



# TECHNICAL MEMORANDUM

TO: PacifiCorp Energy  
FROM: Kleinfelder  
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## **Mercury Demethylation Considerations for Condit Dam Sediments**

Many factors influence the speciation, bioavailability, bioaccumulation, and toxicity of mercury in the environment. Due to the number of factors and the complexity of interactions among them, the question regarding the timing of establishment of demethylating bacteria that could reduce methylmercury after the sediments are released into the White Salmon River from Condit dam cannot be easily answered. Without a substantial amount of experimental work and testing (e.g., measuring the rates of mercury methylation and demethylation in project sediments) it is not possible to provide a meaningful estimate of the time required for mercury in sediments impounded behind Condit dam to be demethylated following project removal. The following provides additional background information about the mercury methylation and demethylation processes and discusses how those processes may be impacted by known and expected conditions following project removal.

Inorganic mercury is readily dispersed and transported in the environment (Beyer et al., 1996). Mercury occurs in natural waters in many forms, including elemental mercury, dissolved and particulate ionic forms, and dissolved and particulate methylmercury (Beyer et al., 1996). Methylmercury (organic form) is more toxic and bioaccumulative than the inorganic forms (USDI, 1998). Inorganic mercury is methylated in the environment, primarily by microbes (Beyer et al., 1996). Methylation in aquatic systems can occur in the sediment and water column. Sediment can be a sink and a source of mercury in the environment and is a source of methylmercury to biota and to the water column (USDI, 1998). Mercury levels in water tend to be greatest downstream of wetlands due to the high organic content of the water, and disturbance and re-



suspension of wetland sediments can mobilize mercury associated with sediments (USDI, 1998).

Nearly all of the mercury found in fish is methylmercury, even though little of the total mercury found in freshwater and sediments exists as methylmercury (Beyer et al., 1996). Inorganic mercury is absorbed less efficiently and excreted more efficiently than methylmercury. Inorganic mercury is not methylated by fish tissue, though it is methylated in the gut. The methylmercury in fish is obtained mostly from the diet and to a smaller extent from the water passing across the gills (Beyer et al., 1996; USDI, 1998). Thus, concentrations of dissolved organic mercury compounds are more useful than total dissolved mercury concentrations for predicting mercury concentrations in fish (USDI, 1998).

Uptake of mercury from water into fish is affected by temperature, pH, and water hardness, as well as mercury speciation (USDI, 1998). A large body of data supports the generalization that mercury concentrations in freshwater fish and other aquatic organisms and fish-eating animals tend to increase as the pH, alkalinity, hardness, conductivity, and neutralizing capacity of the water decrease (see discussion below and Table 1). Methylmercury is created primarily from bioavailable inorganic mercury Hg(II). Both represent only a very small proportion of total mercury in sediment or water. Aquatic organisms preferentially accumulate methylmercury, and this is the main form of Hg found in fish. Inorganic forms of mercury comprise the main repository of mercury in sediments. In oxygenated fresh water, bioavailability of Hg(II) is enhanced in the range of Cl<sup>-</sup> levels and pH values at which dissolved inorganic Hg(II) is mostly in the form of the lipophilic species HgCl<sub>2</sub>. Lipophilic thiol and inorganic sulphide complexes probably account for much of the bioavailability of Hg under reducing conditions. However, bioavailability of Hg is much lower if the dissolved Hg(II) is mostly in the form of ionic complexes or Hg(OH)<sub>2</sub>. Briefly, inorganic Hg(II) is probably most bioavailable to methylators in acidic fresh water in which it is mainly in the form of HgCl<sub>2</sub> or Hg(SH)<sub>2</sub>, and it should be less bioavailable in weakly acidic or alkaline fresh water in which Hg(OH)<sub>2</sub> exceeds HgCl<sub>2</sub> or Hg(SH)S<sup>-</sup> exceeds Hg(SH)<sub>2</sub>. In the presence of high pH and low Cl<sup>-</sup> levels sufficient to allow Hg(OH)<sub>2</sub> to exceed HgCl<sub>2</sub>, bioavailability of inorganic Hg(II) should be relatively low for two reasons: (a) Hg(OH)<sub>2</sub> penetrates membranes less



easily than  $\text{HgCl}_2$ , and (b) in comparison with  $\text{HgCl}_2$ ,  $\text{Hg}(\text{OH})_2$  is more readily sorbed by suspended matter.

Although smaller fish (due to their relatively faster metabolic rates) tend to accumulate mercury more rapidly than larger fish (USDI, 1998), mercury concentrations in fish tissue generally increase with increasing age or body size (Beyer et al., 1996), and piscivorous (fish-eating) fish and other animals at higher trophic levels (particularly long-lived species) will generally accumulate more methylmercury than animals at lower trophic levels (Beyer et al., 1996).

Elemental mercury and mercuric ions are predominant forms of mercury in the atmosphere and in water, while mercuric sulfide (naturally occurring cinnabar ( $\text{HgS}$ )) occurs most commonly in soil and in anaerobic sediments (Boening, 2000; D'Itri, 1990). Bacteria in the environment methylate inorganic mercury to produce both monomethyl and dimethylmercury (Clarkson, 1997). Both aerobic and anaerobic bacteria can methylate mercury (D'Itri, 1990). Dimethylmercury is highly volatile and can enter the atmosphere, where it is degraded into monomethyl and inorganic forms (Clarkson, 1997). Environmental levels of methylmercury depend on the balance between bacterial methylation and demethylation (Boening, 2000).

Monomethylmercury enters aquatic food chains to become the predominant source of dietary mercury to humans (Clarkson, 1997). Monomethylmercury is transferred through biological cycles involving aquatic organisms and is probably converted to inorganic forms that can once again enter reduction and methylation pathways (Clarkson, 1997). Monomethylmercury undergoes biomagnification in aquatic food webs, while inorganic mercury  $\text{Hg}(\text{II})$  does not (Langston and Bebbiano, 1991). Thus, even though inorganic mercury predominates in water and sediments, most of the mercury found in fish occurs as methylmercury (Langston and Bebbiano, 1991). Elevated methylmercury in fish may be found not only in areas polluted with mercury but also in virtually unpolluted ones where conditions favor methylmercury production (Langston and Bebbiano, 1991).

Results of the tests of mercury uptake into nematodes (roundworms) provide some limited information about the potential differences in bioavailability of



mercury in sediments impounded behind Condit dam and sediments collected at other locations. However, it is unclear at this time whether sediments are the only source of mercury at the locations that were investigated, and the testing that has been conducted did not involve measuring or quantifying the multiple factors that control mercury speciation and bioavailability. The following paragraphs provide some insight into the complexity of mercury behavior in aquatic ecosystems.

The net rate of methylmercury production depends on the abundance of bioavailable inorganic Hg(II) species and the activities of methylating and demethylating microbes. Bioavailability of Hg(II) (and consequently susceptibility to methylation) and activities of methylating and demethylating microbes are controlled by a wide range of environmental variables. Furthermore, the kinetics of methylmercury bioaccumulation depend not only on the supply of methylmercury but also on the characteristics, behavior, activities, stage of development, and food web structure of the organisms involved. (Langston and Bebbiano, 1991)

Many water quality parameters influence production and bioaccumulation of methylmercury, including dissolved oxygen (DO), pH, alkalinity, hardness, buffering capacity, and humic matter (completely decomposed organic matter that is readily soluble in acids or bases). Generally, mercury concentrations in freshwater fish and other aquatic organisms and fish-eating animals tend to increase as the pH, alkalinity, hardness, conductivity, and neutralizing capacity of the water decrease. Physical variables - through their influence on biological activities, redox conditions, and water chemistry - can also strongly influence methylmercury production and bioaccumulation of mercury. Water depth, thermal stratification, water dynamics (turbulent mixing, flushing), and maximum depth are all important. For example, low flow conditions tend to favor methylation (Langston and Bebbiano, 1991). Lake turnover time and mixing are also important, and these are affected by depth and temperature. Mercury transport on particulates is greatest in the smallest size fractions of organic matter. Lakes with longer turnover times allow smaller particles with greater concentrations of mercury more time to settle to the bottom, enriching sediment mercury concentration. The following example illustrates the importance of



thermal stratification, depth, and productivity, as well as interactions among these three factors. Microbial methylation commonly occurs with greatest intensity at the sediment/water interface, but microbial methylation of mercury can also take place in certain regions of the water column where labile organic matter and local DO depletion may support a level of methylating activity comparable to that observed in surface sediments (Langston and Bebbiano 1991). This phenomenon is sometimes observed in the hypolimnion of a lake just below the thermocline or even in the epilimnion of an extremely eutrophic lake following a phytoplankton bloom (Langston and Bebbiano 1991).

Optimal conditions for production and bioaccumulation of methylmercury in aquatic ecosystems include: high levels of biodegradable organic substances (e.g., dead algae or plants and other detritus, as would typically be observed in productive lakes), anoxic or oxygen-poor environments with weakly acidic or neutral pH, and absence/low levels of sulphides. These conditions are inter-related (e.g., microorganisms using labile organic matter consume oxygen and generate sulfides). Methylating activity tends to correlate with heterotrophic (an organism that requires organic substrates to get its chemical energy for growth and development) microbial activity, in general. Methylmercury bioaccumulation is favored in acidic fresh water by at least two factors: inorganic Hg(II) is more available to methylators, and biological uptake of methylmercury occurs rapidly. However, it is possible that demethylation will also occur more rapidly under these conditions due to increased availability of mercury to demethylators. Exceptions to these generalizations are common under a wide variety of conditions (Langston and Bebbiano, 1991).

Microbial methylation of mercury is commonly concentrated in surface sediments (i.e., at the sediment/water interface), but in certain regions of the water column, labile (relatively available) organic matter and local DO depletion may support a level of methylating activity comparable to that observed in surface sediments (Langston and Bebbiano, 1991). Consequently, both waterborne and sediment-associated mercury may be important sources to methylating microbes.

Methylation of mercury in sediments occurs most intensely at the sediment/water interface where microbial activity is greatest (Langston and Bebbiano, 1991). If deeper sediments impounded behind Condit dam are released to the river



downstream, this will presumably expose a greater amount of sediment to microbial activity. The balance of factors favoring methylation versus demethylation will determine the fate of mercury in those sediments. The net effect of all of the modifying factors cannot be estimated reliably without additional testing and measurements.

## References

- Balistrieri, L. S., Murray, J. W., and Paul, B., 1992. "The Biogeochemical Cycling of Trace Metals in the Water Column of Lake Sammamish, Washington: Response to Seasonally Anoxic Conditions." *Limnology and Oceanography*, 37(3), 529-548.
- Boening, D. W., 2000. "Ecological Effects, Transport, and Fate of Mercury: a General Review." *Chemosphere*, 40(12), 1335-1351.
- Beyer, W. N., Heinz, G. H., and Redmon-Norwood, A. W., 1996. *Environmental Contaminants in Wildlife: Interpreting Tissue Concentrations (SETAC special publications series)*, CRC Press, Boca Raton, Florida.
- Clarkson, T. W., 1997. "The Toxicology of Mercury." *Critical Reviews in Clinical Laboratory Sciences*, 34(4), 369-403.
- D'Itri, F. M., 1991. "Mercury Contamination- What We Have Learned Since Minimata." *Environmental Monitoring and Assessment*, 19 (1-3), 165-182.
- D'Itri, F. M., 1990. "The Biomethylation and Cycling of Selected Metals and Metalloids in Aquatic Sediments." Pages 163-214, In: *Sediments: Chemistry and Toxicity of In-Place Pollutants*, R. Baudo, J. P. Giesy, and H. Muntau (eds.), Lewis Publishers, Ann Arbor, Michigan. \*\*\*Ordered on ILLIAD
- Eisler, R., 2000. "Mercury." Pages 313-409, In: *Handbook of Chemical Risk Assessment: Health Hazards to Humans, Plants, and Animals. Volume 1. Metals*, Lewis Publishers, New York.
- Farrell, R. E., Huang, P. M., and Germida, J. J., 1998. "Biomethylation of Mercury(II) Adsorbed on Mineral Colloids Common in Freshwater Sediments." *Applied Organometallic Chemistry*, 12(8-9), 613-620.



- Fitzgerald, W. F., and Clarkson, T. W., 1991. "Mercury and Monomethylmercury: Present and Future Concerns." *Environmental Health Perspectives*, 96, 159-166.  
<http://www.ehponline.org/members/1991/096/96026.PDF>
- Fleming, E. J., Mack, E. E., Green, P. G., and Nelson, D. C., 2006. "Mercury Methylation from Unexpected Sources: Molybdate-inhibited Freshwater Sediments and an Iron-reducing Bacterium." *Applied and Environmental Microbiology*, 72(1), 457-464.  
<http://aem.asm.org/cgi/content/abstract/72/1/457>
- Gilmour, C. C., Henry, E. A., and Mitchell, R., 1992. "Sulfate stimulation of mercury methylation in freshwater sediments." *Environmental Science & Technology*, 26(11), 2281-2287.
- Harris, H. H., Pickering, I. J., and George, G. N., 2003. "The chemical form of mercury in fish." *Science*, 301(5637), 1203. <http://www.sciencemag.org>
- Hintelmann, H., Keppel-Jones, K., and Evans, R. D., 2000. "Constants of Mercury Methylation and Demethylation Rates in Sediments and Comparison of Tracer and Ambient Mercury Availability." *Environmental Toxicology and Chemistry*, 19(9), 2204-2211.
- Hunerlach, M. P., Alpers, C. N., Marvin-DiPasquale, M., Taylor, H. E., and De Wild, J. F., 2004. "Geochemistry of Mercury and other Trace Elements in Fluvial Tailings Upstream of Daguerre Point Dam, Yuba River, California, August 2001." *Scientific Investigations Report 2004-5165*, United States Geological Survey (in cooperation with the Bureau of Reclamation and the California Department of Fish and Game), Sacramento, California.  
<http://pubs.usgs.gov/sir/2004/5165/>
- Kim, E. H., Mason, R. P., Porter, E. T., and Soulen, H. L., 2006. "The Impact of Resuspension on Sediment Mercury Dynamics, and Methylmercury Production and Fate: A Mesocosm study." *Marine Chemistry*, 102(3-4), 300-315.
- Langston, W. J., and Bebianno, M. J., 1991. *Metal Metabolism in Aquatic Environments (Ecotoxicology Series 7)*, Chapman & Hall, London.
- Mason, R. P., Laporte, J.-M., and Andres, S., 2000. "Factors Controlling the Bioaccumulation of Mercury, Methylmercury, Arsenic, Selenium, and Cadmium by Freshwater Invertebrates and Fish." *Archives of Environmental Contamination and Toxicology*, 38, 283-297.



- Morel, F. M. M., Kraepiel, A. M. L., and Amyot, M., 1998. "The Chemical Cycle and Bioaccumulation of Mercury." *Annual Review of Ecology and Systematics*, 29(1), 543-566.
- Newman, M. C., and McIntosh, A. W., 1991. *Metal Ecotoxicology: Concepts & Applications (Advances in Trace Substance Research)*, Lewis Publishers, Chelsea, Michigan.
- Paulson, A. J., and Cox, S. E., 2007. "Release of Elements to Natural Water from Sediments of Lake Roosevelt, Washington, USA." *Environmental Toxicology and Chemistry*, 26(12), 2550-2559.
- Peterle, T. J., 1991. *Wildlife Toxicology*, Van Nostrand Reinhold, New York.
- Ullrich, S. M., Tanton, T. W., and Abdrashitova, S. A., 2001. "Mercury in the Aquatic Environment: a Review of Factors Affecting Methylation." *Critical Reviews in Environmental Science and Technology*, 31(3), 241-293.  
<http://www.informaworld.com/10.1080/20016491089226>
- USDI, 1998. "Guidelines for Interpretation of the Biological Effects of Selected Constituents in Biota, Water, and Sediment." 3, United States Department of the Interior: Bureau of Reclamation, U.S. Fish and Wildlife Service, U.S. Geological Survey, and Bureau of Indian Affairs, Denver, Colorado.
- Wang, Q., Kim, D., Dionysiou, D. D., Sorial, G. A., and Timberlake, D., 2004. "Sources and Remediation for Mercury Contamination in Aquatic Systems—a Literature Review." *Environmental Pollution*, 131(2), 323-336.
- Watras, C. J., Morrison, K. A., Host, J. S., and Bloom, N. S., 1995. "Concentration of Mercury Species in Relationship to Other Site-specific Factors in the Surface Waters of Northern Wisconsin Lakes." *Limnology and Oceanography*, 40(3), 556-565.
- Whalin, L., Kim, E.-H., and Mason, R., 2007. "Factors Influencing the Oxidation, Reduction, Methylation and Demethylation of Mercury Species in Coastal Waters." *Marine Chemistry*, 107(3), 278-294.
- Wiener, J. G., Krabbenhoft, D. P., Heinz, G. H., and Scheuhammer, A. M., 2003. "Ecotoxicology of Mercury." Pages 409-464, In: *Handbook of Ecotoxicology*, D. J. Hoffman, B. A. Rattner, G. A. Burton, Jr., and J. Cairns, Jr. (eds.), Lewis Publishers, New York.
- Wood, J. M., 1974. "Biological Cycles for toxic Elements in the Environment." *Science*, 183(4129), 1049-1052.