of Biostatistics and

Epidemiology, Dartmouth University; e) Allan Smith, Professor of Epidemiology, University of California, Berkeley; f) X. Chris Le, Professor of Public Health Sciences, University of Alberta; g) Peggy O'Day, Associate Professor of Natural Sciences, University of California, Merced; and h) James Davis, USGS. Several of these senior scientists were selected because they are also potential future collaborators. The most recent November External Advisory Committee meeting was attended by Drs. Szabo, Smith, Le, O'Day and Karagas. Each of our seven research project PIs, as well as the PIs of the Research Translation Core, made presentations and received useful feedback and suggestions from the Committee.

The Administrative Core was also instrumental in assuring an excellent representation of investigators, post-doctoral fellows and students at the recent December, 2007, annual meeting of SBRP programs held at the Washington Duke Inn in Durham, NC.

**Core A: *Data Management Core***
**PI: Diane Levy**

During the past year the data management staff provided services to each of the three projects with which it works. The following summarizes the tasks that were performed.

1. Questionnaire Design:
    a. Project 2
        i. Consulted with project manager regarding design of follow up 3 questionnaire for Arsenic Cohort Study
    b. Project 3
        i. Consulted with project manager regarding design of home tracking questionnaire for US based (New Hampshire & Maine) children's study
    c. Additional projects:
        i. Consulted with Khalid Khan regarding design of questionnaire for interviews of children in arsenic education project
2. Programming Services:
    a. Project 2
        i. Programming modifications to original Microsoft Access application to accommodate data-entry for the expansion of the baseline cohort.
        ii. Developed update processes to periodically move expanded cohort data to Microsoft SQL Server database for permanent storage.
        iii. Programmed Microsoft SQL Server database for collection of follow up 3 data.
        iv. Supervise design and programming of an outside consultant for a customized system that will allow data-entry of follow up 3 data to occur in Bangladesh. The new system will collect data on the local area network in Bangladesh and will monitor the availability of a stable Internet connection. When a connection is available, data will automatically be sent to an SQL database located at Columbia University, in New York.
    b. Project 3
        i. Completed programming of database tables and web-based data-entry screens for child studies in New Hampshire and Bangladesh. Tables and screens were programmed to accept test and questionnaire data for these studies.
    c. Project 4
        i. Periodic uploads of laboratory data to Microsoft SQL server database. The following data have been added: plasma folate, B12, homocysteine, cysteine, Cystatin C; leukocyte DNA methylation; urinary 8-OHdG (8-hydroxydeoxyguanosine); serum retinol and carotenoids (including

leutein/zeaxanthin (one variable); beta-cryptoxanthin, lycopene, alpha-carotene, and beta-carotene) serum tocopherol.

3. Data-entry
    a. Project 2:
        i. Data-entry completed for Arsenic Cohort follow up 2 subjects. 11,619 were questionnaires entered.
        ii. 3,145 new baseline questionnaires have been added to our database since October, 2006 bringing the current total number of participants in the Arsenic study database to 14,891. Data-entry is continuing for this effort.
    b. Project 3
        i. Home questionnaires and WASI, Bruininks and Wisc exams have been piloted in Bangladesh. The paper copies of these questionnaires and tests were sent to New York where data-entry occurred. Currently 73 home questionnaires have been entered. Test entries include: 56 Wasi (28 each of observer and participant), 182 Bruininks (91 each of observer and participant) and 18 WISC (9 each of observer and participant).
4. Maintenance of secure database and web servers has continued. Projects 2, 3 and 4 are the direct beneficiaries of these services.
5. Ongoing creation of targeted datasets has occurred; data have been distributed to PIs for projects 2, 3 and 4.
6. Management of data flow continues using the Issue Tracking System and the Query Tracking Systems.

**Core B: *Trace Metals Core Laboratory***
**PI: Joseph Graziano**
Laboratory Director: Vesna Slavkovich

The primary purpose of the Trace Metals Core Laboratory is to provide Center investigators with the capability to obtain analyses of biological samples for a broad array of metals. In addition, the facility provides method development for these analyses, standardization, and quality control.

During the past year, we conducted more than 15,000 "routine" analyses of biological samples from projects 2, 3 and 4. Last year, this lab developed two new analytical methods that have since led to significant research breakthroughs. Until now, the measurement of arsenic in blood samples has been considered to be of little value, since blood arsenic concentrations are exceedingly low and undetectable by conventional graphite furnace atomic absorption methods. Using ICP-MS-DRC, the Trace Metals lab developed a new method for arsenic in blood. Last year, working with Project #2, we demonstrated that blood arsenic is an extremely useful biomarker of arsenic exposure, and is strongly associated with water arsenic, urine arsenic, and skin lesion status (Hall et al, 2006). This year, this method has enabled Project #4 to discover that folic acid supplementation, to arsenic-exposed people, produces a significant decline in blood arsenic concentration (Gamble et al, 2007).

Given the potential utility of blood arsenic measurements in epidemiologic research, we are now devoting time to the development of a new blood arsenic method that could use tiny blood samples obtained by fingerstick. Epidemiologic studies employing repeated blood arsenic measurements over time have the potential to answer many issues concerning the bioavailability and toxicokinetics of arsenic. Yet people in the developing world are generally reluctant to give blood samples for research purposes. We believe that this new methodology will facilitate important new areas of investigation. The Columbia University IRB has approved a protocol that will enable us to test the validity and reproducibility of fingerstick/capillary tube blood arsenic measurements, as compared to measurements obtained from venous blood samples. Approval of this protocol by the Bangladesh Medical Research Council is pending.

Last year, this lab utilized a high pressure liquid chromatographic (HPLC) method in conjunction with ICP-MS-DRC to analyze the concentrations of arsenic metabolites in blood. This year, we published novel observations employing this new blood method. First, in Project #3, in a study of mother-cord pairs of samples, we discovered that blood contains much higher proportions of inorganic arsenic and monomethylarsenic (MMA), the more toxic species, than urine; this occurs because dimethylarsenic (DMA), the less toxic fully methylated form, is much more readily excreted by the kidney; this work was recently published in EHP (Hall et al, 2007). In addition, in Project #4, we discovered the decline in blood arsenic that occurs in response to folic acid treatment (mentioned above) is due almost entirely to a decline in blood MMA; this work was published in the American Journal of Nutrition in 2007, and received a great deal of attention and press coverage (Gamble, 2007). Collectively, these observations have enormous public health significance, and indicate that folic acid treatment may represent a new therapeutic modality for arsenic-exposed people.

**Students involved with this work**:

Marni Hall, a former Ph.D. student in Environnmental Health Sciences, Mailman School, and now employed at Pfizer.

J. Richard Pilsner, a former Ph.D. student in Environnmental Health Sciences, Mailman School, now a Robert Wood Johnson Fellow in the EHS Department at the University of Michigan.

Christine George, a new minority Ph.D. student who has a degree in Environmental Engineering from Stanford University, who has developed the fingerstick blood arsenic method during her first lab rotation.

**Publications**: Virtually every publication listed for Projects 2, 3 and 4 has relied on the Trace Metal Core.

**References:**

Hall M, Gamble M, Slavkovich V, Liu X, Levy D, Cheng Z, van Geen A, Yunus M, Rahman M, Pilsner JR, Graziano J. Determinants of arsenic metabolism: blood arsenic metabolites, plasma folate, cobalamin, and homocysteine concentrations in maternal-newborn pairs. *Environ Health Perspect*. 2007;**115**(10):1503-9.

Gamble MV, Liu X, Slavkovich V, Pilsner JR, Ilievski V, Factor-Litvak P, Levy D, Alam S, Islam M, Parvez F, Ahsan H, Graziano JH. Folic acid supplementation lowers blood arsenic. *Am J Clin Nutr*. 2007;**86**(4):1202-9.

**Core C: *Biogeochemistry Core***
**PI: Alexander van Geen**
Co-investigators: Yan Zheng, Steve Chillrud, Brian Mailloux,
Outside collaborators: Benjamin Bostick (Dartmouth U.), John Stolz (Duquesne U.)

The Biogeochemical analytical core laboratory is housed at Lamont-Doherty Earth Observatory (LDEO). It provides sample preparation and analyses to six projects of the

Columbia Superfund program (biomedical projects 2, 3 and 4 and earth science projects 5, 6 and 7) and trains students and post-docs. Many of the publications and exciting new discoveries under these 6 projects are directly linked to contributions from this core. Sample preparation and analyses have been carried out by high-resolution inductively coupled plasma mass spectrometry for up to 33 elements for water, soil, sediment, leachate, and plant material (HR ICP-MS). In addition, subcontracts with two outside collaborators have boosted the core's capabilities in two new areas to include extended X-ray absorption fine structure spectroscopy (EXAFS) of aquifer particles for Fe and As and detailed characterization of bacterial species interacting with As using 16S rRNA techniques.

On behalf of biomedical projects 2, 3, 4 a total of 4200 new groundwater samples collected from Araihazar, Bangladesh, with support from project 7, have been analyzed by HR ICP-MS for As and Mn. In support of project 5, over 800 groundwater or sediment leachates collected in Maine and Bangladesh were analyzed by HR ICP-MS for As, Mn, U and additional constituents of potential geochemical interest or health concern. A total of 1100 groundwater and leachate samples for material collected from the Vineland Superfund sites were analyzed by HR ICP-MS on behalf of project 6. Finally, a total of 950 groundwater and sediment leachate samples from Araihazar, Bangladesh, and other regions affected by arsenic have been analyzed by HR ICP-MS on behalf of project 7.

On the microbial side, we have been performing molecular studies to understand the effect of elevated arsenic concentrations on the microbial ecology of the subsurface. Interestingly, we have found that the arsenic reductase gene, arrA, is present in only small concentrations and is non-detectable at many locations. This is in direct contrast to other environments such as Mono Lake where arrA is thought to be the driver of arsenic cycling. Instead, we observe a diverse population of microbes with the arsenical compound resistance acr3, gene. This gene is at best poorly studied in the environment yet our results indicate it may be important in arsenic cycling. Our initial studies have focused on the Vineland Superfund site but we are observing patterns in Union Lake, downstream of the Vineland Superfund site, and potentially in the shallow aquifers of Bangladesh.

Recent analysis has shown that methane and arsenic are correlated in the shallow aquifer in Bangladesh. Analysis of mcrA a functional gene required in the terminal step of methane production indicates a divers and unique microbial population. Interestingly, quantitative PCR indicates that the concentrations of arsenic and mcrA are not correlated. We hypothesize that methane is an indicator of overall microbial activity and that this is another indicator that ancillary arsenic release is an important mechanism.

We have performed laboratory experiments and analysis of Bangladesh sediments that indicate a novel arsenic release mechanism, we have termed ancillary arsenic release may be the primary arsenic mobilization mechanism in Bangladesh. We show that phosphate-limited cells of *Burkholderia fungorum* mobilize ancillary arsenic from apatite as a by-product of mineral weathering for nutrient acquisition. The rate of arsenic release is independent of the initial arsenic concentration. We also demonstrate the presence of the same phenotype in Bangladesh sediments. These results suggest that microbial weathering for nutrient acquisition could be an important mechanism for arsenic mobilization under a wide range of conditions.

**Submitted Manuscripts:**

Mailloux, B. J., Alexandrova, E., Keimowitz, A., Wovkulich, K., Freyer, G., Herron, M. M., Stolz, J. F., Kenna, T., and Pichler, T., 2007. Microbial Mineral Weathering for Nutrient Acquisition Releases Arsenic. Appl. Environ. Microbiol. SUBMITTED.

**Students supported in part by the Biogeochemistry Core over the past year**
Peter Wagner. Undergraduate, Columbia University
Jared Fox, Frederick Douglass Academy III in the south Bronx. This past summer as a part of Columbia University's Science Teacher Research Program
Sasha Sasha Harbajan George Washington Carver High School Harlem Children Society. www.harlemchildrensociety.org.
Rachel Foster, Post-doc Lamont Doherty Earth Observatory
Ekaterina Alexandrova, Undergdraduate, Barnard College
Elizabeth Trembath-Reichert, Undergraduate, Barnard College

**Core D: *Hydrogeology Support Laboratory***
**PI: Martin Stute**
Co-Investigators: Peter Schlosser, Juerg Matter, Steve Chillrud

The Hydrogeology Support Core provides information on the groundwater and surface water flow and transport regime at our field sites in the US and Bangladesh, and supports projects number 5, 6, and 7, as well as the RTC.

**Notable advances for the last period**

**Field efforts** This year's focus of the hydrogeology support laboratory has been to instrument a ~2 $km^2$ site in Araihazar, Bangladesh (project 5). Our goal at this site (K) is to track the geochemical evolution of groundwater from recharge to discharge area. We have installed 10 wells, completed three of them as multi level well nests, and instrumented the wells with pressure transducers and temperature data loggers. We performed slug tests, pumping tests, and other hydraulic measurements on wells at two sites (K and X). We built two automated stations that monitor water levels in the near-by stream. We also set up an automated weather station, which unfortunately was lost in the cyclone Sidr this November.
In preparation for a series of push/pull experiments (project 7) planned for a remote site in Bangladesh (I) to study the effects of intrusion of shallow groundwater into the deeper, low arsenic aquifer, a tracer experiment was successfully conducted in March. 97 percent of the tracer injected into the aquifer was recovered in the pumping phase.

**Sample Measurements** We performed 14 noble gas measurements on ground water samples collected at site K in Bangladesh and 40 stable isotope ($^{18}O$ and $^{2}H$) analyses on precipitation and groundwater (projects 5 & 7). In order to better understand recharge mechanism in the area of study, soil gas profiles were obtained at 3 sites in March and May.

**Modeling** Core personnel supported groundwater flow modeling activities using the codes MODFLOW and MODPATH at site 'X' in Bangladesh (projects 5 & 7) with the goal to quantify the groundwater/surface water interactions. With support of the Philadelphia office of ACE, an MT3D model was developed that allowed us to design a forced gradient experiment at the Vineland Superfund site to evaluate enhanced arsenic removal by amendment with oxalic acid (project 6).

**Instrument development** We continued testing of a prototype of a novel sampler for gases dissolved in groundwater. This sampler separates gases from the water in the field with a membrane and potentially considerably simplifies the transport of the samples to the lab and the measurement by gas chromatographs and mass spectrometers (projects 5-7).

All publications in Projects 5, 6, and 7 have been supported by the Hydrogeology Core.

2007 Abstracts supported by the core:

Alexander, P, Loose, B, and Stute, M. (2007) A portable membrane-based gas sampler for gases Dissolved in Groundwater, Eos Trans. AGU, 88(52), Fall Meet. Suppl., Abstract H11C-0680.

Radloff K.A., Zheng, Y., Stute, M., Matter, J., Aziz, Z. , Rahman, M.M., Huq, M.R, Chowdury, T., Ahmed, K.M., and van Geen, A. Influence of Groundwater Flow on As Distribution in Shallow Aquifers. Poster at the annual Superfund Basic Research Program Meeting. Durham, N.C., 2007.

Wovkulich, K., M. Stute, H.J. Simpson, B. Mailloux, A. Lacko, A. Keimowitz, Z. Cheng, S. Chillrud. Mobilization of Arsenic from Contaminated Sediments for Improved Remediation. Poster at the annual Superfund Basic Research Program Meeting. Durham, N.C., 2007.

Wovkulich, K., H.J. Simpson, M. Stute, B. Mailloux, A. Keimowitz, Z. Cheng, S. Chillrud. Improving Arsenic Remediation Through Chemistry: Laboratory and Modeling Data for a Superfund Site Highly Contaminated with Arsenic (Vineland, NJ). Oral presentation at the annual Superfund Basic Research Program Meeting. Durham, N.C., 2007.

**Research Translation Core: *Collaborating with Government & the Public: As & Mn Exposure via Groundwater***

**Co-PIs: H. James Simpson, Meredith L. Golden**

Co-investigators: Joseph Graziano, Mark Becker, Martin Stute, Steve Chillrud, Yan Zheng, Alexander van Geen

Columbia University SBRP Research Translation Core central theme, *Collaborating with Government & the Public: As & Mn Exposure via Groundwater*, focuses on working with selected governmental agencies to minimize human exposure to arsenic, manganese, and other contaminants through domestic water supplies derived primarily from groundwater.

CU-RTC activities encompass four states: New York, New Jersey, New Hampshire, and Maine. In NY, Columbia with NYSDEC Region 3 is evaluating older landfills as potential sources of elevated As and Mn in groundwater. CU-RTC scientists are collaborating with Rockland County Legislature and DOH, USGS-NY (Paul Heisig), and United Water New York to develop effective strategies to address current and future public water supply/quality issues, including arsenic and manganese contamination. At the Vineland Superfund Site in NJ, CU-RTC is assisting in the modification of well maintenance protocols. In ME, we have partnered with the ME Geological Survey, ME DOH, and the USGS (Charles Culbertson). Part of our work with the USGS in ME has been to develop sampling strategies and methodologies plus a real time As monitoring device. In ME and NH, our researchers have made presentations to schools and communities on the effects of arsenic exposure on cognitive and motor functioning in children. Our geospatial specialists have helped visualize the potential for exposure to arsenic and manganese by integrating physical geography (hydrology, surface and bedrock geology, topography, land use/land cover, and aerial photography), with USGS arsenic data for NY and New England, NYSDEC Region 3 inactive landfill locations, and well data from UWNY and RCDOH.

CU-RTC scientists' involvement with arsenic in groundwater in Rockland County exemplifies how SBRP programs can assist governmental agencies, private companies, and the general public in addressing complex environmental health issues. When UWNY disclosed in 2007 that two Rockland wells had exceeded EPA's annual average arsenic MCL, RC Legislature Environmental Committee responded to public concern convening several special sessions, with presentations by United Water, RCDOH, USGS-NY, and Columbia SBRP. CU-

RTC scientists submitted a Letter-to-the-Editor translating available science. The RCDOH utilized our expertise on geophysical processes and biomedical mechanisms to develop appropriate health messages. CU-RTC also assisted USGS with analyzing well water for the Rockland Water Assessment using state-of-the-art equipment/techniques at CU-SBRP core labs. UWNY has proposed a MOA including Columbia to conduct the “Arsenic Study Report”. CU-RTC now partners with RC, NYS, UWNY and public interests to develop long-term strategies to monitor and assess water quality and supply.

Overall, our RTC provides the framework for sustained communication among research projects, cores, governmental agencies, and interested parties through monthly seminars, CU-SBRP website, and focused meetings. Columbia SBRP seminars offer presentations on biomedical and geoscience topics by our own scientists and visitors. Other events have included: Columbia/University of Dhaka/UNDP Symposium: New Findings Concerning the Health Effects and Geochemistry of Arsenic; Arsenic in Drinking Water Exhibit at Lamont Open House; workshops on As at Siemens Science Day at CU; and panel discussions as part of the Margaret Mead Film Festival at the American Museum of Natural History.

Publications:

Parisio, S., A.R. Keimowitz, H.J. Simpson, A. Lent and V. Blackman. Arsenic-rich iron floc deposits in seeps downgradient of solid waste landfills, Soil & Sediment Contamination 15: 443-453, 2006.

Keimowitz, A.R., B. J. Mailloux, P. Cole, M. Stute, H.J. Simpson and S.N. Chillrud. Laboratory investigations of enhanced sulfate reduction as a groundwater arsenic remediation strategy. Environmental Science & Technology 41: 6718-6724, 2007.

Graziano, J., S. Chillrud, H.J. Simpson, M. Golden, and others at LDEO. Local health risks from arsenic appear ‘vanishingly’ small. The Journal News, a Gannett Co (Westchester, Rockland and Putnam Counties, NY), Editorial Section, March 8, 2007.

Chillrud, S., A. Keimowitz, K Wovkulich, H.J. Simpson, J. Ross, M. Stute and S. Parisio. Older landfills & arsenic: Can triage assessments help focus limited resources? Federation of NY Solid Waste Associations Solid Waste/Recycling Conference – Landfills & Water Quality Session, May 6-9, 2007 (abstract and oral presentation).

**Training Core**
**PI: Paul Brandt-Rauf**

The Training Core continued its Workshop Program with a week-long, all-day workshop on “EPA Lead Paint Inspection and Risk Assessment” given by Dr. Marco Pedone, an expert on hazardous waste management. In addition to covering the didactic requirements for EPA training in this area, the workshop included hands-on exercises on the evaluation of lead paint hazards. Besides the monthly Superfund Seminar Series, the Training Core also participated in the Annual Granville H. Sewell Distinguished Lecture in Environmental Health Sciences which this year featured Professor Wallace Broecker from Columbia’s Lamont-Doherty Earth Observatory speaking on “What Should We Do about Fossil Fuel $CO_{2?}$” concerning the challenges and possible solutions for global climate change. In addition, the Training Core continued to offer trainees participation in a web-based course on “Hazardous Waste and Public Health” during the summer semester which can be done by anyone with a computer and internet access from any location and which has proven highly successful in past years. The course includes practical case studies in managing hazardous waste issues as problem-solving exercises for the participants. Finally, an environmental justice field trip visiting local environmental hazards in the New York City area (“Toxics and Treasures Tour”) is planned under the auspices of West Harlem Environmental Action, one of our community partners.

**Patent Updates:**

None

**Superfund Site Updates:**

The Joplin, MO and Ottawa County, OK  sites have been removed and the attached list is updated.

**Contact Information Updates:**

Updated in the attached file.

**Student Information Updates:**

Embedded within test and also updated in attached excel file.