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The mercury isotope composition of Arctic coastal seawater

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ABSTRACT

For the first time, Hg isotope composition of seawater in the Canadian Arctic Archipelago is reported. Hg was pre-concentrated from large volumes of seawater sampling using anion exchange resins onboard the research vessel immediately after collection. Elution of Hg was performed in laboratory followed by isotope composition determination by multi-collector inductively coupled plasma mass spectrometry (MC-ICP-MS). For comparison, seawater from two stations was shipped to the laboratory and processed within it. Results showed negative mass-dependent fractionation in the range from –2.85 to –1.10‰ for δ^{202}Hg, as well as slightly positive mass-independent fractionation of odd Hg isotopes. Positive mass-independent fractionation of ^{200}Hg was also observed. Samples that were pre-concentrated in the laboratory showed different Hg isotope signatures and this is most probably due to the abiotic reduction of Hg in the dark by organic matter during storage and shipment after sampling. This emphasizes the need for immediate onboard pre-concentration.

1. Introduction

Mercury (Hg) is a global pollutant, which enters the Canadian Arctic Archipelago (CAA) waters through (i) dry and wet deposition from the atmosphere, (ii) influx from adjacent ocean basins and (iii) continental inputs through riverine discharge (AMAP, 2011; Fisher et al., 2012; Kirk et al., 2012; Sonke et al., 2013; Sunderland and Mason, 2007). In its methylated form, Hg is particularly toxic and concentrates in marine organisms with highest levels found in species at the top of the trophic chain, posing ecological threats to top predators, including humans (Mergler et al., 2007; Oostdam et al., 2005). The CAA connects the Arctic Ocean to the Atlantic Ocean (Dickson et al., 2008). In the CAA seawater, exchange between Arctic and Atlantic Oceans takes place through the relatively long channels of the Nares Strait, the Cardigan Strait, and the Lancaster Sound. Although water exchange occurs in both directions, the net average flow of approximately 1.8 Sv/year (Sverdrup/year) is towards the Atlantic Ocean (Dickson et al., 2008). The CAA thus plays an important role in the global cycling of seawater as well as in that of Hg.

Recent developments in Hg isotope ratio measurements show the potential of this technique for the identification of Hg biogeochemical reactions in the environment, as well as for tracing and distinguishing among different sources of Hg (Feng et al., 2010; Foucher et al., 2009; Perrot et al., 2010). Hg isotope ratio measurement could allow a better understanding of Hg biogeochemical cycling in Arctic environment and consequently in establishing policies aiming at minimizing harmful effects of Hg in the Arctic and reduce Hg contamination in the Arctic. Hg isotopes are fractionated during biogeochemical processes due to difference in mass (mass-dependent fractionation, MDF) (Bigeleisen and

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Mayer, 1947; Urey, 1947), as well as due to differences caused by the magnetic isotope effect and nuclear field shift (mass-independent fractionation, MIF) (Bigeleisen, 1996; Schauble, 2007). MIF was first shown to be limited to odd Hg isotopes (Bergquist and Blum, 2007; Bigeleisen, 1996; Schauble, 2007; Zheng and Hintelmann, 2009), but recent results of Hg isotope ratio measurements in precipitation show significant positive MIF for even Hg isotopes also (Chen et al., 2012; Demers et al., 2013; Gratz et al., 2010; Rolison et al., 2013).

Hg isotope ratios in Arctic Ocean water has not been determined yet, mainly due to the relatively low Hg concentrations in Arctic seawater, varying between 0.14 and 2.9 ng/L (Kirk et al., 2008; Wang et al., 2012). To overcome this analytical challenge, a technique for the pre-concentration of Hg on an anion exchange resin, developed by Štrok et al. (2014), was used. This technique utilizes quantitative Hg pre-concentration from large seawater sample volumes (more than 20 L) to gain sufficient mass of Hg for precise Hg isotope measurement using multi-collector inductively coupled plasma mass spectrometry (MC-ICP-MS). Due to the challenges associated with storage and transportation of large volumes of seawater, this procedure was tested in the laboratory to provide reliable Hg isotope ratios results after long-term storage of the anion exchange resin with adsorbed pre-concentrated Hg (Štrok et al., 2014). Consequently, this procedure was deemed to be suitable for Hg pre-concentration immediately after sampling on board research vessels and shipping anion exchange resin columns instead of large volumes of seawater.

The objectives of this study were: (i) to field-test the suitability of this novel procedure to pre-concentrate Hg from seawater on board research vessels and (ii) to acquire first-of-a-kind results for Hg isotope ratios in seawater samples in locations of interest in the CAA. Although the procedure developed by Štrok et al. (2014) was capable of producing reliable results in the laboratory, performing the same procedure under field conditions can be affected by the different laboratory environment resulting in much less control over Hg contamination issues, as well as the limited time available for sample treatment between the sampling stations. These and other limitations of the method can only be assessed by conducting practical fieldwork in order to fully understand the advantages and limitations of the method. In this study, time constraints did not allow onboard pre-concentration for the last two stations (117 and 304, Fig. 1) and water samples collected from those stations were shipped back to the laboratory for pre-concentration. Although the samples pre-concentrated in the laboratory were not collected at exactly the same locations as those pre-concentrated on board to allow direct comparison of different sampling methods, they were used to assess the two methods since there are no known large point sources of Hg that could significantly alter total Hg concentrations, present in those regions. Consequently, it was expected that total Hg concentrations in samples from these two stations would be in the same range as samples from other stations.

The second objective was constrained by the pre-defined route of the ArcticNet 2013 expedition in Baffin

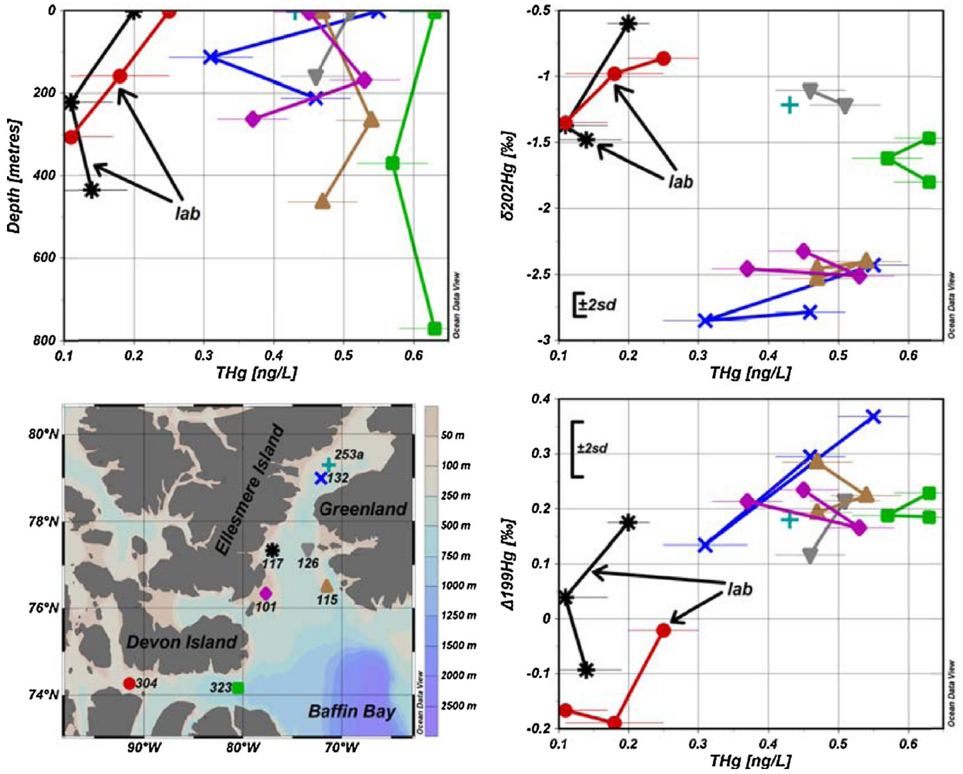

Fig. 1. (Color online.) Seawater sampling sites and results for total Hg concentrations (THg) versus depth, δ^{202}Hg and Δ^{199}Hg with ± 2SD of the UM-Almadén reference solution. Results acquired from samples pre-concentrated in the laboratory are identified by arrows.