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Separation of monomethylmercury from estuarine sediments for mercury isotope analysis

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ABSTRACT

Estuarine sediments support the production of monomethylmercury (MeHg) which accumulates in aquatic organisms. While natural variation in mercury stable isotope ratios can potentially be used to track sources and transformations of mercury in the environment, the isotopic signature of MeHg in sediments has not been measured directly. The isotopic composition of MeHg has been studied in laboratory experiments and fish using tandem gas chromatography-multicollector inductively coupled plasma mass spectrometry (MC–ICP-MS) systems; however, the precision and sensitivity of this method may be too low for the analysis of many environmental samples including sediments in which MeHg constitutes 1% or less of the total mercury. In this study, we developed an offline separation method for the precise measurement of the Hg isotopic composition of MeHg in estuarine sediments. Separation of MeHg from inorganic species was accomplished by distillation and chemical ethylation-GC, and was followed by gold amalgam trapping to collect and preconcentrate pyrolyzed MeHg, which was then released into an oxidizing solution. MeHg standards processed in this way were collected with an average yield of 97.5%. External precision for all replicate isotope analyses of MeHg process standards was ±0.14‰ (2 SD, n = 8) for δ^{202}Hg and no detectable fractionation of Hg stable isotopes occurred during the separation. δ^{202}Hg values for MeHg separated from estuarine sediments using our approach varied from −0.41 to +0.41‰ and were generally higher, and spatially and temporally more variable, than those for total Hg (−0.21 to −0.48‰).

1. Introduction

Mercury (Hg) is a ubiquitous and toxic trace metal known to bioaccumulate in its organometallic form, monomethylmercury (MeHg). In aquatic ecosystems, up to 90% of Hg in fish is present as MeHg (Bloom, 1992; Grieb et al., 1990). The methylation of Hg in soils and sediment is mediated by anaerobic microorganisms (Compeau and Bartha, 1985; Hamelin et al., 2011; Kerin et al., 2006), and although predictive models of Hg methylation in sediments have been developed (Benoit et al., 1998; Hammerschmidt and Fitzgerald, 2004; Jonsson et al., 2014) the environmental controls on MeHg production remains an active area of research (Schartup et al., 2013).

Mercury stable isotopes are increasingly used to study the sources of Hg to contaminated sediments (Donovan et al., 2013; Foucher and Hintelmann, 2006; Foucher et al., 2009; Gehrke et al., 2007; Liu et al., 2011; Ma et al., 2013; Mil-Homens et al., 2013; Perrot et al., 2010; Sonke et al., 2010) and to characterize the extents of abiotic and biotic transformations of Hg in the environment (Bergquist and Blum, 2007; Jiménez-Moreno et al., 2013; Kritee et al., 2007, 2009; Perrot et al., 2013; Rodriguez-Gonzalez et al., 2009; Zheng and Hintelmann, 2010). However, few studies have examined the Hg isotopic composition of specific pools of Hg in aquatic systems (Smith et al., 2014; Yin et al., 2013). In particular, analytical challenges have limited the examination of the Hg isotopic composition of MeHg in environmental samples and the isotopic composition of MeHg in marine sediments, where MeHg typically accounts for less than 1% of the total Hg (Hammerschmidt et al., 2004; Mason and Sullivan, 1999; Schartup et al., 2013), has not been measured directly.

Sulfate reducing bacteria in pure culture have been shown to cause mass dependent fractionation (MDF) of Hg stable isotopes during Hg methylation resulting in isotopically lighter (depleted in ^{202}Hg) MeHg (Perrot et al., 2015; Rodriguez-Gonzalez et al., 2009). Similar results were obtained in abiotic methylation experiments with methylcobalamin and other methyl group donors (Jiménez-Moreno et al., 2013; Malinovsky and Vanhaecke, 2011; Perrot et al., 2013). In contrast, the Hg isotopic composition of sediment MeHg, inferred from the isotopic analysis of total Hg and the proportion of total Hg present as MeHg in aquatic food chains, indicates that MeHg in sediment is isotopically enriched in ^{202}Hg relative to total Hg (Gehrke et al., 2011; Kwon et al., 2014; Sherman and Blum, 2013). Similarly, MeHg in various aquatic animals with a range of MeHg concentrations has been shown to be enriched in ^{202}Hg relative to total Hg (Masbou et al., 2013). Direct measurement of the isotopic composition of MeHg in sediments is needed to understand these observations and evaluate the extent of isotopic

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fractionation during Hg methylation and demethylation in the environment.

The Hg isotopic composition of MeHg has been measured by coupling gas chromatography (GC) separation of ethylated Hg species to a multicollector inductively coupled plasma mass spectrometer (MC–ICP-MS) (Dzurko et al., 2009; Epov et al., 2008, 2010). However, chromatographic separation of MeHg may cause up to 0.5‰ variation in δ^{202}Hg between the start and end of peak elution (Dzurko et al., 2009) resulting in low precision of isotope ratios reconstructed from the transient signal (Rodriguez-Gonzalez et al., 2009). Analytical precision could be improved through the offline preconcentration of MeHg prior to isotope analysis. However, conventional MeHg separation systems are designed for a maximum load of only ~2 ng of MeHg (Liang et al., 1994) whereas at least 10 ng is needed for the highest precision Hg isotope analysis. Overloading GC columns may result in peak broadening or isotopic fractionation (Wehmeier et al., 2003).

The purpose of this study was to develop a procedure for the separation of large quantities of MeHg from estuarine sediment samples for Hg isotope analysis. In order to improve precision relative to online methods, MeHg was separated prior to introduction into the mass spectrometer using a high capacity GC column which could accommodate 10 to 20 ng of MeHg. Elemental Hg from separated MeHg was then collected on gold traps and subsequently desorbed offline for transfer to an oxidizing solution (Gratz et al., 2010; Sun et al., 2013). Since incomplete ethylation (Yang and Sturgeon, 2009) and other analytical steps (Dzurko et al., 2009; Wehmeier et al., 2003) may cause Hg isotope mass biases, the fractionation of Hg isotopes was evaluated for each step of the separation system. With this separation and pre-concentration system, we were able to obtain high precision measurements of the Hg isotopic composition of MeHg from estuarine sediments containing elevated concentrations of inorganic Hg.

2. Materials and methods

2.1. Sediment collection

Sediment samples for MeHg separation and isotope analysis were collected over five seasons from August 2012 to August 2013 along a salinity gradient (S = 2 to 14) in the Hackensack River estuary and at one site in the Passaic River estuary (S = 6.6), New Jersey, USA (Table S1). Surface sediment (to approximately 10 cm depth) was collected from a small boat using a pole-mounted Ekman grab and subsamples were transferred to 500 mL acid-cleaned glass jars with a stainless steel scoop. Sediment-filled jars were placed in plastic bags and stored on ice immediately after collection and during transport to the laboratory. Sediment samples were stored at 4 °C for no longer than 3 days prior to freeze-drying and extraction. All sampling tools were rinsed with ambient surface water between samples. After sampling, equipment was leached in de-ionized water and tested for mercury carryover. The amount of total Hg in these leachates was typically less than 0.005 ng g^{-1} of Hg in the 100 mL wash.

2.2. Preparation of sediment for Hg and MeHg analysis

Samples for total Hg analysis were prepared by acid extraction according to the appendix to EPA Method 1631B (U.S. EPA, 1999). Approximately 0.5 to 1 g of dry sediment was weighed into glass flasks fitted with Teflon caps. A small volume (10 mL) of a 4:1 mixture of hydrochloric and nitric acids (Trace Metal Grade, Fisher Scientific) was added to each flask and they were then incubated at room temperature for 24 h. Sample digests were preserved with 0.07 N bromine monochloride and diluted to 40 mL with ultra-pure water.

Methylmercury was separated from sediment by distillation according to Horvat et al. (1993). Briefly, 0.5 g of dry sediment was weighed into Teflon distillation vials and 30 mL of ultra-pure water was added. Trace metal grade sulfuric acid and reagent grade potassium chloride were added to final concentrations of 0.8% v/v and 0.2% v/v, respectively. Distillation lines were attached to 50 mL Teflon receiving vessels containing 5 mL of ultra-high purity water and purged with ultra-high purity Ar (60 mL min^{-1}). The distillation was performed at 125 °C in a custom aluminum heating block and was run for approximately 4 h until 75% of the original volume was distilled. Method recovery was tested using a 10 ng g^{-1} MeHgCl spiking solution prepared from a 1 μg g^{-1} stock (Brooks Rand Labs); sediment recovery spikes (2 ng MeHg) ranged between 80 and 110% (mean = 90.6%, 1 SD = 8%, n = 15). While these spiked sediments were used to evaluate MeHg recovery, they were not analyzed for Hg isotopes since they contained too little MeHg. All distillation blanks were below 0.03 ng of Hg per distillate (mean = 0.025, 1 SD = 0.016, n = 16). Relative percent difference was calculated for duplicate samples and averaged 8.4% (n = 47). Samples were analyzed within two days of distillation. For samples with low MeHg concentrations, multiple distillates were pooled.

2.3. Sample analysis and separation

Total Hg was analyzed by tin chloride reduction, cold vapor atomic absorbance spectrometry (CVAAS) according to EPA Method 245.1 using a Hydra AA Mercury Analyzer (Teledyne-Leeman Labs) (U.S. EPA, 1994). A 0.1 to 0.5 mL aliquot of the sediment digest was added to Teflon sample tubes and excess BrCl was reduced with 0.1 mL of 15% (w/w) hydroxylamine hydrochloride (certified ACS grade, Fisher Scientific). Samples were reduced online with 10% (w/w) tin chloride (certified ACS, Fisher Scientific). Method performance was verified using the European Reference Material (ERM) CC580 (estuarine sediment). Our average measured value for ERM CC580 (130 ± 5 μg g^{-1}, n = 6) was within 2% of the certified value (132 ± 3 μg g^{-1}).

Methylmercury was analyzed by cold vapor atomic fluorescence spectrometry (CVAFS) of distillates following isothermal gas chromatographic (GC) separation of ethylated derivatives according to Liang et al. (1994). Distillates (25–30 mL) were added to glass impingers and ethylated with sodium tetraethylborate (8 μg g^{-1} final concentration; Alfa Aesar). Ethylation yields are known to vary with the concentration of tetraethylborate and reaction time (Liang et al., 1994). Since ethylation can cause large mass-dependent fractionation of Hg at yields below 90% (Yang and Sturgeon, 2009), we tested various ethylation reagent concentrations to achieve the highest possible chemical recovery. The efficiency of ethylation was tested by oxidizing a portion of the ethylated and purged distillate with bromine monochloride (2% w/w) for 24 h and measuring total Hg as described above. We found, consistent with Liang et al. (1994), that with 8 μg g^{-1} tetraethylborate, ethylation efficiencies averaged 99 ± 0.3% (n = 12) and the amount of Hg remaining in the impingers was comparable to equipment blanks. Ethylated products were purged from solution with 4.5 L of ultra-high purity nitrogen, collected on 100 mg Tenax TA 60/80 traps (Supelco Analytical), and subsequently introduced into a GC column prepared with 15% OV-3 Chromosorb W-AW 60/80 (Ohio Valley Specialty Chemical).

2.4. Collection of total Hg for Hg isotope analysis

For isotope analysis of total Hg in estuarine sediment, dried sediment samples were weighed into ceramic boats and combusted in a custom made, two-stage furnace as described previously (Gehrke et al., 2011; Tsui et al., 2012). A stream of Hg-free O_2 carried released Hg(0) into an oxidizing trap filled with 24 g of 1% (w/w) potassium permanganate. Samples were analyzed for concentration using a Nippon Instruments MA-2000 CVAAS. Before isotope analysis, samples were reduced with tin chloride and preconcentrated into a smaller potassium permanganate trap (5.5–6.5 g) using Hg-free air with an automatic sample changer (Nippon Instruments, SC-3) to final concentrations of 5 ng Hg g^{-1}.