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Do wood fibers from a pulp mill affect the distribution of total and methyl mercury in river sediments?

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ABSTRACT

The St. Lawrence River near Cornwall Ontario is affected by industrial mercury contamination of sediments and biota. It has been suggested that pulp and paper mill effluents may stimulate bacterial mercury methylation in these sediments, leading to contamination of aquatic biota. To test this hypothesis, we examined sediment–porewater dynamics of total mercury (THg) and methyl mercury (MeHg) at a site with high concentrations of wood fibers from a pulp and paper mill effluent and a nearby reference site with low wood fiber content. Dissolved phase THg (THg_{diss}) and MeHg ($MeHg_{diss}$) in porewater profiles showed that $38 \pm 30.9\%$ (SD) of THg in porewaters was in the methylated form regardless of wood fiber content. $MeHg_{diss}$ and THg_{diss} concentrations were homogeneous between porewater and overlying water, indicating (a) that there is minimal net diffusion of $MeHg_{diss}$ and THg_{diss} and (b) that redox-dependent processes such as sulfate reduction and Fe reduction were not associated with $MeHg_{diss}$ distribution in these sediment profiles. MeHg and THg in solid phase showed coincident subsurface peaks at depths > 40 cm suggesting either that historical deposits of MeHg on particles ($MeHg_{(p)}$) are preserved in deep sediments, or that Hg methylation is active in deep sediments.

Introduction

The St. Lawrence River at Cornwall, Ontario and Massena, NY was designated as an Area of Concern (AOC) by the International Joint Commission (IJC) in 1986 due to environmental contamination including high sediment concentrations of Hg along its northern coast and high PCBs (polychlorinated biphenyls) on its southern coast. Considerable attention has been given to an area downstream of a former pulp and paper mill (designated Zone 1) which contains wood fibers and high anaerobic microbial activity evidenced by rapid methane gas production and ebullition (Biberhofer and Rukavina, 2002; Delongchamp et al., 2010). This zone supports the most Hg contaminated fish and invertebrates within the AOC, despite having similar or lower Hg concentrations in sediment than in other embayments along the Cornwall waterfront (Fowlie et al., 2008; Yanch, 2007), suggesting Hg methylation may be an important mediating process in the Hg contamination of Zone 1 (Delongchamp et al., 2009; Yanch, 2007).

MeHg is a toxic form of Hg (Scheulhammer et al., 2007) that poses a potential risk to humans and aquatic animals. It is the only Hg form that biomagnifies in aquatic food webs leading up to fish and ultimately humans (Lindqvist et al., 1991). Sediments are the main Hg reservoir in the aquatic environment (Benoit et al., 1998) and play a major role in Hg cycling of aquatic systems (Ramalhosa et al., 2001). Microbial methylation usually occurs under low oxygen or anoxic conditions near the sediment–water interface (Gilmour and Henry, 1991; Siciliano et al., 2002). Sulfate reducing bacteria (SRBs) are believed to be the primary Hg methylators (Avramescu et al., 2011; Compeau and Bartha, 1985) in freshwater and estuarine sediments. While sulfate reducing bacteria are the most important in this process (Avramescu et al., 2011), other microorganisms including methanogens and iron reducing bacteria may also contribute to Hg methylation (Pak and Bartha, 1998). Although abiotic methylation of Hg has been suggested (Celo and Scott, 2006), it is generally considered to be a small contribution to MeHg when compared to biotic pathways. Once deposited to sediments, Hg and MeHg may be subjected to postdepositional processes. For example, reduction of Fe and Mn oxides and their dissolution as a consequence of the microbial degradation of the organic matter, may remobilize Hg to the porewater (Froelich et al., 1977), though subsequent precipitation by sulfides may mediate this process (Ullrich et al., 2001). Fe and Mn oxides which are known as scavengers of trace metals in the environment (Lockwood and Chen, 1973) can scavenge Hg from surface waters to surface sediments and form stable complexes (Murray, 1975). Dissolved organic matter may also mediate Hg speciation, bioavailability, and facilitate its mobility in sediments and porewaters (Ramalhosa et al., 2006).

Here we examine how sediment mercury dynamics relate to the presence of wood fibers from a local pulp mill with a detailed seasonal analysis of total Hg and MeHg in sediments and porewaters.

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Previous studies on mercury in sediments at this site speculated on the role of wood fibers on mercury dynamics, but this study is the first to examine their impacts in a case-control design. Two sites were chosen for this comparison, one site containing high wood fibers in sediments (HWF site) and a nearby reference site with low wood fiber content in sediments. Based on underwater video and core sampling in the same area of the river, Biberhofer and Rukavina (2002) observed a correspondence between sites with high wood fiber and amounts of gas released when mechanically disturbed. Gas ebullition rates from the sediments of up to 2800 ml m^{-2} day^{-1} have been measured near these study sites, of which 29–84% was methane (Razavi et al., in press), indicating active populations of methanogens in these sediments. We hypothesized that increased methanogen activity in sediments containing wood fibers may elevate MeHg production in sediments, and enhanced respiration rates may lead to depletion of terminal electron acceptors, including oxygen and ferric iron, which may facilitate diffusion of MeHg from sediments to overlying water. Porewater analysis was used to study mercury dynamics in sediments because porewaters mediate the fluxes of metals between sediment and water column (Boudreau, 1996) and they also may reveal zones of active Hg methylation in sediments (e.g. Clarisse et al., 2011).

The specific objectives of this study were: (1) to compare the distributions of dissolved and particulate Hg and MeHg in sediments, porewaters, and overlying waters of two nearby sites in Zone 1 of the Cornwall AOC, one site containing high wood fibers in sediments (HWF), and a reference site with low wood fiber content; (2) to determine whether sediments containing high densities of wood fibers diffuse more THg and MeHg to overlying waters than sediments with low wood fiber content; and (3) to relate the distribution of THg and MeHg in sediments and pore waters to redox sensitive constituents (SO_4^{2-}, S^{2-} and Fe^{2+}) to identify areas of active MeHg production in sediments.

Materials and methods

Study site

The St. Lawrence River AOC includes an 80 km stretch of the St. Lawrence River, from the Moses-Saunders Power dam to the eastern outlet of Lac St. Francois in Quebec. This stretch of the river encompasses many jurisdictions, including the provinces of Ontario and Quebec, the state of New York, the federal governments of Canada and U.S.A, the St. Regis Tribe and the Mohawks of Akwesasne.

The St. Lawrence River drains the Great Lakes to the Estuary and Gulf of the St. Lawrence. Water discharge, which averages about 8000 m^3/s at Cornwall, has been regulated since the 1950s with the construction of the Moses-Saunders Dam. Below the dam the river splits around Cornwall Island, with about one third of the flow passing along the north shore by Cornwall. River flow is primarily from west to east, with back eddies creating depositional zones in bays along the waterfront. Our study sites were located along the Cornwall waterfront of the northern channel (Fig. 1), approximately 1 km downstream from the discharge of two local industries, the Domtar pulp and paper mill (closed in 2006), and ICI Forest Products, a chlor alkali plant (closed in 1995).

Despite regulations established in the1970s by the federal government to limit the discharge of Hg to the river in liquid effluent by local industries, concentrations of Hg in surface sediments of Zone 1 have remained elevated and often exceed the sediment quality guideline (SQG) of 0.85 nmol g^{-1}, a limit set for the protection of biota by Environment Canada (Environment Canada, 1981). Also, MeHg concentration in large walleye in this area exceeded 2.32 nmol g^{-1}, the OMOE (Ontario Ministry of the Environment) guideline for fish consumption to protect the general population (Grapentine et al., 2003; OMOE, 2011) and this area is still listed as an AOC. A full history of industrial development at this site, as well as an account of total mercury and methyl mercury deposits in sediments of the Cornwall AOC is given in Delongchamp et al. (2009) and Ridal et al. (2009).

The high wood fiber (HWF) site is located immediately downstream of the pulp mill effluent discharge (45° 0′44.65″N, 74°43′43.73″W) and the reference site (45° 0′42.80″N, 74°43′51.31″W) is located nearby to the south west (Fig. 1). Samples were collected from June to August 2007. The physical setting of the two sites was similar low energy environments with depth integrated current velocities at the two sites <0.1 m/s (Nettleton 2004), total depths of approximately 8 m, and surface sediments consisting of brown-black clayed mud with a brownish surface. Benthic invertebrate species at nearby sites consist mainly of chironomids, tubificid worms, naidid worms, and gammarid amphipods (Milani and Grapentine, 2009).

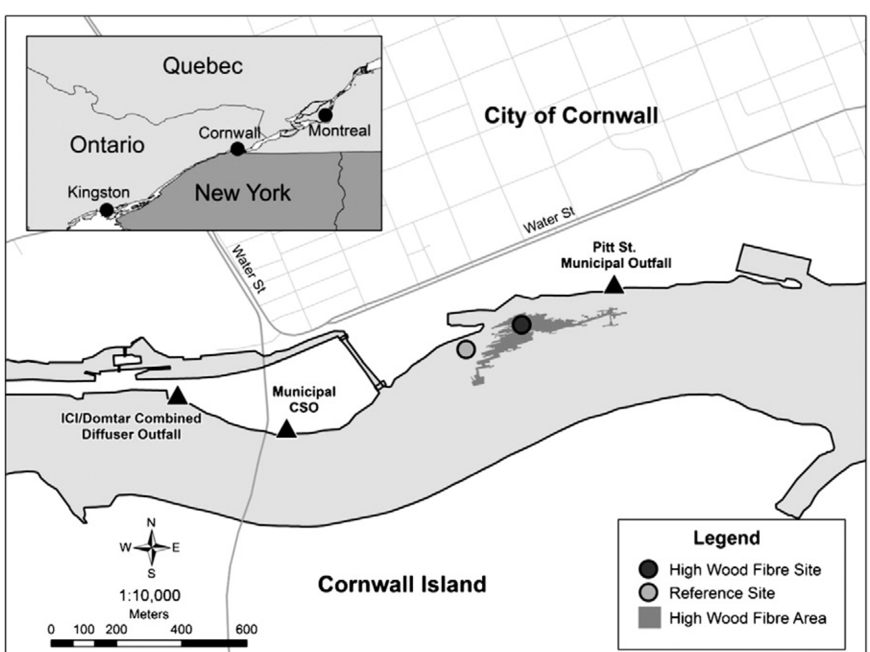

Fig. 1. Location of mercury sampling sites in the St. Lawrence River, showing the high wood fiber site and reference site.