



Mass-dependent and mass-independent variations in the isotope composition of mercury in cores from lakes polluted by a smelter: Effects of smelter emissions, natural processes, and their interactions

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ABSTRACT

Analysis of sediment cores from three lakes polluted by a smelter and located 3.8, 9.4, and 21.0 km from it revealed that mercury (Hg) in smelter fallout has an isotope signature which denotes enrichment in lighter isotopes by mass-dependent fractionation (MDF), suggesting volatilisation as isotopically light Hg(0) followed by oxidation to reactive gaseous Hg(II) by flue gas constituents. However, the signature was detected only in the lake closest to the smelter; elsewhere it was obliterated by MDF and mass-independent fractionation (MIF) due to natural processes, whose effects varied with environmental factors, including smelter emissions. MIF caused depletion in ¹⁹⁹Hg and ²⁰¹Hg in all three lakes and was enhanced by dissolved organic matter but inhibited by heavy metals from the smelter; yet inter-lake comparison showed that the inhibition increased with decreasing metal concentration (i.e. with increasing distance from the smelter). Inhibition of MIF by metals was strongest in acidic and oxidising environments, and the inhibitory effects of individual metals depended on the metal's atomic polarisability. MDF was controlled by different processes, was more sensitive to local conditions, correlated with sulphate concentrations in lake water, and showed weaker net inhibition by metals; and inhibition by individual metals depended on the standard enthalpy of formation of the aqueous metal cation. Moreover, the combined effects of MDF and MIF varied with the sediment's Zn/Cu ratio but not with its Zn or Cu concentration alone. MIF is attributable to activities of anaerobic heterotrophic bacteria which were inhibited by the metals, whose toxicity depended on the properties, speciation, bioavailability, and interactive effects of the metals. The exacerbation of metal toxicity under acidic and oxidising conditions, and with increasing distance from the smelter, can be explained by enhanced bioavailability. MDF, too, is attributable to effects of bacteria, metals, and environmental variables but involved different mechanisms and pathways.

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1. Introduction

Several thousand tonnes of the toxic heavy metal mercury (Hg) are released into the atmosphere every year from different sources of pollution, including base metal smelters, and a comparable amount is emitted by natural sources, such as volcanoes (Nriagu and Pacyna, 1988; Pirrone et al., 1996, 2009; Jackson, 1997, 1998a; Fitzgerald et al., 1998). Hg emanates from diffuse sources as well as point sources, and there are secondary sources in the environment as well as the primary sources. Atmospheric Hg is mostly in the form of Hg(0) gas but includes variable quantities of particulate Hg(II) (PHg) and “reactive gaseous mercury” (RGM), which consists of low-molecular weight Hg(II) compounds such as HgCl₂ and HgO (Galbreath and Zygarić, 1996; Carpi, 1997; Lindberg and Stratton,

1998; Manolopoulos et al., 2007). Hg(0) has the longest residence time in the atmosphere, because, besides being gaseous, it is relatively inert and only slightly soluble in water. It is eventually oxidised to Hg(II) and returned to the earth's surface as wet and dry fallout, but this is apt to occur far from the point of origin. In contrast, PHg and RGM tend to come down relatively close to the source. When introduced into a body of water, inorganic Hg(II) is efficiently scavenged by fine particulate matter and deposited in fine-grained bottom sediments, but bacteria in the water and sediments convert small, variable portions of it to the toxic species methylmercury (CH₃Hg⁺) and may produce gaseous (CH₃)₂Hg and Hg(0) as well. CH₃Hg⁺ is subject to preferential accumulation by aquatic organisms, with biomagnification from lower to higher trophic levels, but is also prone to decomposition by bacteria, which reduce its Hg(II) moiety to Hg(0). Moreover, Hg is subject to many abiotic as well as biochemical reactions, including oxidation and reduction, photochemical as well as “dark” reactions, and the binding of Hg(II) by ligands, notably

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sulphide species and thiol groups. Thus, the biogeochemical cycle of Hg is extremely complex (Jackson, 1998a).

A major cause of uncertainty in research on atmospheric Hg contamination is the difficulty of identifying and quantifying contributions from different sources once they have been dispersed and intermingled in the environment (Jackson, 1997, 1998a; Lindberg et al., 2007), and the problem is compounded by the complexity of the biogeochemical cycle of Hg. The discovery that the stable isotope composition of Hg in aquatic ecosystems shows significant variations caused by both mass-dependent fractionation (MDF) (Jackson et al., 2004) and mass-independent fractionation (MIF) (Jackson et al., 2006, 2008a), 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 new, potentially fruitful lines of inquiry, 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, 2008a; Bergquist and Blum, 2009; Yin et al., 2010; Sonke and Blum, 2013).

MDF yields products whose isotope abundances increase or decrease as a linear function of the isotope's mass, whereas MIF usually yields 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, 2008a,b; Bergquist and Blum, 2007; Schauble, 2007; Biswas et al., 2008; Ghosh et al., 2008; Buchachenko, 2009a,b; Carignan et al., 2009; Das et al., 2009, 2013; 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; 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, to the best of our knowledge, has never been observed in Hg from other natural media. During fractionation of Hg isotopes, isotope depletion in certain Hg fractions is balanced by enrichment in others in accordance with the principle of mass conservation. As with lighter elements, such as C and N (Hoefs, 2004), spatial and temporal variations in the isotopic makeup of Hg in natural environments may reveal valuable information about sources and biogeochemical pathways of Hg (Jackson et al., 2004, 2008a; Bergquist and Blum, 2007, 2009; Yin et al., 2010; Jackson and Muir, 2012).

Evidence for MDF of Hg isotopes by natural processes has been found in sediments from various aquatic environments (Jackson et al., 2004, 2008a,b; Gantner et al., 2009; Feng et al., 2010; Liu et al., 2011; Jackson and Muir, 2012). MDF in a meromictic lake was ascribed to oxidation-reduction reactions mediated by bacteria (Jackson et al., 2004), and subsequent laboratory experiments lent credence to this inference by showing that MDF occurred during microbial reduction of Hg(II) to Hg(0) (Kritee et al., 2007, 2008, 2009, 2013). In addition, MDF may be brought about by chemical and photolytic reduction of Hg(II) (Yang and Sturgeon, 2009), atmospheric processes (Gratz et al., 2010; Rolison et al., 2013), sorption of Hg(II) by goethite (Jiskra et al., 2012), evaporation of Hg(0) (Ghosh et al., 2013), abiotic methylation of Hg(II) (Jiménez-Moreno et al., 2013), and solubilisation of bio-available Hg species in soil (Yin et al., 2013a). Moreover, MDF may result from the methylation of Hg by sulphate-reducing bacteria (Rodríguez-González et al., 2009; Kritee et al., 2013) and has been ascribed to microbial activities in a lake polluted by emissions from coal-burning power plants (Jackson and Muir, 2012). MDF is also caused by hydrothermal activity, including the deposition of Hg ores, and by industrial processes such as the smelting and calcination of ore, the leaching of calcines, and the combustion of coal, leading to production of Hg isotope signatures which could be used to trace Hg in the environment to particular sources of pollution (e.g. mines,

smelters, and power plants) (Hintelmann and Lu, 2003; Smith et al., 2005, 2008; Jackson et al., 2008b; Foucher et al., 2009; Stetson et al., 2009; Feng et al., 2010; Estrade et al., 2011; Gehrke et al., 2011; Liu et al., 2011; Jackson and Muir, 2012; Sherman et al., 2012; Foucher et al., 2013; Ma et al., 2013; Mil-Homens et al., 2013; Sonke and Blum, 2013; Sun et al., 2013; Yin et al., 2013b).

Evidence for MIF of Hg isotopes was observed in an experiment on the inhibition of an enzyme by CH_3Hg^+ (Buchachenko et al., 2004), raising the possibility that certain biochemical processes mediate MIF in nature. Shortly afterwards, Jackson et al. (2006, 2008a) reported the discovery that CH_3Hg^+ accumulated by crustaceans and fish in food webs of lakes was invariably enriched in ^{199}Hg and ^{201}Hg as a result of naturally occurring MIF, which they ascribed to microbial activities. Their findings were corroborated by others, who reported that the same isotope signature of MIF was a characteristic feature of Hg in the fish and invertebrates of other freshwater ecosystems (Bergquist and Blum, 2007; Das et al., 2009; Gantner et al., 2009; Laffont et al., 2009; Perrot et al., 2012). Hg isotope signatures indicative of MIF have also been found in sediments, lichens, peat, coal, fly ash, hot springs, atmospheric precipitation and ambient air, and Arctic snow exposed to sunlight (Biswas et al., 2008; Ghosh et al., 2008; Jackson et al., 2008b; Carignan et al., 2009; Sherman et al., 2009; Feng et al., 2010; Gratz et al., 2010; Liu et al., 2011; Jackson and Muir, 2012; Das et al., 2013; Ma et al., 2013; Mil-Homens et al., 2013; Rolison et al., 2013), and analysis of a sediment core from a lake polluted by emissions from coal-burning power plants yielded evidence for MIF mediated by microorganisms (Jackson and Muir, 2012). Moreover, experiments have revealed that MIF may be caused by various abiotic processes, including photochemical reduction of Hg(II), "dark" reduction of Hg(II), photochemical demethylation of CH_3Hg^+ , evaporation of Hg(0), and the binding of Hg(II) by thiol groups (Bergquist and Blum, 2007; Buchachenko et al., 2008; Estrade et al., 2009; Zheng and Hintelmann, 2009, 2010; Sherman et al., 2010; Wiederhold et al., 2010; Ghosh et al., 2013; Kritee et al., 2013). The fundamental mechanisms of MIF evidently involve [1] effects of the nuclear magnetic moment of the isotope (a consequence of its nuclear spin) or the nuclear field shift (nuclear volume) effect, or both, and [2] specific chemical properties of the reactants, notably the tendency of valence electrons to penetrate the inner electron shells of Hg, thereby coming into close contact with the nucleus, and preferential reactions of free radicals with Hg isotopes that have nuclear magnetic fields (Buchachenko et al., 2004; Jackson et al., 2006, 2008b; Schauble, 2007; Buchachenko, 2009a,b). In brief, MIF may be caused by a wide range of mechanisms and pathways – biochemical as well as abiotic ones, dark as well as photochemical ones, and nuclear field shift effects as well as effects of nuclear magnetic moment. The process has been reviewed elsewhere (Buchachenko, 2009a,b; Epov et al., 2011; Malinovsky and Vanhaecke, 2011; Jackson and Muir, 2012; Sonke and Blum, 2013), and a global model of it has been proposed (Sonke, 2011).

Hg isotope signatures are potentially useful for tracing environmental Hg to specific sources of contamination but are beset with uncertainties and limitations because isotope fractionation by natural processes in the environment may alter or obliterate the original signature (Jackson et al., 2004; Gratz et al., 2010; Gehrke et al., 2011; Jackson and Muir, 2012; Sherman et al., 2012). Another problem is that the mixing of variable quantities of Hg from different sources may obscure the individual signatures, causing ambiguity, especially in remote environments contaminated with Hg from many distant sources. Furthermore, even if a distinctive signature is imprinted on the Hg at the source, it may not be unique to that source or sufficiently different from signatures of Hg from other sources. A logical approach to the question of source attribution would be to investigate isotope signatures of Hg from individual point sources. Accordingly, we studied historical variations in the isotopic makeup of Hg in sediment cores from three lakes that have been polluted with Hg and

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