Mercury in aquatic ecosystems on the Oak Ridge Reservation - paradoxes provide a key to a more complete understanding of the global mercury cycle

Oak Ridge National Laboratory – ERSP Science Focus Area

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Abstract The accumulation of methylmercury in aquatic organisms is a world-wide problem arising from the global transport of gaseous mercury and the conversion of that mercury to highly toxic methylmercury when it is deposited to aquatic ecosystems. Paradigms developed from the extensive study of Hg transport, transformation, and bioaccumulation in systems affected by atmospheric mercury deposition often fail to describe the behavior of mercury at sites contaminated by industrial sources. The Oak Ridge Reservation (ORR) contains multiple mercury-contaminated aquatic ecosystems that provide examples of the paradoxical differences between sites contaminated by local versus global sources. Ultimately, a single model incorporating a full understanding of the transport and transformation of mercury in aquatic systems should be universally applicable to all sites. Investigating the causes of the apparent paradoxes associated with mercury on the ORR will advance the science toward this universal understanding.

Mercury contamination on the Oak Ridge Reservation

History

Approximately 11,400 metric tons of mercury were shipped to the Oak Ridge Y-12 Plant in the early 1950's for use in isotopic enrichment of lithium. About 3% of that mercury was lost to the environment, 2/3 of which contaminated soil and rock under the facility. That subsurface elemental Hg continues to act as a source of dissolved Hg in groundwater that eventually contaminates surface waters draining the site. Smaller amounts of mercury were handled at the other Oak Ridge facilities, with similar results. Inorganic mercury is converted to methylmercury by chemical and biological processes at the groundwater:surface water interface, and that methylmercury accumulates in fish to levels posing risks to consumers.

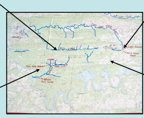
Remedial efforts initiated in the 1980's at the Y-12 facility have focused on identifying and eliminating point sources of mercury. Among actions completed to date are: filling and capping New Hope Pond and eventually bypassing its replacement, treatment of building sump waters (groundwater),cleaning, relining, and replacement of subsurface storm and process drains, stabilizing contaminated streambanks, and building a treatment system for contaminated spring water. These and other actions reduced waterborne mercury export from the site from over 100 g/d in 1985 to approximately 10 g/d at the present time. Mercury in East Fork Poplar Creek (EFPC) now approaches 200 ng/L, the interim cleanup goal.

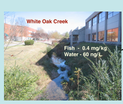
Mercury-contaminated ecosystems

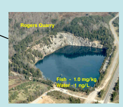
The Oak Ridge Reservation contains multiple Hg-contaminated aquatic ecosystems. Relationships between inorganic mercury concentration and the net production of methylmercury (indicated by the accumulation of mercury in fish) vary widely among them.

Aquatic systems where Hg in fish exceeds 0.3 mg/kg (EPA Water Quality Criterion)

Bear Creek	0.8 mg/kg
White Oak Creek	0.4 mg/kg
Rogers Quarry	1.0 mg/kg
East Fork Poplar Creek	
Upper	1.1 mg/kg
Lower	0.9 mg/kg



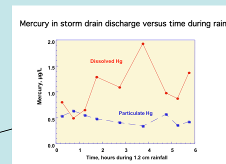


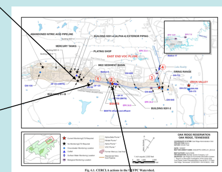


Subsurface sources of mercury to aquatic ecosystems

Storm drain network

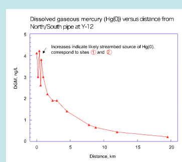
Mercury-enriched groundwater infiltrates the storm-drain system, where residual chlorine (from process water discharges) oxidizes Hg and maintains it in solution. The highly reactive dissolved Hg is rapidly taken up by the stream-bed biofilm and suspended solids after the water exits the pipe. Typical Hg levels at this site is ~ 700 ng/L. The response to rainfall indicates the presence of a reservoir of dissolved Hg in close hydrologic proximity to the storm drain system.

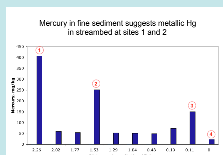




Metallic mercury in stream sediments

Metallic Hg in deep in the streambed generates dissolved Hg(0) and Hg(II) that sorb to sediments and infiltrate surface flow. The 200 m reach at right (site 1 on map) accounts for ~25% of Hg flux in the creek. Hg levels in interstitial streambed water is > 30 µg/L and > 400 ppm in sediment.





Mercury in the solution cavity system (karst)

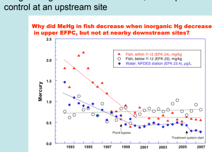
The bedrock underlying EFPC contains a solution cavity network that conveys groundwater to a spring. Mercury in that groundwater is > 20 µg/L, while that in the spring was typically 2 - 10 µg/L. Hg(0) constitutes ~ 30% of total mercury in Outfall 51, and >50% of the remainder is reducible with near stoichiometric amounts of $SnCl_2$. A treatment system completed in 2005 effectively removes Hg from the spring water, but ~ 20% of the spring flow is not captured by the system

Dye injected into a Hg-contaminated solution cavity 700-m upstream emerges from a spring.

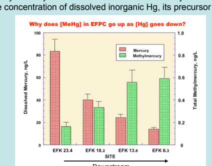
Mercury transport and transformation on the Oak Ridge Reservation

Paradoxical observation of Hg at Oak Ridge sites

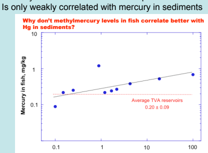
Mercury bioaccumulation was not proportional to waterborne inorganic Hg downstream from Y-12, but responded to source control at an upstream site



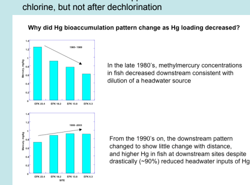
Methylmercury concentration in EFPC is inversely related to the concentration of dissolved inorganic Hg, its precursor



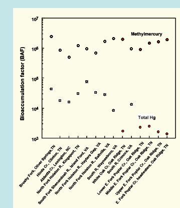
Mercury in bass from contaminated ponds and reservoirs Is only weakly correlated with mercury in sediments



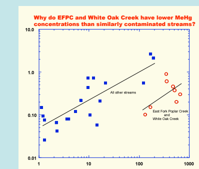
Mercury accumulation in EFPC fish closely matched downstream dilution when upper EFPC contained residual chlorine, but not after dechlorination



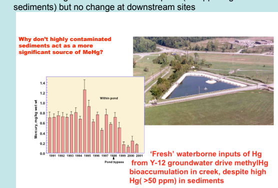
Differences between ORR and other sites are not caused by differences in the ecological biomagnification of MeHg, but rather by differences in net MeHg production from inorganic Hg



Relationship between aqueous inorganic Hg and methylmecury in Contaminated ORR streams differs from other ecologically similar streams



Diversion of Hg-rich streamflow around this pond resulted in decreased Hg bioaccumulation in the pond (>50 ppm Hg in sediments) but no change at downstream sites



Groundwater-derived mercury at Y-12 has greater affinity for particulates than 'natural' (background) mercury

Site	$[Hg]_{water,\ dissolved}$ ng/L	$[Hg]_{solids}$ mg/kg	K_d L/kg
East Fork Poplar Cr. (EFK 23.4)	54 - 135	47 - 230	1.8×10^6
Hinds Cr. (reference site)	0.6 - 11	0.10 - 2.8	1.6×10^5

Why is Hg from Y-12 subsurface sources more reactive toward soil than 'natural' Hg?

The global mercury problem arises from the atmospheric transport and deposition of Hg and its subsequent delivery to aquatic ecosystems by runoff and groundwater. Even minute concentrations of inorganic mercury (< 2 ng/L) can be transformed into hazardous methylmercury in sensitive ecosystems. At sites with local Hg contamination, inputs are subsurface point sources, and mercury in groundwater is likely to be a mix of dissolved inorganic Hg(II), Hg(I), and Hg(0) species complexed with various ligands. Such sources are likely to be chemically distinct from inputs associated with the global cycling of Hg, in which Hg complexes with natural organic matter predominate. In the local scenario, point source inorganic Hg is added to surface flow in a localized reach and returned to the subsurface (streambed sediments) for processing into methylmercury over an extensive downstream reach. Consequently, chemical speciation of Hg in subsurface source water plays a critical role in how Hg is converted to methylmercury in receiving waters, as do chemistry and microbial ecology of the downstream waters. The apparent paradoxes observed at ORR sites may provide a key to understanding how differences in the chemistry of mercury within groundwater sources affects its conversion to methylmercury at the surface water:groundwater interface.