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Mass-dependent and mass-independent variations in the isotope composition of mercury in a sediment core from Lake Ontario as related to pollution history and biogeochemical processes

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ABSTRACT

Historical variations in the isotope composition of mercury (Hg) in Lake Ontario were examined for the purpose of characterising the isotope signatures of the sources of Hg contamination and investigating their fate in the environment. The lake has been polluted with Hg, organochlorine compounds, and other contaminants from industrial and urban sources, chlor-alkali plants being, historically, the principal sources of Hg. The pollutants were discharged into the Niagara River, transported to the lake by fluvial action, and deposited in fine-grained sediments. Analysis of a dated sediment core from the lake revealed that the Hg concentration increased sharply in the 1890s, peaked in the 1930s–1940s and 1960s, and then declined, levelling off in the late 1900s. The δ-values of the ^{198}Hg/^{202}Hg, ^{199}Hg/^{202}Hg, ^{200}Hg/^{202}Hg, and ^{201}Hg/^{202}Hg ratios of the Hg that formed the peaks decreased with increasing total Hg concentration. Thus, the isotope signature of the anthropogenic Hg was formed by mass-dependent fractionation (MDF) which caused preferential depletion in the lighter isotopes, suggesting evaporation from Hg(0) electrodes in the chlor-alkali plants. The background Hg above and below the peaks also showed inverse correlations with total Hg but formed separate regression lines, reflecting the fact that its origins and pre-depositional history were different. The isotope signatures were altered appreciably by both MDF and mass-independent fractionation (MIF) attributable to natural processes in the lake. MDF caused secondary *enrichment* in lighter isotopes, and MIF caused intermittent ^{201}Hg enrichment associated with episodes of Fe and Mn oxyhydroxide precipitation. FeOOH abundance showed a marked dip coinciding with maximum concentrations of organochlorine compounds in the 1960s, but ^{201}Hg enrichment by MIF increased significantly with the concentrations of certain chlorobenzene compounds. These findings suggest that MIF was mediated by bacteria, including oxyhydroxide-precipitating species, and that organochlorines inhibited FeOOH-producing bacteria, whereas the chlorobenzenes stimulated bacterial enzyme activity involved in MIF.

1. Introduction

Contamination of aquatic ecosystems with the toxic heavy metal mercury (Hg) by aqueous or atmospheric transport from various anthropogenic and natural sources has long been a serious worldwide problem (Nriagu and Pacyna, 1988; Pirrone et al., 1996; Jackson, 1997; Fitzgerald et al., 1998; Jackson, 1998; Pirrone et al., 2009); and in North America the widespread occurrence and quantitative importance of Hg pollution following the onset of the Industrial Revolution has been well documented by analysis of ice cores from a glacier (Schuster et al., 2002) and sediment cores from a large assortment of lakes ranging from the mid-latitudes to the High Arctic (e.g. Lucotte et al., 1995; Lockhart et al., 1998; Muir et al., 2009; Kirk et al., 2011). Research on Hg in the environment, however, is challenging because of the enormous complexity of the biogeochemical cycle of Hg (Jackson, 1998) and the difficulty of distinguishing and quantifying the effects of discharges from different sources of contamination, especially distant ones, after the Hg has been released into the environment. The discovery that the stable isotope composition of Hg in aquatic ecosystems varies as a result of both mass-dependent fractionation (MDF) (Jackson et al., 2004) and mass-independent fractionation (MIF) (Jackson et al., 2006, 2008), and that Hg ores from different sources have different isotope signatures (Hintelmann and Lu, 2003), along with reports of experimental data demonstrating biochemically mediated MIF (Buchachenko et al., 2004) and abiotic MIF (Bergquist and Blum, 2007), opened up a new and rapidly expanding field of research on Hg in the environment, raising the possibility that isotope signatures of Hg can help to identify sources of Hg contamination and may yield important information about the biogeochemical cycling of Hg (Jackson et al., 2004, 2008; Bergquist and Blum, 2009; Yin et al., 2010; Jackson and Muir, 2012; Jackson et al., 2013; Sonke and Blum, 2013).

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Processes that mediate MDF of Hg isotopes yield products whose Hg isotope abundances increase or decrease as a linear function of the mass of the isotope. In contrast, processes that bring about MIF of Hg isotopes usually yield products that are anomalously enriched or depleted in the isotopes of odd mass number (^{199}Hg and ^{201}Hg) (Buchachenko et al., 2004; Jackson et al., 2006; Bergquist and Blum, 2007; Schauble, 2007; Biswas et al., 2008; Ghosh et al., 2008; Jackson et al., 2008; Buchachenko, 2009a,b; Carignan et al., 2009; Das et al., 2009; Gantner et al., 2009; Laffont et al., 2009; Sherman et al., 2009; Feng et al., 2010; Epov et al., 2011; Lefticariu et al., 2011; Liu et al., 2011; Malinovsky and Vanhaecke, 2011; Sonke, 2011; Chen et al., 2012; Jackson and Muir, 2012; Perrot et al.., 2012; Das et al., 2013; Jackson et al., 2013; Ma et al., 2013; Mil-Homens et al., 2013; Sonke and Blum, 2013). Evidence for MIF of an isotope of even mass number (^{200}Hg) has reportedly been detected in atmospheric Hg (Gratz et al., 2010; Chen et al., 2012; Rolison et al., 2013) but has not been detected in Hg from other natural media, such as sediments and biological material. During MDF or MIF, isotope depletion in certain Hg fractions is balanced by corresponding enrichment in other fractions in accordance with the principle of mass conservation; and separation of isotopically distinct fractions (e.g. loss of isotopically light Hg(0) by evaporation, leaving an isotopically heavy nonvolatile Hg(II) residue) leads to isotope enrichment in some natural media and depletion in others. Both MDF and MIF have been attributed to a variety of natural and industrial processes, including both biotic and abiotic processes (Jackson and Muir, 2012; Jackson et al., 2013; Sonke and Blum, 2013).

Evidence for MDF and MIF of Hg isotopes has been found in freshwater and marine sediments (Jackson et al., 2004; Ghosh et al., 2008; Jackson et al., 2008; Gantner et al., 2009; Feng et al., 2010; Liu et al., 2011; Jackson and Muir, 2012; Das et al., 2013; Foucher et al., 2013; Gray et al., 2013; Jackson et al., 2013; Ma et al., 2013; Mil-Homens et al., 2013; Yin et al., 2013). Although isotope signatures traceable to different natural and anthropogenic sources of Hg contamination have reportedly been detected in natural media, including lake sediments, Hg ores, and coal (Hintelmann and Lu, 2003; Smith et al., 2005, 2008; Foucher et al., 2009; Stetson et al., 2009; Feng et al., 2010; Estrade et al., 2011; Gehrke et al., 2011; Lefticariu et al., 2011; Liu et al., 2011; Jackson and Muir, 2012; Das et al., 2013; Foucher et al., 2013; Gray et al., 2013; Jackson et al., 2013; Ma et al., 2013; Mil-Homens et al., 2013; Yin et al., 2013), there is also evidence for alteration or obliteration of these signatures by MDF and MIF mediated by natural processes, including microbial activities in aquatic ecosystems, after the Hg has been released into the environment (Jackson et al., 2004, 2008; Jackson and Muir, 2012; Jackson et al., 2013).

The research whose results are presented here involved analysis of a sediment core from a lake basin polluted with Hg from industrial effluents which had been discharged into river water and transported to the lake by fluvial action. The purposes of the research were to characterise the isotope signatures of the Hg from the major sources of pollution, to compare them with the isotope signature of the background Hg, to differentiate between isotope signatures imprinted on the anthropogenic Hg at the sources of pollution and secondary isotope effects caused by natural processes in the environment, and to draw comparisons between the waterborne anthropogenic isotope signatures dealt with here and airborne ones described in previous publications with respect to their characteristics and their fate in the environment.

2. Field area, materials, and methods

The Niagara River flows northward from the east end of Lake Erie and empties into the Niagara Basin at the west end of Lake Ontario (Fig. 1). Starting in the 1890s and rising to peak intensity in the mid-twentieth century, the Niagara Basin was polluted with Hg and a wide range of other toxic contaminants, including other heavy metals and a variety of xenobiotic chlorinated hydrocarbons, which were discharged into the Niagara River from a large number of industrial and urban sources located mostly in the heavily industrialised cities of Buffalo, Tonawanda, and Niagara Falls in New York State, U.S.A. (Thomas, 1972; Hang and Salvo, 1981; Vincent and Franzen, 1982; Allan et al., 1983; Durham and Oliver, 1983; Mudroch, 1983; Thomas, 1983; Whittle and Fitzsimons, 1983; Breteler et al., 1984; Joshi, 1988; Mudroch, 1993; Wong et al., 1995; Jackson, 2001; Coakley and Lewis, 2003). The principal sources of the anthropogenic Hg were Hg(0) electrodes used for the production of caustic soda and chlorine in two chlor-alkali plants operated, respectively, by the Olin Corporation and the Hooker Chemical Corporation (also known as Hooker Chemicals and Plastics Corporation or Hooker Electrochemical) in Niagara Falls (Breteler et al., 1984), although there were other sources as well, including a steel foundry and a steel manufacturing plant (Hang and Salvo, 1981). The chlor-alkali plants are situated near each other on the bank of the Niagara River ~25 km upstream from the mouth of the river (Fig. 1). The Olin plant began its operations in 1893, inaugurating a period of major Hg pollution, and the pollution problem was compounded in the early 1960s, when the Hooker plant was set up. Starting in 1970, however, pollution abatement measures were implemented in both of these plants to minimise the Hg content of their effluents (Breteler et al., 1984).

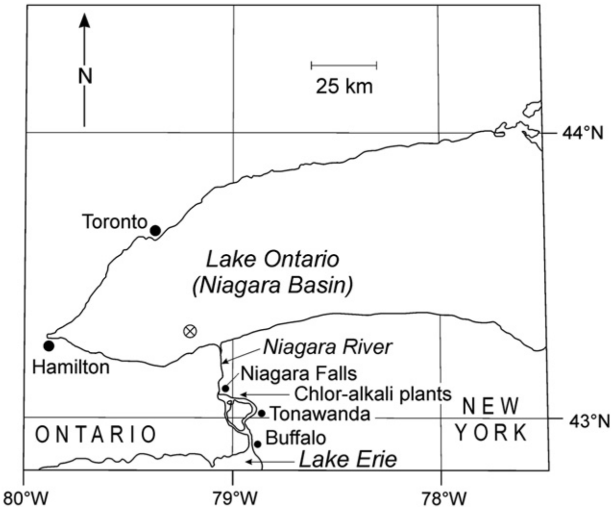

Fig. 1. Map of the field area showing the location of the sampling site (⊗) and the chlor-alkali plants.

In May, 1999 a core of fine-grained sediment 6.7 cm in diameter and 30 cm long was collected from the profundal zone of the Niagara Basin of Lake Ontario at a site located at latitude 43° 20′ 12″ North and longitude 79° 11′ 45″ West (~12 km northwest of the mouth of the Niagara River and ~40 km downstream from the chlor-alkali plants), where the water was 92.6 m deep (Fig. 1). The core was cut into 1 cm sections, which were stored in plastic bags and frozen. The core sections were then freeze-dried and subjected to chemical and isotopic analyses and radiometric dating.

Total Hg concentrations were determined by digesting weighed portions of the core sections with hot HNO_3/HCl (*aqua regia*) and $KMnO_4$ to convert all Hg to dissolved inorganic Hg(II), which was then reduced to Hg(0) gas by treatment with $SnCl_2$ and analysed by cold vapour atomic absorption spectrophotometry. Aliquots of the sample digests, along with aliquots of a standard solution consisting of Hg(II) dissolved in dilute HNO_3 (Inorganic Ventures Inc.) were then analysed for Hg isotopes in the order standard-sample-standard. The solutions were treated with $SnCl_2$ to reduce the dissolved Hg(II) to Hg(0) gas, and the Hg(0) was stripped from the solution phase (which was then discarded) in a gas–liquid separator to avoid matrix effects, whereupon the isotopic composition of the Hg(0) was determined by multi-collector inductively coupled plasma mass spectrometry