

SCIENTIFIC PROGRESS REPORT

Health Effects and Geochemistry of Arsenic and Lead
Principal Investigator: Joseph Graziano, PhD
January 31, 2002

The Columbia University SBRP made remarkable progress during the past year toward achieving its specific aims. In addition, the Columbia SBRP organized and held a highly successful international meeting entitled "Arsenic in Drinking Water," held on November 26-27, 2001, that was attended by 187 participants from all over the world.

Project 1: Bioavailability of Soil Lead and Arsenic in Humans

PI: Conrad Blum, MD

This project builds on our previous published work using the stable isotope dilution method to estimate the bioavailability of soil Pb in human volunteers who ingest milligram quantities of soil (and microgram quantities of Pb) in gelatin capsules. The primary aims of this project are to: 1) determine estimates of the bioavailability of Pb 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 humans.

During the past year, significant progress has been made regarding the evaluation of a phosphate-amended soil sample obtained from the Joplin, Missouri, Superfund smelting site. Thus far, a total of 32 potential study volunteers have been screened for blood Pb concentration, Pb isotope composition, and overall health. Of these, eight subjects have completed the study protocol; final Pb isotope and bioavailability data are complete for six of these. Of the six, three subjects received "ordinary" non-amended soil from the site, while three received soil that was amended with 1% phosphate at the site by the U.S. EPA. The six volunteers had blood $^{206}\text{Pb}/^{207}\text{Pb}$ ratios that ranged from 1.15 to 1.19, and included Caucasian (3), African-American (2) and Asian (1) subjects. The Joplin soil had a higher $^{206}\text{Pb}/^{207}\text{Pb}$ ratio of 1.38, providing an ideal experimental situation for the stable isotope technique. The six subjects ranged in weight from 60 to 90 kg, and received doses of soil of 42 to 77 mg.

The findings are extremely interesting and potentially important. Among the three subjects who received the non-amended soil, the mean Pb bioavailability was 42%, with a range from 26-52%. In contrast, among those who received the phosphate-amended soil, mean Pb bioavailability was 13%, with a range of 11-16%. This represents a 69% reduction in bioavailability. These findings clearly indicate that this phosphate amending agent, a widely available agricultural phosphate fertilizer, has potential as a means of substantially reducing Pb bioavailability in humans. It is important to note that the soil utilized in this study was treated 18 months prior to the collection of the sample, and was allowed to weather in its natural outdoor environment during that time. Thus, the effect of phosphate treatment was not short-lived. Upon completion of laboratory analyses from the last two subjects, this data will be published.

Of interest is the fact that Pb bioavailability of the exact same Joplin soil sample has been

simultaneously tested in other experimental models of bioavailability, including a swine animal model (by Dr. Stan Casteel), and in an *in vitro* model (by Michael Ruby). Their models found identical reductions in Pb bioavailability of 38% and 38%. The swine model involves the administration of exceptionally large doses of soil and Pb, which might saturate intestinal Pb absorption. The *in vitro* model is clearly a potentially useful, yet artificial system. Thus, because our human model found a 69% reduction in bioavailability, we believe that those artificial models have substantially underestimated the utility of soil-amending agents as a means of reducing Pb bioavailability.

Publications:

Graziano, JG, LoIacono, NJ, Maddaloni, M, Chillrud, S, Blum, CB: Assessing the oral bioavailability of lead in soil in humans. *The Toxicologist* 60: 331, 2001 (abstract).

Project 2: Genotoxicity of Arsenic

PI: Tom K. Hei, PhD

1) The overall goal of Project II is to elucidate the mutagenic mechanism of the trivalent sodium arsenite and the pentavalent arsenate in mammalian cells. Specifically, the role of reactive oxygen and nitrogen species and the contributing function of mitochondria damage in mediating the genotoxic process are being examined. The specific aims of the studies remain unchanged.

2) During the current funding period, we used electron spin resonance (ESR) together with the spin trap probe Tempo-H to identify the radical species in arsenite-treated human-hamster hybrid (A_L) cells. Addition of sodium arsenite, 4 $\mu\text{g/ml}$, increased the ESR signal of Tempol by ~ 3 fold based on the amplitude of the signals. On the other hand, the addition of catalase and superoxide dismutase to the reaction mixture reduced the signal by $\sim 70\%$ and 50% , respectively. These findings provide convincing evidence that reactive oxygen species, particularly hydroxyl radicals, play an important causal role in the genotoxicity of arsenical compounds in mammalian cells.

To ascertain if the nucleus is the only target for arsenite-induced genotoxicity in mammalian cells, we exposed anucleated cytoplasts to arsenite followed by rescue fusion with karyoplasts to determine whether gene mutations can be induced in the absence of nuclear exposure to arsenite. Exponentially growing A_L cells were enucleated using cytochalasin B followed by centrifugation. The cytoplasts collected were treated with graded doses of arsenite for 3 hr and fused with karyoplasts at a ratio of 3:1 using polyethylene glycol. Reconstituted cells were subcultured in medium containing uridine overnight to provide cells with deficient respiratory chain an additional source of pyrimidine for better recovery. Cultures formed by fusion of non-treated cytoplasts with nuclei in a similar manner were used as controls. Treatment of cytoplasts alone with arsenite resulted in an induced mutant yield of 119 ± 9 $CD59$ mutants per 10^5 survivors over the corresponding controls. The data provide strong evidence that extranuclear target(s), including mitochondria, contribute to the genotoxic response induced by arsenite.

3) The metalloid arsenic, while a natural component of the earth crust, is a serious environmental concern worldwide, because of the large number of known contaminated sites and millions of people at risk from drinking arsenic-contaminated water. A better understanding of the mutagenic

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

4) In the coming year, we will examine the induction of oxidative DNA damage product, 8-OHdG in arsenic-treated A_L cells using immunohistochemical assay. In addition, we will ascertain the type of mutants induced by arsenite-treated whole cells versus those induced by cytoplasmic treatment.

Publications:

Liu, S.X., Athar, M., Lippai, I., Waldren, C.A., and **Hei, T.K.**, Induction of oxyradicals by arsenic: implications for mechanisms of genotoxicity. *Proceedings 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. *Cell and Molecular Biochemistry* **223**: (In press 2002).

Project #3: A Cohort Study of the Health Effects of Arsenic Exposure in Bangladesh

PI: Habibul Ahsan, MD, MPH

The overall goal in the previous year was to recruit a cohort of 10,000 adults in Bangladesh who have been exposed to a wide range of water arsenic concentrations. Data collection has proceeded well for our baseline survey, and has involved a structured questionnaire, a full dietary assessment instrument, a clinical examination, and the collection of biological samples. Progress can be summarized as follow:

a. Recruitment of the cohort has proceeded very well. As of January 15, 2002, nearly 8,500 of the targeted 10,000 adult males and females have been recruited into the cohort study. About 95% and 90% of the study participants donated urine and blood samples, respectively.

b. After piloting the sample collection, storage and shipping procedures for heat and light sensitive biological samples, we have successfully transported (on dry ice) more than 7,500 urine, blood, serum and 1,000 plasma samples to Columbia University from Bangladesh. Please note that this is easier said than done, particularly since 9/11/01.

c. The Trace Metals Core Lab completed the analysis of more than 3,500 urine samples for total urinary arsenic.

d. Each of the cohort study questionnaires is checked for its completeness, consistency, accuracy and reliability by two supervisors in Bangladesh after an interview is completed. Appropriate coding is done and necessary values are added for foods and other variables that are time consuming to do during an interview. To date, we have completed checking and coding more than 5,000 questionnaires and brought them to Columbia University for entry into our central database.

e. The Biostatistics/Data Management Core Laboratory of Columbia's P30 NIEHS Center for Environmental Health in Northern Manhattan is acting as the central data management core for

this study, and is supervised by senior faculty in the Department of Biostatistics. A complex multi-dimensional database was designed to enter, storage, manipulate and accommodate data form different sources. The database is now in use after extensive testing for its consistency, performance and transaction. Data entry is proceeding extremely well, with data from more than 3,700 study participants completed.

f. In order to accurately assess an individual's dietary intake pattern and evaluate whether the questionnaire measures it with sufficient accuracy, a dietary validation study was conducted among 200 cohort members in the summer of 2001 (first phase). A complete food frequency and portion was recorded by direct observation for seven days and every food item eaten by a respondent was measured in this survey.

g. The 5,000 tube-wells involved in this study were revisited and their owners/caretakers were informed about the arsenic concentration in the wells and alternate safe water options. All the tube wells were labeled by a permanent pictorial metal tag with date of collection, arsenic concentration and safety information. An education and outreach program was initiated, with collaboration from social scientists at Columbia's School of International & Public Affairs (SIPA), the goal of which is to reduce arsenic exposure in our study region.

h. In order to provide primary health care for the cohort study participants and their family members, a field clinic has been set up by the Columbia University arsenic research project in Araihasar. The field clinic is run by trained physicians and assisted by a nurse, and a health assistant. More than 4,000 people of the area have received treatment for primary care and arsenic related symptoms form the field clinic. Within a very short time, the field clinic has become an important health care provider in the area and patients are very satisfied with the quality of treatment they receive in the clinic.

i. We established a second laboratory in Bangladesh to perform biological sample processing, such as separation of white blood cells to yield higher amounts of DNA. A graduate level technician was recruited and trained by a Columbia University laboratory scientist to run the lab. The lab has separated high quality samples (100) and transported them to New York.

j. Approval for this study was renewed from the Columbia University Institutional Board and Bangladesh Medical Research Council (Bangladesh IRB). The director of the Bangladesh Medical Research Council visited our study area and was very satisfied with the field work.

Presentations and Publications:

Ahsan, H., Parvez , F., A.Z.M.I. Hussain, H. Momotaj, Y. Chen, G.R Howe, W.Y Tsai, R.M. Santella, P.W. Brandt-Rauf, J. Longley, van Geen, and J.H. Graziano. A Cohort study of Arsenic Exposure in Bangladesh: Progress and Preliminary Findings. *Arsenic in Drinking Water, an International Conference, Columbia University, November 26-27, 2001.*

Parvez, M. F., H. Ahsan, Y. Chen, A. van Geen, A.Z.M.I. Hussain, H. Momotaj, A. Horneman, R. Dhar Y. Zheng, M. Stute, H.J. Simpson, V. Slavkovich, N.J. Lolacono, M. Shahnewaz, K.M. Ahmed, and J.H. Graziano. The Arsenic Problem and Its Awareness in Bangladesh Population:

Results of A Large Population-based Survey. *Arsenic in Drinking Water, an International Conference, Columbia University, November 26-27, 2001*

Ahsan, H, Y. Chen. Lifetime Excess Risk of Internal Cancers Due to Arsenic Exposure among Bangladesh Population. *Arsenic in Drinking Water, an International Conference, Columbia University, November 26-27, 2001.*

Project #4: Environmental Arsenic, Pregnancy, and Child Development

PI: Joseph Graziano, PhD

This project is examining dose-response relationships between chronic arsenic exposure and selected outcomes in pregnant women and children. It also seeks to characterize arsenic metabolism in adults and children in Bangladesh, and determine whether folate and/or vitamin B₁₂ status (i.e., methylation potential, estimated via measurements of plasma homocysteine) is associated with arsenic methylation.

It is important to note that due to the 25% overall program budget cut, the progress of this project has been seriously hampered. The children to be studied in the project are children of couples enrolled in Project #3, i.e., the cohort study. We have had to devote all of our Bangladesh/NIPSOM field staff efforts to the cohort study, since the proposed studies of children cannot take place until recruitment of the adult cohort is completed. As mentioned above, recruitment of the adult cohort will be finished within the next few months, at which point field staff will shift their efforts toward the initiation and completion of cross-sectional studies of 6- and 10 year old children. Progress during the past year includes the following:

- a. We completed a pilot study of a questionnaire designed to ultimately ascertain rates of spontaneous abortion and stillbirth in 2000 women. Implementation of the full study awaits the new fiscal year budget.
- b. An HPLC method for the analysis of homocysteine in plasma has been established, and we have begun to analyze 500 plasma samples from adults in the cohort study. The same samples will also be simultaneously analyzed for folate and B12. Dr. Mary Gamble, who recently completed a post-doctoral fellowship at Columbia's Institute of Human Nutrition, has joined our study team and is heading up this component of the project. This preliminary work is required so that we can determine the prevalence folate and/or B12 deficiencies. Because the methylated arsenic metabolites are relatively less toxic than inorganic arsenic, we aim to eventually conduct a clinical trial of folate and B12 in order to determine whether supplementation facilitates methylation.
- c. A study of arsenic metabolism in 5-year old children has been completed. Urine samples were obtained on two different occasions from 40 Bangladeshi children, who were selected based on strata of well water arsenic concentration. Their well water and urinary arsenic concentrations span a remarkably wide range. Total urinary As measurements, as well as the proportions of MMA, DMA, As⁺³, As⁺⁵, and arsenocholine + arsenobetaine, have been completed this week. The only other study of arsenic metabolism in children, conducted by Marie Vahter in Argentina, concluded that children are poor methylators of arsenic, eliminating 42-49% as inorganic arsenic.

This is certainly not the case in Bangladesh. Our preliminary descriptive statistical analysis indicates that, on average, children eliminate approximately xx% as DMA, yy% as MMA, and only zz% as inorganic species. We are just about to begin analyses that will determine whether arsenic metabolism in children is saturable.

d. Planned cross-sectional studies of 6- and 10-year old children will test the hypothesis that arsenic exposure may be associated with neuropsychological deficits, and other health outcomes. Our collaborator for this work in Bangladesh, Dr. L. Kahn, visited the Mailman School of Public Health in May to work with Drs. Graziano and Wasserman in developing culture-appropriate psychometric test batteries. Dr. Wasserman, a developmental psychologist who worked with Dr. Graziano on the Yugoslavia Prospective Study of Pb in Children, will visit Bangladesh for the first time in February, 2002, to conduct pilot studies of the instruments to be used in the cross-sectional studies. We aim to begin these cross-sectional studies in the fall of 2002.

e. In order to test the hypothesis that arsenic exposure may be associated with an increased risk for diabetes, 2,100 blood samples from the cohort study were analyzed for total and glycated hemoglobin (HbA1c). The results of these HbA1c analyses indicate that at the water arsenic concentrations encountered in Araihasar, Bangladesh, there is no association between arsenic exposure and diabetes mellitus. While previous studies in the literature suggest an association, the participants of those studies were chronically exposed to much higher arsenic concentrations, i.e., > 1 mg/L.

Slavkovich, V, Parvez, M. F., Ahsan, H., A. Z. M. I. Hussain, H. Momotaj, N. J. Lolocono, Factor-Litvik, P., and J. Graziano. Relationship Between Arsenic Exposure and Diabetes in Residents of Araihasar, Bangladesh. *Arsenic in Drinking Water, an International Conference, Columbia University, November 26-27, 2001.*

Project #5: Arsenic Mobilization in Bangladesh Ground Water

Co-PIs: Yan Zheng, PhD, and Martin Stute, PhD

In the Ganges-Brahmaputra Delta, concentrations of arsenic in groundwater can vary from < 5 ug/L to > 1000 ug/L within lateral and vertical scales of tens of meters. This extreme degree of variability is probably the result of complex geological, hydrological, geochemical, and microbial interactions that reflect heterogeneity inherent to the sedimentary evolution of the delta over the past 10,000 years. The main objectives of our study during the past year have been to understand the factors that contribute to such spatial variability of arsenic at the local scale (# 1 km) and to investigate any potential temporal variability of groundwater arsenic concentrations.

Multi-disciplinary field investigations conducted in January 2001 and June 2001 focused on two villages within a 20-km² region in Araihasar Upazila, about 20 km east of Dhaka. This is precisely the same region where the public health studies described in Projects #3 and #4 are taking place. The activities included geophysical surveys using resistivity and conductivity, installation and sampling of two nests of monitoring wells, as well as collection of two sediment cores. Our collaborator, Dr. K. M. Ahmed and his students from Dhaka University are monitoring water level and As concentrations of our well nests at biweekly to monthly intervals. About 50 shallow

groundwater wells that are representative of a range of chemical conditions found in shallow, As-containing aquifer were also re-sampled in June and September to investigate variability of arsenic with time. Key findings to date are:

Extreme spatial variability of arsenic concentrations (< 5 to ~ 800 ug/L) is observed in the shallow, presumed Holocene sedimentary aquifers. A suite of redox-indicators measured in parallel with arsenic indicates that As mobilization generally follows the reduction of Fe-oxyhydroxides, and, in some cases, even extends into sulfate-reducing conditions as evidenced by the low SO_4/Cl ratio. Monitoring wells installed in both villages (20 - 300ft) show similar depth profiles of arsenic with low arsenic concentrations at shallower depths (20-30ft) and greater depths (>100 -130 ft), and high arsenic concentrations of ~ 600 ug/L at a depth of ~ 50 ft. Although the depth profiles of arsenic suggest that the vertical redox gradient at a given location influences arsenic mobilization, almost the entire dynamic range of arsenic concentrations (from ~ 100 to ~ 600 ug/L) was observed in existing tube wells at very similar depths of 40 ft (before correction to a single reference level was made) located in one village (Dari Satyabandi). Factors controlling the apparent variability of arsenic concentration at the same depth interval, as well as the well-defined sub-surface arsenic maximum concentration at ~ 50 ft is the focus of our on-going investigation. Graduate student R. Dhar is now in Bangladesh with a work plan designed to address such questions.

Drilling identified a 50-ft thick clay formation at depth ranging from 44 ft to 94 ft in Dari Satyabandi village (23.785°E , 90.603°N), with a thin interval of silt at depth from 63 ft to 68 ft. This clay formation is likely the Madhupur clay of Pleistocene age, because the radiocarbon content of a thin peat layer within the clay was below detection limit. A resistivity survey confirmed that the clay formation underlies the entire village area of Dari Satyabandi. This clay formation separates the shallow, As-containing aquifer from the deep, low As aquifer that is chemically distinct. The water table from 4 shallow monitoring wells was always ~ 1 -2 m higher than that of the 3 deep monitoring wells since Jan. 2001 to present indicating isolation of the two aquifers. Furthermore, radiocarbon analyses of monitoring wells (100 ft, 140 ft and 300 ft) found 28 percent modern carbon in dissolved inorganic carbon. In contrast, bomb-radiocarbon was found in monitoring wells at 20 ft and 40 ft.

In Baylakandi village (23.780°E , 90.640°N), two ~ 10 ft thick clay formations were recovered at depths ranging from 106 ft to 120 ft, and again from 146 ft to 156 ft, with very fine to fine sand between the two clay layers. However, a resistivity survey could not confirm that these clay formations were continuous. The temporal water table fluctuations of 5 shallow and 2 deep monitoring wells (135 and 175 ft) were similar. Together, they suggest that the shallow and deep aquifers in village Baylakandi are not as well separated as those in village Dari Satyabandi. Although deep aquifer waters in both villages are low in arsenic (< 50 ug/L), dissolved sulfate concentrations in deep aquifer water from Baylakandi village is extremely low (< 0.05 mg/L) when compared to that from village Dari Satyabandi (~ 1 mg/L). We are investigating the causes for the difference in chemistry, not only between the shallow and deep aquifers, but also between the two deep aquifers to address the long-term sustainability of the deep aquifer.

Despite the extensive spatial variability of arsenic concentrations at the local scale (< 1 km), we observed little temporal variability of arsenic concentrations. About 50 shallow groundwater

wells (< 50 ft) from Dari Satyabandi village were re-sampled in January, June and September 2001. When compared with the arsenic concentrations during the initial sampling from March to June 2001, only one well showed a difference greater than the analytical uncertainty. Monitoring wells installed at both villages have been sampled at monthly intervals and also show little variation of arsenic concentrations with time. However, much lower sulfate concentrations were observed in June 2001 than that of January 2001 in the shallow monitoring wells (40-ft and 50-ft, As > 500 ug/L) from Dari Satyabandi village. Despite intensification of sulfate reduction in the shallow aquifer during the wet season, little arsenic concentration changes were observed. The results show that seasonal water table fluctuations do not alter conditions sufficiently to cause variations in arsenic mobilization. Residence time of the shallow groundwater aquifer by $^3\text{H}/^3\text{He}$ dating, as well as the potential source of the heterogeneity of the redox driver in solid and dissolved phases will be the focus of next year's investigation.

Presentations and Publications

Y. Zheng, M. Stute, A. van Geen, I. Gavrieli, R. Dhar, H. J. Simpson, and K. M. Ahmed, Redox control of arsenic mobilization of Bangladesh groundwater, submitted to Appl. Geochem., Jan. 2002.

Goodbred, Jr, S.L., S.A. Kuehl, M.S. Steckler, and M.H. Sarker, Controls on facies distribution and stratigraphic preservation in the Ganges-Brahmaputra delta sequence, Sedimentary Geology, in press, 2001.

Y. Zheng, 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, and M. Shahnewaz. 2001. Variability of Arsenic Concentrations in Tube Wells from two Villages in Araihasar Upazila, Bangladesh, *Arsenic in drinking water, an international conference, Columbia University, Nov. 26-27, 2001*. <http://superfund.ciesin.columbia.edu/Conference.html>

Zheng, Y., R. Dhar, M. Stute, A. van Geen, A. Horneman, I. Gavrieli, R. Versteeg, M. Steckler, S. Goodbred, K. M. Ahmed. 2001. Variability of Arsenic Concentrations in Tube Wells from one Village in Araihasar Upazila, Narayanganj District of Bangladesh (Abstract), GSA annual meeting, Boston, vol. 33, No. 6, pA116.

Dhar, R. , Zheng, Y., M. Stute, A. van Geen, I. Gavrieli, R. Versteeg, M. Steckler, S. Goodbred, A. Horneman, H. J. Simpson, K. M. Ahmed. 2001. Spatial variability of arsenic concentrations in two villages in Araihasar Upazila, Narayanganj district of Bangladesh *_EOS. Trans. AGU 82(20):S204*, Spring Meet. Suppl. Abstract H61C-02

Project #6: Redistribution of Arsenic and Other Contaminants at Sites in NJ and Maine Co-PIs: Martin Stute, PhD, and Jim Simpson, PhD

During the past year, two major tracer experiments involving SF₆, NaCl and NaBr were conducted at a Superfund site in Winthrop (ME), which is characterized by elevated arsenic (100 to 400 ppb)

in groundwaters beneath a closed and capped landfill. The subsurface water, similar to Bangladesh groundwaters in some properties, is strongly reducing, high in dissolved Fe(II) and sulfate, but relatively low in dissolved phosphate. The lack of evidence for any arsenic-enriched point sources in the landfill supports the working hypothesis that elevated dissolved arsenic at this site appears to be natural arsenic from the heterogeneous glacial deposits underlying the landfill that is mobilized by subsurface reducing conditions. A similar mobilization process appears likely in Bangladesh groundwaters. The first tracer experiment was initiated in November of 2000, after installation of monitoring wells, as a pilot to establish tracer sensitivities in this groundwater system. The second, which began in January 2001, was designed as a tracer injection experiment including Oxygen Release Compound (ORC: primarily Mg_2 as a source of O_2 to the subsurface) in an attempt to substantially alter groundwater redox conditions to effect large reductions in dissolved iron and arsenic. The primary hypothesis being tested was that it is feasible to manipulate subsurface redox conditions through economically practical amounts of chemical injections sufficient to prevent mobilization of arsenic into groundwaters.

The two SF₆ tracer experiments conducted at the Winthrop site allowed us to estimate groundwater transport velocities that ranged from less than 0.1 to at least 3 m/d. We were also able to demonstrate which wells, and which levels in each well, were in the influence zone of the injected ORC. The tracer data revealed extreme heterogeneity of the groundwater flow pattern. There was no convincing evidence of significantly altered groundwater redox conditions during the second experiment despite the addition of large quantities of oxidizing slurry designed to release oxygen continuously over about half a year (about 1400 kg of dry MgO_2), and the relatively short flow paths (< 5 meters) to the first series of multi-level monitoring wells and other monitoring wells over a total transport path of the order of 25 meters to the continuously pumped extraction well. Thus, elevated levels of dissolved arsenic and iron in the monitoring wells persisted through the entire seven months of the experiment. Samples which contained substantial concentrations of SF₆ and bromide were not systematically different in [Fe(II)] and [As(III+V)] from samples which contained little or no evidence of tracer transport to that sampling level. We plan to continue to collect monitoring data and supporting information to further explore the viability of in situ redox manipulation of aquifer properties to alter mobilization of arsenic in highly-reducing groundwaters. The results of these field experiments indicate that direct intervention to alter redox conditions in the subsurface where elevated [As] is observed can be quite difficult. However, the use of SF₆ as a groundwater tracer in such systems proved to be extremely sensitive and critical to interpretation of the processes which can mobilize dissolved arsenic. This work is directly relevant to accessing potential remediation interventions at other Superfund sites, as well as in location of natural As mobilization, such as Bangladesh groundwaters. Clearly, chemically inert tracer injection experiments can provide importance new constraints on the time-scale and spatial dimensions of processes which can lead to elevated dissolved arsenic in groundwaters of current management importance.

We also studied the sulfur geochemistry at the Winthrop site, because formation of highly insoluble sulfide precipitates of many elements such as As and Fe can be important removal pathways for these elements in reducing groundwater. Using differential pulse cathodic stripping voltametry (DPCSV) capable of detecting nM levels of dissolved sulfide, we found that groundwater sulfide concentrations ranged from < 4 nM to ~ 2000 nM and <4 nM to ~ 7300 nM for about a dozen multi-level observation wells under a landfill cap, and several monitoring wells outside the landfill, respectively. Sulfide concentrations generally increased when the ORP values

became more negative. Despite the three orders of magnitude difference of dissolved sulfide concentrations, arsenic concentrations were all elevated under the land fill cap, suggesting that As still remains mobile under mildly sulfate-reducing conditions. Only in one well outside of landfill area with extremely negative ORP (-321 mV) and ~ 7300 nM of dissolved sulfide, groundwater is depleted in dissolved As, Fe, and sulfate, suggesting that precipitation of arsenopyrite is a plausible mechanism for removing As in reducing groundwater.

Publications:

Stute M., H.J. Simpson, S.N. Chillrud, N. Santella, E. Law-wai, J. Ross, D.T. Ho, P. Schlosser, Y. Zheng, Y. He (2001) SF₆/Br tracer experiments at the Winthrop (ME) site. In: Butler, B. et al., Report on Winthrop, ME Oxygen Release Compound Experiments, United Technologies Corporation, 2002.

Santella, N., D.T. Ho, P. Schlosser, M. Stute (2001) The vadose zone as an archive of atmospheric SF₆ near a large urban area. Submitted to *Env. Sci. Tech.*

He Y., Y. Zheng, D.C. Locke (2001) Differential pulse cathodic stripping voltammetric determination of nanomolar levels of dissolved sulfide applicable to field analysis of groundwater. Submitted to *Anal. Chim. Acta.*

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? *Arsenic in drinking water, an international conference, Columbia University, Nov. 26-27, 2001.* <http://superfund.ciesin.columbia.edu/Conference.html>

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Santella, N., P. Schlosser, D. Ho, M. Stute (2001) The vadose zone as an archive of atmospheric SF₆ near a large urban area, *EOS. Trans. AGU* 82(47), Fall Meet. Suppl., Abstract H52D-12.

Schlosser, P., M. Stute, D.T. Ho, W.M. Smethie (2001) Role of environmental tracers for hydrologic investigations. *EOS. Trans. AGU* 82(47), Fall Meet. Suppl., Abstract H42A-0341. 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.

Project #7: Assessment and Remediation of Arsenic in Groundwater

Co-PIs: Alexander van Geen, PhD, and Poniseril Somasundaran, PhD

This project focuses on investigating Fe-As interactions at various physical scales to (a)

understand the source of As enrichments in reducing groundwater and (b) to develop cost-effective treatment technologies that are effective under the diverse socio-economic conditions that exist in the US and Bangladesh. Considerable progress was made both in the field and in the lab during the second year of this project.

Progress made by our team members at the Lamont Doherty Earth Observatory can be described as follows:

(1) Household arsenic-removal systems designed by co-Investigator X. Meng were used for a period of 3 months by six families in Bangladesh that were trained and supplied with the necessary ferric chloride and bleach reagents. Treated water samples collected weekly to bi-weekly samples from the households by students of our colleague Dr. K. M. Matin from the Geology Department of Dhaka University. While As concentrations in treated water depended on the extent to which instructions were followed, all but one of these samples contained <50 ug/L As for a range of input water of As concentrations of 200-600 ug/L range. Co-investigator N. Nikolaidis also successfully deployed an As removal system based on Fe filings for a limited period in Bangladesh.

(2) Based on the spatial distribution of arsenic in existing wells established in the previous year of this project, a total of seven community wells were installed in the most afflicted parts of our study area. Two of these wells required repeated drilling before safe water was reached at 500-ft depth. These wells are heavily used by the local communities and continue to be regularly monitored for arsenic. We have struck an understanding with two local teams of well installers such that they collect sediment cuttings from each new well they install (based on our advice) in return for a measurement by us to confirm that the water is indeed low in As. We expect to learn a great deal about factors leading to As mobilization based on our growing collection of sediment cuttings from the study area.

(3) Chemical, spectroscopic, and magnetic analysis of sediment cuttings and comparison with groundwater As in surrounding wells indicate that the conversion of Fe III oxyhydroxides to mixed Fe II/III oxyhydroxides such as magnetite is a key step in the release of As naturally present in the sediment. Incubation experiments of Bangladesh sediment under anoxic conditions indicate that this process requires microbial activity. Our results suggest that an inexpensive spectroscopic device could perhaps detect the conversion of iron oxyhydroxides to magnetite as cuttings are generated during drilling in the field and, hereby, predict whether groundwater As levels will be high before the installation of a tube well has been finalized.

(4) The prototype of a simple device to measure arsenic concentrations in groundwater by colorimetry using the molybdate-based method of Johnson and Pilson (1972) was built and tested in collaboration with P. Perona at Caltech. The inexpensive device measures infra-red light absorption in two solutions simultaneously at very high precision. Tests conducted in the laboratory indicate promising performance characteristics, once the response of the two channels of the device is intercalibrated for various factors. In June 2001, the prototype was taken to Bangladesh for evaluation under realistic conditions. Although the high humidity affected the electronics, arsenic concentrations in several Bangladesh groundwater samples were measured accurately in the 10-100 ug/L range. These promising results, and the potential use of such a

device in the US as well as Bangladesh, led to an SBIR proposal that was recently submitted in collaboration with a small California company.

Additional work by Dr. P. Somasundaran at Columbia's Henry Krumb School of Mines can be summarized as follows:

(1) Removal of Arsenic Species by the Flotation of Ions

Foam Flotation, a relatively inexpensive technique, has been employed for the first time for enhanced removal of arsenic species from the solution. This method involves interactions between arsenic species and surfactants and removal of hydrophobic complexes formed by air bubbles under quiescent conditions. The system in our experiments consists of Arsenic (V) oxide hydrate, dodecylamine ($\text{CH}_3(\text{CH}_2)_{11}\text{NH}_2$), sodium dodecyl sulfate ($\text{CH}_3(\text{CH}_2)_{11}\text{OSO}_3\text{Na}$) and aluminum chloride, and frothers. It was found that as much as 98 % removal of arsenic species can be obtained, the removal being depended upon the solution pH and the interactions between As species and surfactants used as activators or collectors. These preliminary results suggest that foam flotation based on the interactions between As species and surfactants is a new effective method either by itself or in combination with other techniques for the removal of As species from the solution.

(2) Cyclic voltammetric study of redox reactions of arsenic

The redox reactions between As (III) and As(V) in acidic solution were investigated using cyclic voltammetric technique with a Pt rotating disk electrode (RDE). In the potential region corresponding to the reduction or oxidation of arsenic species only one cathodic and one anodic peak were observed, indicating that the redox reactions between As(III) and As(V) are controlled by one slow reaction, although two electrons are transferred. Judged by the shift of the peak potential when changing scan rate and the distance between anodic peak potential and cathodic peak potential, the redox reactions between As(III) and As(V) are irreversible slow reactions. Digital simulation will be employed in the coming year to obtain kinetic information of the reactions.

(3) Atomic force microscopy study of arsenic binding on glass surfaces

Many treatment technologies are capable of removing arsenic from potable water. But the socio-economic situation in Bangladesh and other parts of the world complicates the choice of treatment technologies. So far, adsorption of Arsenic (III and IV) by oxides of Aluminum, Iron and their mixtures has shown encouraging results. We are working to understand the basic interaction mechanism of arsenic species with such surfaces, using atomic force microscopy. We studied the deposition of arsenic species on glass surfaces, activated by ferric ions, after activation by ferric oxide particles failed to provide any evidence of arsenic deposition. Initial results show the deposition of the arsenic species on the glass surface, as sharp jagged precipitates.