



Biogeochemistry of mercury in wetlands

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The environmental behavior and accumulation of Hg in aquatic organisms is subtly complex and driven by chemically and biologically mediated reactions involving exceedingly small quantities of Hg in the atmosphere and natural waters. The atmospheric and aquatic biogeochemical Hg cycle associated with wetlands and their environs will be affected not only by localized discharges (e.g., rivers; waste water treatment facilities), and tidal exchange, but from direct and indirect (via watershed leaching) airborne transport and deposition of Hg from regional and longer range sources. Increasing control of potential polluting activities and the development of 'clean' technologies have resulted in a substantial decrease in Hg emissions to the environment from point sources especially in developed countries. Unfortunately, there is no evidence suggesting that there has been a decline in total global pollution related Hg emissions. Indeed, it appears that emissions and discharges in developing regions (e.g., Asia, Africa, South America) are reducing the potential improvements gained through environmental legislation and other initiatives. Such global pollution is apparent in elevated levels of total gaseous mercury (TGM) in the Arctic (Schroeder et al., 1998) and in the equatorial Atlantic (Lamborg et al., 1999) as compared to mid-continent regions of the north-central United States (Lamborg et al., 1995; 2000). Further, effects of pollutants from longer range and diffuse sources can present a time-delayed and spatially-displaced response which depends on the ecological characteristics of the receiving ecosystems (Salomons and Stigliani, 1995).

Biogeochemical properties of a given ecosystem may increase or decrease the chances of a pollutant of reaching toxic levels, irrespective of the original magnitude in source. In aquatic ecosystems, wetlands are among the most sensitive to pollutants such as Hg. These environments may not only concentrate

elements, but in most cases, biogeochemical reactions can change their chemical form, mobilization and bioavailability. For example, relatively innocuous levels of inorganic Hg can be transformed by wetland and salt marsh bacterial activity into toxic methylmercury (MMHg). Methylmercury levels in marine and freshwater fish exceeding national and international public health guidelines are common to aquatic systems in the northern and southern hemispheres, and in settings ranging from urban/regional to remote oceanic environs. Methylmercury is considerably more toxic to humans than either elemental Hg or inorganic Hg salts. Humans are exposed MMHg principally from consumption of fish and fish products, and prenatal life is more susceptible to MMHg-induced brain damage than adults (Fitzgerald and Clarkson, 1991). Fish consumption advisories are common internationally.

The recognition of the ecological significance and socio-economic importance of wetlands has resulted in the enforcement of regulations on the use of wetland resources and on the restriction to development of many anthropogenic activities on wetland areas. Nevertheless, these ecosystems not only respond to direct environmental changes but to the combined or integrated influences of different anthropogenic activities taking place along their watersheds. Indeed, they are permanently at risk (Behrendt, 1993). Localized inputs of Hg include waste water sewage and industrial discharges, and emissions/deposition from energy generation (e.g., coal combustion), incineration, gold mining, and smelting. Long range anthropogenic contributions include river-borne Hg species and atmospheric Hg transport from distant sources (e.g., high temperature emissions on other continents). A thorough understanding of the Hg biogeochemistry in wetland ecosystems and its effects and availability to aquatic biota are crucial for the successful monitoring,

risk assessment and remediation of Hg contaminated areas. In this special issue of **Wetlands Ecology and Management**, some major topics relating to the biological and chemical cycling of Hg in tropical and temperate wetlands are discussed.

A decrease of Hg concentrations in natural indicators, fish and bottom sediments, has been reported for coastal areas, particularly where major Hg inputs were from industrial sources, such as the Argentine coast of Buenos Aires province and Ria do Aveiro, Portugal. Although both studies confirm the decreasing importance of Hg from industrial point sources, they illustrate the potential for remobilization of Hg from contaminated sites. This is exemplified by migratory fish at the Ria do Aveiro, Portugal. These fish show a significant incorporation of Hg when entering contaminated areas, even when migration is only seasonal. Also, notwithstanding the sharp decrease of Hg in Argentine coastal areas, methylation still occurs and results in relatively high Hg levels in fish from these areas. More discouragingly, however, are remote sites affected by artesian gold mining, such as the Pantanal wetlands in central Brazil, which show increasing Hg contamination. This source of Hg is responsible for a global emission of over 400 tons annually, mostly in the tropics, with enormous potential for environmental impacts and human health risks due to the difficulty in monitoring such activities (Lacerda and Salomons, 1998).

Wetlands are understood to play a significant role in the biogeochemical cycles of nutrients and of greenhouse gases. They may act as major conduits for gas exchange between the atmosphere and their substrate sediments and/or enhance the Hg flux from anoxic sediments. Biotic re-emission of Hg from terrestrial wetland vegetation is evidenced, confirming that wetland plants have the ability to mobilize reduced Hg vapor from soils to the atmosphere through root-related processes.

The biogeochemistry of Hg in wetland pore waters, studied under completely different situations, including tropical mangroves and temperate salt marshes, showed some consistent similarities. Hg concentrations in pore waters seem not to be controlled by exchange equilibrium with the solid phase. Hg complexes, with polysulfides or organics, may dominate in sulfidic estuarine waters. On the other hand, methylation occurs at elevated rates at the redox cline of wetland sediments even under high sulfate concentrations. Tidal fluctuation may accelerate dissolved and particulate Hg export from coastal wetlands to

adjacent marine areas. Remobilization and export of Hg from pore waters of salt marshes is reported in temperate areas and from mangroves in the tropics. Formation of complexes with dissolved organic matter and polysulfides, may result in higher concentrations of dissolved Hg than those predicted by the thermodynamic solubility of sulfides. Although comparable processes are occurring in both temperate and tropical areas, the rate may be different, since strong seasonal events do occur in the tropics. However, there are no comparative quantitative studies.

Whereas, these aforementioned papers present a robust group of experimental studies, they are just a beginning; that is a framework for further investigations of the biogeochemical cycling of Hg in wetlands. Indeed, there is an urgent need for much additional comparative research, in particular, between fresh and salt water wetlands, and between tropical and temperate areas.

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