

Arsenic Mobilization from Contaminated Sediments: A Full-scale Experiment in Progress

J.G. Hering and K. Campbell
California Institute of Technology, Pasadena, CA

S. Dixit
Lawrence Livermore National Laboratory, Livermore, CA

P. A. O'Day
University of California, Merced, CA

U.S. Department of Energy

Lawrence
Livermore
National
Laboratory

This article was submitted to
Eleventh International Symposium on Water Rock Interaction (WRI)
Saratoga Springs, New York
June 27, 2004 – July 2, 2004

February 5, 2004

DISCLAIMER

This document was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor the University of California nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or the University of California, and shall not be used for advertising or product endorsement purposes.

This is a preprint of a paper intended for publication in a journal or proceedings. Since changes may be made before publication, this preprint is made available with the understanding that it will not be cited or reproduced without the permission of the author.

This report has been reproduced
directly from the best available copy.

Available to DOE and DOE contractors from the
Office of Scientific and Technical Information
P.O. Box 62, Oak Ridge, TN 37831
Prices available from (423) 576-8401
<http://apollo.osti.gov/bridge/>

Available to the public from the
National Technical Information Service
U.S. Department of Commerce
5285 Port Royal Rd.,
Springfield, VA 22161
<http://www.ntis.gov/>

OR

Lawrence Livermore National Laboratory
Technical Information Department's Digital Library
<http://www.llnl.gov/tid/Library.html>

Arsenic mobilization from contaminated sediments: A full-scale experiment in progress

J.G. Hering, S. Dixit & K. Campbell

Environmental Science & Engineering, California Institute of Technology, Pasadena, CA 91125, USA

P.A. O'Day

School of Natural Sciences, University of California, Merced, CA 95344, USA

ABSTRACT: The mobilization of arsenic was examined in a system where the deposition of iron and arsenic have been substantially modified by large-scale manipulations. This engineering practice was designed to decrease arsenic concentrations in water supplied to the City of Los Angeles. Accomplishing this objective, however, has resulted in significant accumulation of arsenic and iron in the sediments of a reservoir on the Los Angeles Aqueduct. Arsenic and iron are released into the porewater at depth in the sediment, consistent with reductive dissolution of iron(III) oxyhydroxides. Factors influencing the possible re-sorption of arsenic onto residual iron(III) oxyhydroxides solids have been examined. Reduction of As(V) to As(III) alone cannot account for arsenic mobilization since arsenic occurs in the solid phase as As(III) well above the depth at which it is released into the porewater. Competition from other porewater constituents could suppress re-sorption of arsenic released by reductive dissolution.

INTRODUCTION

The mobilization of arsenic (As) from aquifer sediments poses a serious threat to human health in many parts of the world, particularly in South Asia (Nordstrom, 2002). Such mobilization can result in the occurrence of arsenic in groundwater at concentrations of hundreds to thousands of $\mu\text{g/L}$. Arsenic in alluvial sediments is often associated with iron (Fe) oxyhydroxides and is mobilized by conditions that destabilize the solid carrier phase or that promote desorption of As from the solid (Smedley and Kinniburgh, 2002; Welch et al., 2000). Manipulation experiments (e.g., a push-pull experiment in which an organic substrate is injected into an aquifer) can demonstrate the effects of environmental conditions on arsenic mobility (Harvey et al., 2002). However, it is often infeasible to perform large-scale biogeochemical experiments.

In some cases, large-scale manipulations of environmental systems are engineered for specific goals such as ecosystem restoration. A useful opportunity to study the biogeochemical controls on As mobility is provided by a full-scale engineering project that is currently being implemented by the Los Angeles Department of Water and Power (LADWP).

1 THE INTERIM ARSENIC MANAGEMENT PLAN FOR LOS ANGELES

The Los Angeles Aqueduct (LAA) transports water from the eastern Sierra Nevada to the City of Los Angeles for municipal water supply. Because of geothermal inputs, As concentrations in the LAA water supply are naturally elevated with a historical annual average of $20 \mu\text{g/L}$. In 1996, an interim As management plan was implemented to lower the concentration of As in the water delivered by the LAA (Stolarik and

Christie, 1999). Since 1996, ferric chloride and polymer have been added to the aqueduct at the Cottonwood Treatment Plant, an existing facility originally used to control turbidity. Ferric chloride addition results in the formation of an Fe(III) oxyhydroxide floc that is transported as suspended load in the aqueduct and deposited in North Haiwee Reservoir as the flow velocity decreases. Ferric chloride doses are adjusted to remove sufficient As from the dissolved phase that the As concentrations below Haiwee Reservoir are $< 10 \mu\text{g/L}$. This practice has resulted in significant accumulation of As and Fe in the Haiwee sediments since 1996.

2 SIGNAL AND IMPACT OF ARSENIC AND IRON DEPOSITION

Sediments and porewaters have been sampled in the inlet channel where the LAA feeds into North Haiwee Reservoir (Kneebone et al., 2002). Sampling has thus far been limited to locations very near the bank because of restrictions on human contact with the LAA water supply. Thus it cannot be claimed that the samples obtained are entirely representative of conditions throughout the reservoir.

Sediment cores collected from the inlet channel were found to contain elevated concentrations of Fe, As, and Mn relative to sediments at a control site. Sediment concentrations of these elements remain elevated throughout the core length sampled (ca. 4% Fe, 600 $\mu\text{g/g}$ Mn, and 200 $\mu\text{g/g}$ As). Porewater profiles reveal that Mn, Fe, and As are mobilized at depth in the sediment with Mn released into the porewaters at a more shallow depth than either Fe or As. Arsenic concentrations in porewaters at depth in the sediment reached values $>1000 \mu\text{g/L}$ (Kneebone et al., 2002). The depth at which increased porewater concentrations are observed varied in sampling conducted in different seasons but, in general, Mn, As, and Fe porewater concentrations were all low in the surficial sediments and overlying water. At depth in the sediments, As and Fe concentrations in the porewaters were always strongly correlated (Dixit, unpubl.; Campbell, unpubl.).

From the water supply perspective, the interim As management plan is fulfilling its objectives. Arsenic concentrations in water delivered to the LAA Filtration Plant in Sylmar, CA are consistently below 10 and often below 5 $\mu\text{g/L}$. Thus, the As deposited to the sediments in association with the Fe(III) oxyhydroxide floc must be almost entirely retained within the sediment. The low porewater concentrations of As in the surficial sediment despite elevated concentrations at depth in the sediment indicate that As diffusing upward in the sediment is sequestered into the solid phase before reaching the sediment-water interface. Nonetheless, numerous questions remain regarding the controls

on the rate and extent of As mobilization in this system.

3 BIOGEOCHEMICAL CONTROLS ON ARSENIC MOBILITY

Even though elevated concentrations of As are observed at depth in the Haiwee sediments, the As concentration in the sediments is fairly constant with depth. The amount of As that would need to be released from the sediments in order to support the observed porewater concentrations can be estimated by assuming reasonable waters for the porosity of the sediment and the density of the Fe(III) oxyhydroxide floc. This estimate suggests that $<2.5\%$ of the As and $<1\%$ of the Fe in the sediments is released into the porewaters. Notably the molar ratios of Fe-to-As are similar in the sediments and porewaters and in the calculated values for the original floc (Hering and Kneebone, 2001).

These observations raise the question of what factors control the rates of release of As and Fe. For Fe, mobilization into the porewaters can be attributed to reductive dissolution but, for As, other processes (e.g., competitive desorption) could also play some role. A related question is whether the Fe and As released by reductive dissolution are partly repartitioned (i.e., by sorption) to the solid phase, which contains the bulk of the deposited oxyhydroxide floc. And, if such re-sorption does not occur, whether that is due to alteration of the solid phase or because the porewater composition does not favor As sorption.

Several hypotheses can be stated regarding the biogeochemical processes controlling As mobility in Haiwee sediments:

- 1 Arsenic oxidation state hypothesis. It may be hypothesized that reduction of As(V) to As(III) is responsible (in whole or in part) for As mobilization from the sediments into the porewater.
- 2 Solid diagenesis hypothesis. The Fe(III) oxyhydroxide floc could have undergone some alteration such that the residual solid in the sediment is not as good a sorbent for As as the original floc.

3 Porewater composition hypothesis. Resorption of As onto the residual floc may not be favored under the chemical conditions prevailing in the porewater. In particular, resorption of As could be inhibited by elevated concentrations of Fe(II), phosphate, or dissolved organic matter (DOM) in the porewater.

3.1 Arsenic oxidation state hypothesis

A substantial body of work on As removal from drinking water by coagulation with hydrolyzing Fe(III) salts demonstrates that, under conditions relevant to water treatment, better removal efficiencies are achieved with As(V) than with As(III) (Hering et al., 1996; Jekel, 1994; Shen, 1973; Sorg and Logsdon, 1978). Similar results have been observed for adsorption of As(III) and As(V) onto pre-formed Fe(III) oxyhydroxides at comparable sorbate and sorbent concentrations (Wilkie and Hering, 1996). Such studies, however, focus on low sorbent concentrations (typically $[Fe]_T < 120 \mu M$ corresponding to a solids concentration of ca. 12 mg/L) and sorbate-sorbent ratios at which As(V) removal from solution is nearly complete.

In contrast, As sorption studies conducted with Fe(III) oxyhydroxides at higher sorbate and sorbent concentrations and higher sorbate-to-sorbent ratios have demonstrated comparable sorption of As(III) and As(V) at circumneutral pH and preferential sorption of As(III) at higher pH values (Dixit and Hering, 2003; Manning et al., 1998; Raven et al., 1998). However, the relative affinity of the Fe(III) oxyhydroxide surface for As(III) and As(V) is affected not only by pH but also by the presence of competing sorbates such as phosphate. In the presence of phosphate, the extent of sorption of As(III) and As(V) onto hydrous ferric oxide (HFO) are still comparable at $pH \approx 8$ but sorption of As(III) is significantly depressed at lower pH values (Fig. 1).

In Haiwee sediments, examination of cores using X-ray Near Edge Spectroscopy (XANES) indicated that As in the solid phase was present as As(III) throughout the sediment core; As(V) was detected only in the surficial sediment

(Kneebone et al., 2002). Since As occurs as As(III) in the sediment well above the depth at which As is released into the porewater, it is apparent that reduction of As(V) to As(III) is not, in itself, sufficient to account for the mobilization of As at depth.

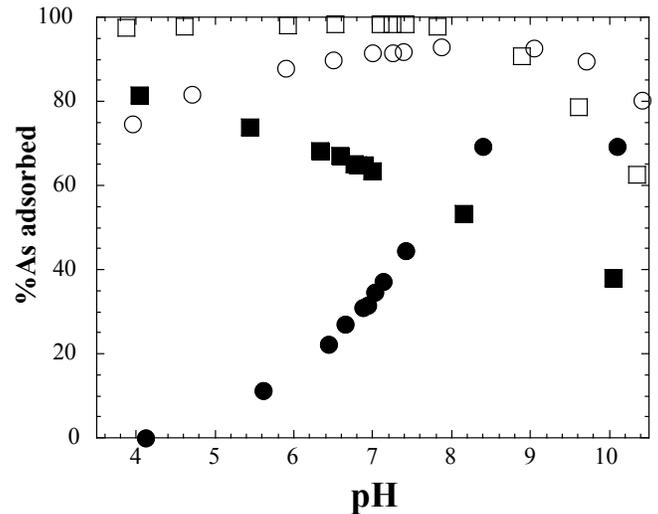


Figure 1. Sorption of As(III) (circles) and As(V) (squares) on HFO in the presence (closed symbols) or absence (open symbols) of phosphate. Experimental conditions: 0.03 g/L HFO, $[As]_T = 10 \mu M$, $[PO_4]_T = 100 \mu M$, 0.01 M NaClO₄. From Dixit and Hering (2003).

3.2 Solid diagenesis hypothesis

At the Cottonwood Treatment Plant, the Fe(III) oxyhydroxide floc is formed under conditions that would produce an amorphous solid. This solid material might become increasingly crystalline as it aged in the sediment. Amorphous Fe(III) oxyhydroxides can also undergo transformation to the mixed Fe(II), Fe(III) solid magnetite during reductive dissolution (Benner et al., 2002).

The bulk Fe signature in a sediment core taken at Haiwee reservoir in December 2001 was examined by Extended X-Ray Fine Structure (EXAFS) Spectroscopy. Iron EXAFS spectra were collected at the Stanford Synchrotron Radiation Laboratory using a Lytle fluorescence detector at room temperature. Spectra were fit using assuming that Fe-bearing phases in the sediment are primarily a mixture of detrital phyllosilicate minerals (indicated by X-ray dif-

fraction analyses of a control core) and ferrihydrite floc. Sediment spectra are similar but not identical to a reference spectrum of synthetic ferrihydrite (Fig. 2), consistent with the presence of additional detrital phyllosilicate minerals in the core. Spectra for surficial and deeper sediments were remarkably similar to each other and least-squares fits indicated no major structural change with depth. These spectra show no evidence of iron reduction or conversion to magnetite. The possibility of ferrihydrite conversion to goethite is not excluded on the basis of EXAFS alone because the local atomic structure of both phases is nearly identical (O'Day et al., in press). However, bulk X-ray diffraction analysis of sediment cores collected in 2003 has indicated an absence of crystalline Fe(III) oxide or oxyhydroxide phases.

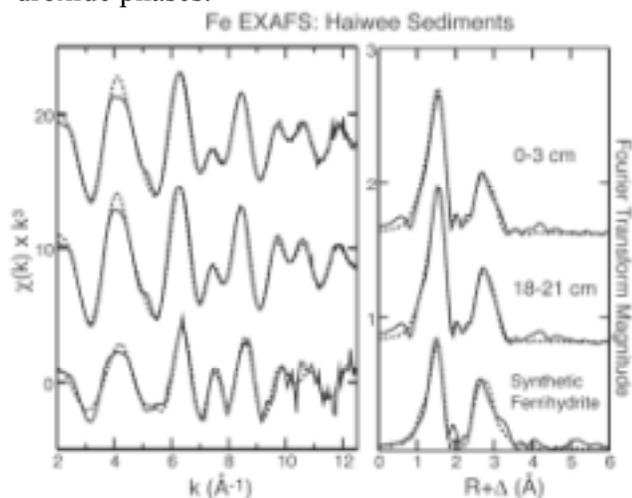


Figure 2. Iron EXAFS and Fourier transforms of bulk sediments from a Haiwee core at two intervals, 0-3 cm and 18-21 cm, compared to a reference sample of synthetic ferrihydrite. Solid lines are experimental data; dashed lines are non-linear least-squares fits.

Laboratory studies of As(III) sorption onto HFO and goethite indicate comparable sorption for both solids when sorbed As(III) is normalized to surface site densities (Dixit and Hering, 2003). In this study, the maximum sorption density for As(III) on HFO was ca. 20-fold higher than on goethite. This would imply that the capacity of the surface for As sorption would decrease with alteration of the solid to goethite. However, this difference largely reflects the lower surface area of synthetic

goethite (relative to HFO). If alteration to goethite in the sediments occurred without substantial decrease in specific surface area, then the sorption capacity of the solid would not be affected. A recent laboratory study showed that aging of HFO did not result in the desorption of As(V) (Ford, 2002).

3.3 Porewater composition hypothesis

The composition of the porewater changes with depth in the sediment as a result of the respiration and mineralization of organic matter. In the Haiwee sediments, pH measured with a microelectrode in September 2003 decreased only moderately (from 7.8 to 6.7) with depth (Dixit, unpubl.). Total dissolved P concentrations in the porewater (like those of As, Fe, and Mn) were elevated only deeper in the sediment column. It is possible that the release of phosphate associated with the remineralization of organic matter could lead to competitive desorption of As from the Fe(III) oxyhydroxide floc. Consistent with this hypothesis, it was observed that a significant fraction (ca. 80%) of the As associated with the sediment was released by leaching with 1 M phosphate at pH 4. The presence of elevated phosphate in the porewaters may also inhibit the re-sorption of As (released by reductive dissolution) onto the residual Fe(III) oxyhydroxide solids in the sediment. Note that, in this study, only total dissolved P (not phosphate, per se) was measured in the porewater. In addition, it has not yet been possible (given the small volumes of porewater recovered) to distinguish between As(III) and As(V) in the porewaters though the preponderance of As(III) in the solid phase suggests that As(III) may also dominate the dissolved pool.

Dissolved organic matter (DOM) has not yet been measured in the porewaters of Haiwee sediments but DOM concentrations are often elevated in sediment porewaters. If present at sufficient concentrations, DOM could promote desorption of As and/or inhibit As re-sorption onto the Fe(III) oxyhydroxide floc (Redman et al., 2002).

Elevated concentrations of total, dissolved Fe have been measured in Haiwee sediments. As with As and P, the speciation of Fe in the porewaters has not yet been determined but it may be assumed that inorganic Fe(II) is predominant (van der Zee et al., 2002). A laboratory study of competitive sorption of Fe(II) and As(III) was conducted using goethite as the sorbent. Sorption of Fe(II) was shown to be reversible. In single sorbate experiments, sorption of both Fe(II) and As(III) was observed. In the presence of both sorbates, however, competition between Fe(II) and As(III) was not observed (Fig. 3) (Dixit, unpubl.). Although the potential for competition between Fe(II) and As(III) needs to be assessed for conditions relevant to Haiwee reservoir, these results suggest that Fe(II) is not likely to suppress As(III) sorption dramatically.

4 *IN SITU* SORPTION EXPERIMENTS

Because of the difficulty of obtaining sufficient volumes of porewaters for sorption experiments (or even for complete analytical characterization), an alternative approach was adopted in which freshly-prepared HFO could be exposed to *in situ* conditions with minimal disturbance of the sediments. The gel probe sampler (Kneebone et al., 2002; Krom et al., 1994), which was used to obtain porewater profiles, was modified for this purpose. In the original gel probe sampler, polyacrylamide (clear) gel slabs held in a plexi-glass ladder were introduced into the sediment and allowed to equilibrate with the porewater. For the modified sampler, the gels were doped with HFO before being loaded into the sampler. The sampler was loaded with both HFO-doped and clear gels. It was hoped that the clear gels could be used (as previously) to obtain porewater profiles of various elements and that the HFO-doped gels would provide information on the extent of sorption of those elements in response to their porewater concentrations.

In obtaining porewater profiles using the (clear) gel probe sampler, it can be assumed that the equilibration of the clear gels does not perturb the ambient porewater composition signifi-

cantly. This assumption is reasonable because the volume of water in the gel slabs is quite small and the porewater constituents are not concentrated in the (clear) gel. This is not the case, however, with the HFO-doped gels.

Since significant concentration of porewater constituents onto the HFO-doped gels (i.e., by sorption) may be expected, the concentration of these species in the porewater in contact with the sampler could be substantially depleted (Ernstberger et al., 2002; Zhang et al., 1995; Zhang et al., 2002). Thus, the accumulation of sorbates in the HFO-gels and the concentrations of solutes in the clear gels will reflect the ambient porewater composition only if the sorbing constituents are resupplied to the porewater from the sediments on the timescale of equilibration of the (mixed clear and HFO-doped) gel probe sampler. Preliminary deployment of the sampler (for several hours) suggested some artifacts associated with kinetic limitations of either As resupply from the sediment or uptake onto the HFO-doped gels or both. Further work is in progress to assess performance of the HFO-doped gel probe sampler.

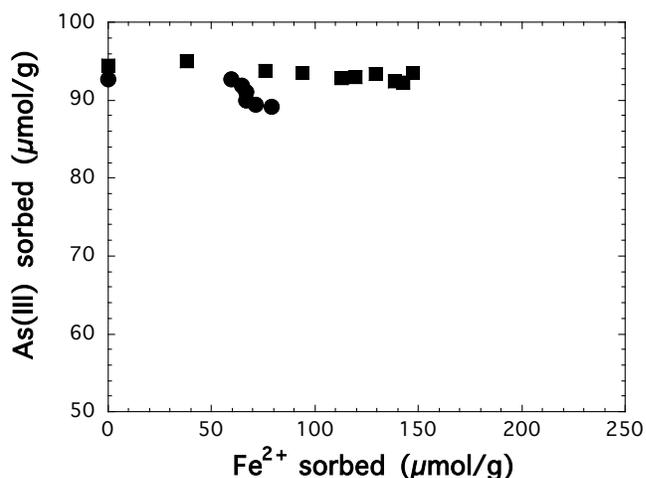


Figure 3. Sorption of As(III) and Fe(II) onto goethite at pH 6.5 (circles) and 7.5 (squares). Experimental conditions: $I = 0.01$, 2.5 g/L goethite, $[As(III)]_T = 250 \mu M$, $[Fe(II)]_T = 0-1.5 \text{ mM}$.

CONCLUDING COMMENTS

The deposition of As-enriched Fe(III) oxyhydroxide floc to the sediments of Haiwee Reservoir provides a unique setting for the study of As mobilization. Sediment deposition patterns in Haiwee reservoir have been significantly perturbed by the addition of ferric chloride to the LAA. Because this manipulation is designed to substantially decrease dissolved As concentrations in the LAA water supply, it has necessarily been carried out at a large scale. Geochemical studies in this system, in which As and Fe inputs are relatively well defined, provide insight into the biogeochemical controls on As mobility.

REFERENCES

- Benner, S.G., Hansel, C.M., Wielinga, B.W., Barber, T.M. and Fendorf, S., 2002. Reductive dissolution and biomineralization of iron hydroxide under dynamic flow conditions. *Environmental Science & Technology*, 36(8): 1705-1711.
- Dixit, S. and Hering, J.G., 2003. Comparison of arsenic(V) and arsenic(III) sorption onto iron oxide minerals: Implications for arsenic mobility. *Environ. Sci. Technol.*, 37: 4182-4189.
- Ernstberger, H., Davison, W., Zhang, H., Tye, A. and Young, S., 2002. Measurement and dynamic modeling of trace metal mobilization in soils using DGT and DIFS. *Environmental Science & Technology*, 36(3): 349-354.
- Ford, R.G., 2002. Rates of hydrous ferric oxide crystallization and the influence on coprecipitated arsenate. *Environmental Science & Technology*, 36(11): 2459-2463.
- Harvey, C.F. et al., 2002. Arsenic mobility and groundwater extraction in Bangladesh. *Science*, 298(5598): 1602-1606.
- Hering, J.G., Chen, P.Y., Wilkie, J.A., Elimelech, M. and Liang, S., 1996. Arsenic removal by ferric chloride. *Journal American Water Works Association*, 88(4): 155-167.
- Hering, J.G. and Kneebone, P.E., 2001. Biogeochemical Controls on Arsenic Occurrence and Mobility in Water Supplies. In: W.T. Frankenberger (Editor), *Environmental Chemistry of Arsenic*. Marcel Dekker, New York, pp. 155-181.
- Jekel, M.R., 1994. Removal of Arsenic in Drinking Water Treatment. In: J.O. Nriagu (Editor), *Arsenic in the Environment. Part I: Cycling and Characterization*. Wiley-Interscience, New York, pp. 119-132.
- Kneebone, P.E., O'Day, P.A., Jones, N. and Hering, J.G., 2002. Deposition and Fate of Arsenic in Iron- and Arsenic-Enriched Reservoir Sediments. *Environ. Sci. Technol.*, 36: 381-386.
- Krom, M.D., Davison, P., Zhang, H. and Davison, W., 1994. High-Resolution Pore-Water Sampling with a Gel Sampler. *Limnol. Oceanogr.*, 39: 1967-1972.
- Manning, B.A., Fendorf, S.E. and Goldberg, S., 1998. Surface structures and stability of arsenic(III) on goethite: Spectroscopic evidence for inner-sphere complexes. *Environmental Science & Technology*, 32(16): 2383-2388.
- Nordstrom, D.K., 2002. Public health - Worldwide occurrences of arsenic in ground water. *Science*, 296(5576): 2143-2145.
- O'Day, P.A., Rivera, N., Root, R. and Carroll, S.A., in press. X-ray absorption spectroscopic study of iron reference compounds for the analysis of natural sediments. *American Mineralogist*.
- Raven, K.P., Jain, A. and Loeppert, R.H., 1998. Arsenite and arsenate adsorption on ferrihydrite: Kinetics, equilibrium, and adsorption envelopes. *Environ. Sci. Technol.*, 32: 344-349.
- Redman, A.D., Macalady, D.L. and Ahmann, D., 2002. Natural organic matter affects arsenic speciation and sorption onto hematite. *Environmental Science & Technology*, 36(13): 2889-2896.
- Shen, Y.S., 1973. Study of Arsenic Removal from Drinking Water. *Journal of the American Water Works Association*, 65(8): 543-548.
- Smedley, P.L. and Kinniburgh, D.G., 2002. A review of the source, behaviour and distribution of arsenic in natural waters. *Applied Geochemistry*, 17(5): 517-568.
- Sorg, T.J. and Logsdon, G.S., 1978. Treatment Technology to Meet the Interim Primary Drinking Water Regulations for Inorganics: Part 2. *J. Am. Water Works Assoc.*, 70(7): 379-393.
- Stolarik, G.F. and Christie, J.D., 1999. Interim Arsenic Management Plan for Los Angeles, Proc. Amer. Water Works Assoc. Annual Conference, Chicago, IL.
- van der Zee, C., van Raaphorst, W. and Helder, W., 2002. Fe redox cycling in Iberian continental margin sediments (NE Atlantic). *Journal of Marine Research*, 60(6): 855-886.
- Welch, A.H., Westjohn, D.B., Helsel, D.R. and Wanty, R.B., 2000. Arsenic in ground water of the United States: Occurrence and geochemistry. *Ground Water*, 38: 589-604.
- Wilkie, J.A. and Hering, J.G., 1996. Adsorption of arsenic onto hydrous ferric oxide: Effects of adsorbate/adsorbent ratios and co-occurring solutes. *Colloids and Surfaces A-Physicochemical and Engineering Aspects*, 107: 97-110.
- Zhang, H., Davison, W., Miller, S. and Tych, W., 1995. In-Situ High-Resolution Measurements of Fluxes of Ni, Cu, Fe, and Mn and Concentrations of Zn and Cd

in Porewaters by Dgt. *Geochimica Et Cosmochimica Acta*, 59(20): 4181-4192.

Zhang, H. et al., 2002. Localised remobilization of metals in a marine sediment. *Science of the Total Environment*, 296(1-3): 175-187.

This work was performed under the auspices of the U.S. Department of Energy by University of California Lawrence Livermore National Laboratory under contract No. W-7405-Eng-48

University of California
Lawrence Livermore National Laboratory
Technical Information Department
Livermore, CA 94551

