# Response | Mercury and the FLUDEX project

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# Letters

## Mercury and the FLUDEX project

Bodaly et al. recently outlined the results of the first three years of the Flooded Uplands Dynamics Experiment (FLUDEX) but included hardly any interpretive discussion of the observed phenomena (*1*). It might have helped the authors to interpret their data more adequately and with greater insight if they had studied certain previously published papers concerning the effects of flooding on the biogeochemistry of mercury (Hg) in hydroelectric reservoirs of northern Manitoba, Canada (*2–4*). Several of the phenomena highlighted in their article were reported and discussed at length in this literature, which includes some studies that are particularly pertinent to the FLUDEX project and related work by Bodaly and associates (*5–8*).

Thus, comparison of sediments from two Manitoba reservoir sites, one rich and the other poor in submerged terrestrial organic matter, and a reference lake unaffected by impoundment demonstrated that microbial decomposition of the organic matter involved production of copious $CO_2$, $CH_4$, and methyl mercury (MeHg) accompanied by consumption of $O_2$ and the creation of reducing conditions (*2*). Understandably, the sediment richest in organic matter had the largest total (mainly inorganic) Hg content as well as the most intense Hg methylating activity and highest MeHg concentration (cf. *9*, *10*). However, it also had the highest ratio of MeHg to total Hg, implying that the elevated rate of MeHg production was due primarily to stimulation of the growth and activity of methylating microbes by organic nutrients and by the anoxic conditions created by general heterotrophic microbial activity, rather than the increased abundance of inorganic Hg. This is an important distinction that Bodaly et al., in their sketchy description of similar phenomena, failed to address. The net rate of MeHg production from a given quantity of inorganic Hg depends on microbial activities and the supply of bioavailable inorganic Hg(II) species. Consequently, it is a complex function of the many spatially and temporally varying environmental factors that affect the growth, biochemical activities, and species composition of the microflora and the bioavailability of the local pool of unmethylated Hg(II) (*9*).

Comparable effects of organic matter occur in other kinds of aquatic ecosystems. Bodaly et al. mentioned the role of leaf litter in prairie streams (*11*) but neglected to note the important fact that strong enhancement of MeHg production by phytoplankton blooms has also been reported (*11–14*). There is evidence, moreover, that the species composition of the bloom affects the balance between Hg methylation and demethylation, probably by determining the species composition of the associated bacterial community (*14*).

Furthermore, laboratory experiments on the effects of labile terrestrial organic matter on microbial production of MeHg, $CO_2$, and $CH_4$ in sediments from Manitoba lakes and reservoirs (*4*) yielded results comparable to observations reported by Bodaly et al. With increasing concentration of organic matter, the rates of MeHg production and bioaccumulation rose progressively, peaked at a critical point, and then declined despite a concurrent increase in $CO_2$ and $CH_4$ levels and a decrease in sediment Eh, which proved that there was no decline in overall microbial activity (*4*). The investigator inferred that MeHg production dropped because the rate of demethylation exceeded the rate of methylation owing to ecological succession in the microbial community (*4*; cf. *15*, *16*), and because Hg-binding agents, such as thiols and sulfides generated by anaerobic bacteria, rendered inorganic Hg(II) less available for methylation (*9*). Similarly, comparison of FLUDEX soils with "low", "medium", and "high" concentrations of organic matter showed that the MeHg flux was greatest in soil of medium organic content (*1*). This phenomenon, however, was not adequately explained or discussed. Without any supporting evidence or consideration of possible alternative explanations, Bodaly et al. simply speculated that MeHg production depended on "carbon quality (lability)." Although this inference is plausible (*14*, *17*), it is unsubstantiated and is probably not sufficient to explain the observed effect (*4*). As for the high concentration but low flux of MeHg in the high-carbon reservoir (*1*), it suggests that the MeHg produced there is efficiently scavenged by organic ligands, especially thiol groups (*9*), but possible explanations were not discussed.

Finally, investigation of physicochemical and biological variables controlling Hg accumulation by fish in the reservoirs and reference lake in Manitoba (*4*) revealed relationships between Hg concentrations in fish (data extracted from publications and government archives) and the speciation and bioavailability of Hg in the habitat of the fish. The results showed that the Hg content of walleye (*Stizostedion vitreum*), a species that appears to be particularly suitable for whole-lake bioassays of MeHg production (*4*, *14*), could be predicted by means of an empirical compound variable (the "Hg methylating capability" of the sedimentary microflora multiplied by the abundance of bioavailable Hg in the sediment), which was formulated to measure the relative rate of MeHg production in samples of fine-grained offshore sediments (*4*; cf. *2*, *14*). Hg concentration in walleye muscle increased significantly as a function of this compound variable but correlated much more weakly with its component variables, demonstrating that it was the combination of the two complementary factors that regulated the bioaccumulation of MeHg. Furthermore, Hg concentrations in plankton and benthic invertebrates depended mainly on environmental factors affecting Hg availability but were unrelated, or inversely related, to inorganic Hg and MeHg concentrations and rates of Hg methylation in their habitats (*3*; cf. *18*). It must also be borne in mind that MeHg concentrations in fish and other food-web organisms are functions of many biological variables, such as habitat preference, diet, age, size, growth rate, metabolic rate, and biochemical mechanisms for excretion or demethylation of MeHg (*4*), as well as the numerous environmental factors that affect the growth, biochemical activities, and interactions of microorganisms and the speciation, binding and release, and bioavailability of inorganic Hg and MeHg (*2–4*, *9*, *18–20*). Given that the biogeochemical cycle of Hg in an aquatic ecosystem is the net result of such a complex interplay of physicochemical and biological processes, it is hardly surprising that Bodaly et al. found that "MeHg accumulation in the food chain was generally not closely linked to the rates of MeHg production in the reservoirs."

What is surprising and disappointing, though, is that the authors merely described their findings in a cursory manner without attempting to explain them in terms of biogeochemical processes, compounding this deficiency by inadequate coverage of relevant literature. As Bodaly and associates themselves acknowledged earlier (*21*), the bioaccumulation of Hg in reservoirs is controlled by many variables, and much remains to be learned about this complex phenomenon; however, their paper on the FLUDEX project (*1*) gives no indication that they have advanced our knowledge of it.

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(1) Bodaly, R. A., et al. Experimenting with Hydroelectric Reservoirs. *Environ. Sci. Technol.* **2004**, *38*, 346A–352A.
(2) Jackson, T. A. The Mercury Problem in Recently Formed Reservoirs of Northern Manitoba (Canada): Effects of Impoundment and Other Factors on the Production of Methyl Mercury by Microorganisms in Sediments. *Can. J. Fish. Aquat. Sci.* **1988**, *45*, 97–121.
(3) Jackson, T. A. Accumulation of Mercury by Plankton and Benthic Invertebrates in Lakes of Northern Manitoba (Canada): Importance of Regionally and Seasonally Varying Environmental Factors. *Can. J. Fish. Aquat. Sci.* **1988**, *45*, 1744–1757.
(4) Jackson, T. A. Biological and Environmental Control of Mercury Accumulation by Fish in Lakes and Reservoirs of Northern Manitoba, Canada. *Can. J. Fish. Aquat. Sci.* **1991**, *48*, 2449–2470.
(5) St. Louis, V. L.; et al. The Rise and Fall of Mercury Methylation in an Experimental Reservoir. *Environ. Sci. Technol.* **2004**, *38*, 1348–1358.
(6) Kelly, C. A.; et al. Increases in Fluxes of Greenhouse Gases and Methyl Mercury Following Flooding of an Experimental Reservoir. *Environ. Sci. Technol.* **1997**, *31*, 1334–1344.
(7) Rosenberg, D. M.; et al. Large-Scale Impacts of Hydroelectric Development. *Environ. Rev.* **1997**, *5*, 27–54.
(8) Hecky, R. E.; et al. Increased Methylmercury Contamination in Fish in Newly Formed Freshwater Reservoirs. In *Advances in Mercury Toxicology*; Suzuki, T., Imura, N., Clarkson, T. W., Eds.; Plenum Press: New York, 1991; pp 33–52.
(9) Jackson, T. A. Mercury in Aquatic Ecosystems. In *Metal Metabolism in Aquatic Environments*; Langston, W. J., Bebianno, M. J., Eds.; Chapman & Hall: London, 1998; pp 77–158.
(10) Lucotte, M.; et al. Mercury in Natural Lakes and Unperturbed Terrestrial Ecosystems of Northern Québec. In *Mercury in the Biogeochemical Cycle*; Lucotte, M., et al., Eds.; Springer: Berlin, Germany, 1999; pp 55–87.
(11) Balogh, S. J.; et al. Episodes of Elevated Methylmercury Concentrations in Prairie Streams. *Environ. Sci. Technol.* **2002**, *36*, 1665–1670.
(12) Jackson, T. A. Methyl Mercury Levels in a Polluted Prairie River-Lake System: Seasonal and Site-Specific Variations, and the Dominant Influence of Trophic Conditions. *Can. J. Fish. Aquat. Sci.* **1986**, *43*, 1873–1887.
(13) Jackson, T. A. Effects of Environmental Factors and Primary Production on the Distribution and Methylation of Mercury in a Chain of Highly Eutrophic Riverine Lakes. *Water Pollut. Res. J. Can.* **1993**, *28*, 177–216. (Also see Erratum, *Water Pollut. Res. J. Can.* **1993**, *28*, after p 512.)
(14) Jackson, T. A. The Influence of Phytoplankton Blooms and Environmental Variables on the Methylation, Demethylation, and Bio-Accumulation of Mercury (Hg) in a Chain of Eutrophic Mercury-Polluted Riverine Lakes in Saskatchewan, Canada. In *Heavy Metals in the Environment*, Vol. 2 (Proc. Intl. Conf., Toronto, Canada, Sept 1993); Allan, R. J., Nriagu, J. O., Eds.; CEP Consultants Ltd.: Edinburgh, UK, 1993; pp 301–304.
(15) Jackson, T. A. The Influence of Clay Minerals, Oxides, and Humic Matter on the Methylation and Demethylation of Mercury by Micro-Organisms in Freshwater Sediments. *Appl. Organomet. Chem.* **1989**, *3*, 1–30.
(16) Jackson, T. A. Effects of Heavy Metals and Selenium on Mercury Methylation and Other Microbial Activities in Freshwater Sediments. In *Heavy Metals in the Environment*; Vernet, J.-P., Ed.; Elsevier: Amsterdam, The Netherlands, 1991; pp 191–217.
(17) Thérien, N.; Morrison, K. *In Vitro* Release of Mercury and Methylmercury from Flooded Organic Matter. In *Mercury in the Biogeochemical Cycle*; Lucotte, M., et al., Eds.; Springer: Berlin, Germany, 1999; pp 147–164.
(18) Tremblay, A. Bioaccumulation of Mercury and Methylmercury in Invertebrates from Natural Boreal Lakes. In *Mercury in the Biogeochemical Cycle*; Lucotte, M., et al., Eds.; Springer: Berlin, Germany, 1999; pp 89–113.
(19) Schetagne, R.; Verdon, R. Mercury in Fish of Natural Lakes of Northern Québec. In *Mercury in the Biogeochemical Cycle*; Lucotte, M., et al., Eds.; Springer: Berlin, Germany, 1999; pp 115–130.
(20) Schetagne, R.; Verdon, R. Post-Impoundment Evolution of Fish Mercury Levels at the La Grande Complex, Québec, Canada (from 1978 to 1996). In *Mercury in the Biogeochemical Cycle*; Lucotte, M., et al., Eds.; Springer: Berlin, Germany, 1999; pp 235–258.
(21) Bodaly, R. A., et al. Bioaccumulation of Mercury in the Aquatic Food Chain in Newly Flooded Areas. In *Metal Ions in Biological Systems*; Sigel, A., Sigel, H., Eds.; Marcel Dekker: New York, 1997; pp 259–287.

## Response

We thank Togwell Jackson for his interest in our feature article on the experimental flooding (FLUDEX) project (*1*). His main complaints were that our article lacked interpretation and inadequately reviewed the relevant literature. Unfortunately, Jackson seems to have misunderstood that *ES&T* feature articles have a different function than primary research articles. The purpose of *ES&T* feature articles is the "examination of significant developments and issues affecting the environmental community, to probe timely topics from multiple perspectives—scientific, regulatory, and technical—and to provide readers with an authoritative and up-to-date understanding of the subject" (*2*). Features are limited as to length and the number of literature citations. Our article provided an overview of the environmental impact that hydroelectric reservoirs create and specifically included the production of methyl mercury (MeHg) and greenhouse gases; the policy implications of these environmental impacts; the experimental design of our study, hypotheses, and the study area and sites; and the preliminary conclusions from the first three years of the flooding of the five-year experiment. Future scientific papers will reference this introduction to the problem and the study design of the project.

Jackson raised the issue of the relationship among organic carbon storage, decomposition, and MeHg production. Our feature clearly stated that elevated concentrations of MeHg in reservoirs are related to elevated rates of mercury (Hg) methylation, as compared with natural lakes, and that high rates of methylation are associated with high rates of organic carbon decomposition. We noted that community respiration was fairly similar among reservoirs but that MeHg production varied (*3*). The situation is complicated by many factors, including the fact that the bacteria decomposing carbon are not the same as those methylating Hg. Also, initial rates of MeHg production appear to change rapidly with reservoir aging. Thus, although MeHg production slowed significantly in all of the FLUDEX reservoirs after the first year of flooding, it did not slow equally among the reservoirs. The quality of organic carbon may have differed among the reservoirs, especially with regard to the stimulation of Hg methylation (*1*, *4*), but because of the low levels of oxygen in the medium-carbon reservoir, redox conditions may also have played a role. Of course, redox conditions were influenced by rates of decomposition, which were also affected by organic carbon quality.

Regarding the lack of a relationship between MeHg production and Hg concentrations in fish, the situation is complicated by numerous factors, including the fact that most MeHg produced in flooded soils and peat does not enter the water column and the food chain (*4*, *5*). Therefore, we were also not surprised by the lack of a relationship between MeHg production and Hg in fish, as we have detailed in previous studies of experimental reservoirs (*5*–*7*). The factors affecting Hg concentrations in fish are many, including fish growth, feeding behavior and prey selection, fish activity levels, and Hg concentrations in food; many of these factors probably differed among the FLUDEX reservoirs, even though many variables, such as water temperatures, light, and water renewal times, were similar among the reservoirs.

We are well aware of the complexities of the biogeochemical cycling of Hg in reservoirs and the scientific literature in this area. The literature that Jackson suggested we should have included in our article formed, with other works, the basis for the hypotheses and study design for the FLUDEX project. Several papers delve into the experimental results in much more detail than could be included in this feature article (*3*, *4*, *8*, *9*), and others have been submitted or are in preparation.

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(1) Bodaly, R. A.; et al. Experimenting with Hydroelectric Reservoirs. *Environ. Sci. Technol.* **2004**, *38*, 347A–352A.
(2) *Guidelines for Authors of ES&T A-page Features and Viewpoints*, http://pubs.acs.org/journals/esthag/apage_authorguide.pdf.
(3) Matthews, C. J. D.; et al. Carbon Dioxide ($CO_2$) and Methane ($CH_4$) Production in Small Reservoirs Flooding Upland Boreal Forest. *Ecosystems* **2005**, *8*, in press.
(4) Hall, B. D.; et al. The Impact of Reservoir Creation on the Biogeochemical Cycling of Methyl and Total Mercury in Boreal Upland Forests. *Ecosystems* **2005**, *8*, in press.
(5) St. Louis, V. L.; et al. The Rise and Fall of Mercury Methylation in an Experimental Wetland Reservoir. *Environ. Sci. Technol.* **2004**, *38*, 1348–1358.
(6) Bodaly, R. A.; Fudge, R. J. P. Uptake of Mercury by Fish in an Experimental Boreal Reservoir. *Arch. Environ. Contam. Toxicol.* **1999**, *37*, 103–109.
(7) Kelly, C. A.; et al. Increases in Fluxes of Greenhouse Gases and Methyl Mercury Following Flooding of an Experimental Reservoir. *Environ. Sci. Technol.* **1997**, *31*, 1334–1344.
(8) Hall, B. D.; St. Louis, V. L.; Bodaly, R. A. The Stimulation of Methylmercury Production by Decomposition of Flooded Birch Leaves and Jack Pine Needles. *Biogeochemistry* **2004**, *68*, 107–109.
(9) Mailman, M.; Bodaly, R. A. Total Mercury, Methyl Mercury, and Carbon in Fresh and Burnt Boreal Plants and Soil. *Environ. Pollut.* **2005**, in press.