

## Mercury cycling in the environment

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The potential consequences of mercury contamination of aquatic food webs were first recognized in the 1950s and 1960s in Minamata and Niigata, Japan, where human consumers of contaminated fish were severely poisoned. These and other tragic incidents prompted widespread reductions in direct releases of mercury into surface waters in many countries. Since about 1985, however, widespread mercury contamination of aquatic biota has become evident in systems remote from obvious anthropogenic mercury sources. Investigations at these sites have shown that in most cases, atmospheric transport and low rates of mercury deposition are largely responsible for the observed widespread mercury contamination of aquatic ecosystems across the globe. In some cases, concentrations in fishes from these remote sites have equalled or exceeded those in fishes from waters that have been heavily contaminated by direct industrial discharges. The key to understanding the apparent discordance between these despairing contamination levels, yet similar levels in fish is the methylation process. In brief, this process involves the conversion of inorganic mercury that is the dominant form in deposition to methylmercury, which is the dominant form in fish (>95%). Presently, researchers are engaged in unravelling the many complexities of the environmental mercury cycle, including source-receptor relationships, bioavailability of various mercury sources, speciation of the precise forms of mercury in various environmental media, bioaccumulation processes, and toxic effects to humans and wildlife. Although mercury contamination of the environment is an enormously complex area of research, significant advances in our understanding have been made over the past 15 years. Presently, however, one of the greatest challenges in integrating this improved understanding with policies that will lead to improved environmental conditions in the future.

## Mercury in coal and its impact on utility mercury emissions

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### Mercury in Coal

U.S. coal-burning utility power stations emit 64% (1999) of input mercury (U.S. EPA, 2002), and remain the largest anthropogenic point source category of mercury emissions not regulated by the EPA. Efforts to reduce mercury output require knowledge of coal characteristics. Mercury contents differ by coal basin, by rank, and within individual coal beds, reflecting diagenetic differences at various scales. Mercury loading to combustion sources is a function of both the mercury and energy content of fuels.

We have investigated the modes of occurrence of mercury in various coal samples using selective chemical leaching and reconnaissance laser-ablation ICP-MS. In bituminous coals, pyrite is the primary host of mercury, whereas the proportion of organic-hosted mercury is generally greater in lignite and sub-bituminous coals. Coal preparation (to reduce sulfur) is effective in achieving modest reductions of mercury contents in bituminous coals by reducing pyrite contents. Higher ( $\geq 35\%$ ) mercury reductions likely require engineered approaches. The average mercury content of coals delivered to U.S. power plants in 1999 is 0.10 ppm (U.S. EPA, 2002).

### Impact of Coal Choice on Mercury Speciation

Knowledge of coal rank, chemistry, and mineral content is important in determining flue gas mercury speciation and capture efficiency of a given combustion system. Compared to bituminous coals, combustion of low rank coals evolves a greater proportion of elemental mercury ( $\text{Hg}^0$ ), relative to oxidized (reactive) species ( $\text{Hg}^{2+}$ ). For most emission control devices, capture of elemental mercury is less efficient than oxidized mercury (Pavlish and others, 2003). Chlorine present in coal also influences mercury speciation, by promoting oxidation of elemental mercury, leading to formation of  $\text{HgCl}_2$  (Kilgroe and Senior, 2003). Detailed coal chemical and rank characterization, and knowledge of power station set-up are needed to predict mercury capture by emissions control devices and flue gas mercury speciation.

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## New insights into mercury exchange between air and substrate

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Mercury (Hg) can be emitted to the air from Hg-enriched and unenriched substrates, as well as deposited to terrestrial surfaces from the air as wet and dry deposition and subsequently re-emitted. The relative magnitude of these processes is important to understand for developing regional and global biogeochemical mass balances, and assessing the effectiveness of regulatory controls. Mercury emissions often follow a diel pattern with emissions highest during midday. Light is thought to be a dominant parameter driving emissions with temperature, atmospheric turbulence and precipitation all demonstrated to exert some control. This paper presents new insights into other parameters important in controlling Hg air-substrate exchange.

Recent work has shown that soil moisture content and atmospheric ozone significantly enhance Hg emissions from enriched and unenriched substrates. Evaporation of moisture from soils is also thought to be an important process whereby Hg within the soil column is transported by mass flow to the soil-air interface. It has been suggested that with increasing anthropogenically derived atmospheric oxidants in the air Hg emission from soils may increase.

Little work has been done to investigate the potential for dry deposition of elemental Hg to soils and the potential for re-emission of Hg deposited by dry or wet processes. Field and laboratory studies have shown that elemental Hg is dry deposited to substrate. Laboratory experiments have shown that factors controlling deposition include air Hg concentrations, dark versus light conditions, soil pH, and atmospheric chemistry. Data from a field experiment using stable Hg isotopes amended in a simulated light rain event to desert soils indicated that HgCl<sub>2</sub> is not rapidly re-emitted.

## Mercury geochemistry of the Scioto River, Ohio: Impact of agriculture and urbanization

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In April 2003 during a high flow event we sampled the Scioto River, a major central Ohio tributary to the Ohio River, for a number of chemical and physical constituents, including total and dissolved Hg. Seven locations were sampled, from the headwaters, which run through row crop agricultural lands, to just south of Columbus, the 15<sup>th</sup> largest city in the USA. The total Hg concentration increased continually downstream with the highest concentrations observed at Commercial Point, just below two large sewage treatment plants that serve metro Columbus. The highest Cl<sup>-</sup> concentration was also observed there. The highest NO<sub>3</sub><sup>-</sup> concentrations were found in the agriculturally dominated portion of the river. The highest dissolved Hg concentration occurred in downtown Columbus. Using the flow data from the day that the samples were collected, Hg yields were calculated at three locations within the basin: at Prospect (P) in the northern, ag-dominated part of the basin; at Bellepoint (B) located between two reservoirs, just north of Columbus proper; and at Downtown Columbus (D). The dissolved Hg yields in ng km<sup>-2</sup> sec<sup>-1</sup> increased by a factor of 2 from P to B and then another 50% at D. The particulate Hg yields increased only 10% from P to B, but 30% from B to D, with the particulate Hg yields being about ~2.5 to 4.5X greater than the dissolved ones. These data suggest that yields of particulate Hg are more affected by urbanization than agricultural activities. The cause of the increasing yields of dissolved Hg as the river proceeded downstream is not clear at this time. We assume the last increase is due to input from the urbanized portion of the watershed. As demonstrated previously by Mason and Sullivan (1998) in Washington, DC, it appears that urbanized regions retain a lower percentage of atmospherically deposited Hg than other landscape types.

## Hydrothermal mercury in the Yellowstone lake ecosystem

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Sublacustrine hydrothermal vents in Yellowstone are strongly enriched in Hg, as well as As, B, Cl, CO<sub>2</sub>, Ge, H<sub>2</sub>S, K, Li, Mo, Na, Rb, Sb, Si, and W. Sublacustrine hot springs have dissolved Hg concentrations up to 170 µg/L.

Mercury concentrations in cutthroat and lake trout populations are significant in muscle (cutthroat=0.07-0.53, lake trout=0.03-0.88 µg/g, wet weight; both ave.=0.21) and liver (cutthroat = 0.13-0.89 µg/g, 0.32 ave.; lake trout = 0.11-0.93 µg/g, 0.50 ave., wet weight) relative to trout collected elsewhere in the Yellowstone River basin. Methylation of Hg in thermal waters is probably carried out by bacteria that live around hot springs and these bacteria are consumed by amphipods. Stomach contents of cutthroat trout, which contain amphipods in many cases, average 0.20 µg Hg/g, wet weight. Hg in cutthroat trout has implications for grizzly bear, otter, eagle, and osprey populations that feed on the cutthroat trout that spawn in the rivers. For example, the hair of grizzly bears collected (by the Interagency Grizzly Bear Study Team) near Yellowstone Lake have higher Hg concentrations (0.6-1.7 µg/g, dry weight) than bear hair sampled at more remote areas in the Greater Yellowstone Ecosystem (0.006-0.09 µg/g, dry weight). Other grizzly bear foods, such as pine nuts and various megafauna show insignificant Hg concentrations.

## The isotopic composition of mercury as a tool in understanding the natural and anthropogenic cycling of a highly toxic element

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The industrialised countries have varying degrees of regulatory control on the uses and disposal of Hg, but in many developing countries anthropogenic usage of Hg is poorly regulated. Consequently, the persistence, high mobility, bioaccumulation, biomagnification, and toxicity of mercury (Hg) indicate that anthropogenic use continues to be an issue in regard to global health. Global sources, sinks, rates and loads that comprise the general Hg cycle in the surficial environment have been established. More importantly, however, the complex regional and local sub-cycles, determined by climate, geology, and biology are quite uncertain. Here, I present a review of Hg isotope systematics that suggests an additional tool in understanding Hg cycling. Second generation multi-collector ICPMS instruments provide opportunities to make precise measurements of Hg isotope ratios although there is much to be learned regarding methodologies. In particular, the degrees of mass fractionation during chemical processing of samples and appropriate application of instrumental mass bias corrections are areas requiring attention. There is also a lack of certified standards for Hg isotopes although this situation is slowly being rectified, mainly by IRMM. Hg isotope fractionation should occur during natural processes given the physical and organic chemistry of Hg. There is an emerging body of literature indicating Hg isotopes are fractionated in cinnabar deposits, meteorites, and during coal combustion and the natural /anthropogenic variation is likely to exceed 5 per mil; quite large considering the small relatively mass range (<4%).

## Methylmercury in food webs in northern midcontinental lakes: Bioaccumulation, adverse effects, and trends

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This presentation illustrates key aspects of the environmental mercury (Hg) problem, with emphasis on mid-continental lakes (USA). Atmospheric deposition is the dominant source of Hg in many of these waters, and much of the deposited Hg is from anthropogenic sources. Nearly all of the mercury in fish is methylmercury (MeHg), a toxic compound that bioaccumulates and can biomagnify to high concentrations in organisms atop aquatic food webs. The microbial methylation of inorganic Hg(II) strongly influences the concentration of MeHg in food webs; thus, concentrations of Hg in prey and piscivorous fishes can vary several fold among nearby lakes, in response to variations in ecosystem factors that influence the microbial production and abundance of MeHg. Concentrations of MeHg in predatory fish from many lakes exceed the USEPA fish-tissue criterion of 0.3 mg/kg wet weight, established to protect the health of humans who consume non-commercial fish. Consumption of fish is the primary pathway for exposure of wildlife and humans to MeHg, and documented consequences of MeHg contamination of fish include (1) direct adverse effects on the health of fish-eating humans and wildlife; (2) diminished nutritional, socioeconomic, cultural, and recreational benefits of fishery resources; and (3) adverse socio-cultural effects in some communities that had fished for subsistence. Northern pike with high MeHg concentrations exhibit depressed concentrations of sex hormones essential for development of gonads and gametes, a finding in agreement with recent experimental results. Rates of accumulation of total Hg in lacustrine sediments have recently declined, and data from Minnesota and Ontario lakes suggest concomitant decreases in concentrations of MeHg in game fish.

## Microbial transformations in the mercury geochemical cycle

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Microorganisms play a critical role in the geochemical cycling of mercury by carrying out oxidation and reduction reactions and by transforming mercury between the organic and inorganic forms, thus affecting the accumulation of methylmercury (MeHg) in the environment.

Sulfate reducing bacteria (SRB) in anoxic sediments methylate mercury. However, the biochemical pathways of methylation are not fully understood and recent new data suggest that more than one pathway may be implicated in mercury methylation by SRB.

Methylmercury may be degraded either oxidatively to carbon dioxide and, most likely, inorganic mercury (Hg(II)), or reductively to methane and elemental mercury (Hg(0)), by bacteria that produce the enzymes organomercury lyase, which splits the carbon mercury bond, and mercuric reductase, which reduces the resulting Hg(II) to Hg(0). These enzymes are encoded by mercury resistance (*mer*) operons in mercury resistant prokaryotes in diverse environments. Because *mer* operon functions depend on induction by nM concentrations of Hg(II), we hypothesized that MeHg degradation and Hg(II) reduction by *mer*-specified functions affect mercury speciation in highly contaminated environments while other processes take place in less impacted environments. This hypothesis was accepted by demonstrating *mer* induced reductive demethylation in an industrially contaminated site in New Jersey, USA, while in pristine sites in New Jersey impacted by atmospheric deposition of mercury MeHg was degraded oxidatively [Schaefer et al., 2004] and Hg(II) was reduced photochemically or as a result of phytoplankton activities at the Experimental Lakes Area, Ontario, Canada [Poulain et al., 2004]. The demonstration that inducible reductive MeHg degradation is stimulated in contaminated environments provides the first plausible explanation for the commonly observed trend of low MeHg accumulation in highly contaminated, relative to more pristine, aquatic environments.

Finally, Hg(0) may be oxidized to Hg(II) by enzymes that lessen oxidative stress in microorganisms. The significance of this process in production of Hg(II), the substrate for methylation, in the mercury geochemical cycle is at present unknown.

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## Mercury transformations in mine wastes and natural habitats adjacent to abandoned mercury mines

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Abandoned Hg mines pose an environmental threat due to high Hg concentrations in waste materials. Hg mobilized during past mining activities is capable of being methylated and transported hundreds of km downstream, a process that may continue for decades into the future. To investigate the ability of Hg-laden materials to be mobilized due to bacterially-mediated transformations, activities were assessed in samples of calcine, retort ash, soil, and stream sediment surrounding abandoned Hg mines. Samples were collected from mines in Spain (Almadén), Slovenia (Idrija), Texas (Terlingua and Mariscal), Nevada (McDermitt), California (Mt. Diablo), and Alaska (Red Devil). Transformation activities were determined using radiotracers (Hines *et al.*, 2000) and Hg speciation by CVAFS (Bloom and Fitzgerald, 1988; Bloom, 1989).

### Results and discussion

Mine wastes, soils and sediments actively methylated and demethylated Hg, and activity data agreed with the distribution of Hg species. Calcines that are generally dry and oxic exhibited little methylation, but demethylated Hg readily. An exception was calcine material near a retort in Spain that contained very high methyl-Hg levels and methylated Hg rapidly. C-rich retort ash also methylated Hg rapidly. Calcines and soils demethylated methyl-Hg via the reductive path suggesting that bacteria express lyase genes coded by the *mer* operon genetic system. Stream sediments rapidly methylated and demethylated Hg, but the latter was via the oxidative path that may lead to a re-methylation of Hg released during demethylation. Wastes near Hg mines are subject to active bacterially-mediated transformations and thus are capable of supplying high levels of methyl-Hg to downstream environments.

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## Overview of mercury contamination related to mercury mining and small-scale gold mining worldwide

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Areas of past and active Hg mining and small-scale (artisanal) Au mining worldwide are of environmental concern because of toxic Hg compounds in mine wastes and in surrounding sediment, water, and biota. The most significant environmental concerns of these mining activities are direct exposure of humans to elemental Hg, transference of Hg to surrounding ecosystems, and chemical and microbial conversion to bioavailable, compounds such as methyl-Hg, which are water soluble and readily transferred to biota such as fish. Methyl-Hg is the most toxic of the Hg compounds, is a human neurotoxin, and is the dominant Hg form in fish. Worldwide Hg mining produced an average of about 2,000 t/yr in the past decade and the primary Hg producing countries were Algeria, China, Kyrgyzstan, and Spain. Use of elemental Hg for separation of Au in artisanal mining results in significant loss of Hg to surrounding environments and is estimated to be about 500-800 t Hg/yr worldwide. Elemental Hg-Au amalgamation is an easy and inexpensive technique dating back to about 2700 BC. Although elemental Hg is used in artisanal mining worldwide, it is most common in developing countries, particularly those in South America, Africa, and Asia. Present estimates indicate that >10 million people in about 40 countries are involved in artisanal Au mining. Mine wastes and surrounding soils collected near Hg mines are often highly elevated in total Hg, exceeding 10,000 µg/g, and methyl-Hg concentrations exceed 1,000 ng/g in some instances. Freshwater fish collected in areas of artisanal Au mining may contain total Hg concentrations >4.0 µg/g (muscle, wet weight), significantly exceeding the 0.5 µg/g safe level recommended by the World Health Organization for human consumption of fish.

## Sources, transport, and fate of mercury at some representative mining sites

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Mercury contamination related to historic and to some contemporary mining comes mainly from 1) the contemporary, reckless use of mercury by artisanal miners to recover gold from ores and 2) from the historic mining of mercury itself. These mining activities often occur near waterways, either because the waterway sediments are being processed to remove placer or alluvial gold, or because of the need for water during the processing or milling of many types of ores.

For reasons that will be discussed, there is often a juxtaposition of upland mining coupled with lowland agriculture, ensuring maximum environmental impact from released contaminants. These settings are common worldwide. This makes the understanding of source, transport, environmental impacts, and fate of pollutants in these settings an important contemporary research topic. In the absence of this interesting juxtaposition, as in most contemporary artisanal alluvial mining, an understanding of sources, transport, and fate of contaminants is still important and many of the same issues pertain.

An understanding of the chemistry, geochemistry, biogeochemistry, biochemistry, and atmospheric chemistry of mercury helps with our understanding of the nature of the transport, fate, and environmental impacts of mercury. The geochemistry of mercury is the main topic of this contribution, and through a review of several examples of mercury contamination from both mercury mining and the use of mercury in artisanal gold mining, an understanding of the transport and fate of mercury, mainly in fluvial systems, can be developed.

The natural protective mechanisms present in nature which minimize the environmental impacts of mercury, as well as examples of significant environmental impacts from mercury, will be explored through the use of examples from Nevada, California, Brazil, and Guyana. It will be shown that sulfur-rich environments can fix fugitive mercury as its relatively-immobile sulfide in reducing environments of reservoirs, lakes, and soil horizons. It will also be shown that environmental impacts of mercury in other environments can arise far from the source of mercury in fluvial environments, and linkage to a specific source can be elusive.

## Hydrologic control on mercury biogeochemistry in a closed river basin: The Carson River System, Nevada

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The Carson River flows in a closed basin system and the total flow of the river tends to decrease downstream due to evaporation and consumptive uses. This river system is fed primarily by the snow pack, which accumulates in the Sierra Nevada during winter and flows downward following melting in spring and summer. Water loss through evaporation in the Carson River results in a downstream buildup of conservative elements such as chloride and certain oxyanion forming elements known to interfere with the transformation of mercury within the sulfur cycle. In 1859, the Comstock Lode was discovered in western Nevada, USA and this discovery was followed by an intensive use of metallic Hg for over 50 years in the amalgamation process to extract Au and Ag from crude ores. Wastes from mining operations previously accumulated in mill tailings were dispersed throughout the Carson River drainage basin over time, in large part due to fluvial processes. Hg contamination in the Carson River system is now well documented and published Hg levels in different environmental compartments are extremely high.

In this study, hydrologic driven changes in water chemistry of the river system and their impact on the behavior and fate of Hg were examined. Obtained results show that periods of low water flow regimes correspond to high water pH values (up to 8.5), relatively high concentrations of Group VI oxyanion forming elements (e.g., Se, Mo, and W), and low Hg methylation potential in sediments. In contrast, periods of high flow regimes bring about dilution, which results in lower pH (around 7), lower oxyanion concentrations, but higher Hg methylation potential. In "Stillwater", a wetland and protected wildlife refuge fed by the Carson River water, the dry/wet cycle results in trends of methyl-Hg production and degradation that follow changes in water levels and water content of the wetland soil. Overall, the evapoconcentration of group VI elements in the terminal basins of the studied system limits the rates of Hg methylation. This limitation is likely related to: (1) the interference of group VI elements with Hg transformation by sulfate reducing bacteria, and (2) Hg speciation imposed by changes in hydrologic conditions and the resulting limited Hg-bioavailability.

## Mercury emissions from artisanal zinc and mercury smelting in Guizhou, PR China

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Both artisanal zinc smelting and mercury mining activities are still in operation in Guizhou, China. Artisanal (small scale) zinc smelting activities in Hezhang, Guizhou started since 17<sup>th</sup> century. Zinc production in this area increased during the last decade, and reached 48,098t in 2000. Meanwhile, artisanal mercury mining activities in Wuchuan, Guizhou have also a long history since 1950s. The annual mercury production reached 20 to 70 t in the past few years. The techniques used for both cases are very simple. The ores are heated in a furnace for a few hours, and zinc metal and liquid mercury are produced. There are no pollution control devices employed at all during the melting processes.

A mass balance method is employed to calculate mercury emission factors from both zinc smelting and mercury mining activities. Mercury is an important associate element for zinc ores, and the maximum mercury concentration in zinc ore reached 160 mg/kg. The mercury emission factors from artisanal zinc smelting activities vary from 79 to 155 g Hg t<sup>-1</sup> of Zn produced, which are much higher than the literature value used to estimate mercury emission from zinc smelting in developing countries that is 25 g Hg t<sup>-1</sup> of Zn produced. We estimated that 30-50% mercury in mercury ores are released into the atmosphere during mercury smelting processes. The miners and local inhabitants may suffer from mercury vapor poisoning, and total mercury concentrations in hair samples collected from the mercury miners reached 20 to 80 mg/kg.

Up to 2003, a few metric tons of mercury was annually emitted to ambient air from zinc smelting in such a small area (<150 km<sup>2</sup>) in Hezhang, Guizhou, China. Meanwhile 6 to 21 metric tons of mercury was annually released into the atmosphere in Wuchuan, Guizhou. The mercury emissions from zinc and mercury smelting activities in Guizhou not only contribute significantly to global atmospheric mercury pool, but also pose a threat to the local ecosystem and to the health of local inhabitants. Much work is needed to scrutinize mercury contaminations from zinc and mercury smelting in Guizhou.

## Mercury and methylmercury distribution in sediments affected by historical gold mining, Sierra Nevada, California

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Mercury (Hg) is widely dispersed in stream sediments affected by historical gold mining in the Sierra Nevada, California. This presentation describes the downstream transport and microbially mediated transformation of elemental mercury, introduced in the 1850s to enhance gold recovery. U.S. Geological Survey studies of Hg bioaccumulation in sport fish have led to the first consumption health advisories in this area. Mercury is transported primarily by the episodic mobilization of fine-grained particles during high rainfall and runoff events. The degree of subsequent inorganic Hg(II)-methylation rates vary depending on the interaction of numerous environmental factors such as dissolved sulfate and iron (likely derived from localized pyrite oxidation) concentrations, pH, redox potential, dissolved oxygen, organic carbon, and microbial community composition and activity.

Sluice and tunnel sediments at hydraulic mine sites typically contain visible elemental mercury (Hg<sup>0</sup>) (up to 45 g/kg) and gold-mercury amalgam (AuHg). Methylmercury (MeHg) concentrations are locally elevated, although the ratio of MeHg to total (Hg<sub>T</sub>) in these settings tends to be low.

Sediments trapped in two reservoirs downstream of hydraulic mine sites have average Hg<sub>T</sub> concentrations from about 200 to 800 ng/g (nanograms per gram). Concentrations of MeHg in the top 4 cm of reservoir sediments range from 0.2 to 7 ng/g. At Englebright Lake (Yuba River), MeHg concentrations > 0.1 ng/g persist to depths as great as 33 meters in cores sampling a 62-year stratigraphic record.

Flood-plain sediments downstream of reservoirs are affected both by hydraulic mining and bucket-line dredging. Creeks traversing the Folsom gold fields have yielded both visible Hg<sup>0</sup> and AuHg from subsurface sediments. Potential rates of Hg(II) methylation and demethylation correlate with sediment organic-carbon concentrations. Methylation rates also correlate with pore-water Fe(II) concentrations, but do not vary systematically with sulfate reduction rates, suggesting either (1) a relationship between iron-reducing bacteria and Hg(II) methylation, or (2) increased availability of reactive Hg(II) in the iron-reducing zone.

## Mercury loss from stream water by evasion and sedimentation

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In northern New Brunswick, Canada, a contaminated groundwater plume, originating from gold-mine tailings, discharges to a small headwater stream. Elevated concentrations of Hg (Hg<sub>T</sub> up to 60 µg/L) and CN (up to 27 µg/L) occur in the stream water. Around 95% of the aqueous Hg<sub>T</sub> load is attenuated by processes such as evasion and sedimentation within 4 km from the source. A method was developed to quantify Hg evasion from the stream, and mineralogical investigations were conducted to determine the forms of Hg that have accumulated in the sediment.

The evasion rate of Hg from the stream was estimated by combining a measured relationship between Hg and propane evasion coefficients in turbulent systems with propane tracer experiments in the field (Maprani et al. in press).

Mineralogical investigations indicate that Hg is stored in the sediments in the form of Au-Ag-Hg amalgam and HgS. Similar to Hg, the Au and Ag were transported to the creek as aqueous CN complexes in groundwater from the tailings (Leybourne et al. 2000). Nano particles of HgS +/- Au occur commonly at a scale of approximately 5-10 nm (Fig. 1).

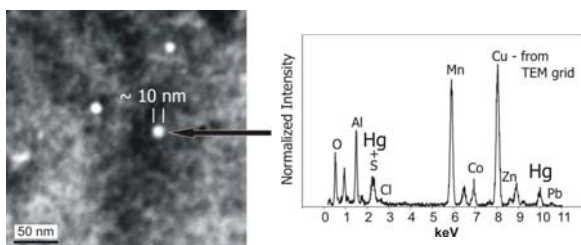


Figure 1. Dark-field STEM image of HgS nanoparticles within Mn-Al-oxyhydroxide precipitate from the stream sediments (left) and corresponding EDS analysis (right).

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## The potential for methyl mercury production in constructed wetlands and a riparian setting

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Many watersheds of the western United States have mercury (Hg) contamination that originated from mining and processing of gold and silver ores during the late 1800's. Wetland and riparian areas are important aquatic habitats in the water limited west, but may also be potential sites for formation of methyl Hg (MeHg), a subtle neurotoxin that is bioaccumulated in ecosystems.

This project investigated the potential for MeHg production in flow-through wetland mesocosms as a function of 1) soil and water Hg concentrations on a seasonal timestep; and 2) experimental manipulations using chemical additions and regulating water flow. Some mesocosms had sediment (0.1 to 2.0 mg/kg) and water (20 to 350 ng/L) derived from a creek contaminated with mine waste containing Hg that was used to amalgamate gold and silver ore. Wetland mesocosms (10 total) were densely vegetated and consisted of four replicated experimental designs. Water quality parameters and Hg concentrations in all mesocosms were monitored for > two years. In addition, the potential for MeHg production associated with a vegetated reach of the contaminated creek was investigated.

In general, the wetlands were a sink for total Hg and seasonally dependent sources for MeHg with greater production in the summer. Mesocosms with contaminated sediments and uncontaminated waters were the most significant MeHg sources. Drying and wetting resulted in flushing of MeHg from the wetlands and increased water retention time enhanced MeHg release. Chemical manipulations using sulfate and nitrate additions produced no significant change in MeHg concentrations.

No trends in MeHg concentrations along the stream reach were observed. However, sampling of shallow ground water in piezometers showed that the hyporheic zone could be an area of significant MeHg formation in riparian areas with mercury contamination.

## Mercury dynamic in a mountainous catchment polluted by chlor-alkali activity (Alsace, France)

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Total atmospheric mercury contamination was measured using CV-AFS in soils, river bottom sediments, river waters and bryophytes (*Hypnum cupressiform*) samples collected in a French mountainous catchment upstream from a chlor-alkali industrial activity. Natural and atmospheric/anthropogenic contributions to total Hg contents in soils and stream sediments were assessed using Hg concentrations in the deepest soil mineral horizon and in the stream bottom sediments. Soil Hg stock and mean annual particulate and dissolved Hg river fluxes coming from the upper part of the basin are estimated for the first time in this catchment.

The natural background level of Hg content deriving from rock weathering was estimated to  $32 \pm 9 \text{ ng g}^{-1}$  in the deepest soil layers. The soils appear to be Hg contaminated in two ways: atmospheric deposition and Hg-organic matter complexes leaching through the soil profiles. Hg concentrations in upper stream sediments varied between 108 and  $639 \text{ ng g}^{-1}$ . The Hg enrichment factor ( $EF_{\text{Hg}}$ ) which could be calculated by normalization to Sc, allow to estimate the major contribution (63 to 95%) of the atmospheric inputs, even in the upper part of the basin. This contribution may be attributed to diffuse regional atmospheric deposition of Hg and is mainly due to the geographic location of this chemical plant. The suspended matter was the main phase of Hg fluvial transportation in the different tributaries, with concentrations close to those of river bottom sediments. The Hg flux due to the weathering of the upper basin ( $0,58 \cdot 10^{-3} \text{ mg m}^{-2} \text{ y}^{-1}$ ) was negligible in comparison with the yearly Hg discharges in the Thur River due to the anthropogenic activities. The calculation of the Hg residence time indicates that Hg is trapped in the soils of the upper catchment for a long time in such a polluted hydrosystem.

## Mercury speciation in water and microbial mats of Yellowstone National Park hot springs

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### Background

Despite the significant flux of Hg to the atmosphere from natural sources, the biogeochemistry and impacts of mercury on microbes within geothermal features are poorly understood. We conducted preliminary sampling of waters and microbial mats from chemically diverse hot springs of Yellowstone National Park for analysis of Total Mercury (THg), Monomethylated Mercury (MeHg), pH, total sulfides, and other constituents important to mercury biogeochemistry.

### Results

THg and MeHg levels varied by orders of magnitude among individual hot springs. Filtered THg levels ranged from 6 to over 1200 ng/L; filtered MeHg levels varied from below detection ( $<.020 \text{ ng/L}$ ) to 9.041 ng/L. Highest levels of filtered and particulate THg and MeHg were observed in low pH and high specific conductivity (SC) waters typical of acid-chloride-sulfate springs.

Filtered concentrations of THg and MeHg did not correlate with each other, total sulfide levels or Eh. Correlations of filtered MeHg with pH and SC were weak, ( $r^2 = 0.82$  with SC;  $r^2 = 0.44$  with pH), with regression lines influenced strongly by waters from two acid-chloride-sulfate springs.

Preliminary data suggests that methylation of mercury may be occurring in some Yellowstone geothermal waters. Additionally, a limited set of preliminary samples indicate the presence of MeHg in microbial mats. Filamentous microbial bacteria and vegetation in two hot springs revealed that 5-10 % of Hg was in the form of MeHg while less than .1 % of Hg was MeHg in the hot spring waters. The bioconcentration factors are 1,210 and 12,000 (L/kg) for microbial and plant communities in these two hot springs.

## Biological Hg isotope fractionation

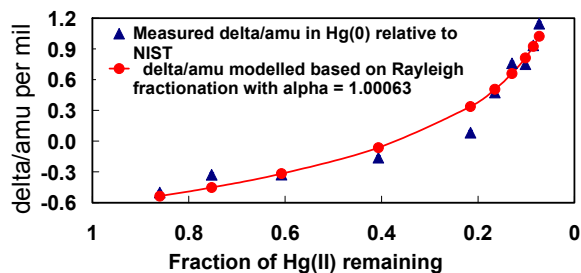
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The extreme toxicity of mercury (Hg) compounds warrants the search for new methods that can be used to track sources of Hg and dominant pathways leading to formation and bioaccumulation of methylmercury. Since Hg has seven stable isotopes (0.15 – 30% abundance; mass spread of 4%) and its compounds have a high degree of covalent character, it may undergo stable isotopic fractionation, and if so, the isotopic signatures of Hg may attest to its origin and/or redox history.

The purpose of this study was to determine the extent of mercury isotopic fractionation during the reduction of Hg(II) to Hg<sup>0</sup> by the mercuric reductase, an enzyme found in a broad range of Hg resistant bacteria from diverse environments. We measured the isotopic composition of Hg<sup>0</sup> formed by pure cultures of *Escherichia coli* and *Bacillus Cereus*, as a function of the extent of Hg substrate utilized using MC-ICPMS (Lauretta et al., 2001). We found that Hg(II) supplied as NIST 3133 undergoes Rayleigh fractionation with a fractionation factor ( $\alpha$ ) of ~1.0006 per amu during its reduction by *E. coli* (see graph below) and *B. cereus* at 37°C.  $\alpha$  values of similar magnitude were observed when Hg<sup>0</sup> was produced by a natural microbial community following enrichment of Hg(II) reducing microbes.



This is the first evidence of biologically induced mass dependent fractionation of Hg, the heaviest metal for which biological fractionation has been detected to date. This report opens up the possibility of use of Hg isotope fractionation for identifying its sources and sinks in the environment, in situ pathways leading to its toxicity and the nature and evolution of redox reactions in both modern and paleo environments.

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## Mercury in the Wabash River, Indiana: A preliminary assessment

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Unlike in the neighboring states, there is very little information on mercury (Hg) in streams in Indiana. Current research has focused mainly on the industrialized northern part of the state, close to Chicago, and on the Ohio River valley at the southern end of the state, which is impacted by numerous coal-fired power plants. For the other rivers draining Indiana, including the Wabash River, numerous Hg-based fish advisories are posted, but very little to no data on Hg in water or sediments exist.

In this paper, we present the first Hg data for the Wabash River in western Indiana. The river section under study extends from just upstream of Lafayette to Terre Haute in western Indiana. This section of the river has no input from tributaries that drain reservoirs, as encountered upstream of this section. Potential sources for Hg are the two cities along the river, as well as a power plant upstream of Terre Haute. Our first results suggest that concentrations vary between ~0.57 and 1.7ng/L for dissolved Hg, and total mercury (THg) concentrations range from ~1.6 to 5.0 ng/L. Hg concentrations are lowest in Lafayette, increase further downstream, and then decrease again towards Terre Haute. These values observed by us are similar to those reported for streams in neighboring states. We will discuss the connections between dissolved Hg, particulate Hg, and Hg in Wabash River sediments, determine potential local sources for Hg, and link our findings with the fishing advisories currently posted along the Wabash River. Finally, we will also discuss our results in connection with water data from neighboring, well-investigated states such as Wisconsin.

## Mercury mobilization to the aquatic environment from cyanide-rich gold mine tailings

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### Introduction

Gold was extracted by cyanidation from a gossan that overlies a Cu-Zn massive sulfide deposit in northern New Brunswick, Canada. Approximately one Mt of tailings are stored on-site in an unsaturated pile that contains residual CN and Hg, mainly in the form of cinnabar. Elevated Hg concentrations have been detected over the past 15 years in the groundwater adjacent to the tailings pile (up to 8,000 mg/L in 1991) and down gradient in the water of Gossan Creek, a local 1<sup>st</sup>-order stream.

### Experimental Methods

The relationship between observed Hg contamination in the aquatic environment and residual CN in the tailings was investigated through: 1) tailings column leach experiments; 2) geochemical sampling of the groundwater and Gossan Creek; 3) geochemical speciation calculations.

### Results and Discussion

Initially CN leaches conservatively from the columns but as time progresses the data suggest that geochemical reactions control the release of CN. A strong correlation is observed between Hg and CN concentrations in the column leachate, groundwater and surface water in Gossan Creek. Geochemical modeling suggests that Hg-CN complexes account for > 99% of the measured Hg, predominantly as Hg(CN)<sub>2</sub>.

### Conclusions

Residual CN in the tailings mobilizes Hg from cinnabar into the pore-water through the formation of Hg-CN complexes. These complexes facilitate the transport of Hg to the surrounding environment.

## Dissolved, adsorbed, organic bound and mineral bound mercury transport by rivers, British Columbia, Canada: The role of rock weathering

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Water and suspended particulate from the Fraser, Skeena and Nass river systems of the western Canadian Cordillera have been analysed for mercury (Hg) concentrations in the dissolved, adsorbed, organic bound and mineral bound phases. The total annual export of Hg to coastal waters by these rivers is determined to be  $10.9 \times 10^3$  kg·yr<sup>-1</sup>, of which 6% (630 kg·yr<sup>-1</sup>) is in the labile phases (dissolved < adsorbed < organic bound). Dissolved Hg concentrations range from <0.3 to 1.4 ng·L<sup>-1</sup> (ppt). Particulate Hg concentrations (dry weight) range from 3 to 88 ppb (adsorbed), 4 to 270 ppb (organic bound), and 5 to 2000 ppb (mineral bound).

Chemical weathering of bedrock transfers Hg from bedrock to the pedosphere, biosphere, atmosphere, and hydrosphere. Using measured chemical weathering rates and conservative estimates of Hg in bedrock, Hg release by weathering in the study area is calculated by mass balance. Results indicate weathering is the dominant source of Hg in the Cordilleran rivers, with sulphide oxidation having the greatest influence on Hg release bedrock weathering.

Comparison of data collected during the high stage (June) and low stage (October) of the hydrograph shows a seasonal variability in Hg concentrations and relative distribution between the adsorbed, organic bound and mineral bound phases. In June, the labile Hg dominantly exists in the adsorbed phase, with little organic bound Hg. The opposite distribution is observed in October. This is consistent with a change in composition and source of the suspended particulate matter from relatively unweathered rock flour in June (alpine source) to substantially more weathered material in October (valley source) containing a greater percentage of organic material and secondary minerals that form during soil development.

The mineral bound Hg concentrations also show seasonality, with Fraser, Skeena and Nass main stem samples having as much as an order of magnitude more Hg in June than October. Lower Hg concentrations in the low-land derived particulate suggests that soil development may be associated with direct loss of Hg to the atmosphere.