

Risk & Remediation

Emerging Issues in Mercury Cycling

The site-specific nature of mercury cycling demands an in-depth understanding prior to selecting a remedy.

Mercury (Hg) is a naturally occurring element in the earth's crust and is found in both elemental form and complexed with organic and other inorganic elements. Mercury of both natural and anthropogenic origins cycles between the atmosphere, water bodies, soil, and sediment. Although it is difficult to assess the amount of mercury in the environment that has arisen from anthropogenic sources, the U.S. EPA (1997) estimates that between 40% and 75% of the current atmospheric mercury concentrations are the result of anthropogenic releases. Anthropogenic releases over the last several decades have been dominated by emissions from

Although much has been learned about mercury in the environment in the last 10 to 20 years, much remains to be understood.

combustion sources, power plants, and chlor alkali plants. Mercury levels in remote water bodies across the northern parts of the world have increased over the last 100 to 200 years (Swain *et al.*, 1992), and this

increase is believed to be due to an increased atmospheric fallout of mercury that predominantly affects the northern latitudes. However, at this time it is unclear whether atmospheric mercury concentrations are increasing or decreasing (U.S. EPA, 1997).

A host of biogeochemical and physical transport and transformation processes in the environment contribute to the "mercury cycle" (see figure). Mercury can transform from elemental to divalent mercury in the atmosphere, a form that is removed more rapidly, and deposited on land and water. A portion of mercury deposited into lakes and other water bodies is converted by aquatic organisms to methylmercury, which bioaccumulates in the food chain, ultimately providing a source of exposure to humans through fish consumption. Mercury reduced to its

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Letter to our Readers

September 2000

Dear Colleague,

In this issue of *Trends*, we return to metals, examining recent proposals for regulation of arsenic in water, and focusing attention on the wealth of new information being generated for mercury, both in terms of mercury cycling in the environment and mercury toxicity. Metals are a part of our natural environment, and pose unique risk assessment questions as a result. Here, we discuss some of the current concerns arising from this unique position of metals in our environment.

Contributors to this issue include Dr. Teresa Bowers, Gradient Principal, geologist, and metals risk assessor. Joining her are Ms. Tracey Slayton, a toxicologist who specializes in exposure assessment, and Dr. Barbara Beck, Gradient Principal and nationally recognized expert in toxicology and health risk assessment. And finally, we welcome Dr. Christopher P. Weis, a U.S. EPA Region 8 Toxicologist, who shares his thoughts on metal bioavailability testing.

We hope you will find the information in this issue of *Trends* thought-provoking and helpful in your daily work.

Yours truly,



Neil Shifrin
President

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Emerging Issues in Mercury Cycling

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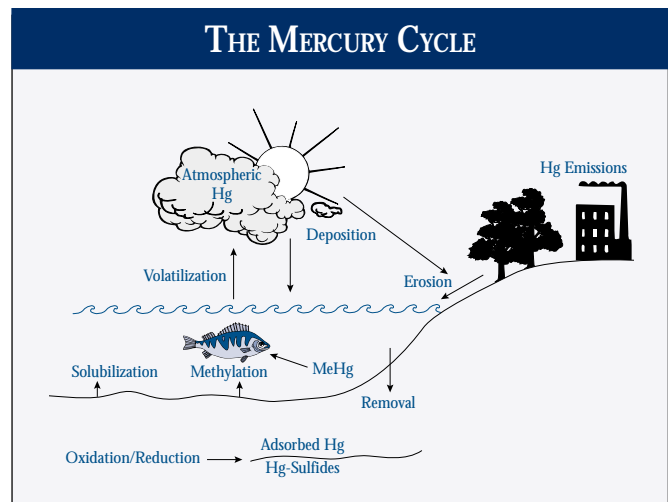
elemental form in water bodies, volatilizes and cycles back into the atmosphere. Mercury is also removed from the water column by sedimentation, and is eventually buried sufficiently to effectively remove it from the environmental cycle. Mercury deposited on land participates in a variety of chemical and biological reactions that take place in soil. Much of it ends up bound to organic matter in the soil. Some mercury in soil enters water bodies through erosion and runoff from the watershed.

Because fish ingestion is the primary pathway for mercury exposure to humans, much of the attention is focused on the potential for mercury in soils and sediments to enter the food chain. Mercury entering the food chain can be thought of as a two-step process: (1) mercury must be solubilized from soil or sediment so that it enters pore water and/or the water column, and (2) mercury dissolved in water must be transformed to methylated mercury, the primary form taken up by fish.

The extent to which any of the above processes occur is very site-specific. Binding of mercury to soils and sediments depends on temperature, pH, redox conditions, and sediment concentrations of sulfides, ferric oxides, and organic carbon. Mercury combines with available sulfides to form relatively insoluble minerals. It is also immobilized by adsorption onto the surfaces of ferric oxides and organic carbon. The formation of mercury sulfides occurs under reducing conditions, while adsorption of mercury onto ferric oxides occurs under more oxidizing conditions. Seasonal or other fluctuations in the redox state of a sediment may result in cycling of mercury between these two removal mechanisms. For these reasons, a site-specific "mercury cycling model" should be assembled to describe the movement of mercury in a given system.

An understanding of these processes can have a profound impact on remedy selection. For example, dredging of sediments that results in the removal of a surface oxidized layer may expose underlying reduced sediments to oxygenated conditions, resulting in the remobilization of mercury that had been previously isolated from the environment.

Although much has been learned about mercury in the environment in the last 10 to 20 years, much remains to be understood. The factors that control the bioavailability of mercury in sediments to the food chain are numerous and site-specific, and it is clear that measurements of total mercury do not give an indication of the amount of bioavailable mercury. Dredging and other sediment removal operations have the potential to mobilize buried mercury, possibly increasing the bioavailable fraction. Although it is known that diagenetic reactions, redox cycling, and microbial activity all affect the level of mercury in aquatic systems, it is not possible to generalize about these processes. As a result, mercury assessments must



Mercury movement in the environment is mediated by a variety of processes.

remain site-specific. Investigators need to provide sufficient time and studies to generate the development of a site-specific mercury cycling model as a tool to guide informed decision-making.

Teresa S. Bowers, Ph.D.

Email: tbowers@gradientcorp.com

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BY THE WAY...

Does the recent deciphering of the human genome mean that we will soon be able to predict who will and will not get cancer? According to a recent editorial by Robert Hoover in the *New England Journal of Medicine* (July 13, 2000), such nature versus nurture debates are overly simplistic and fail to consider the multifactorial nature of cancer. As stated in the editorial, the wise approach is to focus on identifying and manipulating "...both environmental and genetic risk factors to improve control of cancer."

Developments in Mercury Toxicity

Discrepancies in the outcomes of two recent mercury epidemiology studies are adding to the debate over a regulatory criterion for this metal.

Methylmercury (MeHg) is a common contaminant in fish and marine mammals due to its persistence in the environment and ability to accumulate up the food chain. Results from two large, well-conducted epidemiology studies investigating prenatal MeHg exposures have been published recently.

Although exposure levels in the two studies were similar, their findings were dramatically different – the study conducted in the Seychelles Islands found no evidence of neurodevelopmental effects, while the Faroe Islands study reported developmental abnormalities, primarily in memory, attention, and language skills. Differences in these two studies are emblematic of the current uncertainty regarding mercury toxicity.

To understand the current debate regarding mercury toxicity, it is important to understand the uncertainties underlying the Seychelles and Faroe studies. One particularly confounding issue is the manner by which PCB exposure was assessed in the Faroe study. While the Seychelles Islands are relatively pristine, the Faroe population was also exposed to PCBs from whale blubber, which some investigators thought could influence the study. However, reanalysis of the Faroe Islands data found an equally strong association between MeHg and language and verbal deficits among the subset of Faroe children with lowest PCB exposures, and a series of sensitivity analyses indicated that PCB exposures were unlikely to be causing serious bias.

Similarly, there were other study uncertainties, including differences in exposure patterns, biomarkers, and types of

neurological tests administered. Consumption of MeHg in fish was consistent among the Seychelles population (12 fish meals per week), while exposure was more episodic in the Faroe population (most MeHg exposure from pilot whale, more highly contaminated but consumed less than once per month). The Seychelles study used maternal hair as a biomarker, while the Faroe study relied primarily on cord blood measurements. Moreover, the Seychelles study used neurological tests that integrate performance over many neuropsychological domains, while the Faroe study used more focused, domain-specific tests. Recent studies also have suggested other types of effects, including immunotoxicity and cardiovascular effects. Lastly, the Seychelles population may have been less sensitive, possibly due to protective effects of selenium, omega-3 fatty acids, or other fish components.

Differences in the interpretation of these two studies is being manifested in the considerable controversy among regulatory and scientific agencies responsible for setting acceptable levels of MeHg exposure (see table). The current EPA Reference Dose (RfD) for MeHg is 0.1 µg/kg-day, based on developmental effects in infants due to a grain poisoning incident in Iraq (U.S. EPA, 2000). In contrast, the ATSDR (1999) recommends a Minimal Risk Level (MRL) of 0.3 µg/kg-day, based on the finding of no adverse effects in the Seychelles study. A TERA independent peer review panel (2000) has approved an RfD range of 0.3 to 1 µg/kg-day based on the Seychelles study. Congress directed the National Research Council (NRC) to perform an independent review of MeHg and their report was just released (NRC, 2000). The NRC recommends an RfD of 0.1 µg/kg-day based on the Faroe study. An integrative analysis, using combined results from the Faroe, Seychelles, and New Zealand studies, yielded similar results.

From a scientific perspective, the differences in acceptable exposure levels are slight. Overall, it is encouraging that

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ACCEPTABLE LEVELS OF MeHg EXPOSURE SET BY VARIOUS REGULATORY AND SCIENTIFIC AGENCIES

Agency	RfD/MRL (µg/kg-day)	Critical Dose (ppm maternal hair)	Critical Dose (µg/kg-day)	Total UF	Study
EPA	0.1	11 (10% BMDL)	1.1	10	Iraq
ATSDR	0.3	15.3 (NOAEL)	1.3	4.5	Seychelles Islands
TERA	0.3 – 1.0	21 (10% BMDL)	0.9 – 3	3	Seychelles Islands
NRC	0.1	12 (5% BMDL)	NR	10	Faroe Islands

Mercury criteria span roughly an order of magnitude among various regulatory agencies.

The Arsenic Debate

The U.S. EPA's pending regulatory decision on arsenic in drinking water needs to consider the strengths and weaknesses of the underlying science.

On June 22, 2000, the U.S. EPA proposed to modify the current maximum contaminant level (MCL) for arsenic from 50 µg/L to 5 µg/L, with requests for comments on 3 µg/L, 10 µg/L, and 20 µg/L (U.S. EPA, 2000). This modification could result in multibillion-dollar compliance costs to industry, municipalities, and individual citizens as additional treatment facilities are constructed and maintained to meet this new standard. The proposal uses a risk assessment based largely upon studies of

...by failing to adequately address the implications of these uncertainties, particularly in a quantitative way, the analysis gives the impression of greater confidence in the risk assessment than warranted.

identifying sources of uncertainty in the risk assessment; however by failing to adequately address the implications of these uncertainties, particularly in a quantitative way, the analysis gives the impression of greater confidence in the risk assessment than warranted. While the EPA suggests that risks could approach one in 100 at the present MCL of 50 µg/L, this conclusion is likely biased for much of the U.S. population. Some specific difficulties with the analysis include:

- Selection of low dose extrapolation model: The EPA calculates risks assuming the relationship between dose of arsenic and cancer is linear, even though, according to an EPA-sponsored expert panel, non-linearity is more plausible for arsenic (U.S. EPA, 1997). Moreover, recent biochemical and cellular studies provide evidence of protective effects of arsenic at sub-toxic levels (see for example, Snow *et al.*, 1999), further supporting departure from a linear model. The NRC report demonstrates that, at arsenic levels in the range under debate, the risks calculated using the Weibull model (a no threshold model that can allow non-linearity) can be orders of magnitude below those with the Poisson model (which assumes linearity at low doses). This model selection decision alone will impact the outcome of the analysis by a factor of 15 to 94 fold.
- Consideration of inorganic arsenic in food: While acknowledging that food was a significant source of inorganic arsenic intake in Taiwan, the EPA did not quantify the impact on risk. Such quantification would have yielded lower risk estimates for U.S. populations whose intake of inorganic arsenic in food

is likely less than that of the Taiwanese population.

- Variability in responsiveness of U.S. *versus* Taiwanese populations: The Taiwanese population, particularly those individuals in whom arsenic toxicity was manifest, was nutritionally disadvantaged in several ways, including total caloric intake, selenium intake, and methionine intake. Such deficiencies can enhance susceptibility to arsenic. Thus, the EPA's risk estimates may be overestimates for the majority of the U.S. population who do not experience such dietary deficiencies.
- Inappropriate reliance on a Utah Mortality Study: The EPA notes that this study of individuals in Utah exposed to mean concentrations of arsenic in water up to 191 µg/L supports consideration of heart disease in evaluation of the potential benefits of lowering the MCL. However, the Utah study is inconclusive with respect to heart disease. Although elevated, the rate for hypertensive heart disease did not show a dose-response relationship with arsenic, and the risk for all heart disease showed a negative dose-response relationship. Thus, by emphasizing this study in the analysis, the EPA is potentially overstating the arsenic risk.

Numerous organizations are commenting on the proposed MCL, arguing that it is not supported by the current science. The Science Advisory Board also expressed concern about the EPA's selection of 5 µg/L, noting that uncertainties in the risk assessment "...certainly provide the Agency with sufficient grounds to consider higher MCLs for arsenic (*BNA*, 2000)."

The EPA has not provided sufficient evidence to support a reduction to a level as low as 5 µg/L. Given the breadth and magnitude of the impact of the regulation, (10% or more drinking water systems in the U.S. are estimated to currently exceed 5 µg/L), the EPA would be well served to consider both the strengths and the limitations of their analysis, which may well result in a higher MCL than the current proposal.

Barbara D. Beck, Ph.D., DABT
Email: bbeck@gradientcorp.com

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What's New at Gradient

Gradient Welcomes Dr. Rosalind Schoof

Dr. Rosalind A. Schoof has joined Gradient as a Principal. Dr. Schoof is a board-certified toxicologist and expert in risk assessment, exposure assessment, toxicology, metals, mining and smelting pollutants, pesticide manufacturing pollutants, soil contaminants, and coordination of complex risk assessment projects. She plans to continue her practice and open a Gradient office based in Seattle, WA. She earned her Ph.D. in toxicology from the University of Cincinnati and her B.A. in molecular biology from Wellesley College.

Gradient's Web-Site Gets New Look

Please visit Gradient's newly redesigned web-site at www.gradientcorp.com. Our new site contains information about our services, our staff members, and their accomplishments. *Trends* can also be accessed through our site.

Dr. Barbara Beck Reappointed to Board of Health

Dr. Barbara Beck was recently reappointed by a unanimous vote to the Watertown Board of Health. Dr. Beck has served on the Board of Health in her hometown since 1995.

Recent and Upcoming Presentations

Washington, D.C. August 8, 2000. Eric Butler, A. Dallas Wait, *et al.* "Field Application of ASTM Method D5831 at Fuel-Contaminated Sites," presentation at the U.S. EPA Waste Testing and Quality Assurance 2000 Conference.

Washington, D.C. September 18-19, 2000. Lorenz Rhomberg. Participant in the U.S. EPA Risk Assessment Forum Colloquium on Distributional Methods in Noncancer Risk Assessment.

Boston, MA. September 27, 2000. Lorenz Rhomberg. "Cancer Dose Response and the Implications of Mechanistic Research," lecture in the Harvard Center for Risk Analysis Continuing Education Course, Analyzing Risk.

Research Triangle Park, NC. October 10-12, 2000. Lorenz Rhomberg. Panelist, "Endocrine Disruptors Low-Dose Peer Review."

Piscataway, NJ. October 12, 2000. A. Dallas Wait. "Environmental Forensic Chemistry-Tools for Discerning Contaminant Liability," presentation to the Environmental and Occupational Health Sciences Institute at Rutgers.

Amherst, MA. October 18, 2000. A. Dallas Wait. Moderator for Risk Session at the 16th Annual International Conference on Contaminated Soils, Sediments, and Water, University of Massachusetts.

Amherst, MA. October 18, 2000. Eric Dube. "Are You Underestimating Health Risk from Inhalation Exposure?" Presentation at the 16th Annual International Conference on Contaminated Soils, Sediments, and Water, University of Massachusetts.

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Developments in Mercury Toxicity

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acceptable exposure levels based on different scientific studies, calculated by numerous agencies and organizations using a variety of approaches, are all reasonably consistent. From a regulatory perspective, however, the acceptable levels set by regulatory agencies have important implications for setting criteria for MeHg in fish, air, water, and other environmental media. For that reason, an informed debate on the merits and limitations of mercury toxicity studies leading to harmonization among various regulatory agencies is clearly needed.

Tracey M. Slayton, M.S.
Email: tslayton@gradientcorp.com

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Guest Editorial: Progress in Measurement of Soil Lead Bioavailability¹

Ongoing in vivo and in vitro research on lead bioavailability continues to reduce uncertainties in risk assessment.

Regulatory limits for human exposure to hazardous chemicals in soil are protective by design. Most would agree that such protectiveness is desirable in light of uncertainty and variability in risk estimates. Agreement upon the exact margin-of-safety necessary for adequate protection is quite a different matter! Understanding human health risk through thoughtful collection of environmental data is the key to agreement about necessary margins-of-safety. The resultant reduction of uncertainty represents sound public health practice and good economics. A case in point is the study of lead bioavailability from soil.

Bioavailability is a measure of contaminant uptake and can be a very sensitive parameter in any risk evaluation. Thus, over or underestimates of this parameter can have costly or dangerous consequences. While perhaps seeming unreasonable for some metals, regulatory agencies often assume a contaminant to be completely bioavailable to help assure public safety.

Over the past several years, U.S. EPA Region 8 scientists in cooperation with investigators from Michigan State University, the University of Missouri, and the University of Colorado have explored the empirical relationship between soil lead characteristics and bioavailability of this metal to humans. To do so, we have characterized the gastrointestinal absorption of lead mixtures from a physico-chemically diverse set of 17 Superfund site soils and three reference materials (lead acetate, lead-based

paint, and galena) using a swine model as a surrogate for young children and pregnant adults. Our results indicate that absorption of soil lead is highly variable and dependent upon geophysical-chemical characteristics of the lead matrix as well as the physiological status of the test animal.

More recently, EPA Region 8 has supported the development and independent validation of an *in vitro* solubility assay which reasonably mimics the results of our *in vivo* measurements made in weanling swine. Although highly dependent upon results derived from lead absorption in the swine model, the *in vitro* solubility test shows considerable promise as a screening tool for estimating bioavailability of lead in soils. Correlations between the *in vivo* and *in vitro* estimates of lead bioavailability ranging from 0.89 to 0.93 for three participating labs. With demonstrated relevance to the *in vivo* studies, the *in vitro* assay for estimating soil lead absorption may provide an alternative and more efficient means of estimating lead bioavailability in areas where animal studies are not warranted.

Environmental protection will always benefit by reducing uncertainties in risk assessment practice. Convincing industries and policy-makers to support investigations and adopt the conclusions is likely to require persistence and patience on the part of practitioners.

Christopher P. Weis, Ph.D., DABT
Regional Toxicologist, U.S. EPA Region 8,
Denver, Colorado.

¹ The work described was funded by EPA Region 8. The findings and conclusions represent the work and opinions of the author and do not necessarily represent the official policy of the U.S. Environmental Protection Agency.

Environmental protection will always benefit by reducing uncertainties in risk assessment practice.

In the next issue:

Overview of Dioxin Issues

Dioxin Sampling: When, Where, and How

New Developments in Dioxin Toxicity

Guest Editorial: Is Our Food Safe?

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T R E N D S • I N
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Produced by:

Gradient Corporation

238 Main Street

Cambridge, Massachusetts 02142

Phone: (617) 395-5000

Fax: (617) 395-5001

internet: trends@gradientcorp.com

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