

Annual Progress Report of P42 ES 10349 “Health Effects and Geochemistry of Arsenic and Lead”, Joseph H. Graziano, P.I., 12/15/2003

Section 1: Highlights for 2003

We present below two research highlights. Please also note the development of a strategic plan to solve the arsenic problem in Bangladesh, presented under the Administrative Core, might also be of interest to the general public.

Highlight #1:

Project 3: A Refined Dose-Response Relationship Between Water Arsenic and Skin Lesions in Bangladesh

P.I.: Habibul Ahsan

As part of Columbia University’s SBRP, Dr. Ahsan and his colleagues have established a large prospective cohort study in Araihasar, Bangladesh, to investigate the health effects across a wide range of arsenic concentrations in drinking water. Arsenic exposure is associated with a wide array of adverse health effects. They have initially focused on skin lesions and skin cancers, and have established a bank of biological specimens for future studies. To date, 11,753 men and women, with water arsenic concentrations ranging from 0.1 to 864 µg/L have been recruited and questionnaire, clinical data and biological samples have been collected. This unique cohort is being actively repeatedly examined over time. Using the cross-sectional data from their initial examination of the 11,753 cohort participants, they conducted full dose-response analyses of the relationships between arsenic exposure and risk of skin lesions; in many individuals these lesions go on to become skin cancers. They have estimated adjusted prevalence ratios and odds ratios as measures of relative risks (RR) and associated 95% confidence intervals (CI) of skin lesions for subjects at each category of arsenic exposure using those at the lowest level of exposure as a reference group.

Overall, a very clear and strongly linear dose-dependent effect of arsenic exposure on the risk of skin lesions was found, based on both drinking water and urinary arsenic measurements. In fact, there was a clearly distinct dose-effect even within the

Adjusted Prevalence Ratios and Odds Ratios for Skin Lesions by Levels of Arsenic Exposure in 11,753 Cohort Members

	Adjusted Prevalence Ratios [†]	Adjusted Prevalence Odds Ratios [†]
Well arsenic (µg/l)		
<6	1.0	1.0
6-20	1.6 (1.1-2.4)	1.7 (1.2-2.5)
21-38	2.3 (1.6-3.2)	2.4 (1.7-3.5)
39-61	2.5 (1.8-3.5)	2.8 (1.9-3.9)
62-91	3.0 (2.2-4.2)	3.4 (2.4-4.8)
92-127	3.0 (2.2-4.2)	3.4 (2.4-4.7)
128-178	3.0 (2.1-4.1)	3.3 (2.4-4.7)
179-262	3.2 (2.3-4.4)	3.6 (2.6-5.1)
263-864	5.3 (3.9-7.1)	6.8 (5.0-9.3)
Urinary creatinine-adjusted arsenic (µg/l)		
6.6-90.1	1.0	1.0
90.2-123.1	1.2 (0.8-1.7)	1.2 (0.8-1.8)
123.2-159.4	2.3 (1.7-3.2)	2.5 (1.8-3.5)
159.5-199.1	2.0 (1.4-2.7)	2.1 (1.5-3.0)
199.2-245.9	2.3 (1.7-3.2)	2.5 (1.8-3.5)
245.9-308.0	2.5 (1.9-3.5)	2.8 (2.0-3.9)
308.1-406.0	2.9 (2.1-3.9)	3.2 (2.3-4.5)
406.1-597.7	3.7 (2.7-4.9)	4.4 (3.2-6.0)
597.8+	5.6 (4.2-7.5)	7.7 (5.6-10.5)

[†] Prevalence rate ratios and odds ratios were adjusted for age, gender, education, BMI, and TV ownership

low end of exposure ranging 0-60 µg/L of drinking water arsenic – a range in which ~77 million people in Bangladesh and ~13 million people in the US are chronically exposed. For exposure measures based on drinking water arsenic, compared to those exposed to the lowest category of exposure (<6µg /L) the RR for skin lesions increased steadily from 1.6 (95% CI 1.1-2.4) for people at the second lowest exposure category (6-20µg /L) up to 6.8 (95% CI 5.0-9.3) for people at the highest exposure category (263-864µg /L). Similarly, when exposure was estimated using total urinary arsenic (adjusted for creatinine), compared to those exposed to the lowest category of exposure (<90µg /L) the RR for skin lesions increased steadily from 1.2 (95% CI 0.8-1.8) for people at the second lowest exposure category (90-123µg /L) up to 7.7 (95% CI 5.6-10.5) for people at the highest exposure category (>598µg /L). These results, have major public health significance, and are currently being prepared for publication [Ahsan et al., in preparation]. In short, these data indicate that the recent EPA decision to lower the allowable amount of arsenic in drinking water from 50 to 10 µg /L is highly justified.

Highlight #2:

Project 7 Assessment and Remediation of Arsenic in Groundwater

P.I.: Alexander van Geen

Investigations of arsenic geochemistry prompted us to improve analytical methods for the determination of dissolved arsenic in natural waters, especially those that work well in the field with low instrumentation cost. We have successfully modified a classic colorimetric method used to assay dissolved As in seawater in order to achieve the precision (< 5%) and detection limit (< 2 µg/L) required for groundwater analyses in the presence of high concentrations of phosphate (Dhar et al., in revision). The low detection limit is achieved through a double-beam photospectrometer with 4 decimal points absorbance recording capability. We have also successfully developed and modified an electrochemical method (Differential Pulse Cathodic Stripping Voltammetry) that can detect As level at < 1 µg/L levels and has a < 5% precision (He et al., accepted). Both of these methods can differentiate dissolved arsenite and arsenate. When the electrochemical method was combined with an anoxic extraction of synthetic iron oxides with adsorbed As, arsenite could be quantitatively extracted. This suggests that this technique has the potential be applied to the analysis of oxidation state of sediment As. Simultaneous measurements of oxidation state of As in dissolved and solid phases in the field will address the question whether reduction of sedimentary As is necessary for the mobilization of As or not. This progress was reported earlier this year as a Research Brief, presented below.

Research Brief 98: Arsenic Mobilization in Bangladesh Groundwater

In the early 90's, an epidemic of arsenic poisoning began to emerge in Bangladesh. This epidemic is the indirect consequence of a well-intentioned campaign by donor agencies approximately 20 years ago to shift water consumption patterns in Bangladesh away from microbial disease-ridden surface water to "safe" clean tube well groundwater. It is now estimated that nearly one-third of these wells is contaminated with levels of arsenic greater than 50 µg/L (or 50 ppb), the drinking water standard for Bangladesh. This crisis has now been recognized in other areas of Asia, including India and Vietnam. Health experts estimate that 40 million people

have been chronically exposed to arsenic, making this the worst environmental health disaster of the 20th century.

Development of national and international strategies to reduce levels of arsenic in drinking water supplies is hampered by a serious lack of information concerning a complex set of geochemical, public health, and remediation issues. The SBRP supports seven interrelated, multidisciplinary research projects at Columbia University with the goal of addressing some of these issues. Yan Zheng (Queens College, CUNY and Lamont-Doherty Earth Observatory [LDEO], Columbia University) and Martin Stute (Barnard College and LDEO) are leading an investigation to identify the fundamental processes that result in the arsenic enrichment of groundwater in Bangladesh. SBRP-funded research of Alexander van Geen (LDEO) focuses on translating this new knowledge into practical mitigation strategies to provide the rural population of Bangladesh access to safe water. Arsenic occurs in high concentrations under a wide range of hydrological and hydrochemical conditions in Bangladesh - making it an ideal study site for gaining a better understanding of arsenic mobilization.

Zheng and Stute began with a pilot study of the geochemistry of six sites in eastern Bangladesh. These sites represent three distinct geological units (uplifted Pleistocene terrace, fluvial flood plain, and delta plain). Arsenic concentrations in collected groundwater samples ranged from $< 10\mu\text{g/L}$ to $\sim 1200\mu\text{g/L}$. Despite regional differences and spatial variability of groundwater arsenic concentrations, there are systematic patterns between arsenic and other properties of the groundwater such as dissolved oxygen, nitrate, iron and manganese concentrations and sulfate/chloride ratios. The sulfur isotopic composition of dissolved sulfate suggests that oxidation of sulfide is not the dominant process in arsenic release. These observations (soon to be published in *Applied Geochemistry*) confirm that reduction of iron oxyhydroxides is likely the dominant mechanism of arsenic release to groundwater in Bangladesh. Although the reason groundwater systems in Bangladesh are driven to reducing conditions remains somewhat enigmatic, the researchers suspect the cause may be the oxidation of dispersed organic matter in sandy aquifers formed over the past 20,000 years, as sea level rose by about 100 m. They believe that bacterial decomposition of deltaic sediments consumes all of the oxygen in the water. The resulting "reducing" water causes arsenic to be chemically reduced from arsenate to arsenite, thereby making it soluble in water.

Zheng and Stute suggest that exhaustion of labile organic matter is the likely explanation for the much lower groundwater arsenic levels associated with aquifers made of older sediments ($> 100,000$ years). Although these deeper aquifers are more difficult to reach, they appear to be a promising source of water that is both low in arsenic and free of infectious human pathogens.

Data from the pilot study were also used to identify the area where Columbia University SBRP-funded biomedical studies are being conducted and where major remediation effort has taken place. To set the stage for the epidemiological study conducted by scientists from Columbia's Mailman School of Public Health, van Geen spearheaded an effort to collect and analyze groundwater samples from nearly 6000 contiguous tube wells covering a 25 km² area of Bangladesh. The location of each well was determined with handheld Global Positioning System receivers. A statistical analysis from this unprecedented geo-referenced data set shows that although only half the resident population of 70,000 has access to water that meets the Bangladesh drinking water standard, nearly 90% live within 100 m of a low-arsenic well.

This striking observation (reported in a recent issue of the Bulletin of the World Health Organization) indicates that the extreme spatial variability of groundwater arsenic offers an opportunity for mitigation in the short-term through the sharing of water from the safe wells. Social barriers to such sharing need to be better understood and, if possible, overcome.

The patchiness of the groundwater arsenic distribution is somewhat less bewildering when the depth dimension is added to the picture. In a manuscript which builds on the same 6000 well data set (and was recently accepted for publication by Water Resources Research) the researchers show that the proportion of wells that does not meet the Bangladesh standard for drinking water arsenic increases with depth from 25% between 8-10 m to 75% between 15-30 m, then declines gradually to less than 10% at 90 m. Some villages within the study area do not have a single well that meets the standard, while others have wells that are nearly all acceptable. In most villages, the distribution of arsenic is highly variable in the 8-30 m depth range and does not follow any obvious pattern. The distribution of arsenic in the 30-90 m depth range, instead, appears to be controlled by the depth of the transition from relatively young Holocene to older Pleistocene sand deposits, which typically contain low-arsenic groundwater. In some parts of the SBRP study area, these older deposits are separated by a thick clay layer from shallower aquifers with elevated levels of arsenic. In other parts of the study area where there is no such clay layer, there is concern that tapping into the deeper aquifers may be only a temporary solution if withdrawal leads to downward entrainment of high-arsenic water from the shallower aquifers.

This project is a critical component of the overall SBRP program at Columbia University - it provides the necessary foundation for long term resources management, and in turn, may greatly reduce the population at risk of exposure to arsenic in the United States, Bangladesh and elsewhere. The findings to date, obtained in close collaboration with Dr. Kazi Matin Ahmed of the Geology Department of the University of Dhaka, could assist the Government of Bangladesh in finding safe sources of groundwater for the people of Bangladesh. SBRP-funded researchers, along with the President of Columbia University (Lee Bollinger) and the Director of the Columbia Earth Institute (Jeffrey Sachs), traveled to Bangladesh in January, 2003, to meet the Bangladesh Prime Minister and discuss Columbia's ability and interest in tackling mitigation problems in Bangladesh on a much wider geographic scale.

To learn more about this research, please refer to:

- van Geen, A.F., H. Ahsan, A. Horneman, R. Dhar, Y. Zheng, I. Hussain, K.M. Ahmed, A. Gelman, M. Stute, H. James Simpson, S. Wallace, C. Small, F. Parvez, V. Slavkovic, N.J. LoIacono, M. Becker, Z. Cheng, H. Momotaj, M. Shahnewaz, V. Seddique, J.H. Graziano. 2002. Promotion of well-switching to mitigate the current arsenic crisis in Bangladesh. *Bulletin of the World Health Organization* 80:732-737.
- van Geen, A., Y. Zheng, R. Versteeg, M. Stute, A. Horneman, R. Dhar, M. Steckler, A. Gelman, C. Small, H. Ahsan, J. Graziano, I. Hussein, and K. M. Ahmed. 2003. Spatial Variability of Arsenic in 6000 Tube Wells in a 25 km² Area of Bangladesh. *Water Resources Research* 2003; 39(5): 1140-1151.
- Zheng, Y., M. Stute, A. van Geen, I. Gavrieli, R. Dhar, H. J. Simpson, and K. M. Ahmed. 2003. Redox control of arsenic mobilization in Bangladesh groundwater. *Applied Geochemistry* (In Press).

Section 2: Progress Reports for Research Projects and Cores

Project 1: Bioavailability of Soil Lead and Arsenic in Humans

P.I.: Conrad Blum

The primary aims of this project are to 1) determine estimates of the bioavailability of lead in soils from a mining site, smelting site and urban site; 2) to test the hypothesis that phosphate-based soil amending agents reduce this bioavailability in adult humans; and 3) to examine the correlation between the human and *in vitro* estimates of bioavailability in these soils. This study involves the ingestion of tiny amounts of sterilized soils, which contain lead but no other contaminants of concern. The method utilizes the technique known as stable isotope dilution, and takes advantage of the fact that the presence of non-radioactive isotopes of lead in soil allow one to track tiny amounts of lead that are actually absorbed into blood.

Sixteen subjects have completed the protocol designed to assess the bioavailability of lead in soil. The first twelve study participants were randomly assigned to ingest either the phosphate amended or non-amended soil. This soil from a former smelting site in Joplin, MO, was treated with 1% phosphate at the site, by the U.S. EPA, and sampled at 6 month intervals. We have evaluated an “amended” and “non-amended” soil specimen that was sampled 18 months post-treatment. Final Pb isotope and bioavailability data were analyzed in the Geochemistry Core Laboratory.

The findings are extremely interesting and potentially important. Among the six subjects who received the non-amended soil, the mean Pb bioavailability was 34.7%. In contrast, among those who received the phosphate-amended soil, mean Pb bioavailability was 19.9%, significantly less. While there is a wide range of inter-individual variability, this represents an average reduction in bioavailability of 43%. Studies evaluating the bioavailability of these same soil samples in animals, by Casteel et al, and in an *in vitro* system, by Ruby et al, reported a 38% reduction in bioavailability, by both methods, validating the relative effect that phosphate inactivation has on soil lead bioavailability in these samples. It is particularly important to note that our work to date appears to validate the use of the *in vitro* and animal models, in that the values obtained for bioavailability in all three systems are coherent with each other.

The use of phosphate inactivation appears to be a viable method to reduce the bioavailability of lead in contaminated soils, however it is important to determine whether the observed reductions in bioavailability persist over longer periods of time. Particularly given its relatively low cost, compared with other methods used to reduce human exposure to lead in soils, the use of phosphate inactivation, at certain sites, may not only be a viable cleanup alternative, but a cost-effective one at that. A manuscript describing these findings is in preparation.

We are currently evaluating of the next set of soils which have been collected from a former mining site in Tar Creek, OK. The soils were analyzed by the EPA laboratory in Edison, NJ, for over 200 priority pollutants, and were found to be otherwise safe for human consumption. Before the soils were administered to the subjects, as in the past, they were also sterilized by gamma irradiation. Four subjects have been clinically evaluated thus far and several additional volunteers are being screened for admission within the next 4-6 weeks. Analysis of the blood

samples are in progress. Thus far, a total of 54 potential study volunteers have been screened for blood Pb concentration, Pb isotope composition, and overall health.

Project 2: Genotoxic Mechanisms of Arsenic in Mammalian Cells

P.I.: Tom Hei

During the current funding period, we examined the role of mitochondria in mediating the genotoxicity of arsenite using two complementary approaches. Treatment of enucleated cells with arsenic followed by rescue fusion with karyoplasts from controls resulted in significant mutant induction. An important corollary of this finding is that the nucleus is not necessarily the only and sufficient target for arsenic carcinogenesis. Treatment of cytoplasts with arsenic, in the absence of the nucleus, initiated similar oxyradical production, as detected by using the radical probe, 5',6'-chloromethyl-2',7'dichlorodihydro-fluorescein diacetate (CM-H₂DCFDA). In contrast, treatment of mitochondrial DNA depleted cells followed by rescue fusion with cytoplasts produced very few mutations. Mitochondrial damage can lead to the release of superoxide anions which then react enzymatically with nitric oxide to produce the highly reactive peroxynitrites. The mutagenic damage was dampened by the nitric oxide synthase inhibitor, N^G-methyl-L-arginine. Thus, the genotoxicity of arsenic is mediated by a combination of both reactive oxygen and nitrogen species.

Arsenic is paradoxical in that it is a well established human carcinogen and is associated with a variety of cancers including those of skin. On the other hand, it has also been used, albeit at low doses, in the treatment of leukemia for over a century. Melanoma is often a deadly disease due to the lack of effective treatment options. During the current funding period, we have shown that short term treatment with low concentrations of sodium arsenite (2-10 μ M) which has little or no effects on normal melanocytes induces apoptosis of human melanoma including highly metastatic ones in a process independent of binding to Fas ligands. The apoptotic response depends on low nuclear NF- κ B activity and an endogenous expression of TNF α . Simultaneous inhibition of PI3K-AKT and MEK-ERK pathways induces TRAIL-mediated apoptosis of human melanoma cells that can be substantially enhanced by low dose of arsenite treatment. Taken together, these data suggest that arsenite may be a powerful therapeutic agent in the treatment of disseminated melanoma.

Arsenic is an important environmental carcinogen that affects millions of people worldwide through contaminated water supplies. For decades, arsenic was considered a non-genotoxic carcinogen. Using the highly sensitive A_L mutation assay, we showed previously that arsenic is indeed a potent gene and chromosomal mutagen and that its effects are mediated through the induction of reactive oxygen species. However, the origin of these radicals and the pathways involved are not known. Our studies illustrate that mitochondria are a primary target of the arsenic-induced genotoxic response and that 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.

Publications:

Hei, T.K., Liu, S.X., and Waldren, C.A., Mutagenicity of arsenic in mammalian cells: Role of reactive oxygen species. *Proc. National Academy Science U.S.A.* 95:8103-8107, 1998.

Liu, S.X., Athar, M., Lippai, I., Waldren, C.A., and Hei, T.K., Induction of oxyradicals by arsenic: implications for mechanisms of genotoxicity. *Proc. National Academy Science U.S.A.* 98:1643-1648, 2001.

Kessel, M., Liu, S.X., Xu, A., Santella, R., and Hei, T.K., Arsenic induces oxidative DNA damage in mammalian cells. *Mol. & Cell. Biochem.* 234: 301-308, 2002.

Metka, F., and Hei, T.K., Mutagenicity of cadmium in mammalian cells: Implication of reactive oxygen species and inhibition of oxidative DNA damage repair. *Mutation Research* 542: In press, 2004.

Hei, T.K., and Filipic, M. Role of oxidative damage in the genotoxicity of arsenic. *Free Radical Biology and Medicine* 36: In press 2004.

Liu, S.X., Davidson, M.M., Tang, X.W., Athar, M., and Hei, T.K. Mitochondrial damage mediates genotoxicity of arsenic in mammalian cells. In revision: *Proc. National Academy Science U.S.A.*

Ivanov, V.N., and Hei, T.K., Arsenite treatment sensitizes human melanoma to apoptosis via TNF α or TRAIL-mediated pathways. Submitted for publication.

Project 3: A Cohort Study Of Health Effects Of Arsenic Exposure In Bangladesh

P.I.: Habibul Ahsan

In Bangladesh, nearly 40 million people have been chronically exposed to elevated concentrations of arsenic in drinking water for the past several decades, resulting in an epidemic of arsenicosis. This situation arose as a result of the well-intentioned efforts of UNICEF, which installed a million tube wells in an effort to shift the population away from microbially-contaminated surface water, not realizing that the groundwater is naturally enriched in arsenic. Three of our seven SBRP projects take place in Bangladesh, in an effort to learn about health and geochemistry issues that are of importance in the U.S., while at the same time trying to help the people of Bangladesh reduce their exposure to arsenic.

This project is our largest biomedical project. It has established a prospective cohort study that has recruited 11,753 men and women in Arahazar, Bangladesh, to investigate the health effects of arsenic exposure with an initial focus on skin lesions and skin cancers, and also to establish a biorepository for future studies. 99% of the eligible participants who were approached agreed to be in the study and were recruited an 18 months recruitment period from October 1, 2000 to April 2002. In order to set the stage for the cohort study, especially to build a sampling frame, we tested all 5,966 contiguous tube wells for arsenic within a well-defined area of approximately 26 square kilometers in collaboration with our hydrology and geochemistry colleagues. We also enumerated all 65,876 people in the study area who were drinking water from these 5,966 wells. Findings from this pre-cohort study survey are published in a series of papers [van Geen et al., 2002 and 2003; Parvez et al., Submitted].

The biological samples have been processed and baseline questionnaire data have been processed and stored for all 11,753 cohort members. We already completed the analysis of total urinary arsenic of all these individuals at baseline and are currently in the process of analyzing

arsenic metabolites in a subset of 1200. Using baseline cross-sectional data on arsenic exposure and prevalent skin lesion cases we have conducted full dose-response analyses of the relationship between arsenic exposure and risk of skin lesions (see Highlight #1). These novel results, with major public health significance, are being written up for publication. We have also collected full dietary data from all 11,753 cohort members using a modified meal-based dietary questionnaire. In addition, we completed a dietary validation study by collecting complete records of a seven-day food diary of a randomly selected 200 cohort participants in two different seasons of the year. The results of this validation study, which have been submitted for publication [Chen et al., Submitted], showed very good agreements between the information on most of the food items collected through the cohort instrument used for all cohort participants and the in-depth data collected through complete 7-day food records. Thus, this dietary information will enable us to examine possible nutritional effects on arsenic metabolism and disease.

We are currently actively following the cohort members through in-person home visits every 2 years, in addition to the passive follow-up through the participants' visits to a field clinic established to provide primary care study participants and their families. Our first follow-up visits started in October, 2002; to date, we completed in-person follow-up home visits and have collected questionnaire, clinical data and biological samples from 9,500 of our 11,753 cohort members. Almost all published epidemiological studies have used either retrospective assessments of arsenic exposure or examined ecological associations without individual exposure assessments. Our ongoing cohort study is the first to prospectively examine the dose-response relationship between arsenic exposure and skin lesions using individual-level exposure data. Results of our prospective analyses will undoubtedly shed light on the health effects of arsenic at dose ranges that are relevant for both Bangladesh and the U.S.A.

Publications for Project 3

- Ahsan H, Perrin M, Rahman A, Parvez F, Stute M, Zheng Y, Milton AH, Brandt-Rauf P, van Geen A, Graziano J. Association between drinking water and urinary arsenic levels and skin lesions in Bangladesh. *Journal of Occupational and Environmental Medicine* 2000; 42(12): 1195-1201.
- Do T, Perrin M, Ahsan H, Parvez F, Hasnat A, Graziano J, Brandt-Rauf P. Transforming growth factor- expression, urinary arsenic and arsenic-induced skin lesions in Bangladesh. *Biomarkers* 2001; 6(2): 127-132.
- van Geen, Y. Zheng, R. Versteeg, M. Stute, A. Horneman, R. Dhar, M. Steckler, A. Gelman, C. Small, H. Ahsan, J. Graziano, I. Hussain, and K. M. Ahmed. Spatial Variability of Arsenic in 6000 Contiguous Tube Wells of Araihasar, Bangladesh. *Water Resources Research* 2003; 39(5): 1140-51.
- van Geen, Y. Zheng, R. Versteeg, M. Stute, A. Horneman, R. Dhar, M. Steckler, A. Gelman, C. Small, H. Ahsan, J. Graziano, I. Hussain, and K. M. Ahmed. Spatial Variability of Arsenic in 6000 Contiguous Tube Wells of Araihasar, Bangladesh. *Water Resources Research* 2003; 39(5): 1140-51.
- Ahsan H, Chen Y, Wang C, Slavkovich V, Graziano JH, Santella RM. DNA repair gene *XPD* and susceptibility to arsenic-induced hyperkeratosis. *Toxicology Letters* 2003; 143(2): 123-131.

Ahsan H, Chen Y, Kibriya MG, Slavkovich V, Graziano JH, Santella RM. Oxidative stress genes myeloperoxidase and catalase and susceptibility to arsenic-induced hyperkeratosis. *Cancer Letters* 2003; 201(1): 57-65.

Chen Y, Ahsan H. Excess risk of internal cancers due to arsenic exposure from drinking water in Bangladesh. *American Journal of Public Health*. In press.

Gamble MV, Ahsan H, Liu X, Factor-Litvak P, Slavkovich V, Parvez F, Hussain I, Momotaj H, Graziano JH. Folate deficiency, hyperhomocysteinemia and exposure to arsenic in drinking water in Bangladesh. Submitted for Publication.

Chen Y, Ahsan H, Parvez MF, Graziano JH, Howe GR. Validity of a food frequency questionnaire for a large prospective cohort study in Bangladesh. Submitted for publication.

Parvez MF, Ahsan H, Chen Y, Hussain AZMI, Momotaj H, Dhar R, van Geen A, Graziano, JH. The Prevalence of Arsenic Exposure and Awareness of Its Health Risks in Bangladesh Population - Results from a Large Population-based Study. Submitted for publication.

Project 4: Environmental Arsenic, Pregnancy and Children's Health

P.I.: Joseph Graziano

Substantial progress has been made with each of the four specific aims of this project. This report focuses one aim, i.e., our effort to determine whether arsenic exposure from the consumption of groundwater is associated with diminished intellectual function in children. Sadly, the answer is yes.

Exposure to arsenic has long been known to have neurologic consequences in the occupational setting, but to date there have been no well controlled studies in children. In Bangladesh, nearly 40 million people have been chronically exposed to naturally occurring arsenic in groundwater used for drinking and cooking. We have completed a cross-sectional investigation of intellectual function in 201 ten year-old children in Arai hazar, Bangladesh. Well water arsenic concentrations, measured with sophisticated technology (ICP-MS) at Columbia University ranged from 0.1 to 790 µg/l. Roughly 80 of these were in the low range, less than 50 µg/l. Children and their mothers came to a field clinic in Arai hazar, where the children received a medical examination, and provided a small blood and urine sample. Their intellectual function was assessed using a culturally modified version of the WISC-III, which yields a Total Score, a Verbal Score, and a Performance Score; the latter score, which reflects visual-motor functioning, is the domain of function known to be particularly adversely affected by lead. Since the WISC-III has not been standardized (i.e., "normed") in Bangladesh - which would require testing of many thousands of children across the country - we can report only raw exam scores rather than traditional IQ scores.

After taking into account other well known factors that influence a child's intelligence (e.g., mother's education, mother's intelligence, child's height, head circumference, blood lead, socioeconomic status, etc.) water arsenic concentration was significantly and adversely associated with child intelligence, particularly the Performance Score. Since many wells in Bangladesh have water manganese concentrations above the WHO standard of 500 µg/l, we also measured and controlled for water manganese. This did not alter the observed association between water arsenic and child intelligence. *Of particular concern, children with water arsenic*

concentrations greater than approximately 10 µg/l performed significantly more poorly than those with less than 10 µg/l.

The importance of these findings is profound in the U.S. and elsewhere. The recent EPA decision to lower the allowable limit of arsenic in drinking water from 50 to 10 µg/l appears highly justified. For example, today, 10% of the population of New Hampshire and thousands in the Southwestern states are drinking water in excess of 10 µg/l and even 50 µg/l. If the new EPA arsenic policy is implemented, it will offer protection to countless thousands of children. The Columbia University scientists are now conducting additional studies in younger (6 year-old) children in Bangladesh, and are planning a study of U.S. children.

Manuscripts in preparation for Environmental Health Perspectives:

Wasserman, GA, Liu, X, Parvez, F, Ahsan, H, Factor-Litvak, P, Van Geen, A, Slavkovich, V, Hussain, I, Momotaj, H, Graziano, JH: Water arsenic exposure and children's intellectual function in Araihasar, Bangladesh.

Gamble, MV, Ahsan, H, Liu, X, Factor-Litvak, P, Slavkovich, V, Parvez, F, Hussain, I, Momotaj, H, Graziano, JH: Folate deficiency, hyperhomocysteinemia and exposure to arsenic in drinking water in Bangladesh.

Project 5: Arsenic mobilization in Bangladesh Groundwater

P.I.s: Yan Zheng and Martin Stute

The goal of project 5 is to document the spatial and temporal variability of groundwater As concentrations in Araihasar, Bangladesh where biomedical Projects 3 and 4 are being conducted, and to gain a better understanding of the geophysical, hydrological, and geochemical processes that regulate As levels in groundwater. There have been several notable advances during the past year:

Hydrological setting of the shallow Holocene aquifer: Precise GPS surveys of the region and water level monitoring allowed us to establish hydrographs for the rivers and our 7 monitoring well nests and a network of existing private tube wells. They indicate that surface and ground waters in Araihasar are well connected and that surface waters contribute most recharge. Residence times derived from $^3\text{H}/^3\text{He}$ data range from a few years, beneath sandy surfaces, to decades for water beneath silty clay surfaces. Residence time of ground waters increase with depth at all sites corresponding to vertical recharge rates for the shallow aquifer below the lowest seasonal water level ranging from 10 to 70 cm/year.

Groundwater and sediment redox state of the shallow Holocene aquifer: Investigation of arsenic geochemistry of both water and sediment samples in two villages from Araihasar demonstrate that As is mobilized from a dispersed sedimentary source, likely upon reduction and/or reductive dissolution of Fe-oxides with sorbed As. It is noteworthy that ground waters in the shallow aquifer are all anoxic and usually have elevated dissolved iron concentrations, indicating that groundwater has reached a redox condition that is thermodynamically plausible to mobilize As. Even ground waters sampled in sandy areas with a few years residence time displayed highly elevated dissolved Fe concentrations and low but consistently detectable As at ~ 10 µg/L, with all of the As being arsenite. Arsenic increases at a

surprisingly constant rate as a function of residence time, indicating that water/sediment contact time plays an important role in As mobilization. These observations suggest factors other than redox conditions of groundwater control the spatial variability of As. The likely candidates other than residence time of groundwater for these factors include mobility of sedimentary As and redox state and sorption capacity of Fe-oxides.

Depth distribution of Arsenic and aquifer sustainability: Geochemical and hydrogeological investigations in Araihasar, Bangladesh identified an As-containing, shallow Holocene aquifer and low As (i.e., safe) deeper aquifers of either Holocene or Pleistocene/Pliocene age. Three factors have been identified that contribute to low dissolved As concentrations in deep aquifers of our study area in central eastern Bangladesh, namely, 1) the hydrological separation provided by the impermeable muddy sediments, 2) the redox state of groundwater and sediment, and 3) the lack of sedimentary sources of arsenic. These results (Zheng et al., in revision) *point to the great potential of the deeper aquifer in this region as a long-term drinking water supply*. This is because these deep aquifer waters are reasonably well separated from the shallow As containing aquifer, and the sediments of the aquifer do not contain appreciable amounts of phosphate extractable As. Recharge rates of the deeper aquifer derived from hydraulic and tracer data are comparable to withdrawal rate of water for domestic usage. However, abstraction rates would increase by one or two orders of magnitude, if irrigation wells would tap the deeper aquifers as well. Some of that increased demand might be met by an increased recharge rate, but a danger remains that deeper aquifers become contaminated with shallow ground water high in As. Therefore, *the deep aquifer water should not be used for irrigation* until the aquifer's hydrological and chemical response to increased withdrawal is better understood.

Publications

- Ahsan H, Perrin M, Rahman A, Hasnat A, Parvez MF, Brandt-Rauf P, Zheng Y, Stute M, van Geen A, Graziano J, Association between drinking water and urinary arsenic levels and skin lesions in Bangladesh, *J. Occup. Environ. Med.* 42(12): 1195-1201, 2000.
- Stute, M., Tritium (³H) in precipitation in Bangladesh, in "Groundwater contamination in the Bengal delta plain of Bangladesh", Royal Technical Institute (KTH) Special Publication TRITA-AMI Report 3084, pp. 109-117, 2001.
- van Geen, A., H. Ahsan, A. H. Horneman, R. Kdhar, Y. Zheng, I. Hussain, K. M. Ahmed, A. Gelman, M. Stute, H. J. Simpson, S. Wallace, C. Small, F. Parvez, V. Slavkovich, N. J. LoIacono, M. Becker, Z. Cheng, H. Momotaj, M. Shahnewaz, A. A. Seddique, and J. H. Graziano, Promotion of well switching to mitigate the current arsenic crisis in Bangladesh, *Bulletin of the World Health Organization*, 80, 732-737, 2002.
- He, Y., Y. Zheng, and D.C. Locke (2002) Differential pulse cathodic stripping voltammetric determination of nanomolar levels of dissolved sulfide applicable to field analysis of groundwater. *Analytica Chimica Acta* 459 (2): 209-217.
- van Geen, Y. Zheng, R. Versteeg, M. Stute, A. Horneman, R. Dhar, M. Steckler, A. Gelman, C. Small, H. Ahsan, J. Graziano, I. Hussein, and K. M. Ahmed, Spatial variability of arsenic in 6000 tube wells in a 25 km² area of Bangladesh, *Water Resources Research*, 35(5), 1140, 2003.
- van Geen A, Zheng Y, Stute M, Ahmed KM, Comment on "Arsenic mobility and groundwater extraction in Bangladesh" (II) *Science*, 300, 584C-584C, 2003.

Zheng, Y., M. Stute, A. van Geen, I. Gavrieli, R. Dhar, H. J. Simpson, P. Schlosser, and K. M. Ahmed, Redox control of arsenic mobilization in Bangladesh groundwater, *Applied Geochemistry*, in press since March, 2002.

Submitted

Zheng, Y., A. van Geen, M. Stute, R. Dhar, Z. Mo, Z. Cheng, A. Horneman, I. Gavrieli, H. J. Simpson, R. Versteeg, M. Steckler, S. Goodbred, K. M. Ahmed, M. Shanewaz, and M. Shamsudduha, Contrast in groundwater arsenic in shallow Holocene and deeper older aquifers: a case study of two villages in Araihasar, Bangladesh, submitted to *Water Resources Research*, October 2002, under revision.

Dhar, R. K. Y. Zheng, J. Rubenstone, and A. van Geen, Rapid spectrophotometric determination of dissolved inorganic arsenic in groundwater, *Environmental Science and Technology*, submitted, January 2003.

He, Y., Y. Zheng, M. Ramanaraine, D. C. Locke. Differential Pulse Cathodic Stripping Voltammetric Speciation Analysis of Trace Level Inorganic Arsenic in Natural Waters, *Anal. Chim. Acta.*, accepted, Oct. 2003.

Project 6: Redistribution of arsenic (As) and other contaminants at sites in New Jersey and Maine

P.I.s: Harry J. Simpson, Martin Stute, and Steven Chillrud

Arsenic mobilization in surface and ground waters presents major challenges for minimizing chronic human As exposure. We are currently working at two Superfund sites, both of which have elevated As concentrations. The Superfund site which has been the focus of our field efforts during the past year is Vineland NJ, the location of a manufacturing facility for arsenical biocides which operated for about three decades beginning in the late 1940s. Many hundreds of tons of arsenic from this facility were dispersed in local soils, ground waters, streams and sediments.

A major treatment facility at the site has been in operation for about two years to remove both organic and inorganic As from the groundwater beneath the site. One of the primary goals and design criteria for the extraction wells was to eliminate off-site migration of As occurring via groundwater discharge to the Blackwater Branch, which flows along one perimeter segment of the site. We have used environmental samples of sediment, pore waters and surface waters along the stream to establish the extent of ongoing dispersal of As from the plant site during full operation of the treatment facility. During July 2003, concentrations of dissolved As increased by an order of magnitude (2.5 to 24 ppb) in this stream as it transited about 1.4 km around the property. Preliminary assessment of our results indicate that the dominant source of dissolved As to the stream was current inflows of contaminated ground waters, rather than diffusion of highly contaminated pore waters out of the stream sediments.

Another significant difficulty associated with remediation of the Vineland site, which is projected to have cumulative costs on the order of \$100 million over the next several decades, is rapid clogging of a number of the extraction well screens. This reduces groundwater extraction rates, contributes to continued outflow of ground into surface waters, and makes treatment plant

operations less efficient due to frequent interruptions for chemical flushing of the wells. We conducted experiments that allowed us to exclude the hypothesis that entrainment of O₂ through the well by rapid pumping was responsible for the clogging. Field testing at Vineland of an experimental system for removing both organic and inorganic As was quite promising. The concept of this remediation approach is based on using zero-valent iron (metallic iron filings) as a medium for extraction of dissolved As. One of the advantages of this approach is that it doesn't require oxidizing the inflowing water to achieve precipitation and removal from solution of iron. If this approach can be further refined, it offers an alternative strategy to further decrease dissolved As levels beyond those now provided by the treatment plant in place at Vineland.

The second Superfund site at which we are working (Winthrop, ME) is a closed landfill that has undergone extensive remediation, including operation of pump and treat facilities for a number of years, but continues to have high dissolved As concentrations in ground waters (200-400 ppb). These elevated As groundwater levels appear to be derived from "natural" sediment As, present at average abundances (5 mg/kg) typical of soils and other unconsolidated crustal materials, which is mobilized by intense reducing conditions associated with landfill leachate. *Our findings suggest that As mobilization associated with landfills could be a widespread problem at locations not currently designated as national priority sites*, since it appears as if natural abundances of As in sediment are sufficient to generate quite elevated dissolved arsenic when reducing conditions are induced.

Publications

- He, Y., Y. Zheng, and D.C. Locke (2002) Differential pulse cathodic stripping voltammetric determination of nanomolar levels of dissolved sulfide applicable to field analysis of groundwater. *Analytica Chimica Acta* 459 (2): 209-217.
- Santella, N., D.T. Ho, P. Schlosser, and M. Stute (2003). The distribution of atmospheric SF₆ near a large urban area as recorded in the vadose zone. *Environmental Science and Technology*, 37 (6) 1069-1074. (Project 6, Core C).
- Keimowitz, A.R., S. Datta, M. Stute, H.J. Simpson, S.N. Chillrud, J. Ross, and M. Tsang (2003). Naturally-occurring arsenic: mobilization at a landfill in Maine and implications for remediation. Submitted to *Applied Geochemistry*.

Abstracts

- He Y, Y. Zheng, D.C. Locke, H.J. Simpson and M. Stute (2001), Dissolved sulfide in groundwater with elevated arsenic concentrations at Winthrop, Maine, EOS. Transactions American Geophysical Union 82(47), Fall Meet. Suppl., Abstract H32C-0316, F434.
- Stute M., H.J. Simpson, S.N. Chillrud, E. Law-wai, N. Santella, J. Ross, D.T. Ho, P. Schlosser, Y. Zheng, G.M. Dobbs (2001), Application of SF₆, Bromide and ³H/³He for Tracing Groundwater Transport Beneath a Landfill, EOS. Trans. AGU 82(47), Fall Meet. Suppl., Abstract H22C-0371, F403.
- Stute M., H.J. Simpson, S.N. Chillrud, E. Law-wai, N. Santella, J. Ross, D.T. Ho, P. Schlosser, Y. Zheng, A. van Geen, G.M. Dobbs, B.K. Butler (2001); Arsenic mobilization in reducing groundwaters at a Superfund site in Maine: remediation through aquifer redox

- manipulation? (Abstract). Arsenic in drinking water, an international conference, Columbia University, Nov. 26-27.
- Tsang M., S. Chillrud, M. Stute, H.J. Simpson, J. Ross, A. Keimowitz, Y. Zheng, S. Wallace, Z. Cheng, and A. van Geen (2002), Arsenic mobilization from fine particles under reducing conditions: implications for groundwater remediation (Abstract), Northeastern Geological Society of America, 37th Annual Meeting.
- Datta, S., A.R. Keimowitz, H.J. Simpson, M. Stute, S. Chillrud, M. Tsang, Y. Zheng, A. van Geen and G.M. Dobbs (2002), Redox controls on arsenic mobility beneath Winthrop landfill, Maine, Arsenic in New England, New Hampshire Consortium on Arsenic, May 29-31.
- Stute, M., H.J. Simpson, S.N. Chillrud, E. Law-wai and P. Schlosser (2002), Tracing groundwater transport underneath a landfill with SF₆, Br and ³H/³He (Abstract), Special session S31. Environmental tracers for groundwater dating. Goldschmidt Conference, Davos, August.
- Keimowitz, A.R., S. Datta, M. Stute, H.J. Simpson, S.N. Chillrud, M. Tsang, J. Ross (2003), Arsenic mobilization under reducing conditions beneath a landfill in Maine. Abstracts of Papers, 226th ACS National Meeting, NY.
- Keimowitz, A.R.; Y. Zheng; S.N. Chillrud, Y. He, J. Ross, M. Nanes, J. Ross, S. Datta, F. Family, M. Stute, H.J. Simpson (2003). Estimating Sources of As to a Contaminated Stream. Annual SBRP Meeting, October. (Poster).

Project 7 Assessment and Remediation of Arsenic in Groundwater

P.I.: Alexander van Geen

This project seeks to translate fundamental knowledge on arsenic behavior into improved mitigation for the US and Bangladesh. The project spearheaded the effort to analyze groundwater from approximately 6000 tube wells within a 25 km² area Bangladesh (van Geen et al., 2003a), which serves as the underpinnings of the biomedical studies in Projects 3 and 4. The effectiveness of the project's mitigation through (1) the promotion of well-switching (van Geen et al., 2002; Gelman et al., in review) and (2) the installation of community wells in the most affected villages (van Geen et al., 2003b) has been confirmed by a remarkable drop in urinary arsenic levels for cohort subjects studied for 2 years under Projects 3 and 4. Two kinds of simple arsenic removal systems were also tested in Bangladesh and found to be technically effective, but community wells are clearly preferred in our study area (Cheng et al. b, in review, Nikolaidis et al., in preparation).

On the basis of the above observations, a proposal for arsenic mitigation formulated by the SBRP team was presented to the government of Bangladesh and the World Bank in October 2003. The plan relies on mapping groundwater As and the installation of community wells at the national scale, while generating and keeping the information available at the village scale. A comparison of our data with field tests obtained by the existing national mitigation program indicates that 12% of wells were misidentified by the field tests, in the sense that wells reported as containing <50 µg/L actually contain 50-100 µg/L (van Geen et al., in preparation). Comparison of field kit data broken down to the village level with our results indicates, however, that the field results could be used to install safe community wells (van Geen et al., in preparation).

Project 7 contributed to the fundamental understanding of the mechanisms of As mobilization by demonstrating the key role of micro-organisms through incubations of Bangladesh sediment (van Geen et al., accepted) and by developing new approaches to sediment and groundwater sampling (Horneman et al., submitted; van Geen et al., in preparation). A collaboration with French scientists has produced a detailed comparison of microbial diversity in groundwater pumped from high and low arsenic wells (Thoral et al. a, in preparation). The same collaboration has improved our understanding of interactions between As and Fe at the molecular scale, for both natural and model systems, using X-ray spectroscopy (Thoral et al. b,c, in preparation). The combination of these approaches will help to determine the extent to which irrigation pumping could alleviate or worsen the arsenic crisis in Bangladesh (van Geen et al., 2003c).

Project 7 also contributed significantly to the improvement of a field method for arsenic (Dhar et al., in revision). This work led to a US and international patent application for an inexpensive double-beam infra-red colorimeter (PI and colleagues at Caltech, co-inventors). A rapid and sensitive method for analyzing groundwater for a wide suite of elements including arsenic was also developed (Cheng et al., in review).

Publications led by Project 7

- van Geen, A., S. Thoral, J. Rose, J. M. Garnier, Y. Zheng, and J. Y. Bottero, Decoupling of As and Fe release to Bangladesh groundwater under reducing conditions. Part II: Evidence from sediment incubations, accepted pending minor revision, *Geochim. Cosmochim. Acta*, December 2003.
- van Geen, Y. Zheng, R. Versteeg, M. Stute, A. Horneman, R. Dhar, M. Steckler, A. Gelman, C. Small, H. Ahsan, J. Graziano, I. Hussein, and K. M. Ahmed, Spatial variability of arsenic in 6000 tube wells in a 25 km² area of Bangladesh, *Water Resources Research*, 35(5), 1140, doi:10.1029/2002WR001617, 2003a.
- van Geen, A., K. M. Ahmed, A. A. Seddique, and M. Shamsudduha, Community wells to mitigate the current arsenic crisis in Bangladesh, *Bulletin of the World Health Organization*, 82, 632-638, 2003b.
- van Geen, A., Y. Zheng, M. Stute, and K. M. Ahmed, Comment on “Arsenic mobility and groundwater extraction in Bangladesh” (II), *Science*, 300, 584, 2003c.
- van Geen, A., H. Ahsan, A. H. Horneman, R. K. Dhar, Y. Zheng, I. Hussain, K. M. Ahmed, A. Gelman, M. Stute, H. J. Simpson, S. Wallace, C. Small, F. Parvez, V. Slavkovich, N. J. LoIacono, M. Becker, Z. Cheng, H. Momotaj, M. Shahnewaz, A. A. Seddique, and J. H. Graziano, Promotion of well-switching to mitigate the current arsenic crisis in Bangladesh, *Bulletin of the World Health Organization*, 80, 732-737, 2002.

Publications with a significant contribution from Project 7

- Zheng, Y., M. Stute, A. van Geen, I. Gavrieli, R. Dhar, H. J. Simpson, P. Schlosser, and K. M. Ahmed, Redox control of arsenic mobilization in Bangladesh groundwater, *Applied Geochemistry*, in press since March, 2002.
- Ahsan H, Perrin M, Rahman A, Hasnat A, Parvez MF, Brandt-Rauf P, Zheng Y, Stute, M, van Geen A, Graziano J, Association between drinking water and urinary arsenic levels and skin lesions in Bangladesh, *J. Occup. Environ. Med.* 42(12): 1195-1201, 2000.

Manuscripts submitted/in revision led by Project 7

- Cheng, Z., Y. Zheng, R. Mortlock, A. van Geen, Rapid multi-element analysis of groundwater by high-resolution inductively coupled plasma mass spectrometry, submitted to *Env. Sci. Technol.*, July 2003b.
- Cheng, Z., A. van Geen, C. Jing, X. Meng, A.A. Seddique, K.M. Ahmed, Performance of a household-level arsenic removal system during 4-month deployments in Bangladesh, submitted to *Env. Sci. Technol.*, November 2003a.
- Gelman, A., M. Trevisani, H. Lu, and A. van Geen. Using spatial data for local decision analysis, with application to arsenic in drinking water in Bangladesh, submitted to *Risk Analysis*, June 2003.
- Horneman, A., A. van Geen, D. Kent, P. E. Mathe, Y. Zheng, R. K. Dhar, S. O'Connell, M. Hoque, Z. Aziz, M. Shamsudduha, A. Seddique, and K. M. Ahmed, Decoupling of As and Fe release to Bangladesh groundwater under reducing conditions. Part I: Evidence from sediment profiles, submitted to *Geochim. Cosmochim. Acta*, September 2003.
- Nikolaidis, N. P., Z. Cheng, and A. van Geen, Removal of arsenic with zero-valent iron: pilot applications in Bangladesh, chapter in preparation for *Advances in Arsenic Research*, American Chemical Society Symposium Series Volume, December 2003.
- Thoral, S. C. Yanez-Neaman, R. Christen, J. Rose, J.M. Garnier, A. van Geen, T. Heulin, and V. Chapon, Comparison of bacterial diversity in Bangladesh groundwater with contrasting As and Fe concentrations, in preparation for *Appl. Env. Microbiol.*, December 2003.
- Thoral, S., J. Rose, J.M. Garnier, A. van Geen, T. Heulin, A. Masion, O. Proux, J.L. Hazeman, and J.Y. Bottero, EXAFS analysis of oxidized groundwater from Bangladesh: inhibition of As-Fe interactions by P and Si, in preparation for *Geochim. Cosmochim. Acta*, December 2003.
- Thoral, S., J. Rose, J.M. Garnier, A. van Geen, A. Traverse, and J. Y. Bottero, As and Fe EXAFS study of Fe(II)-As(III) coprecipitates during oxidation, in preparation for *Env. Sci. Technol.*, December 2003.

Manuscripts submitted/in revision with a significant contribution from Project 7

- Dhar, R. K. Y. Zheng, J. Rubenstone, and A. van Geen, Rapid spectrophotometric determination of dissolved inorganic arsenic in groundwater, in revision for *Environmental Science and Technology*, January 2003.
- Zheng, Y., A. van Geen, M. Stute, R. Dhar, Z. Mo, Z. Cheng, A. Horneman, I. Gavrieli, H. J. Simpson, R. Versteeg, M. Steckler, S. Goodbred, K. M. Ahmed, M. Shanewaz, and M. Shamsudduha, Contrasting high-arsenic Holocene alluvial aquifers and low-arsenic deep aquifers in two villages of Araihaazar, Bangladesh, in revision for *Water Resources Research*, November 2002.

Core A: Trace Metals Research Core Laboratory P.I.: Joseph Graziano

The Trace Metals Research Support Core currently provides analytical support to three of the biomedical research cores under this SBRP-Projects 1, 3 and 4. The Core has the capability of measuring a broad range of metals and metalloids in biological samples, including Pb, Hg, As, Cd, Mn, Fe, Cu, Zn, Cr, Co, Pt, K and others. In addition, a number of simple biochemical assays are performed so as to allow for the interpretation of the metal concentration data.

To address one of the major aims of the Core, measuring urinary metabolites in urine, during the past year, a newly acquired Perkin-Elmer Elan II DRC Mass Spectrometer has been installed and is fully operational. This has led to the successful adaptation of an assay established in the Core to measure arsenic metabolites in urine. An HPLC is coupled to the ICP-MS enabling the highly sensitive detection of inorganic and organic arsenic species without on-line digestion of organic forms. The data is fed directly into a computer where data quantification and calibration are achieved via TotalChrom 6.2, after converting the ELAN.nsf data files to TotalChrom.raw files through ChromLink. TotalChrom offers powerful and flexible data review. Throughput of arsenic metabolite measurements has been increased from 1-2 samples per day (by graphite furnace atomic absorption) to 20 samples per day.

Urinary arsenic metabolite data derived from this Core Laboratory is being used to test the general hypothesis that people who are poor metabolizers of arsenic may be at highest risk for disease. For example, 1200 samples analyzed for Dr. Habibul Ahsan (Project 3) will test the hypothesis that cohort participants who have skin lesions are more likely to be poor metabolizers than those without skin lesions. In addition, 300 samples analyzed for Dr. Mary Gamble, who has a separate R01 grant on arsenic, will help to establish which nutritional factors influence arsenic metabolism. Finally, in Dr. Graziano's studies (Project 4) evaluating the effect of arsenic exposure on child intelligence, urine samples are being analyzed to determine if children who are poor metabolizers of arsenic are at increased risk for cognitive deficits.

The number and type of biological samples analyzed during the past grant period are outlined below:

- Total urinary arsenic - 6,100 samples
- Urinary arsenic metabolites - 1000 subjects
- Urinary creatinine - 6,100
- Total hemoglobin - 2,100
- Zinc in purified protein - 15
- Blood lead - 410

Core B: Geochemistry Core

PIs: Steven N. Chillrud and Alexander van Geen

This analytical core laboratory is housed at Lamont-Doherty Earth Observatory (LDEO). It provides sample preparation and analyses to six projects of this Superfund application (biomedical projects 1, 3 and 4 and earth science projects 5, 6 and 7) and trains Ph.D. students and post-doctoral fellows. Sample preparation and analyses are carried out for water, soil, sediment, leachates, plant materials and pre-ashed blood.

Notable advances during the last 3.5 years of funding for this analytical core that are discussed below include increasing the efficiency and amount of information we obtain with environmental analyses, by shifting from measuring a single analyte at a time (by atomic absorption spectrometry; AAS) to measuring multiple elements simultaneously on a high resolution inductively coupled mass spectrometry (HR-ICP-MS). We have also developed a method for rapid sample preparation and analysis of blood samples for lead concentrations and lead isotope ratios via multi-collector ICP-MS. Furthermore, since no standard reference material for a blood matrix existed for stable lead isotope analyses, we created an internal blood

standard for stable lead isotope analysis using out-of-date blood bank red cells. The blood standard was made by adding saline to packed red cells to simulate blood without coagulants, generating 155 frozen “standardized” aliquots. Initial analysis of vials from the beginning, middle and end of the transfer process show that no contamination occurred throughout the process. Thus, these aliquots are now a resource that can be made available to all U.S. investigators who do measurements of stable lead isotopes in blood in their research.

Switching to HR-ICP-MS analysis has allowed routine analysis of 33 major and trace elements, including As, in groundwater samples and has been significant for the projects in two direct ways. First, this method has reduced the detection limit for As to 0.1 µg/L, rather than the 5 µg/L detection limit by GFAA. This proved to be significant, for example, for the interpretation of biomedical data collected under Projects 3 and 4, in that there are no longer any water samples with “non-detectable” arsenic. *This provides enormous power to the biomedical projects to their ability to refine the understanding of arsenic dose-response relationships in the low range, i.e., the range of interest in the U.S.,* and allows all statistical analyses to treat water arsenic as a continuous, rather than categorical variable. In addition, the collection of quality control data has shown a reduction of the standard deviation for replicate measurements from ± 10 µg/L by GFAA to ± 4 µg/L by HR ICP-MS. This increase in precision will also strengthen the ability of the public health scientists to define dose-response relationships. Second, the ICP-MS technique has enabled us to quickly collect data on a wide range of elements “simultaneously” in a very large number of samples. As an example, in a survey of 630 groundwater samples from Northeast Arai-hazar in Bangladesh, about 80% of the samples were found to contain Mn levels above the World Health Organization’s guideline value of 500-µg/L. This information was taken into account in Project 3, in that studies of arsenic exposure and child intelligence were able to control for possible effects of water Mn.

The number of total analyses carried out by the core is shown in Table 1. More than

Table 1. Summary of total analyses by Geochemistry Core over the last 3.5 years

Analysis	Analyte	Samples	QA/QC	Total	# of analytes	Total Analyses
GFAAS	As	6,750	5,230	11,980	1	11,980
FAAS	Fe	985	595	1,580	1	1,580
HR-ICP-MS	As, P or Fe	150	31	181	2	362
HR-ICP-MS	multi	164	35	199	5	995
HR-ICP-MS	multi	841	459	1,300	6	7,800
HR-ICP-MS	multi	42	38	80	16	1,280
HR-ICP-MS	multi	31	16	47	22	1,034
HR-ICP-MS	multi	11	23	34	25	850
HR-ICP-MS	multi	76	36	112	27	3,024
HR-ICP-MS	multi	2,544	840	3,384	33	111,672
HR-ICP-MS	Pb or Fe	0	45	45	1	45
MC-ICP-MS	lead isotopes	267	312	579	4	2,316
COD	COD	79	19	98	1	98
GC	TC& TN	94	19	113	2	226
Colorimetry	As & PO4				2	
Colorimetry	Si	45	18	63	1	63
GC	SF6	100	35	135	1	135
Gamma	Cs-137, Be-7, K-40	924	90	1,014	3	3,042
Totals		12,179	7,751	19,930		146,502

19,000 samples, standards and blanks have been analyzed for a total of over 145,000 analytes in support of these six projects of the Columbia Superfund Basic Research Program.

Published and submitted manuscripts related to Geochemistry Core:

- Ahsan H, Perrin M, Rahman A, Hasnat A, Parvez MF, Brandt-Rauf P, Zheng Y, Stute, M, van Geen A, Graziano J, Association between drinking water and urinary arsenic levels and skin lesions in Bangladesh, *J. Occup. Environ. Med.* 42(12): 1195-1201, 2000.
- Cheng, Z., Y. Zheng, R. Mortlock, A. van Geen, Rapid multi-element analysis of groundwater by high-resolution inductively coupled plasma mass spectrometry, submitted to *Env. Sci. Technol.*, July 2003.
- Cheng, Z., A. van Geen, C. Jing, X. Meng, A.A. Seddique, K.M. Ahmed, Performance of a household-level arsenic removal system during 4-month deployments in Bangladesh, submitted to *Env. Sci. Technol.*, November 2003.
- Chillrud, S.N., N.G. Hemming, J.M. Ross, S. Wallace, N. LoIacono. A rapid and precise procedure for Pb isotopes in whole blood by Fe co-precipitation and MC-ICP-MS analysis. Submitted to *Applied Geochemistry*.
- Gelman, A., M. Trevisani, H. Lu, and A. van Geen. Using spatial data for local decision analysis, with application to arsenic in drinking water in Bangladesh, submitted to *Risk Analysis*, June 2003.
- Horneman, A., A. van Geen, D. Kent, P. E. Mathe, Y. Zheng, R. K. Dhar, S. O'Connell, M. Hoque, Z. Aziz, M. Shamsudduha, A. Seddique, and K. M. Ahmed, Decoupling of As and Fe release to Bangladesh groundwater under reducing conditions. Part I: Evidence from sediment profiles, submitted to *Geochim. Cosmochim. Acta*, September 2003.
- Keimowitz, A.R. S. Datta, M. Stute, H.J. Simpson, S.N. Chillrud, J. Ross, and M. Tsang. Naturally-occurring arsenic: mobilization at a landfill in Maine and implications for remediation. Submitted to *Applied Geochemistry*, 2003.
- van Geen, A., S. Thoral, J. Rose, J. M. Garnier, Y. Zheng, and J. Y. Bottero, Decoupling of As and Fe release to Bangladesh groundwater under reducing conditions. Part II: Evidence from sediment incubations, accepted pending minor revision, *Geochim. Cosmochim. Acta*, December 2003.
- van Geen, Y. Zheng, R. Versteeg, M. Stute, A. Horneman, R. Dhar, M. Steckler, A. Gelman, C. Small, H. Ahsan, J. Graziano, I. Hussein, and K. M. Ahmed, Spatial variability of arsenic in 6000 tube wells in a 25 km² area of Bangladesh, *Water Resources Research*, 35(5), 1140, doi:10.1029/2002WR001617, 2003a.
- van Geen, A., K. M. Ahmed, A. A. Seddique, and M. Shamsudduha, Community wells to mitigate the current arsenic crisis in Bangladesh, *Bulletin of the World Health Organization*, 82, 632-638, 2003b.
- Zheng, Y., M. Stute, A. van Geen, I. Gavrieli, R. Dhar, H. J. Simpson, P. Schlosser, and K. M. Ahmed, Redox control of arsenic mobilization in Bangladesh groundwater, *Applied Geochemistry*, in press since March, 2002.
- Zheng, Y., A. van Geen, M. Stute, R. Dhar, Z. Mo, Z. Cheng, A. Horneman, I. Gavrieli, H. J. Simpson, R. Versteeg, M. Steckler, S. Goodbred, K. M. Ahmed, M. Shanewaz, and M. Shamsudduha, Contrasting high-arsenic Holocene alluvial aquifers and low-arsenic deep aquifers in two villages of Araihaazar, Bangladesh, in revision for *Water Resources Research*, November 2002.

Core C: Hydrogeology Research Support Core Laboratory
P.I.s: M. Stute, M. Steckler, R. Versteeg, and P. Schlosser,

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.

The notable advances during the past year have focused on hydraulic and tracer studies in Bangladesh and at the Vineland Superfund site. For water level data to be useful, the precise elevation of wells and surface water monitoring sites need to be known. In January 2003, we undertook a differential GPS campaign to determine the precise horizontal and vertical positions of the monitoring wells in Araihasar, Bangladesh, and performed topographic surveys to provide elevation data for hydrological modeling. Ten wells or nearby locations, and 3 surface water monitoring sites were occupied for 1 to 7 hours each yielding a mean vertical precision of 20 mm (2 sigma). In addition, we undertook 9 topographic transects with 153 sites. These positions were occupied for between 8 and 30 minutes resulting in mean uncertainties of 22 and 24 mm horizontally and 62 mm vertically. Water-filled 'U'-tubes were used to determine elevations of neighboring wells radiating out from the GPS points with known absolute elevations. These data sets, in combination with our water level observations are being used for a 3-dimensional groundwater flow and transport model currently being constructed for a domain in the southwest of our study area in Araihasar.

Key elements of the hydrogeology core are the environmental tracers, which we use to determine ground water residence times. The most powerful, but also most expensive tracers we use are tritium (^3H) and its decay product, ^3He . It allows us to determine the year of recharge of the sampled ground water parcel. During our 2003 field season, we compared the cheaper transient tracers SF_6 and the chlorofluorocarbons (CFCs) with $^3\text{H}/^3\text{He}$ data, and tested several novel sampling techniques. While the CFCs were clearly affected by degradation, SF_6 showed promising results, and can be used on a larger scale in the future.

The following analysis were performed over the past year:

- a) Approximately 800 hydraulic head time series observations in Bangladesh,
- b) 4 Stream discharge measurements at Vineland site,
- c) 46 environmental SF_6 measurements in Bangladesh and at Vineland,
- d) 32 environmental CFC measurements in Bangladesh,
- e) 30 and 32 mass spectrometric measurements of ^3H and ^3He , respectively,
- f) 15 He, Ne, Ar, Kr, and Xe analyses,
- g) 6 radiocarbon analyses on water samples in Bangladesh,
- h) 60 $\delta^{18}\text{O}$ and $\delta^2\text{H}$ analyses for Bangladesh samples,
- i) characterization of water quality parameters at 11 surface water sampling sites in Bangladesh,
- j) elevation surveys and precise differential GPS positions at Bangladesh sites,
- k) Handheld GPS position measurements at all field locations.

Publications:

- Ahsan H, Perrin M, Rahman A, Hasnat A, Parvez MF, Brandt-Rauf P, Zheng Y, Stute, M, van Geen A, Graziano J, Association between drinking water and urinary arsenic levels and skin lesions in Bangladesh, *J. Occup. Environ. Med.* 42(12): 1195-1201, 2000.
- van Geen, A., H. Ahsan, A. H. Horneman, R. Kdhar, Y. Zheng, I. Hussain, K. M. Ahmed, A. Gelman, M. Stute, H. J. Simpson, S. Wallace, C. Small, F. Parvez, V. Slavkovich, N. J. LoIacono, M. Becker, Z. Cheng, H. Momotaj, M. Shahnewaz, A. A. Seddique, and J. H. Graziano, Promotion of well switching to mitigate the current arsenic crisis in Bangladesh, *Bulletin of the World Health Organization*, 80, 732-737, 2002.
- Stute, M., Tritium (³H) in precipitation in Bangladesh, in "Groundwater contamination in the Bengal delta plain of Bangladesh", Royal Technical Institute (KTH) Special Publication TRITA-AMI Report 3084, pp. 109-117, 2001.
- He, Y., Y. Zheng, and D.C. Locke (2002) Differential pulse cathodic stripping voltammetric determination of nanomolar levels of dissolved sulfide applicable to field analysis of groundwater. *Analytica Chimica Acta* 459 (2): 209-217.
- Santella, N., D.T. Ho, P. Schlosser, and M. Stute. The distribution of atmospheric SF₆ near a large urban area as recorded in the vadose zone. *Environmental Science and Technology*, 37 (6) 1069-1074, 2003.
- van Geen, Y. Zheng, R. Versteeg, M. Stute, A. Horneman, R. Dhar, M. Steckler, A. Gelman, C. Small, H. Ahsan, J. Graziano, I. Hussein, and K. M. Ahmed, Spatial variability of arsenic in 6000 tube wells in a 25 km² area of Bangladesh, *Water Resources Research*, 35(5), 1140, 2003.
- Goodbred, S. L. Jr, S. A Kuehl, M. S. Steckler, M. H. Sarker, Controls on facies distribution and stratigraphic preservation in the Ganges-Brahmuputra delta sequence, *Sedimentary Geology*, 155, 301-316, 2003.
- van Geen A, Zheng Y, Stute M, Ahmed KM Comment on "Arsenic mobility and groundwater extraction in Bangladesh" (II) *Science*, 300, 584C-584C, 2003.
- Zheng, Y., M. Stute, A. van Geen, I. Gavrieli, R. Dhar, H. J. Simpson, P. Schlosser, and K. M. Ahmed, Redox control of arsenic mobilization in Bangladesh groundwater, *Applied Geochemistry*, in press since March, 2002.

Submitted

- Zheng, Y., A. van Geen, M. Stute, R. Dhar, Z. Mo, Z. Cheng, A. Horneman, I. Gavrieli, H. J. Simpson, R. Versteeg, M. Steckler, S. Goodbred, K. M. Ahmed, M. Shanewaz, and M. Shamsudduha, Contrast in groundwater arsenic in shallow Holocene and deeper older aquifers: a case study of two villages in Araihasar, Bangladesh, submitted to *Water Resources Research*, October 2002, under revision.
- Keimowitz, A.R. S. Datta, M. Stute, H.J. Simpson, S.N. Chillrud, J. Ross, and M. Tsang. Naturally-occurring arsenic: mobilization at a landfill in Maine and implications for remediation. Submitted to *Applied Geochemistry*, December 2003.

Abstracts

- Zheng, Y., M. Stute, A. van Geen, J. Simpson, J. Graziano, H. Ahsan, P. Brandt-Rauf, An integrated study of sources, transport and health effects of As in Bangladesh (Abstract), Conference on Arsenic in Bangladesh Ground Water, Wagner College, NYC, February 27-28, 1999.
- Gavrieli, I., Zheng, Y., Van Geen, A., Stute, M., Simpson, J., Dhar, R., Ahmed, K., and Goldstein, S.L., Hydrogeochemical study of arsenic contamination in Bangladesh groundwater - the role of redox condition (Abstract), Tenth V.M. Goldschmidt Conference, 2000.

- Zheng, Y., M. Stute, A. van Geen, I. Gavrieli, H.J. Simpson, R. Dhar, and K.M. Ahmed, Arsenic mobilization in Bangladesh groundwaters: a case study of geochemistry and hydrology in Narayanganj and Laxmipur Districts (Abstract), IGC Workshop on arsenic in groundwater from sedimentary aquifers, Rio de Janeiro, August 3-5, 2000.
- Dhar, R.K., A. Horneman, A. van Geen, M. Stute, J. Simpson, I. Gravrieli, K.M. Ahmed, J. Graziano and Y. Zheng, Redox control of arsenic mobilization in Bangladesh groundwater, (Abstract, poster) NIEHS Superfund basic research meeting, Chapel Hill, North Carolina, 12/15/2000.
- Stute, M., Y. Zheng, A. van Geen, H.J. Simpson, R. Dhar, I. Gavrieli, P. Schlosser and K.M. Ahmed, Groundwater flow dynamics and As geochemistry in the central Ganges-Brahmaputra delta of Bangladesh, (Abstract) American Geophysical Union, San Francisco, CA, Dec. 2000.
- Dhar, R., Y. Zheng, M. Stute, A. van Geen, I. Gavrieli, R. Versteeg, M. Steckler, S. Goodbred, A. Horneman, H.J. Simpson, K.M. Ahmed, Spatial variability of arsenic concentrations in two villages in Araihasar Upazila, Narayanganj District of Bangladesh, (Abstract) EOS Transactions, American Geophysical Union 82 (20), Spring Meeting Supplement, S204, 2001.
- Stute M., H.J. Simpson, S.N. Chillrud, E. Law-wai, N. Santella, J. Ross, D.T. Ho, P. Schlosser, Y. Zheng, G.M. Dobbs, Application of SF₆, Bromide and 3H/3He for Tracing Groundwater Transport Beneath a Landfill, EOS. Trans. AGU 82(47), Fall Meet. Suppl., Abstract H22C-0371, F403, 2001
- He Y, Y. Zheng, D.C. Locke, H.J. Simpson and M. Stute, Dissolved sulfide in groundwater with elevated arsenic concentrations at Winthrop, Maine, EOS. Transactions American Geophysical Union 82(47), Fall Meet. Suppl., Abstract H32C-0316, F434, 2001
- Stute M., H.J. Simpson, S.N. Chillrud, E. Law-wai, N. Santella, J. Ross, D.T. Ho, P. Schlosser, Y. Zheng, A. van Geen, G.M. Dobbs, B.K. Butler; Arsenic mobilization in reducing groundwaters at a Superfund site in Maine: remediation through aquifer redox manipulation? (Abstract). Arsenic in drinking water, an international conference, Columbia University, Nov. 26-27, 2001.
- Zheng Y., R.K. Dhar, M. Stute, A. van Geen, A. Horneman, I. Gavrieli, R. Versteeg, M. Steckler, S. Goodbred, H.J. Simpson, Z. Cheng, K.M. Ahmed, M. Shamsudduha, M. Shahnewaz; Variability of Arsenic concentrations in tube wells from two villages in Araihasar Upazila, Bangladesh. (Abstract). Arsenic in drinking water, an international conference, Columbia University, Nov. 26-27, 2001.
- Tsang M., S. Chillrud, M. Stute, H.J. Simpson, J. Ross, A. Keimowitz, Y. Zheng, S. Wallace, Z. Cheng, and A. van Geen, Arsenic mobilization from fine particles under reducing conditions: implications for groundwater remediation (Abstract), Northeastern Geological Society of America, 37th Annual Meeting, 2002.
- Datta, S., A.R. Keimowitz, H.J. Simpson, M. Stute, S. Chillrud, M. Tsang, Y. Zheng, A. van Geen and G.M. Dobbs, Redox controls on arsenic mobility beneath Winthrop landfill, Maine, (poster), Arsenic in New England, New Hampshire Consortium on Arsenic, May 29-31, 2002.
- Stute, M., H.J. Simpson, S.N. Chillrud, E. Law-wai and P. Schlosser, Tracing groundwater transport underneath a landfill with SF₆, Br and 3H/3He (Abstract), Special session S31. Environmental tracers for groundwater dating. Goldschmidt Conference, Davos, August 2002.

Administrative Core

P.I.: Joseph Graziano

The Administrative Core had a notable year in directing the SBRP program, and in bringing the progress of our program, particularly our work in Bangladesh, to the benefit of thousands of people. In January, 2003, a scientific expedition to Bangladesh by public health and earth scientists involved in Projects 3, 4 and 7 was joined by Columbia University President Lee Bollinger, Earth Institute Director Jeffrey Sachs, and Mailman School of Public Health Dean Allan Rosenfield. Through their efforts, we met with the Bangladesh Prime Minister, the Minister of Finance, the Minister of Health, and the Minister of Local Government. A consensus developed which indicated that the Columbia team, and other institutions working in that country, have developed a sufficient knowledge base to allow for the development of a strategic plan to provide safe drinking water to the entire Bangladesh population within five years.

Thus, the Columbia scientific team came away with the task of developing this strategic plan, and vetting it with major agencies around the world who have been involved with research and service in Bangladesh. A retreat was held in the spring of 2003 at Columbia's School of International and Public Affairs, a plan and national budget was developed, and the plan was vetted with many international agencies including the University of Dhaka, Bangladesh, U.S. Geological Survey (USGS), the British Geological Survey (BGS), UNICEF, BRAC (the largest NGO in Bangladesh) and others. The plan was presented and well received at an international symposium in Dhaka, sponsored by our Fogarty ITREOH training grant, SBRP and the World Health Organization (WHO), held on October 23rd, 2003, and attended by 150 individuals from more than 25 organizations. With the help of Columbia's Jeffrey Sachs, who is special assistant to UN Secretary General Kofi Annan for the implementation of the UN Millennium Goals, we are soon to meet with the Bangladesh delegation of the UN in New York to discuss the plan and have it presented to the Prime Minister. In essence, the plan, which proposes to work at the village level in all 86,000 villages, would rely on the local development of communal wells that tap the deep aquifers which, we have learned, are virtually always low in arsenic and other hazardous materials. (The definition of a "safe depth" varies from village to village, but can readily be determined by surveying all existing wells in a village for depth and arsenic concentrations.) Indeed, through the strategic placement of deep communal wells, for *drinking water*, we have objective evidence based on repeated measures of urinary arsenic in 100 villages, that we have dramatically lowered arsenic exposure in Araihasar, Bangladesh. We have also met with World Bank officials in Washington, D.C., and in Dhaka, and are working toward guiding a demonstration project of the strategic plan in 1000 villages. It is estimated that implementation of the plan throughout Bangladesh would cost roughly \$270,000,000, or about \$2 per person.

In addition, the entire External Advisory Committee of our SBRP, which includes Dr. C.J. Chen, now Minister of Health of Taiwan, joined all of the Columbia SBRP scientists at a two-day retreat in November, 2003, held at Columbia's School of International and Public Affairs. Presentations concerning each project and core were made, and a major planning session was held concerning future directions of our research.

Information Dissemination and Transfer, Government Liaison, and Outreach Activities P.I.: Meredith Golden

Information Dissemination and Transfer, Government Liaison, and Outreach Activities are valuable components of the Columbia SBRP's Administrative Core. The overriding objective is to make available the scientific findings and products generated from Columbia's interdisciplinary suite of projects related to the bioavailability of soil lead in humans and the bioavailability, health effects, and geochemistry of arsenic. The communication of new knowledge among scientists, policymakers, and the private and public sectors promises to stimulate pioneering research, highlight the most urgent priorities, generate innovative products, and promote effective policies.

Even without a separately funded Outreach Core, Columbia has succeeded in integrating these tasks into its research, administrative, and training activities. Columbia SBRP continues to develop its website for seven individual projects, three research laboratories, and administrative and training cores. (Please see www.superfund.ciesin.columbia.edu.) The focus is on facilitating communications and promoting opportunities for meaningful interactions among project scientists and individuals concerned with lead and arsenic exposures.

The Columbia SBRP regularly distributes information on its projects and activities to over 350 individuals from academia, government, private companies, and public interest groups in the US. This year the announcements have been forwarded to the Arsenic Crisis Newsletter whose readership includes over eleven hundred subscribers from more than thirty countries. As a result, the Columbia SBRP is directly in touch with scientists not only in the US, but around the world.

Monthly seminars by Columbia scientists highlight the program's bio-medical and geoscientific research. This year we hosted ten seminars, including presentations by Dr. Chris X. Le from the University of Alberta and Steven Spayd, a research hydrologist with the New Jersey DEP. On average, 20-30 individuals participate in each seminar. Attendees include faculty and students from a variety of Columbia programs, other academics, media specialists, the general public, and city, county, state, and federal officials. Columbia scientists have also interacted in many forums with policymakers, private stakeholders, commercial firms, and non-profit groups. As part of its annual workshop series, the Columbia SBRP Training Core hosted in August 2003 a weeklong workshop on Risk, Crisis, and Emergency Communication in Environmental Health.

Many faculty have presented their SBRP research as part of college courses. Consequently, more students attend the SBRP seminars, become involved in SBRP projects, and incorporate related research into theses and publications. Regarding K-12 education, Columbia researchers work with both elementary and secondary students and teachers. Activities include a hands-on geochemistry workshop for NYC high school students, a "Career Day" presentation at a Queens elementary school, and curriculum development incorporating air pollution studies. SBRP researchers have also participated in Columbia's Earth2Class Program's free "Saturday Workshops for Teachers". For the past two summers, individual high school teachers have worked directly on projects with our researchers.

Finally, a dozen Columbia SBRP scientists, students, and Administrative Core staff participated in all the sessions of the 2003 SBRP Annual Meeting—offering seven posters and

one scientific talk. Columbia's active participation helped to renew old networks, strengthen ongoing collaborations, and initiate future partnerships with other SBRP scientists and outreach coordinators.

SBRP Training Core

P.I.: Paul Brandt-Rauf

The Training Core continued its Summer Workshop Program with a week-long workshop from August 25-29 on "Risk, Crisis and Emergency Communication in Environmental Health" given by Dr. Richard Peters, an expert on risk communication. The workshop included practical exercises in public communication by the attendees that were filmed and critiqued, and the overall feedback was very positive. 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 Edward O. Wilson from Harvard speaking on "Saving the Last Life and Why It Matters" concerning the importance of biodiversity for environmental health. In addition, in lieu of regular meetings to work on case studies in environmental health which has proven difficult to arrange due to the varying schedules and travel demands, the Training Core offered 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. The course includes practical case studies in managing hazardous waste issues as problem-solving exercises for the participants. Finally, trainees and faculty of the SBRP made presentations at the Superfund Conference at Dartmouth and participated in the Fogarty training course on arsenic in drinking water in Bangladesh.

Section 3: Patent Updates

Colorimetric device and procedure to measure Arsenic in natural water and waste waters

U.S. Patent application 60/404,964 filed August 21, 2003

Serial # PCT/US03/26484—International patent application based on U.S. Patent application 60/404,964 filed August 21, 2003, entitled "An Arsenic Meter"

Inventors: Alexander van Geen (Columbia University), Pietro Perona, Dmitri Psaltis, Christophe Moser (California Institute of Technology)

Section 4: Superfund Site Updates

None

Section 5: Contact Information Updates

Government Liaison:

Meredith Golden
Senior Staff Associate
CIESIN at Columbia University
Science Applications Division
Geosciences
PO Box 1000, 61 Route 9W
Palisades NY 10964
phone: 845-365-8968
fax: 845-365-8922
email: mgolden@ciesin.columbia.edu