Columbia University Superfund Basic Research Program
Annual Project and Core Updates – 2009

Health Effects and Geochemistry of Arsenic and Manganese

Director: Joseph H. Graziano

Deputy Director: Alexander van Geen

Highlight #1 - (Project #2): *A prospective study of arsenic exposure from drinking water and incidence of skin lesions in Bangladesh*

Chronic arsenic exposure through drinking water is a growing public health issue affecting millions of people worldwide, including 35 to 77 million in Bangladesh alone. Skin lesions are early manifestations of toxicity to chronic arsenic exposure. The authors evaluated the association between arsenic exposure and skin lesion incidence among 10,182 adults in the Health Effects of Arsenic Longitudinal Study (HEALS), Araihazar, Bangladesh, using data through the third biennial follow-up of the cohort (2000–2009). HEALS was established as part of the Columbia NIEHS-funded Superfund Research Program and provides an invaluable opportunity to investigate the association between arsenic exposure and skin lesion incidence using a prospective design and repeated individual-level assessments of arsenic exposure. Arsenic exposure was measured by individual-level well water and urinary total arsenic concentrations as well as average daily arsenic intake. Discrete time hazard regression models were used to estimate discrete time hazard ratios (HRs) and their 95% confidence intervals (CIs). Compared with individuals consuming well water containing ≤10 µg/L of arsenic at baseline, consuming well water containing 10.1–50.0, 50.1–100.0, 100.1–200.0, and ≥200.1 µg/L of arsenic was associated with sex- and age-adjusted HRs for incident skin lesions of 1.18 (95% CI: 0.93, 1.51), 1.72 (95% CI: 1.35, 2.19), 2.03 (95% CI: 1.62, 2.55), and 3.08 (95% CI: 2.47, 3.85), respectively. Results were similar with the other measures of arsenic exposure. These findings suggest that arsenic exposure is associated with increased incidence of skin lesions, even at low levels of arsenic exposure. Utilizing repeated measures of creatinine-adjusted urinary total arsenic concentration for all cohort members (at baseline and every 2 years), we found that chronic long-term exposure to arsenic (captured at the baseline assessment of exposure) was a more important predictor of skin lesion risk than subsequent short-term changes in exposure (captured at the follow-up visits).

Utilizing six-years of follow-up data from the HEALS cohort, Dr. Ahsan and his colleagues have shown an increased incidence of skin lesions associated with arsenic exposure in a dose-dependent manner. The effect of arsenic exposure on the risk of skin lesions was observed even at the low end of well water arsenic exposure in this population (10.1–100 µg/L). The findings of this study have important public health implications. Prior epidemiologic research has examined the prevalence of skin lesions with arsenic concentrations. This is the first large study to examine the association of arsenic exposure with skin lesion *incidence*. Secondly, 24% of the cohort in the analysis had well water arsenic concentrations less than 10 µg/L and 46% less than 50 µg/L, which makes the exposure levels comparable to other populations that have low level arsenic exposure.

In conclusion, we found that arsenic exposure through drinking water was associated with increased risk of skin lesion incidence, even at water concentrations less than 100 µg/L. Because prior studies have not been sufficiently powered to evaluate skin lesion risk at low levels of arsenic exposure, this work provides important evidence for arsenic toxicity and potential carcinogenic effects at low exposure levels. Additionally, we saw persistent increased risk of skin lesions even among individuals who had reduced their arsenic exposure, which suggests that future chemoprevention interventions should be considered in conjunction with remediation of exposed populations to reduce future cancer risks.

Highlight #2 - (Project #6): ***Strategies for accelerating pump and treat remediation at 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 sites with groundwater contamination, with more than 900 pump and treat 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 need many years to reach desired clean up levels and have high annual costs.

The Vineland Chemical Company located in southern NJ manufactured arsenic-based herbicides and for decades they improperly stored and disposed of their arsenic chemicals. 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 (handling up to 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 a factor of 10. However, several more years of pump and treat as well as remediation efforts focused on excavation, cleaning, and replacing contaminated unsaturated zone soils have led to relatively minor additional improvements in groundwater arsenic levels, which can still be several hundred µg/L. Since the sandy aquifer solids can be elevated in arsenic, they represent a large reservoir, $\sim 10^5$ kilograms of arsenic, for continued groundwater contamination.

Advances: Columbia University scientists hypothesized that the time frame for remediating arsenic contaminated aquifers via pump and treat could be substantially decreased 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 removed from the aquifer with each volume of water pumped out and treated. The scientists have combined laboratory experiments, hydrological modeling, and field studies to evaluate the efficacy of chemical amendments for mobilizing arsenic from aquifer solids. The most promising chemical amendment has been oxalic acid. Oxalic acid is a natural soil acid often responsible for dissolving and transporting iron and aluminum oxides in unsaturated zone soils; these oxide phases are also important on aquifer mineral surfaces.

Laboratory column experiments using arsenic-contaminated aquifer solids (~80 ppm arsenic) from Vineland suggest that oxalic acid can be effective at significantly increasing arsenic mobility compared to groundwater alone. Greater than 85% of the arsenic was removed from the aquifer solids with a 10 mM oxalic acid treatment, while only 5% was released with groundwater alone. 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 ~4 years with 10 mM oxalic acid, based on the clean up goal of lowering the arsenic on the aquifer solids to less than 20 mg/kg.

During 2008 and 2009, Columbia scientists carried out modeling and *in situ* field experiments using tracers and subsurface chemical amendments to build on these laboratory results. Modeling groundwater flow and transport at the site helped design optimal locations for injection and observation wells within the cone of depression near a site pump and treat well, in addition to constraining amendment and tracer concentrations, injection rates and pumping rates for these experiments. In 2009, oxalic acid and two tracers (bromide and SF_6) were injected into a small portion ($\sim 50\ m^2$) of the Vineland site. Groundwater samples indicate that introduction of oxalic acid led to increased arsenic release at an observation well and the nearby pump and treat recovery well. The total amount of arsenic recovered from the two wells was ~3 kg, similar in magnitude to the amount of contaminant arsenic within the pilot study area.

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. Future work will investigate issues related to scaling the chemical additions to the full site.

Significance: Chemical amendments show promise for decreasing 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 traditional pump and treat technologies can be quite expensive. A 2003 survey of annual operation and maintenance costs at pump and treat sites 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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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 determined if long term arsenic treatment of human epithelial cells will result in genomic instability, an indicator of neoplastic potential. Human telomerase immortalized human small airway epithelial cells were treated with graded doses of sodium arsenite for time periods ranging from 24 hours to 48 weeks. A 4.8 fold increase in micronuclei incidence in arsenic treated cells, relative to untreated and comparably propagated cultures, was detected. Using resistance to the chemotherapeutic agent PALA as an index of genomic instability due to the amplification of the CAD gene, we found that long term, low dose arsenic treatment resulted in a 10^3 fold increase in PALA resistance frequency. Taken together, these results strongly suggest that arsenic induces genomic instability in mammalian cells and may provide a mechanism for arsenic induced human cancer.

Our previous studies have shown arsenic to be an efficient inducer of apoptosis in human melanomas. In the present study, we demonstrated that arsenite induced upregulation of TRAIL-R2/DR5 surface expression, but suppressed expression of anti-apoptotic cFLIP (the main inhibitor of caspase-8) and Bcl-xL to promote apoptosis in DR5-positive melanomas. Hence, the primary up-regulation of DR5 surface expression and subsequent down-regulation of anti-apoptotic cFLIP and Bcl-xL (due to arsenite treatment) appear to be an efficient mechanism to recover apoptotic death pathway in TRAIL-resistant melanomas. Furthermore, we showed that suppression of the upstream ATM activity or the downstream STAT3 dramatically increased the sensitivity of melanoma cells to TRAIL-induced death signaling and apoptosis that was correlated with substantial decrease in the melanoma xenotransplant growth in nude mice. Taken together, our results established a molecular mechanism for TRAIL-mediated apoptosis by sodium arsenite.

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 resume our studies on 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 both mitochondrial mediated and non-mitochondrial associated signaling pathways in regulating cell survival and apoptosis in normal and cancer cells.

Project 1-Supported Publications, in 2009:

Partridge, MA, Huang, SX, Kibriya, MG, Ahsan, H, Davidson, M and Hei, TK. Environmental mutagens induced transversions but not translations in regulatory region of mitochondrial DNA. *J. Toxicology & Environmental Health* 2009;**72**:301-4..

Wen, GY, Partridge, MA, Calaf, M, Meador, J, Hu, B, Chau-Echiburu, C, Hong, M, and Hei, TK. Increased susceptibility of human small airway epithelial cells to apoptosis after long term arsenate treatment. *Sci Total Environ.* 2009;**407**:1174-81.

Ivanov, VN, Zhou, H, Partridge, MA, and Hei, TK. Inhibition of ATM kinase activity enhanced TRAIL-mediated apoptosis in human melanoma cells. *Cancer Res.,* 2009;**69**:3510-9.

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. Between 2006 and 2008, the cohort was expanded to 20,033 individuals. Expansion participants were enrolled into the cohort through in-person interviews and had blood and urine samples collected in the same manner as the original cohort. 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 adverse health effects, including prevalent skin lesion cases (Ahsan, Chen et al. 2007; Argos, Parvez et al. 2007; Chen, Hall et al. 2007; Heck, Chen et al. 2008; Parvez, Chen et al. 2008) and are currently conducting longitudinal analyses of mortality and incident skin lesions with the prospective data.

In-person interviews and clinical examinations of the cohort participants are conducted every 2 years. In our previous progress report, we provided a preliminary summary of the six-year follow-up visit of the original cohort. The six-year follow-up visit of the original cohort was completed in February 2009. The questionnaires have been checked and data entry has been completed. The two-year follow-up visit of the expansion cohort was complete in October 2009. The questionnaires have been checked and data entry is in progress. The eight-year follow-up visit of the original cohort and 4-year follow-up visit of the expansion cohort is scheduled to begin in January 2010.

Utilizing the data collected from the first three follow-up visits (2-, 4-, and 6-year visits) of the original cohort, our prospective analyses based on individual-level data clearly suggest *increased mortality in relation to increases in arsenic exposure* based on water and urinary arsenic. Additionally, we utilized the prospective data through 6-years of follow-up to assess skin lesion incidence and observed a clear dose-dependent association between arsenic exposure and skin lesion risk, even at low exposure levels (water arsenic concentration <100 µg/L). Both manuscripts have been drafted and are currently under review.

The objectives of our current analyses and the follow-up interviews are to specifically examine the aims stated in the renewal of this project and have not been modified since the last progress report. Several other manuscripts are being drafted for publication reporting results of our prospective cohort analyses of modification of the effects of arsenic on mortality and incidence of skin lesions.

In addition to the above-mentioned components, resources from this prospective cohort study have also yielded many other ancillary studies and publications including three additional R01 grants from NIH to investigate the genetic and nutritional aspects as well as chemoprevention of arsenic health effects.

Project 2 - Supported Publications, in 2009:

Chen Y, Parvez F, Gamble M, Islam T, Ahmed A, Argos M, Graziano JH, Ahsan H. "Arsenic exposure at low-to-moderate levels and skin lesions, arsenic metabolism, neurological functions, and biomarkers for respiratory and cardiovascular diseases: review of recent findings from the Health Effects of Arsenic Longitudinal Study (HEALS) in Bangladesh." *Toxicol Appl Pharmacol* 2009;**239(2)**:184-92. PMID: 19371619.

Pierce BL, Kalra T, Argos M, Parvez F, Chen Y, Islam T, Ahmed A, Hasan R, Rakibuz-Zaman M, Graziano J, Rathouz PJ, Ahsan H. “A prospective study of body mass index and mortality in Bangladesh.” *Int J Epidemiol* (In press), 2009.

Project 2 - Supported submissions, in 2009:

Argos M, Rathouz PJ, Pierce BL, Kalra T, Chen Y, Parvez F, Slavkovich V, Ahsan H. “Dietary B vitamin group intakes and urinary total arsenic concentration in the Health Effects of Arsenic Longitudinal Study (HEALS) cohort, Bangladesh.” Under Review (2009).

Argos M, Kalra T, Rathouz PJ, Chen Y, Pierce B, Islam T, Ahmed A, Hassan R, Parvez F, Graziano J, Ahsan H. “A Prospective Study of Arsenic Exposure from Drinking Water and Incidence of Skin Lesions in Bangladesh.” Under Review (2009).

Kalra T, Argos M, Rathouz PJ, Chen Y, Pierce B, Parvez F, Islam T, Ahmed A, Rakibuz-Zaman M*,* Hasan R, Graziano J, Ahsan H. “A Prospective Cohort Study of Arsenic Exposure from Drinking Water and All-cause and Chronic Disease Mortality in Bangladesh.” Under Review (2009).

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

This project builds upon our discovery that arsenic (As) and manganese (Mn) exposure from drinking water have adverse effects on intelligence in children. Two studies, in Bangladesh and New England, are in progress. Three years ago we launched a study of elementary school children in New Hampshire to determine whether exposure to As impairs intellectual functioning in a U.S. population. Because recruitment in New Hampshire was not proceeding at a sufficient rate, we expanded our study into Maine where recruitment is excellent and As exposure is more prevalent. To date, 157 children have been recruited and completed the protocol.

Of the 128 children for whom laboratory analyses are complete, 55 had water As levels great than the EPA standard of 10 ppb. Child IQ scores range from 83-140. Thus far, the mean IQ of those with water As < 10 ppb is 108, while the mean for those with water As > 10 ppb is 104. These very preliminary analyses are not conclusive, as we must still employ appropriate regression modeling to determine if there is a significant relationship between As exposure and child IQ.

The second portion of this project takes place in Bangladesh, where our research seeks to determine whether exposure to As and Mn has an adverse effect on motor function and on intelligence. This study involves a 2 x 2 design, i.e., high/low drinking water As and high/low water Mn, with 75 children in each cell. We have completed the recruitment of all 300 children, 7-9 years of age, and all environmental and biological analyses have been completed and entered. Regression analyses are under way and indicate that urinary arsenic is associated with a reduction of Verbal Comprehension, Working Memory, and the WISC Full Scale raw scores. Blood As and blood Mn lowered Working Memory scores, while blood Mn also reduced Perceptual Reasoning and Full Scale scores. A surprise finding has been that blood selenium (Se) concentrations are very strongly and positively associated with motor function, i.e., Fine Manual Control, Manual Coordination, and the Total Motor Function Score (Bruininks Test). All of these new findings are being written up for publication in several manuscripts.

The next phase of the Bangladesh work involves remediation of the ongoing As and Mn exposures via the installation of deep tube wells in each child’s village by our earth science investigators (Project #7). We will reassess motor function and intelligence over time to determine whether the consequences of exposure are reversible. The installation of deep wells had been delayed due to bureaucratic issues, but these have been resolved and a contract has been signed between Columbia University and Water Aid Bangladesh, a highly reputable NGO, to launch this work. Drs. Graziano and van Geen are meeting with Water Aid officials in Dhaka next week to resolve the final placement of the first 50 wells. This phase of our work will not only lower the As and Mn exposure of children in our study, but in thousands of neighborhood residents as well.

Student Involvement:

Christine George, Dr. Graziano's PhD student, is deriving her dissertation from the Bangladesh portion of this project.

Lauden Behrouz is deriving her MPH dissertation in Epidemiology from this project.

Khalid Khan, is a Bangladeshi DrPH student in EHS who is supported by our Fogarty Training Grant. Under the PI's direction, he is conducting an assessment of the impact of a school-based As education program in Araihazar, Bangladesh, in reducing As exposure. He has worked extensively with school teachers, administrators and elementary school students during the past year.

Project 3-Supported Publications, in 2009:

There have been no publications from project #3 during the past year, though the PI has been a co-author of 5 other publications derived from projects #2 and #4. This is due to the fact that we have been conducting field work throughout the year. We anticipate, however, that the fruits of that fieldwork, and the ongoing statistical analyses, will very soon yield a series of novel findings and publications concerning the effects of As and Mn exposure in children. Manuscripts in progress include:

Wasserman, G, Liu, X, Parvez, F, Siddiqui, S, Factor-Litvak, P, Kline, J, van Geen, A, Slavkovich, V, LoIacono, N, Levy, D, Graziano, JH. Adverse associations of arsenic and manganese exposure with child intelligence in 7-9 year old children in Bangladesh. In preparation.

Wasserman, G, Liu, X, Parvez, F, Siddiqui, S, Factor-Litvak, P, Kline, J, van Geen, A, Slavkovich, V, LoIacono, N, Levy, D, Graziano, JH. Positive associations between blood selenium and motor function in 7-9 year old children in Bangladesh. In preparation.

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

Nutritional status may account for some of the considerable variability in progression from arsenic (As) exposure to manifestations of disease. Methylation of ingested inorganic As (InAs) to methylarsonic- (MMA) and dimethylarsinic acids (DMA) relies on folate-dependent one carbon metabolism and facilitates urinary As elimination. Our SBRP project builds upon our Nutritional Influences on As Toxicity (NIAT) studies which demonstrated that folic acid supplementation increases As methylation and lowers blood As and blood MMA concentrations.

The first aim utilizes the repository of biological samples (from Project #2) to conduct a nested case-control study. We tested the hypothesis that at the time of enrollment, participants who subsequently developed As-induced skin lesions (SLs) had lower folate and/or higher homocysteine as compared to non-skin lesion controls; we also analyzed genomic methylation of leukocyte DNA. The odds ratios (95% C.I.s) for subsequent development of SLs for participants who had low folate, high Hcys, or hypomethylated PBL-DNA 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, indicating that folate deficiency, hyperhomocysteinemia, and hypomethylation of genomic DNA are risk factors for As-induced skin lesions.

In this same study, we also proposed to analyze biomarkers of oxidative stress. Analyses of urinary 8-hydroxy-2'-deoxyguanosine suggest that this biomarker is not associated with risk for skin lesions. Additional biomarkers will include malondialdehyde and protein carbonyls.

For the second aim, we proposed to examine the extent to which urinary As metabolites reflect As metabolites in blood in Bangladeshi adults. The Spearman correlations between As in blood and urine ranged from 0.68 to 0.81 ($p < 0.0001$ for all metabolites). However, when the As metabolites were expressed as a percentage of total As, the correlations were less strong (0.32 – 0.44; $p < 0.001$). Most striking were the differences in %MMA (13% in urine vs. 40% in blood) and %DMA (72% in urine vs. 34% in blood), consistent with a short circulating half-life of DMA which is rapidly excreted in urine. These findings suggest that studies analyzing As metabolites in urine have more limitations than previously believed.

Fieldwork for aims 3 and 4 began in January 2008. All 375 participants have been enrolled, and baseline biological samples have been analyzed for reduced and oxidized glutathione. Preliminary data suggest that As exposure is associated with decreased concentrations of reduced glutathione (GSH) in whole blood and increased concentrations of oxidized glutathione (GSSG) in plasma in a dose-dependent fashion. These data are consistent with the hypothesis that As exposure is associated with depletion of glutathione. Since GSH is the body's primary antioxidant, this would be expected to be associated with increased oxidative stress. Other measures of oxidative stress that are currently being evaluated for this aim include malondialdehyde, protein carbonyls and urinary 8-hydroxy-2'-deoxyguanosine.

Project 4-Supported Publications, in 2009:

Hall MN, Liu X, Slavkovich V, Ilievski V, Pilsner JR, Alam S, Factor-Litvak P, Graziano JH, Gamble MV. Folate, Cobalamin, Cysteine, Homocysteine, and Arsenic Metabolism among Children in Bangladesh. *Environ Health Perspect* 2009;**117**(5):825-31.

Pilsner JR, Liu X, Ahsan H, Ilievski V, Slavkovich V, Levy D, Factor-Litvak P, Graziano JH, Gamble MV. Folate deficiency, hyperhomocysteinemia, low urinary creatinine and hypomethylation of leukocyte DNA are risk factors for arsenic-induced skin lesions. *Environ Health Perspect* 2009;**117**(2):254-60. PMCID:PMC2649228

Chen Y, Parvez F, Gamble M, Islam T, Ahmed A, Argos M, Graziano JH, and Ahsan H. Arsenic exposure at low-to-moderate levels and skin lesions, arsenic metabolism, neurological functions, and biomarkers for respiratory and cardiovascular diseases: review of recent findings from the Health Effects of Arsenic Longitudinal Study (HEALS) in Bangladesh. *Toxicol. Applied Pharmacol*, 2009;**239**(2):184-92.

Hall MN, Liu X, Slavkovich V, Ilievski V, Mi Z, Alam S, Factor-Litvak P, Ahsan H, Graziano JH, and Gamble MV. Influence of Cobalamin on Arsenic Metabolism in Bangladesh, *Environ Health Perspect*, 2009;**117**(11):1724-29.

Project 4-Supported Publications submitted, in 2009:

Pilsner JR, Hall M, Liu X, Ahsan G, Ilievski V, Slavkovich V, Levy D, Factor-Litvak P, Graziano JH and Gamble MV. The Influence of Selenium Nutritional Status on Blood and Urinary Arsenic Concentrations, Arsenic Methylation, and Genomic Methylation of Leukocyte DNA. Environ Health Perspect (submitted).

Pilsner JR, Liu X, Hall M, Rahman M, Factor-Litvak P, Graziano JH, and Gamble MV. Influence of maternal arsenic exposure on genomic DNA methylation in maternal-newborn pairs. (manuscript in preparation).

Pilsner JR, Liu X, Ahsan H, Ilievski V, Slavkovich V, Levy D, Factor-Litvak P, Graziano JH, Gamble MV. Influence of folic acid supplementation on DNA methylation in Bangladeshi adults. (manuscript in preparation).

Project 5: ***Mobilization of Natural Arsenic in Groundwater***
PI: Yan Zheng
Co-Investigators: Martin Stute, and Alexander van Geen

We continued field campaigns in Bangladesh (Mar. 09, Oct. 09, and Jan. 10) and New England (Aug. 09) in the past year. We have also made progress to interpret the results from two large group experiments jointly with Project 7 and the Hydrogeology Core that assessed As mobility *in situ* in shallow and deep aquifers in Bangladesh.

Kinetics and Equilibrium of As mobilization: *in situ* and laboratory experiments

The partitioning of As between groundwater and sediment is hypothesized to be controlled by sorption equilibrium locally. This applies to the shallow aquifer where groundwater As is high because sediment As can be high and the affinity of As to reducing sediment is low, i.e., low partitioning coefficient (Kd) and also to the deep aquifer where groundwater As is low because sediment As is low and the affinity of As to oxidized sediment can be high (high Kd).

In the deeper, low-As aquifer, both batch and *in situ* experiments demonstrate that As(III) and As(V) sorption to sediment is fast. Kd's of the orange colored sand are high, with Langmuir isotherms indicating a sorption capacity between 35-40 mg/kg. Combined with groundwater transport modeling, this aquifer is shown to be a sustainable drinking water source.

In the shallow aquifer, both batch and *in situ* experiments demonstrate that adsorption and desorption of As(III) to sediment are also fast. The Kd of the mostly gray colored sand with variable grain size vary from 1-4 L/kg, with Langmuir isotherms with sorption capacity between 2-6 mg/kg. The results suggest that groundwater As concentrations are determined by the "upstream" groundwater concentrations and the local adsorption partitioning (Kd) of the sediment (Radloff et al., 2009).

Arsenic during Groundwater Discharge: Field, Laboratory and Modeling Study

During groundwater discharge along Meghna River in Bangladesh (Datta et al., 2009) and at the Waquoit Bay, MA, the partitioning of As between groundwater and sediment is also controlled by sorptive equilibrium (JUNG and ZHENG, submitted-b). High spatial density piezometers show that groundwater Fe and As showed systematic attenuation from well water to riverbank or bayside porewater, indicating trapping of As in a reactive barrier consisted of amorphous Fe-oxides determined by XAS (JUNG and ZHENG, submitted-a; JUNG et al., submitted). A reactive-transport model has successfully simulated the concentrations of groundwater As plume and the precipitated Fe-oxides at the redox interfaces by incorporating a semi-mechanistic surface-complexation model based on experimentally determined sorption isotherms (Jung et al., 2009).

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. A geostatistical analysis demonstrates for the first time that the bedrock geology controls the spatial pattern of As distribution at intermediate scale (10^0-10^1 km) relevant to community planning applicable to New England (YANG et al., 2009). The detailed hydrogeochemical study has focused our attention on two wells to illustrate the interactions between flow path and As concentrations in fractures using geophysical logging combined with fracture-specific water sampling.

Students and Post-docs whose research is supported completely or in part by Project 5:

Bethany O'Shea, Post-doc fellow, Columbia University Science Fellow
Hun Bok Jung, Ph.D., 2009, Earth and Environmental Sciences, City University of New York (CUNY). Currently post-doctoral research scientist at University of Wisconsin-Madison.
Kathleen A Radloff, 5^{th} yr PhD candidate, Earth and Environmental Engineering, Columbia
Qiang Yang, 4^{th} yr PhD candidate, Earth and Environmental Sciences, CUNY
Ivan Mihajlov, 2^{nd} yr PhD student, Earth and Environmental Sciences, Columbia
Rebecca Fried, MA student,Earth and Environmental Sciences Journalism, Columbia
Ashley MacLean, Undergraduate, Columbia College
Margaret Bounds, Undergraduate, Environmental Science, Barnard College
Hosea Siu, Intel-Westinghouse Contestant, Bronx High School of Sciences

Project 5-Supported Publications, in 2009:

Datta S, Mailloux B, Jung HB, Hoque MA, Stute M, Ahmed KM, and Zheng Y. Redox trapping of arsenic during groundwater discharge in sediments from the Meghna riverbank in Bangladesh. *Proceedings of the National Academy of Sciences* 2009;**106**(40):16930-5. PMCID: 2761342
Jung HB, Charette MA, and Zheng Y. Field, Laboratory, and Modeling Study of Reactive Transport of Groundwater Arsenic in a Coastal Aquifer. *Environmental Science & Technology* 2009;**43**(14):5333-8. PMCID: 2761342
Radloff, KA, Zheng, Y, Stute, M, Ahmed, KM, Schlosser, P, and van Geen, A. Effect of groundwater flow on dissolved As in a Bangladesh aquifer. *Geochimica Et Cosmochimica Acta* 2009;**73**:A1067-A1067.
Stute, M, Horneman, A, and Fried, R. Environmental tracers in hydrogeology: Principles, applications, and challenges. *Geochimica Et Cosmochimica Acta* 2009;**73**:A1287-A1287.
Yang Q., Jung H. B., Culbertson C. W., Marvinney R. G., Loiselle M. C., Locke D. B., Cheek H., Thibodeau H., and Zheng Y. (2009) Spatial Pattern of Groundwater Arsenic Occurrence and Association with Bedrock Geology in Greater Augusta, Maine. *Environmental Science & Technology* 2009;**43**(8):2714-9.

Project 5-Supported Publications submitted, in 2009:

He Y and Zheng Y. (submitted) Mass Balance Approach for Evaluation of Urinary Excretion of Arsenic Metabolites Before and After Rice Diet. *Science of the Total Environment*.
Jung HB and Zheng Y. (submitted-a) Fate of Arsenic during Groundwater Discharge to Meghna River Part II: Aqueous Geochemistry. *Geochimica Cosmochimica Acta*.
Jung HB and Zheng Y. (submitted-b) Mobility of Arsenic in Sediment from Meghna Riverbank, Bangladesh Evaluated by Sorption and Desorption Experiments. *Env. Sci. Tech.*

Jung HB, Zheng Y, Bostick B, Datta S, Rahman MW, Rahman MM, and Ahmed KM. (submitted) Fate of Arsenic during Groundwater Discharge to Meghna River Part I: Sediment Geochemistry. *Geochimica Cosmochimica Acta*.

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

Project 6 investigates the geochemistry and remediation of arsenic associated with the Vineland Superfund site in southern New Jersey. This involves work on the site of the former arsenic herbicide manufacturing facility as well as downstream at a recreational lake impacted by arsenic transport from the site. Due to decades of improper chemical storage and disposal by Vineland Chemical, the Vineland Superfund site was extensively contaminated with arsenic. Concentrations in unsaturated zone soils exceeded 500 ppm As and groundwater [As] exceeded 10,000 ppb prior to the start of treatment. Additionally, contaminated groundwater discharged to a small stream near the site, leading to offsite transport and impacts on the stream, river, and lake downstream. Despite nearly a decade of pump-and-treat remediation groundwater arsenic concentrations can still be several hundred µg/L.

Laboratory soil column experiments had suggested that the current aquifer clean-up strategy, relying on pump-and-treat to flush groundwater through the aquifer, could require hundreds of years before remediation is complete but that this timeframe could be decreased substantially (to <5 yrs) by introducing oxalic acid to the system. Our focus this year was evaluating the potential of chemical additions for increasing As release *in situ* and boosting the efficiency of pump and treat remediation of As. During spring/summer 2009 we conducted a pilot scale forced gradient study on site. A novel system for the injection of chemicals into multiple wells was developed, tested, and a pre-patent application for the device was filed. Oxalic acid and two tracers (bromide and SF_6) were injected into a small portion (~50 m^2) of the Vineland site during a three-month injection phase. Groundwater samples suggest that introduction of oxalic acid led to increased As release at an observation well and the nearby pump and treat recovery well. Approximately 3 kg of arsenic was released by the oxalic acid as monitored at these two wells, similar in magnitude to the amount of solid phase arsenic within the small pilot area. The addition of oxalic acid, therefore, shows promise for accelerating treatment of a highly contaminated site offering the potential to lower the As remediation time-scale.

Another remediation focus for the Vineland Superfund Site is Union Lake, Previous releases of arsenic from the Vineland Chemical Company Superfund site have contaminated the sediments of Union Lake. Field studies have been carried out over the last two summers to examine the effect of summertime eutrophication on the release of Arsenic from sediments and pore waters of Union Lake. Novel genetic sequences corresponding to putative arsenic reductase genes were detected at multiple depths and time points in the lake; however, the transient summertime anoxia allows only minor releases of arsenic from contaminated lake sediments despite the presence of these arsenic-cycling genes and consistent with redox buffering by sediment manganese. Releases of arsenic from the sediments or pore waters within the sediments are therefore relatively minor: bottom water arsenic concentrations reached ~30 ppb at most, representing <13% of the dissolved arsenic content of the lake.

Students and Postdocs involved in studies in 2009:
Alison Keimowitz, PhD 2005, Earth and Environmental Science, post doctoral fellow at Columbia University until July 2009, Currently Assistant Professor at Vassar College

Karen Wovkulich, 5th year graduate student, Earth and Environmental Science, Columbia University
Kamini Doobay, undergraduate, Environmental Sciences, Barnard College
Governmental agency staff we interact with on Vineland Superfund Site:
Ron Naman, EPA Region 2; Steve Creighton, USACE; Laura Bittner, USACE.

Project 6-Supported Publications, in 2009:

2009 Publications and meetings:

Wovkulich, K., M. Stute, T. Protus, B. Mailloux, S. Chillrud, Injection System for Multi-Well Injection Using a Single Pump, (submitted to Ground Water, Nov 2009).
Wovkulich, K., Mailloux, B. J., Lacko, A., Keimowitz, A. R., Stute, M., Simpson, H. J., Chillrud, S.N., "Chemical Treatments for Mobilizing Arsenic from Contaminated Aquifer Solids to Accelerate Remediation" (submitted to Applied Geochemistry Dec 2009).
Wovkulich, K., M. Stute, T. Protus, B. Mailloux, S. Chillrud, Design of an Inexpenseive Injection System as an Example of Technology Transfer from Working Directly at a Superfund Site, Poster at the annual Superfund Research Program Meeting, New York, NY, Nov 2009.
Wovkulich, K., M. Stute, B. Mailloux, A.R. Keimowitz, D. Ntarlagiannis, L. Slater, H.J. Simpson, S. Chillrud, Laboratory and Field Studies to Accelerate Arsenic Remediation at the Vineland Superfund Site, Presentation at the annual Superfund Research Program Meeting, New York, NY, Nov 2009.

Project 7: *Mitigation of Arsenic Mobilization in Groundwater*
PI: Alexander van Geen
Co-Investigators: Yan Zheng, Martin Stute.

Research carried out under this project in 2009 focused on 2 themes: (1) the vulnerability of low-As aquifers to intrusion of high-As groundwater, (2) As mitigation on behalf of biomedical studies in Araihazar. The activities have resulted in 2 published papers and 3 submissions.

(1) PhD student Kathleen Radloff has focused most of her effort this year on analyzing results from push-pull experiments and batch-equilibration experiments conducted in the field in the previous year in collaboration with Proj 5 and with support from Core C. In parallel, PhD student Ivan Mihajlov has conducted laboratory experiments under anaerobic conditions with columns of freshly collected orange sands from Bangladesh to independently measured the retardation of As under representative conditions. The overall conclusion of these experiments is that adsorption of As on orange-colored sands should protect deeper aquifers that are presently low in As for decades to centuries even if unfavorable hydrological conditions were to cause downward advection of shallow groundwater elevated in As. PhD student Zahid Aziz is wrapping up his studies of the distribution of As in very shallow aquifers with a combination of observations and hydrological modeling indicating that enhanced recharge due to irrigation pumping should reduce rather than increase the level of As contamination in groundwater. Such observations are likely to fuel the on-going debate between "sensationalists" claiming that human activities (irrigation pumping and, more recently, digging of ponds) have triggered the release of As to groundwater in Bangladesh and other groups, including ours, believing that As concentrations were elevated well before any likely human impact, even if certain activities may indeed already have modified the distribution of As in the subsurface.

(2) After yet another year of delay caused by various bureaucratic obstacles, a contract has finally been signed with a leading NGO, WaterAid Bangladesh, to install an initial 50 deep low-As wells in villages and schools of Araihazar. This intervention, launched in Dec 2009, will drastically reduce the exposure of several hundred adults and children enrolled in biomedical studies as well thousands more of their neighbors and classmates. As a back-up option in case deep wells could still not be installed, PhD students Christine George and Zahid Aziz have investigated the performance of several hundred As-removal system of three types approved by the government and deployed by UNICEF in a different area of Bangladesh, Shahrasti, where As levels are particularly high. The performance of two of the filter systems (Read-F and Alcan) was found to be acceptable (<10% failure after several months relative to the Bangladesh standard of 50 ug/L) but not the SONO system which showed two-thirds failure. Several months after the SONO filters were replaced by the manufacturer claiming that they had been improperly handled, one third of SONO filters were again failing. A follow-up investigation in collaboration with Proj 5 has shown that dissolved organic carbon levels in Shahrasti groundwater (>30 mg/L) are particularly high and might be the cause of the filter failures.

Project 7-Supported Publications:

Manuscripts published or in press (2) and submitted (3) in 2009

Aziz, Z, B Bostick, Y Zheng, MR Huq, MM Rahman, KM. Ahmed, and A. van Geen, Suppression of arsenic release to shallow groundwater of Bangladesh by reduced sulfur, submitted to *PNAS*, October 2009.

Fendorf, F, HA. Michael, A van Geen, Does the distribution of arsenic in groundwater change over time in South and Southeast Asia? Biogeochemical and hydrological factors to consider, Review commissioned by *Science*, submitted December 2009.

Garnier, J.-M, F. Travassac, V. Lenoble, J. Rose, Y. Zheng, M. Hossain, S. Chowdhury, A. Biswas, K.M. Ahmed; Z. Cheng, A. van Geen, Temporal variations in arsenic uptake by rice plants: The role of iron plaque in paddy fields of Bangladesh irrigated with groundwater, submitted to *Science of the Total Environment*, October 2009.

Leber, J, MM Rahman, MT, Chowdury, KM Ahmed, B. Mailloux, A. van Geen, Seasonal variation of *E. coli* concentrations in the shallow aquifer of two geologically contrasting villages in Bangladesh, *Ground Water*, provisionally accepted by the Guest Editor, November 2009.

van Geen, A, JM. Duxbury, Comment on “Growing rice aerobically markedly decreases arsenic accumulation”, *Environmental Science and Technology,* DOI: 10.1021/es9002982, 2009.

Students supported at least in part under Project 7 in 2009

Kathleen Radloff, Earth & Environmental Engineering, Columbia, PhD candidate.
Zahid Aziz, Earth & Environmental Sciences, Columbia, PhD candidate.
Ivan Mihajlov, Earth & Environmental Sciences, Columbia, PhD candidate.
Christine George, Mailman School of Public Health, Columbia, PhD candidate.
Misheal Artani, Environmental Sciences, Barnard College, Sr Undergraduate.

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 continuously 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. In the past, all of the scientific team has assembled monthly for a two hour seminar, one hour biomedical and one hour non-biomedical. For two reasons, we have had fewer seminars in the past year. First, we have used many of the two hour meetings to hold discussions about the overall progress of our SRP, and to discuss new project ideas that will need to be incorporated into a competitive renewal application in a little more than a year from now. Possible new projects relate to arsenic issues in the Mississippi delta, Vietnam's Red River delta, and the Tennessee coal fly ash disaster have been topics of open discussions. In addition, we have reviewed and discussed each of our seven research projects openly to determine which projects still have novel hypotheses to be explored in the future and which, if any, have reached maturity and will need to be sunsetted. These discussions will continue into the summer of 2010, by which time we will have come to agreement about the structure of our competitive renewal application.

Formal seminars presented included:

"Subjective Risk Assessment and Reactions to Health-related Information: Evidence from Bangladesh" Alessandro Tarozzi
Department of Economics, Duke University

"Mass Balance of Arsenic in Irrigated Paddy Soils: Assessment of Long-Term Arsenic Accumulation Trends in Munshiganj/Bangladesh" Jessica Dittmar
Institute of Biogeochemistry and Pollutant Dynamics (Soil Chemistry) Swiss Federal Institute of Technology Zurich (ETH)

"Climate Change Effects on the Coastal Belt of Bangladesh" M. Qumrul Hassan
Professor and Chair, Department of Geology, University of Dhaka

"Arsenic Adsorption in the Low Arsenic Aquifer after Intrusion of High Arsenic Groundwater in Bangladesh" Karrie Radloff
PhD Student, Department of Earth and Environmental Engineering, Columbia University

"Arsenic in Drinking Water and Adult Mortality" Yu Chen
Assistant Professor of Environmental Medicine, New York University

Our External Advisory Committee continues to provide valuable input to our program. The committee visited Columbia University for a two day retreat on March 2-3, 2009, held at the Lamont Doherty Earth Observatory's new Comer Geochemistry Building. 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; and g) Peggy O'Day, Associate Professor of Natural Sciences, University of California, Merced.

Each of our seven research project PIs, as well as the PIs of the Research Translation Core, made presentations to the Committee at the March meeting and many research issues were discussed at length.

The Administrative Core devoted an extraordinary amount of time to the organization and implementation of the Annual Meeting of the SRP Programs on November 2-5, 2009, entitled "Emerging Issues, Emerging Progress." Drs. Graziano, van Geen and other SRP faculty were intimately involved in the administrative and scientific issues, ranging from the hotel and University venues, to the selection of platform speakers and the solicitation of posters. By all accounts, the meeting was a great success. The Core was also instrumental in assuring an excellent representation of investigators, post-doctoral fellows and students at this meeting. Seven doctoral students and one post-doctoral fellow presented a total of six posters and one platform session.

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. Project 2:
    a. Data from approximately 12,000 follow up 3 questionnaires for HEALS were entered using the customized data entry system in Dhaka, Bangladesh. All data were periodically automatically transferred to our Columbia University SQL database located in New York. Approximately 11,500 follow up 3 questionnaires were entered.
    b. Approximately 8,000 baseline expansion questionnaires were added to our baseline database; the total number of baseline questionnaires in our HEALS database is currently 20,033. Data entry now complete for this effort.
    c. Dhaka staff is in the process of entering data from follow up 1 questionnaires for Arsenic Cohort Expansion (ACE) subjects. As of now approximately 4250 questionnaires have been entered.
    d. Verbal autopsy data have been centralized on a remote server to allow access from Dhaka, Chicago and New York.
    e. Data sets have been provided to Chicago based staff as requested.
2. Project 3:
    a. New Hampshire/Maine
        i. Data for 132 children have been entered. Data entry includes a demographic/well questionnaire, WISC and WASI tests, and a home assessment questionnaire for each participant and family.
    b. Bangladesh
        i. Data entry for 304 children is complete.
        ii. The data were distributed to the PI and Xinhua Liu for analysis.
3. Project 4:
    a. 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.
    b. Targeted data sets have been distributed to PI and biostatistician (as requested) for analyses for studies explained in detail in project related section.

4. Additional efforts:
    a. Health Education of School Children in Bangladesh:
        i. Continued consultations with Khalid Khan.
        ii. Completed programming of Access database data entry screens. Installed database on network for multi-user data entry.
        iii. Supervised entry of data for 1,040 subjects
        iv. In progress: creation of targeted dataset for PI and Xinhua Liu
    b. Community Participation Database
        i. Consultations with Christine Marie George regarding questionnaire design, work flow and database
        ii. Programming complete for Access database for entry of well screening data; in progress: programming of individual screening and baseline questionnaire
    c. Continued support for undergraduate and graduate students working with PIs on Arsenic related projects.
    d. Maintenance of secure database and web servers has continued. All projects detailed above are the direct beneficiaries of these services.
    e. Management of data flow continues using the Issue Tracking System and the Query Tracking Systems.
    f. Attending weekly project team meetings to provide data management consultation as projects move forward.

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. The Trace Metals Core provides analytical support to projects #2, #3 and #4.

During the past year, this Core Lab conducted more than 20,000 "routine" analyses of biological samples from projects 2, 3 and 4. Notably, the Trace Core has supported the expansion of the HEALS Cohort Study (Project #2) from a sample size of roughly 12,000 to 20,000 participants and has conducted analyses of As and creatinine the urine samples of each participant at baseline, and at three biannual follow-up visits. In support of various studies, urinary arsenic metabolites were analyzed for more than 1200 study participants. Three years ago, the Trace Metals Core developed a new method for the analysis of arsenic in blood, using ICP-MS-DRC. That method allowed us to demonstrate that blood As is an extremely useful biomarker of exposure. Moreover, the method allows for the simultaneous measurement of other metals of interest that are covariates in many analyses, namely Pb, Mn and Se. During the past year the lab has continued to provide these blood analyses to several projects, notably Project #4.

Given the potential utility of blood arsenic measurements in epidemiologic research, we have now validated the use of fingerstick blood samples for the analysis of As in blood. With IRB approval, we obtained venous and fingerstick blood samples from NN study participants in Bangladesh who had a wide range of water arsenic exposures. The correlation between fingerstick As and venous blood As was 0.98 ($p < 0.01$), indicating that fingerstick blood samples can be used to accurately measure blood As. (This was not the case for Mn, where we found great discordance (r = 0.20), likely due to ubiquitous contamination of fingers from particulate Mn.)

Epidemiologic studies employing repeated blood arsenic measurements over time have the potential to answer many issues concerning the bioavailability and toxicokinetics of arsenic. We believe that this new method may facilitate this area of research. Indeed, repeated measures of blood As obtained from fingerstick samples are being employed in Dr. Gamble's new RO1 study of folate and creatine as interventions to facilitate As excretion and lower blood As.

Students involved with this work:

Christine George, Dr. Graziano's minority Ph.D. student, who has a degree in Environmental Engineering from Stanford University. She has been awarded a Fulbright Award to spend one year in Bangladesh where she is currently working on her dissertation research project.

Khalid Kahn, Dr. Graziano's Bangladeshi DrPH student, who is supported in part by a training grant from the Fogarty Center. His research is evaluating school performance in elementary school students, as a function of arsenic exposure. He is also evaluating the impact of school-based arsenic education on arsenic exposure.

With an ARRA supplement to this grant, two summer students were hired:

Tiffany Sanchez, a senior at Columbia College, developed the method for the analysis of arsenic in toenails, and completed the analyses of available samples from both the New England and Bangladesh studies.

Larissa Calancie, who has now graduated from Cornell with a degree in nutrition, worked partly in the Trace Metals Lab and partly in Dr. Mary Gamble's lab. She is now permanently employed via Dr. Gamble's new RO1 grant.

Mr. Zhongyuan Mi, an MPH student in EHS, carried out his Master's thesis research in the lab during the past year., resulting in the following publication:

Trace Metals Core-Supported Publications, in 2009:

Hall MN, Liu X, Slavkovich V, Ilievski V, Mi Z, Alam S, Factor-Litvak P, Ahsan H, Graziano JH, and Gamble MV. Influence of Cobalamin on Arsenic Metabolism in Bangladesh, *Environ Health Perspect*, 2009;**117**(11):1724-9.

Every publication listed for Projects 2, 3 and 4 has relied on the Trace Metal Core.

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. 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 spectroscopy (XAS) 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, or 4 a total of 500 new groundwater samples collected from Araihazar, Bangladesh, and 114 wells samples from Maine were analyzed by HR ICP-MS in 2008. In support of project 5, over 300 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. Another 600 samples were analyzed by HR-ICP-MS in support of the field study on increasing the efficiency of the pump and treat operations at Vineland Superfund Site (Proj. 6). For the RTC collaboration with Rockland County Department of Health, 186 groundwater samples were analyzed by HR-ICP-MS to investigate arsenic contamination of drinking water sources. In addition 204 samples were analyzed for pCO2 with a subset analyzed for TCO2.

This past year, the core laboratory also generated XAS data for preserved aquifer material, including for Project 6 analyses of 3 micro-column experiments in situ using microprobe scans and XANES scans for As and Fe to test potential mechanisms for mobilization of As from aquifer solids by oxalic acid.

Core C has also initiated the development of a potential field method for urinary As based on the widely used Hach kit based on arsine generation/Gutzeit method. The idea is that urinary As measurements conducted in the field Bangladesh might provide an even stronger incentive for switching to a low-As well than a well-water measurement. Results to date with spiked urine indicate full recovery of inorganic As(III) and As(V). We are still testing various oxidation procedures for MMA and DMA that don't interfere with arsine generation.

Manuscripts involving collaborators supported by Core C:

Mailloux, B. J., Alexandrova, E., Keimowitz, A., Wovkulich, K., Freyer, G., Herron, M. M., Stolz, J. F., Kenna, T., Pichler, T., P. Knappett, 2007. Microbial mineral weathering for nutrient acquisition releases arsenic. *Appl. Environ. Microbiol*., published 2009.

Aziz, Z., B. Bostick, Y. Zheng, M.R Huq, M.M. Rahman, K.M. Ahmed, and A. van Geen, Suppression of arsenic release to shallow groundwater of Bangladesh by reduced sulfur, Submitted to *PNAS*, November 2009.

Students supported in part by the Biogeochemistry Core over the past year
Misheal Artani, Barnard College

Mailloux BJ, Alexandrova E, Keimowitz AR, Wovkulich K, Freyer GA, Herron M, Stolz JF, Kenna TC, Pichler T, Polizzotto ML, Dong H, Bishop M, Knappett PS. Microbial mineral weathering for nutrient acquisition releases arsenic. *Appl Environ Microbiol*. 2009;**75**(8):2558-65. PMCID: PMC2675215

Datta S, Mailloux B, Jung HB, Hoque MA, Stute M, Ahmed KM, Zheng Y. Redox trapping of arsenic during groundwater discharge in sediments from the Meghna riverbank in Bangladesh. *Proc Natl Acad Sci U S A*. 2009;**106**(40):16930-5. PMCID: PMC2761342.

Students supported were:
Jennifer Cheung, Barnard College
Ekaterina Alexandrova, Barnard College

Core D: *Hydrogeology Core*
PIs: Martin Stute, 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, 7, and the RTC.

Notable advances for the last period

Field efforts: Over the spring/summer of 2009, we conducted a pilot scale *in situ* remediation experiment at the Vineland Superfund site (see report for project 6). The Hydrogeology Core supported the infrastructure of the injection system and measurements of the injected tracers (Br^-, SF_6) and oxalic acid. We developed a novel distribution system that allows for fluid injection into all 15 wells at a uniform rate over several months by using just one pump (Wovkulich et al., 2009). A pre-patent application was filed for this system. The idea of the system was picked up by Sevenson, an environmental consulting firm and was used in other applications at the Vineland Site (RTC). The collection and measurement of a large number of tracer measurements were performed under the core. I collaboration with Rutgers University, a geophysical survey (resistivity) was performed at the site to map the subsurface treatment zone. After completion of the injection experiment, a Geoprobe system was hired to retrieve cores from the influenced area. As concentrations in these cores were compared with those obtained before the treatment to estimate the amount of As that was mobilized.

Laboratory efforts: In preparation of a field experiment to test the sustainability of deeper aquifer use in Bangladesh (P7), a system capable of pumping fluid at constant rates through up to 16 columns was developed and tested over the summer. The system is to a large extent shielded from atmospheric air and succeeds in keeping the water under reducing conditions.

Sample Measurements: We performed about 36 ^3H and 50 ^3He as well as 33 ^{18}O and ^2H and as well as 12 SF_6 and 18 ^{14}C analyses on samples from wells in Bangladesh (P5 & 7). We performed 500 SF_6 measurements by gas chromatography and 900 Br and oxalic acid measurements for the injection experiment at the Vineland site in NJ (P6). Environmental tracer data collected over the years by the hydrogeology core were presented in a larger context this summer (Friedrich et al., 2009; Stute et al., 2009).

Modeling: Core personnel supported the completion of groundwater flow modeling activities (MODFLOW, MT3D) at site 'X' in Bangladesh (P5&7) in order to quantify the groundwater/surface water interactions. The model was able to reproduce the observed groundwater ages as well as some of the variations in well chemistry influenced by the groundwater/surface water interactions.

Instrument development We completed the development of a prototype of a novel sampler for gases dissolved in groundwater (Loose et al, 2009). 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 listed in Projects 5, 6, 7 and RTC have been supported by the Hydrogeology Core. Of particular relevance are the following:

Core D -Supported Publications, in 2009:

Datta, S, Mailloux, B, Jung, HB, Hoque, MA, Stute, M, Ahmed, KM, and Zheng, Y. Redox trapping of arsenic during groundwater discharge in sediments from the Meghna riverbank in Bangladesh. *Proc Natl Acad Sci USA* 2009;**106**:16930-5. PMCID: 2761342.

Friedrich, R, Schlosser, P, Turrin, B, Newton, R, Stute, M, and Plummer, LN. The Lamont-Doherty Tritium/He-3 Dataset for Age Dating of Groundwater. *Geochim Cosmochim Acta* 2009;**73**:A397-A397.

Loose, B, Stute, M, Alexander, P, and Smethie, WM. (2009). Design and deployment of a portable membrane equilibrator for sampling aqueous dissolved gases. *Water Res Research* 2009;**45**. W00D34, doi:10.1029/2008WR006969.

Stute, M., Horneman, A., and Fried, R. (2009). Environmental tracers in hydrogeology: Principles, applications, and challenges. *Geochim Cosmochim Acta* 2009;**73**, A1287-A1287.

Wovkulich, K., M. Stute, T. Protus, B. Mailloux, S. Chillrud, Injection System for Multi-Well Injection Using a Single Pump, Submitted to *Ground Water*, Nov 2009.

Wovkulich, K., M. Stute, T. Protus, B. Mailloux, S. Chillrud, Injection System for Multi-Well Injection Using a Single Pump, *Provisional Patent Application* filed Nov. 2009.

Research Translation Core: *Collaborating with Government & the Public: Arsenic & Manganese Exposure via Groundwater*
Co-PI's: Steve Chillrud, Meredith L. Golden
Co-investigators: Joseph Graziano, Mark Becker, Martin Stute, Yan Zheng, Stuart Braman

The mission of Columbia's Research Translation Core (RTC) is to facilitate communication among Columbia scientists and other SRP-funded groups, and the public. In addition a central theme of RTC activities is direct involvement with ongoing priorities of governmental agencies responsible for minimizing human exposure to arsenic and manganese. Communication has been facilitated by ongoing seminars, workshops, and the project website. Here we highlight some of the activities over the last year.

CU RTC has taken a leadership role in advancing research translation as a vital component of the SRP. In February 2009, it hosted the workshop, "Translating SBRP Triumphs into Public Health Progress: Understanding and Implementing Effective Research Translation". Fifty participants from SRP universities, NIEHS, EPA, and the CDC/ATSDR attended the workshop. The proceedings from this 2½ day workshop are available on Columbia's RT Wiki. After participating in UNC's July workshop "Partnering with USEPA and ATSDR to Improve the Use of SRP Science", the CU RTC organized the Research Translation and Outreach meeting at the SRP Annual Meeting, focusing on the opportunities and obstacles of using SRP Science for government policies and regulations at waste sites. Governmental agency participants are listed below. In addition, the CU RTC gave a presentation to the Administrator's Meeting on "Research Translation Cores: Promoting and Improving the Use of SRP Science to Enhance Public Health".

Our partner agencies are located in NJ, NY, NH and ME and include county, state, and federal personnel. One collaboration grew out of the detection of arsenic in public-supply wells in Rockland County, NY in 2007. RTC scientists began collaboration with County Department of Health officials and the private water supply company on a sampling program of both public supply and private wells. This program was designed to determine the spatial and temporal extent of groundwater arsenic contamination in the region and test reductive dissolution as the primary mobilization mechanism. By monitoring ~60 residential and public supply wells, it has been determined that three of them have As levels consistently above the 10 ppb EPA standard for drinking water. The arsenic from these wells is being removed before use for drinking water. Another 6 wells have had measurable levels, but always below the EPA standard. Further, no seasonal effects have been noted thus far, with all of the wells showing relatively constant arsenic levels over three seasons of monitoring.

RTC scientists developed a public website regarding water quality and supply in Rockland County. The goals of this website are to provide access to current and historical scientific information to allow interested citizens of Rockland County to more fully participate in decision making processes. The web site was launched in April 2009 after testing began in December 2008. To date, the site has been visited 4500 times with 17 different pages visited over 100 times each. RTC scientists have held a number of meetings with NY State Assemblywoman Ellen Jaffee to provide background on Rockland County water quality and water supply issues for state water legislation development.

Students and Postdocs involved in RTC activities in 2008:

Beth O'Shea, PhD in Geology 2006, School of Biological, Earth and Environmental Science, University of New South Wales, Sydney Australia.
Qiang Yang, 5th year graduate student, Queens College and Graduate Center, CUNY.
Karen Wovkulich, 5th year graduate student, Earth and Environmental Science, Columbia University.
Marco Balletta, visiting student from University of Naples, Italy

Governmental Agency Staff who attended the February 2009 RTC meeting at LDEO:
Mark Maddaloni, EPA Region 2; Helen DuTeau, EPA Region 3; Jana Telfer and Olivia Harris, ATSDR; and Beth Anderson and Claudia Thompson, NIEHS

Governmental Agency Staff who attended the Research Translation and Outreach Annual Meeting sessions in Nov 2009 in NYC:
Randall Wentsel, EPA National Land Research Program Director; Sally Perreault Darney, EPA National Human Health Research Program Director; Ronald Landy, EPA Regional Science Program Acting Director; Suzanne Wells, EPA Community Involvement Program and Initiatives Branch Director; Nigel Fields, EPA NCER; Jayne Michaud, EPA OSRTI; William Hagel, ORD STL; Marian Olsen, EPA Region 2; Steve Jones and Deborah Burgin, ATSDR DRO; Racquel Stephenson, ATSDR Region 2; and Dan Walsh, NYC Mayor's Office of Operations; Beth Anderson and Claudia Thompson, NIEHS. Additional staff who could not attend the workshop but who provided comments at the SRP Annual meeting the day before included David Charters, EPA OSRTI, Jon Josephs, EPA Region 2 STL, and Michael Gill, EPA Region 9 STL.

Governmental agency staff we interact with
On Vineland Superfund Site: Ron Naman, EPA Region 2; Steve Creighton, USACE; Laura Bittner, USACE.
On NYS Landfills: Steve Parisio, NYSDEC.
On Rockland County Drinking Water Issues: Dan Miller, RCDOH.

RTC Core-Supported Publications:

Balletta, M. 2009. Arsenic in Iron Floc and Groundwater Downgradient of Unlined Landiflls in Southeastern New York State. Undergraduate Dissertation, Second University of Naples, Naples, Italy, 182 pp.
Golden, M, S Chillrud and T Chai-Onn. "SRP Research Translation: Past, Present, and Future" Presented at the SRP annual meeting in NYC on November 3-4, 2009.

Yang, Q, HB Jung, CW Culbertson, RG Marvinney, MC Loiselle, DB Locke, H Cheek, H Thibodeau, Y Zheng. Spatial Pattern of Groundwater Arsenic Occurrence and Association with Bedrock Geology in Greater Augusta, Maine. *Environ. Sci. Technol.*, 2009;**43**(8):2714-9• DOI: 10.1021/es803141m.

Training Core:
PI: Pam Factor-Litvak

The Training Core continued its annual 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. Dr. Pedone's teaching materials will now be offered as a 3-credit course in the MPH EHS curriculum, and will provide students with an OSHA certificate.

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 Dr. James Hansen, Director, Goddard Institute for Space Studies (Global Climate Change: Beyond the Tipping Point).

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.

A total of seven PhD students are engaged in research related to the ongoing research in our SRP program. This year, one of our students, Karrie Radloff, was awarded the annual Karen Wetterhahn Award for her work concerning the deep aquifers in Bangladesh, while a second student, Karen Wovkulich, made an outstanding platform presentation regarding her work at the Vineland Chemical Superfund site in New Jersey.

Patent Updates:
Wovkulich, K., M. Stute, T. Protus, B. Mailloux, S. Chillrud, Injection System for Multi-Well Injection Using a Single Pump, Provisional Patent Application filed Nov. 2009. Full information provided in attached file.

Superfund Site Updates: None.

Contact Information Updates: Updated in the attached file.

Student Information Updates: Embedded within text and also updated in attached excel file