



Isotopic evidence for distinct sources of mercury in lake waters and sediments



Jiubin Chen^{a,b,*}, Holger Hintelmann^b, Wang Zheng^c, Xinbin Feng^a, Hongming Cai^a, Zhuhong Wang^a, Shengliu Yuan^a, Zhongwei Wang^a

^a State Key laboratory of Environmental Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences, 99 Linchengxi Road, Guiyang, Guizhou 550081, China

^b Chemistry Department, Trent University, 1600 West Bank Drive, Peterborough, Ontario K9J7B8, Canada

^c Department of Earth Sciences, University of Toronto, Toronto, ON M5S 3B1, Canada

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ABSTRACT

Lakes are important ecosystems where mercury (Hg) may undergo extensive methylation and bioaccumulation in the aquatic food web. It is thus crucial to understand the sources of Hg in lake systems. Mercury isotope composition is a powerful tracer of its sources in the environment. However, previous studies on Hg isotope compositions in lake systems mainly focus on the aquatic organism and sediments, whereas lake water that provides the nutrients for the bottom of aquatic food chain has received much less attention. Here we report Hg isotope compositions in surface water and sediments of 8 freshwater lakes in Ontario, Canada. We determined significantly positive $\Delta^{199}\text{Hg}$ and $\Delta^{200}\text{Hg}$ values in surface water of all lakes, which are similar to previously reported isotope signature of local atmospheric precipitation. In contrast, the isotope compositions of lake sediments show predominantly negative $\Delta^{199}\text{Hg}$ and negligible $\Delta^{200}\text{Hg}$ values that are similar to atmospheric elemental Hg(0) and terrestrial soils and plants. We conclude that the source of Hg in lake surface water is likely dominated by direct atmospheric precipitation, while the Hg in lake sediments is primarily derived from watershed inputs of terrestrial particles. The concurrent odd Hg isotope anomalies in surface waters suggest that methylmercury (MeHg) from the watershed wetland, together with Hg(II) derived from the catchment weathering is likely another Hg source to lake waters besides atmospheric deposition. We suggest that the different Hg sources and isotope compositions between lake water and sediments would result in different isotope signatures for MeHg that is produced in water column and in sediments. Therefore, our study not only elucidates the sources of Hg to lake systems, but also has implications in distinguishing between different MeHg sources and in tracing the bioaccumulation of MeHg in aquatic organism.

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1. Introduction

Mercury (Hg) is a globally-distributed metal pollutant. It is deposited into surface ecosystems after long-range atmospheric transport and may be converted to its most toxic form mono-methylmercury (MeHg) that is effectively bio-accumulated and magnified in aquatic food webs, posing significant threats to human health and aquatic biota. Being an important recipient of atmospheric deposition, aquatic systems play a critical role in the biogeochemical cycle of Hg (Mason et al., 1994; Morel et al., 1998). It is thus crucial to identify the linkage between the sources of Hg in aqueous environments (e.g. lakes) and Hg (mainly MeHg) bioaccumulated in aquatic biota. Although impressive progress has been made recently in understanding many aspects of Hg cycling, including the atmospheric deposition (Kirk et al., 2011;

Muir et al., 2009; Prestbo and Gay, 2009; Selvendiran et al., 2009), transport from land to water reservoirs (Buck et al., 2015; Cohen et al., 2004; Lepak et al., 2015; Meili, 1991), surface-atmosphere exchange (Feng et al., 2004; Lindberg et al., 2002; Poissant and Casimir, 1998; Poissant et al., 2000; Southworth et al., 2007; Zhu et al., 2011), and specie transformation (Amyot et al., 1997; Driscoll et al., 1994; Lindberg et al., 2002; O'Driscoll et al., 2006; Sellers et al., 2001; Ullrich et al., 2001), the sources and mechanisms involved in the aquatic Hg cycling still remain poorly understood (Bergquist and Blum, 2009; Krabbenhoft et al., 2002; Morel et al., 1998; Selin, 2009). For example, among many others, one important puzzling question is why Hg (MeHg) concentrations in most Chinese wild fish are generally lower (e.g. <500 ng/g of ww) than those in USA, Canada and northern European countries (>500 ng/g of ww) (Lin et al., 2012; Lindqvist et al., 1991; Pan et al., 2014; Zhang et al., 2014), given the fact that China has the highest Hg production, consumption and emission in the world (Selin, 2009).

Mercury isotopes are an important tracer for the sources and pathways of Hg in the environment. Recent studies have discovered

* Corresponding author at: State Key laboratory of Environmental Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences, 99 Linchengxi Road, Guiyang, Guizhou 550081, China.

E-mail address: chenjiubin@vip.gyig.ac.cn (J. Chen).

both mass-dependent fractionation (MDF, $\delta^{202}\text{Hg}$) and mass-independent fractionation (odd-MIF as $\Delta^{199}\text{Hg}$ and $\Delta^{201}\text{Hg}$, even-MIF as $\Delta^{200}\text{Hg}$ and $\Delta^{204}\text{Hg}$) for Hg isotopes in natural samples (Bergquist and Blum, 2007; Blum et al., 2013; Demers et al., 2013; Point et al., 2011; Sherman et al., 2010, 2015; Sonke, 2011; Sun et al., 2014). Most Hg transformation processes can induce MDF, and large variations of $\delta^{202}\text{Hg}$ (up to 20‰) have been determined in the nature (Chen et al., 2012; Demers et al., 2013; Feng et al., 2010; Ghosh et al., 2008; Rose et al., 2015; Sherman et al., 2015; Sonke, 2011; Zheng et al., 2015). Interestingly, MIF is only observed in a small number of processes, such as photoreduction, photodemethylation, abiotic dark reduction and evaporation (Bergquist and Blum, 2007; Estrade et al., 2009; Kritee et al., 2008; Zheng et al., 2007; Zheng and Hintelmann, 2010a). Except for photoreduction of thiol-bound Hg, photodegradation and photoreduction produce the most significant MIF that typically enriches odd Hg isotopes in the reactant, and are speculated to be responsible for the significant enrichment of ^{199}Hg and ^{201}Hg widely observed in aquatic biota (e.g., fish) (Bergquist and Blum, 2007; Blum et al., 2013, 2014; Point et al., 2011). However, this hypothesis has not been tested by direct determination of the isotope composition of Hg (and MeHg) in natural lake waters.

Atmospheric deposition is a primary pathway by which Hg enters the terrestrial ecosystems (Mason et al., 1994; Morel et al., 1998; Selin, 2009). Intriguingly, recent work has discovered MIF of even Hg isotopes (even-MIF) mainly in atmospheric samples, adding a new aspect to the Hg isotope systematics (Chen et al., 2012; Demers et al., 2013; Gratz et al., 2010; Huang et al., 2015; Rolison et al., 2013; Wang et al., 2015; Yuan et al., 2015). According to these studies, even-MIF of precipitation displayed an increase with latitude (Wang et al., 2015; Cai and Chen, 2016), with the highest $\Delta^{200}\text{Hg}$ values (up to 1.24‰) found in precipitation from southern Ontario, Canada (Chen et al., 2012). The mechanism of even-MIF is not yet understood (Eiler et al., 2014; Mead et al., 2013), but it has been speculated to result from the photo-related processes occurring in the tropopause (Chen et al., 2012). Though recent studies have observed significant $\Delta^{200}\text{Hg}$ in lake sediments, fish, soils, tree moss and seawater (Štrok et al., 2014; Kwon et al., 2015; Lepak et al., 2015; Cai and Chen, 2016; Zheng et al., in review-a), no data was reported for even-MIF in water samples from continental surface reservoirs.

In this study we measured Hg isotopic composition of surface waters and sediments collected from eight lakes in the central and southern Ontario, Canada (Tables 1 and 2, Fig. 1). Surface waters from three Chinese lakes were also measured for comparison (Table S1, Fig. S1). The objectives are 1) to characterize Hg isotope signatures in surface water and sediment of freshwater lakes; 2) to carry out a comparison between Hg isotope compositions in lake system with the published isotope data for atmospheric Hg deposition and terrestrial solid samples (e.g., soils and plants) and 3) to identify the sources of Hg in water and sediment of Canadian lakes using Hg isotope compositions.

2. Methods

2.1. Reagents and materials

All reagents (HCl, HNO_3 , BrCl, L-cysteine, $\text{NH}_2\text{OH}\cdot\text{HCl}$, SnCl_2) used in this study were analytical grade and prepared under Hg-free condition (Chen et al., 2010, 2012). All vessels were glass- or Teflon- made and cleaned with first BrCl, then HNO_3 and a last rinse of H_2O before use. NIST SRM3133 Hg and UM-Almadén Hg were used as reference standards and measured regularly for quality control (Chen et al., 2010).

2.2. Sampling processes

A total of eleven lakes were chosen for Hg isotope study, with eight headwater lakes in the Dorset and Kawartha forest regions of southern-central Ontario, Canada, on the southern margin of Canadian

Table 1
Lake characteristics, mercury concentration and isotopic compositions in lake and stream waters (ON, Canada).

	Date	T°C	pH	DOC (mg/L)	Hg (ng/L)	Recovery (%)	$\delta^{202}\text{Hg}$ (‰)	$\Delta^{199}\text{Hg}$ (‰)	$\Delta^{200}\text{Hg}$ (‰)	$\Delta^{201}\text{Hg}$ (‰)	$\Delta^{199}\text{Hg}/\Delta^{201}\text{Hg}$	A_c (km ²)	A_0 (km ²)	Latitude (N)	Longitude (W)	Max. depth (m)	Av. depth (m)
Lakes																	
Harp (H1)	10/07/10	25	7.4	4.2	0.98	104	-1.49 ± 0.10	1.00 ± 0.04	0.28 ± 0.03	0.63 ± 0.06	1.73	5.09	0.71	45.23	79.07	37.5	13.3
Harp (H2)	22/09/10	17	7.3	4.3	0.61	96	-1.59 ± 0.10	1.02 ± 0.04	0.18 ± 0.03	0.70 ± 0.06	1.46	5.09	0.71	45.23	79.07	37.5	13.3
Plastic	10/07/10	26	6.6	2.2	0.55	93	-1.96 ± 0.10	1.16 ± 0.04	0.08 ± 0.03	0.65 ± 0.06	1.78	0.89	0.32	45.10	78.48	16.3	8
Fairy	16/07/10	26	7.7	4.4	1.19	96	-1.75 ± 0.10	0.97 ± 0.04	0.18 ± 0.03	0.59 ± 0.06	1.64	46.6	7.12	45.19	79.11	74	22
Dikie	23/09/10	16	6.5	6.1	1.15	93	-1.83 ± 0.10	0.73 ± 0.04	0.13 ± 0.03	0.59 ± 0.06	1.24	4.49	0.94	45.09	79.05	12	5
Stoney	12/07/10	27	8.5	4.6	0.51	95	-1.31 ± 0.10	1.91 ± 0.04	0.26 ± 0.03	0.84 ± 0.06	2.27	167	28.2	44.35	78.30	32	6
Coon	25/09/10	17	7.6	6.0	0.51	97	-1.27 ± 0.04	0.78 ± 0.02	0.21 ± 0.04	0.52 ± 0.11	1.50	2.92	0.53	44.36	78.12	18	2.9
Julian	25/09/10	17	8.2	6.5	0.25	98	-1.73 ± 0.10	0.58 ± 0.04	0.22 ± 0.03	0.47 ± 0.06	1.51	3.24	0.78	44.36	78.09	12	4.8
Moir	27/09/10	18	8.4	6.2	0.28	95	-1.82 ± 0.10	0.95 ± 0.04	0.18 ± 0.03	0.63 ± 0.06	1.91	579	8.7	44.30	77.27	8	3
Stream																	
Stream	23/09/10	13	6.0	3.5	1.04	98	-2.22 ± 0.15	0.21 ± 0.07	0.15 ± 0.05	0.11 ± 0.09							

DOC, dissolved organic carbon; A_c , lake catchment area; A_0 , lake surface area; Max. depth, maximum depth of lake water; Av. depth, average depth of lake water; error bars are 2 σ external standard deviations for samples with multiple measurements, or $\pm 0.10\%$, $\pm 0.04\%$, $\pm 0.03\%$, and $\pm 0.06\%$ for $\delta^{202}\text{Hg}$, $\Delta^{199}\text{Hg}$, $\Delta^{200}\text{Hg}$ and $\Delta^{201}\text{Hg}$ of samples measured only one time. Recovery, the percentage of Hg recovered from the preconcentration (measured by MC-ICP-MS) relative to that of the initial solution (measured on Tekran 2600) for the same sample.

Table 2

Mercury concentrations and isotopic compositions in sediments of eight lakes on the southern margin of Canadian Precambrian Shield (ON, Canada).

	Collection date	Hg (ng/g)	$\delta^{202}\text{Hg}$ (‰)	$\Delta^{199}\text{Hg}$ (‰)	$\Delta^{200}\text{Hg}$ (‰)	$\Delta^{201}\text{Hg}$ (‰)
<i>Lake surface sediments</i>						
Harp	10/07/10	171	-1.24 ± 0.21	-0.21 ± 0.07	0.07 ± 0.09	-0.33 ± 0.03
Plastic	10/07/10	149	-0.95 ± 0.10	-0.29 ± 0.04	0.06 ± 0.03	-0.34 ± 0.06
Fairy	16/07/10	399	-0.56 ± 0.10	-0.05 ± 0.04	0.02 ± 0.03	-0.10 ± 0.06
Dikie	23/09/10	407	-1.01 ± 0.10	-0.07 ± 0.04	0.10 ± 0.03	-0.18 ± 0.06
Stoney	12/07/10	408	-1.20 ± 0.10	-0.16 ± 0.04	0.04 ± 0.03	-0.16 ± 0.06
Coon	25/09/10	175	-0.98 ± 0.04	0.06 ± 0.02	0.09 ± 0.04	-0.02 ± 0.11
Julian	25/09/10	232	-0.78 ± 0.09	0.11 ± 0.02	0.11 ± 0.03	0.07 ± 0.02
Moira	27/09/10	1239	-0.68 ± 0.10	-0.10 ± 0.04	0.05 ± 0.03	-0.10 ± 0.06
<i>Sediment core of the Fairy Lake (sampled on 23/09/10)</i> ³						
FC-1	0 ^a	163	-1.67 ± 0.10	-0.17 ± 0.04	0.05 ± 0.03	-0.15 ± 0.06
FC-2	-2.8^a	291	-0.88 ± 0.10	-0.07 ± 0.04	0.05 ± 0.03	-0.12 ± 0.06
FC-3	-5.6^a	296	-0.49 ± 0.10	-0.08 ± 0.04	-0.02 ± 0.03	-0.04 ± 0.06
FC-4	-8.4^a	415	-0.76 ± 0.06	-0.07 ± 0.04	0.02 ± 0.03	-0.05 ± 0.06
FC-5	-9.8^a	430	-0.64 ± 0.10	-0.03 ± 0.04	0.04 ± 0.03	-0.08 ± 0.06
FC-6	-11.2^a	296	-0.90 ± 0.10	-0.02 ± 0.04	0.04 ± 0.03	-0.11 ± 0.06
FC-7	-14^a	404	-0.66 ± 0.10	-0.05 ± 0.04	0.04 ± 0.03	-0.03 ± 0.06
FC-8	-16.8^a	156	-1.07 ± 0.10	-0.17 ± 0.04	0.03 ± 0.03	-0.19 ± 0.06
FC-9	-19.6^a	53	-1.44 ± 0.10	-0.26 ± 0.04	0.05 ± 0.03	-0.21 ± 0.06
FC-10	-22.4^a	109	-1.80 ± 0.15	-0.43 ± 0.09	0.00 ± 0.02	-0.48 ± 0.05
FC-11	-25.2^a	95	-1.59 ± 0.10	-0.45 ± 0.04	0.02 ± 0.03	-0.51 ± 0.06
FC-12	-28^a	121	-1.85 ± 0.10	-0.24 ± 0.04	0.07 ± 0.03	-0.36 ± 0.06

Error bars are 2σ external standard deviations for samples with multiple measurements, or $\pm 0.10\%$, $\pm 0.04\%$, $\pm 0.03\%$, and $\pm 0.06\%$ for $\delta^{202}\text{Hg}$, $\Delta^{199}\text{Hg}$, $\Delta^{200}\text{Hg}$ and $\Delta^{201}\text{Hg}$ of samples measured only one time.

^a Depth in centimeter.

Precambrian Shield (Supplemental materials S1 and Fig. 1) and three lakes in China (Supplemental materials S1 and Fig. S1). Canadian lake surface water samples were collected between July and September 2010 in the center (thus the deepest place) of each lake to avoid the impact of shore input and sediments on Hg budget and isotopic composition (Dove et al., 2012), except for the Moira Lake that is a sluicing lake with very shallow water depth (average 3 m) and short mean water residence time (approximately 0.34 year) (Zheng et al., 2003). An input stream water sample was also collected on the Harp Lake catchment. Due to the low Hg concentration (several ng/L), a large volume of water (varying from 12 to 20 L) was pumped 2 m below the surface through a Teflon tube into a pre-cleaned 12 L (or 20 L) glass container. Harp Lake was sampled twice (H1 and H2, Table 1). Samples were filtered immediately after collection using a four-stage PFA filter system (Savillex) with a final 0.45 μm mixed cellulose membrane filter. Thereafter, the Hg in lake and stream samples refers thus to the total dissolved Hg, including both inorganic (e.g. Hg(II)) and organic (e.g. MeHg) phases. The blank of the whole filtration system is 16 pg Hg ($n = 5$). After filtration, water was acidified with HCl (0.1 M), digested with 0.5% BrCl (0.2 M) and stored at 4 °C until use (Chen et al., 2012). Surface sediments were also sampled from each Canadian lake using a gravity corer to make a comparison with water sample. A sediment core of 30 cm length was also collected from the Fairy Lake in order to evaluate temporal variation of Hg isotopic composition. The core was sectioned into 12 slices. All sediment samples were dried at 45 °C, powdered and digested using HNO₃–HCl mixture for Hg concentration and isotope measurement (Feng et al., 2010). Hg concentration was measured by atomic fluorescence spectrometry (Tekran 2600) (Chen et al., 2012). Dissolved organic carbon (DOC) was measured for water samples on TOC-V_{CSH} (Shimadzu) (Dillon and Molot, 1997a).

2.3. Pre-concentration of Hg

Hg was pre-concentrated from the aqueous matrix using a chromatographic glass column charged with 0.5 mL AG 1 \times 4 resin. The detail of the procedure was described in Chen et al. (2010). The method was carefully validated by testing both synthetic and natural solutions (column-cleaned Hg-free river water spiked with Hg standard) of varying concentrations. Long-term tests with NIST 3133-spiked samples

showed that the recovery of this method was about $101 \pm 6\%$ ($n = 17$), and identical Hg isotope ratio ($\delta^{202}\text{Hg}$ of $0.00 \pm 0.12\%$) to the initial solution, suggesting that no isotopic fractionation was induced using this method (Chen et al., 2010). In brief, after cleaning with L-cysteine (0.05%), 4 M HNO₃ and H₂O, the column was conditioned with 0.1 M HCl. The HCl-acidified water samples were neutralized for excess BrCl using NH₂OH·HCl (0.05%) and then loaded into the column. The loading flow rate of on average 3.5 mL/min was controlled by a peristaltic pump. After rinsing with 10 mL 0.1 M HCl, Hg was finally eluted with 10 mL 0.5 M HNO₃ containing 0.05% L-cysteine. The blank of the whole pre-concentration process (including BrCl and NH₂OH·HCl addition) is about 20 pg Hg, much lower than the total sample Hg mass (>5 ng) obtained for isotope analysis (Chen et al., 2010). The final solution of this process was again treated with BrCl to remove the excess of L-cysteine prior to the Hg isotope ratio measurement. Hg concentration (measured by MC-ICP-MS) of the final pre-concentration solution was compared to that measured by Tekran 2600, no significant difference was found within analytical uncertainty (<10% for Hg concentration) (Table 1).

Since a large volume of dilute lake water (up to 20 L) was needed and a long time (several days) was required for such large amounts of water to pass through the column to accumulate a sufficient mass of Hg for a precise isotope measurement, except for the Coon Lake sample that was measured twice, other lake water samples were only measured once.

2.4. Hg isotope ratio analysis

Hg isotope measurements were performed on a Neptune MC-ICP-MS (Thermo-Fisher, Germany) at Trent University and the technique was detailed in (Chen et al., 2010). Briefly, the pre-concentrated Hg solution was diluted to Hg concentrations between 0.5 (for samples with very low Hg concentration) and 2 $\mu\text{g/L}$ and introduced into the plasma using a cold-vapor generation system, where the SnCl₂ reducing reagent was mixed in-line with Hg solution to generate volatile elemental Hg. TI aerosol was simultaneously introduced into the plasma using an Apex Q Desolvation system (Elemental Scientific Inc.) for instrumental mass bias correction. The Faraday cups were set to measure five Hg isotopes and two TI isotopes. ¹⁹⁶Hg and ²⁰⁴Hg were not measured due to either the very low abundance or the instrument design limitation, though



Fig. 1. Map of eight lakes from the Canadian Precambrian Shield region. The description of the lakes and the sampling is detailed in the text and in the Supplementary materials S1.

the measurement of these two isotopes might be helpful for better understanding Hg isotope systematics (Chen et al., 2012). The typical ion beam intensity of ^{202}Hg was about 2 V for 2 $\mu\text{g/L}$ Hg concentration. The instrumental mass bias was corrected using the modified empirical external normalization (MEEN) method (Chen et al., 2010) that was proved to be more efficient than the simple sample-standard bracketing (SSB) and TI normalized sample-standard bracketing (NSSB) methods (Chen et al., 2010). The MDF of Hg isotope was expressed in delta notation ($\delta^{202}\text{Hg}$, in ‰) as defined by following equation (Blum and Bergquist, 2007):

$$\delta^{202}\text{Hg} = \left(\frac{(^{202}\text{Hg}/^{198}\text{Hg})_{\text{sample}}}{(^{202}\text{Hg}/^{198}\text{Hg})_{\text{std}}} - 1 \right) \times 1000 \quad (1)$$

where “std” represents the international standard NIST SRM 3133 Hg, which was matrix- and Hg concentration-matched to and was measured as bracketing standards for each sample. MIF of both odd and even Hg isotopes was defined by the deviation from the theoretically predicted MDF and was expressed as (in ‰):

$$\Delta^{199}\text{Hg} = \delta^{199}\text{Hg} - 0.252 \times \delta^{202}\text{Hg} \quad (2)$$

$$\Delta^{200}\text{Hg} = \delta^{200}\text{Hg} - 0.502 \times \delta^{202}\text{Hg} \quad (3)$$

$$\Delta^{201}\text{Hg} = \delta^{201}\text{Hg} - 0.752 \times \delta^{202}\text{Hg} \quad (4)$$

The repeated measurements ($n = 53$) of UM-Almadén Hg gave a long-term average $\delta^{202}\text{Hg}$ value of $-0.56 \pm 0.10\%$ (with $-0.52 \pm 0.14\%$ and $-0.57 \pm 0.10\%$ for measurements at Hg concentration of 0.5 and 2 $\mu\text{g/L}$, respectively), consistent with previous reported values (Bergquist and Blum, 2007; Blum and Bergquist, 2007). Measurements of UM-Almadén Hg at 0.5 $\mu\text{g/L}$ concentration gave identical result to those with Hg of 2 $\mu\text{g/L}$. The uncertainties of UM-Almadén (2 standard deviations, 2σ) were 0.10‰, 0.04‰, 0.03‰ and 0.06‰ for $\delta^{202}\text{Hg}$, $\Delta^{199}\text{Hg}$, $\Delta^{200}\text{Hg}$ and $\Delta^{201}\text{Hg}$, respectively, and were considered as the typical external uncertainties for all water samples that were measured only one time, due to limited sample volume. For sediment samples, the uncertainty was calculated as the 2σ external standard deviations of multiple measurements (Table 1).

3. Results and discussion

3.1. Sources of Hg to Canadian lake surface waters

Numerous studies have investigated the potential provenances of Hg in lake waters based on the concentration, speciation, enriched-spike addition and mass balance model (Ethier et al., 2008; Hintelmann et al., 2002; Leermakers et al., 1996; Mierle, 1990; Watras et al., 1996; Zhang

et al., 2012), and showed that lake Hg might derive from variable sources such as precipitation, surface stream, groundwater and anthropogenic input. Here we try to identify the sources to Hg in surface waters of 8 Canadian lakes using Hg isotopic data set.

3.1.1. Atmospheric precipitation as major source

According to previous studies on Hg flux to lakes, the atmospheric deposition (both precipitation and dry deposition) may be the main sources to Hg in lake system (Cohen et al., 2004; Hintelmann et al., 2002; Watras et al., 1996; Wiener et al., 2006). In this study, all lake water samples show significantly negative MDF ($\delta^{202}\text{Hg} = -1.64 \pm 0.48\text{‰}$, 2SD, $n = 9$) and positive MIF for both odd and even Hg isotopes ($\Delta^{199}\text{Hg} = 1.01 \pm 0.76\text{‰}$; $\Delta^{200}\text{Hg} = 0.19 \pm 0.12\text{‰}$, respectively, 2SD, $n = 9$). These isotopic characteristics are similar to those reported for atmospheric precipitation samples collected to date in both North America and Asia, which have predominantly negative $\delta^{202}\text{Hg}$ ($-0.57 \pm 1.29\text{‰}$, 2SD, $n = 88$), positive $\Delta^{199}\text{Hg}$ ($0.42 \pm 0.64\text{‰}$, 2SD, $n = 88$) and $\Delta^{200}\text{Hg}$ ($0.22 \pm 0.46\text{‰}$, 2SD, $n = 84$) (Chen et al., 2012; Demers et al., 2013; Gratz et al., 2010; Sherman et al., 2012; Wang et al., 2015; Yuan et al., 2015). Based on the comparison of Hg isotope compositions, particularly MIF, between lake water and potential sources of the region, we propose that atmospheric precipitation is the major source of Hg to lake surface water (see discussion below).

To our knowledge, this study reports for the first time significant MIF of ^{200}Hg isotopes ($\Delta^{200}\text{Hg} = 0.19\text{‰} \pm 0.12, 2\sigma$) in Canadian lake surface water samples (Table 1, Fig. 2). In contrast to widely-reported and well-established processes generating MIF of odd Hg isotopes, the mechanisms and processes triggering even-MIF remain unclear (Eiler et al., 2014; Cai and Chen, 2016). Chen et al. (2012) proposed that even-MIF is likely triggered by photo-initiated oxidation of gaseous elemental Hg(0) in the upper atmosphere. This may be confirmed by the general increase of $\Delta^{200}\text{Hg}$ in worldwide precipitation with latitude, as the stratospheric intrusion increases with latitude too (Wang et al., 2015; Cai and Chen, 2016), and the fact that even-MIF has been observed mainly in atmospheric samples (e.g. precipitation, Hg(0), particulate bound Hg) (Chen et al., 2012; Demers et al., 2013; Fu et al., 2014; Gratz et al., 2010; Rolison et al., 2013; Wang et al., 2015), with significantly positive $\Delta^{200}\text{Hg}$ for oxidized Hg(II) (mainly in precipitation and particles) but negative $\Delta^{200}\text{Hg}$ (-0.10‰ to 0.00‰) observed for Hg(0) (Chen et al., 2012; Fu et al., 2014; Gratz et al., 2010; Rolison et al., 2013; Wang et al., 2015). Though recent studies also reported even-MIF in terrestrial samples that are directly or indirectly associated with atmospheric deposition (Štok et al., 2014; Kwon et al., 2015; Lepak et al., 2015; Cai and Chen, 2016; Zheng et al., in review-a), the $\Delta^{200}\text{Hg}$ magnitude in these samples is much lower than that (-0.01‰ to 1.24‰) of precipitation samples (Chen et al., 2012; Demers et al., 2013; Gratz et al., 2010; Sherman et al., 2011; Wang et al., 2015). So far, there is no evidence for the occurrence of even-MIF in terrestrial processes (Blum et al., 2014; Eiler et al., 2014). This leads us to propose that even-MIF may behave conservatively in surface ecosystems and thus can be used as a powerful tracer for atmospheric contribution. Although $\delta^{202}\text{Hg}$ ($-0.45 \pm 1.04\text{‰}$, 2SD, $n = 69$) and $\Delta^{199}\text{Hg}$ ($-0.37 \pm 0.63\text{‰}$, 2SD, $n = 69$) of North America precipitation are statistically different from those of lake water samples (ANOVA model, $P < 0.001$), $\Delta^{200}\text{Hg}$ ($0.26 \pm 0.50\text{‰}$, 2SD, $n = 65$) of precipitation is not different from lake water (ANOVA model, $P = 0.347$). This similarity suggests that $\Delta^{200}\text{Hg}$ signatures in lake water are likely derived from the atmosphere and that precipitation is a major Hg source to lake water. Precipitation Hg may be indirectly transported into lakes through watershed streams. For example, the stream sample collected during dry periods has a $\Delta^{200}\text{Hg}$ of 0.15‰ , consistent with the downstream Harp Lake water H2 (0.18‰) collected at the same time (Table 1). However, given the fact that gaseous Hg(0) has generally slightly negative or close to zero even-MIF, the positive $\Delta^{200}\text{Hg}$ values determined in lake waters would suggest that the direct deposition of atmospheric Hg(0) to lake surface is limited, due to probably its low solubility (Morel et al., 1998; Selin, 2009), except if positive even-MIF would be caused during post-depositional processes.

The atmospheric origin of even Hg MIF in lake surface waters is further supported by the positive correlation (ANOVA model, $P = 0.085$, Fig. 3) between $\Delta^{200}\text{Hg}$ in Canadian lake waters and the ratio of catchment area A_c to lake surface area A_0 (A_c/A_0), except for the Moira Lake. The relationship between the recipient area of the atmospheric deposition and the Hg concentrations in lakes was also reported in other studies (Landis and Keeler, 2002; Mason and Sullivan, 1997; Mills et al., 2009; Swain et al., 1992). The lake with the largest A_c/A_0 (7.13) has the highest $\Delta^{200}\text{Hg}$ of 0.28‰ , close to the average value (0.46‰) of local rain samples (Chen et al., 2012). Since the surface processes would not modify (and induce) $\Delta^{200}\text{Hg}$, even-MIF is likely a conservative tracer of atmospheric contribution. The larger the catchment area, the higher the $\Delta^{200}\text{Hg}$, suggesting more contribution of Hg exported to the lake water originating from precipitation onto the catchment. The deviation of the Moira Lake from the linear relationship defined by other lakes (Fig. 3) may be explained by the fact that, the Hg isotopic signature is strongly impacted by resuspended sediments due to its shallow water body (average depth of 3 m) for the whole lake (as seen by the large amount of particles present in the sample), or more likely, the contamination of Hg (with no ^{200}Hg anomaly) from the upstream historic gold mine activities for both lake water and

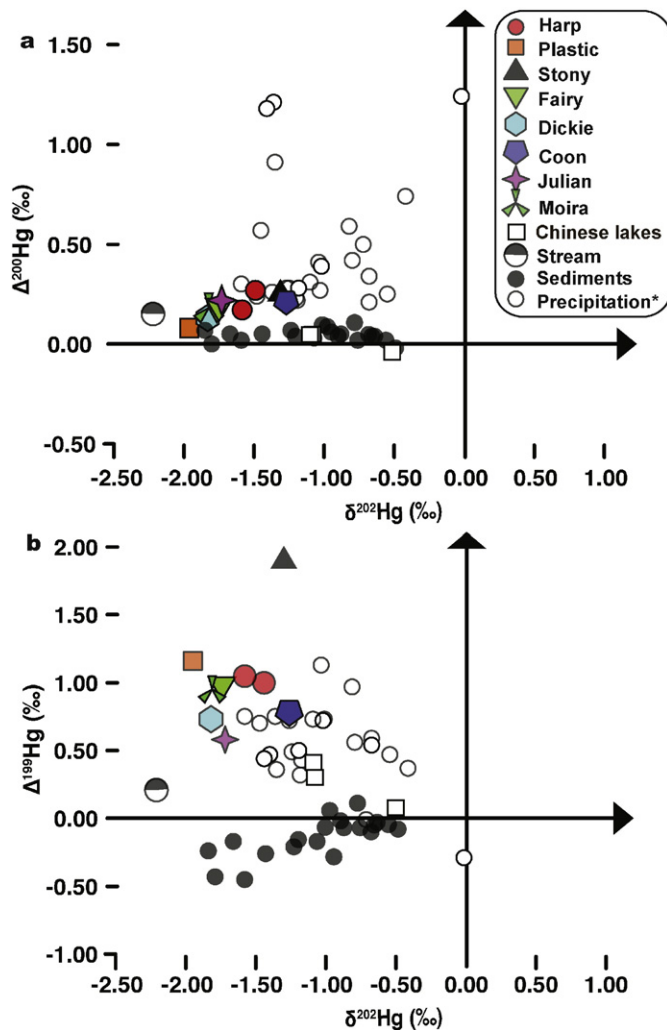


Fig. 2. Mercury isotopic compositions of surface water samples and sediments from eight Canadian Shield lakes (Ontario, Canada) and three Chinese lakes. One stream sample collected in the Harp Lake watershed was also included. Error bars are smaller than the symbols. *data from local precipitation samples reported in Chen et al. (2012) for comparison.

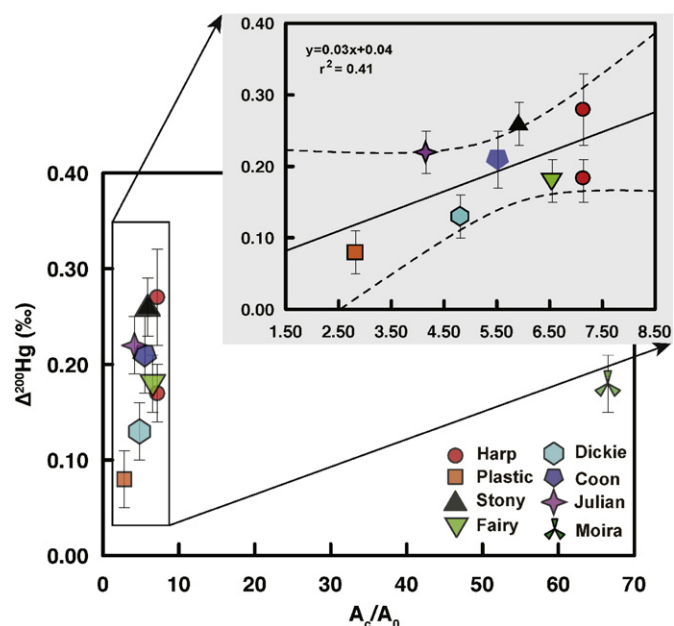


Fig. 3. Relationship between $\Delta^{200}\text{Hg}$ and the ratio of catchment area A_c to lake surface area A_0 (A_c/A_0). Error bars represent the 2σ external standard deviations for the Coon Lake sample that measured twice, or 0.03‰ for $\Delta^{200}\text{Hg}$ of other samples measured only once (see [Methods](#) section). Dashed lines represent the error ellipse on the fit of all data points at a 95% confidential level.

sediments (Zheng et al., 2003), as Hg was used extensively in gold prospecting in order to increase the gold recovery by forming Au–Hg amalgam.

The contribution of wet atmospheric Hg deposition (predominantly via precipitation and surface streams during flood events) to Hg in Canadian lake surface waters can be approximately estimated using the following mixing equation assuming that in-lake processes do not modify even-MIF (Blum et al., 2014). The overall $\Delta^{200}\text{Hg}$ of each lake ($\Delta^{200}\text{Hg}_L$) can be calculated as the following:

$$\Delta^{200}\text{Hg}_L = \chi_A \times \Delta^{200}\text{Hg}_A + \chi_B \times \Delta^{200}\text{Hg}_B \quad (5)$$

where χ_A and χ_B are the proportions of lake water Hg (Hg_L) from direct atmospheric precipitation (A) and the sum of all other Hg sources (streams especially during dry period, groundwater, etc.) that are not directly from atmospheric deposition (B), respectively, with:

$$\chi_A + \chi_B = 1. \quad (6)$$

According to previous studies (see above discussion), $\Delta^{200}\text{Hg}_B$ should be around zero. Taking the average $\Delta^{200}\text{Hg}_A$ value (0.46‰) of the local precipitation (Chen et al., 2012), we estimate that the mean contribution of atmospheric precipitation to the total Hg load in lake waters is about $42\% \pm 26$ (2σ), with a lowest value of 17% for the Plastic Lake, and a highest value of 61% for the Harp Lake. We mention that these values are just an approximate estimation as the calculated results strongly depend on the $\Delta^{200}\text{Hg}_A$ value. The calculation based on the weighted average $\Delta^{200}\text{Hg}_A$ would give more accurate results. However, according to the above discussion (conservative behavior of even-MIF), the accuracy of this calculation may not be influenced by post-depositional processes and lake characteristics. Though long-term monitoring study on Hg isotopes in both lake and watershed samples would give more reliable mass balance, within uncertainties, our calculated values are similar to or slightly lower than those previously reported for lakes of the Canadian Shield region (Harris et al., 2007; Mierle, 1990; Watras et al., 1996). This suggests that even-MIF is a good tracer

of atmospheric wet Hg depositions. Our estimation also suggests that other non-atmospheric Hg inputs (χ_B) may be also significant (around 58%).

Canadian lake waters also exhibit significant positive odd-MIF (a range of 1.33‰ for $\Delta^{199}\text{Hg}$), with the lowest value of 0.58‰ in Julian Lake, and the highest value of 1.91‰ in Stony Lake (Table 1). These values are similar to those of the atmospheric precipitation in North America (Chen et al., 2012; Gratz et al., 2010; Sherman et al., 2011) (Fig. 2b) and previously reported natural river waters (Chen et al., 2010), but contrary to the negative values generally observed for atmospheric Hg(0) and terrestrial samples such as sediments, soils and lichens (Blum et al., 2014; Demers et al., 2013; Sonke, 2011). The first-order information from this odd-MIF similarity between lake water samples and atmospheric precipitation likely supports our earlier argument based on even-MIF that precipitation (rather than atmospheric Hg(0) and terrestrial solid samples) is a major source of Hg in lake surface waters (see also discussion below).

Considering that atmospheric particles may also display positive odd-MIF and even-MIF, we can't exclude the direct or indirect (through streams) contribution of Hg released from atmospheric particulate deposition to Hg in lake surface waters.

3.1.2. Possible effect of in-lake processes

The statistically different $\delta^{202}\text{Hg}$ and $\Delta^{199}\text{Hg}$ between precipitation and lake water can be caused by either isotope fractionation processes within lake water or by additional Hg sources that are not discussed above. Lake water samples generally show higher $\Delta^{199}\text{Hg}$ and lower $\delta^{202}\text{Hg}$ than precipitation (Table 1 and Fig. 2). One possibility is that the current published isotope data of precipitation (and also the lake waters analyzed in this study) may be not fully representative of its heterogeneity. Alternatively, the higher $\Delta^{199}\text{Hg}$ in lake water could be caused by in-lake isotope fractionations (e.g., photochemical transformations, dark reduction and oxidation). Mercury in lake surfaces could undergo significant photoreduction and photodemethylation (Chandan et al., 2014; Garcia et al., 2005; Harris et al., 2007; Jeremiason et al., 2015; Lalonde et al., 2004; O'Driscoll et al., 2006; Poste et al., 2015; Rose et al., 2015). Experimental studies on aqueous photoreduction and photodemethylation in the presence of natural organic matter found that these processes generally enrich odd Hg isotopes (^{199}Hg and ^{201}Hg) in the residual Hg(II) and MeHg pools (Bergquist and Blum, 2007; Zheng and Hintelmann, 2009, 2010a). Although reversed odd-MIF (depletion of odd isotopes in residual Hg(II) phase) has been demonstrated in laboratory experiments of photoreduction of thiol-bound Hg(II) and in photoreduction of Hg(II) on snow (Sherman et al., 2010; Zheng and Hintelmann, 2010a), we argue that these are unlikely major processes in lake water, because 1) the experimental study by (Zheng and Hintelmann, 2009) on Hg(II) photoreduction in natural Ontario lake water found predominantly positive odd-MIF; 2) the lakes in this study are not significantly affected by snow probably due to the re-emission (even partially) of Hg by sunlight-initiated Hg(II) reduction on snow (Lalonde et al., 2003), otherwise the lake surface waters largely impacted by snow or winter samples with relatively higher $\Delta^{200}\text{Hg}$ (up to 1.24‰, Chen et al., 2012) would lead to much higher even-MIF. In fact, the positive $\Delta^{199}\text{Hg}$ reported in Chen et al. (2012) for the compacted surface snow on Greenland (that was collected in summer and thus represented an entire year of snowfall) supports this argument. Dark reduction (both abiotic and biotic) and oxidation are unlikely the major cause of the higher $\Delta^{199}\text{Hg}$ in lake water, because based on experimental studies, these processes either produce no MIF or negative MIF in the residual Hg pool in lake water (Kritee et al., 2008; Kritee et al., 2013; Zheng and Hintelmann, 2010b; Zheng et al., in review-b). However, in contrast to $\Delta^{199}\text{Hg}$, the lower $\delta^{202}\text{Hg}$ in lake water cannot be explained by in-lake photochemical processes as these processes should produce higher (more positive) $\delta^{202}\text{Hg}$ in the residual Hg in lake water, which is opposite to our observation. Most other transformation processes that

result in Hg loss, such as microbial reduction, abiotic dark reduction and volatilization, also preferentially remove lighter isotopes and thus should leave higher $\delta^{202}\text{Hg}$ in the residual Hg in lake water (Estrade et al., 2009; Kritee et al., 2007; Zheng and Hintelmann, 2010b). Aqueous oxidation of Hg(0) also enriches heavier isotopes in the oxidized Hg(II) phase (thus higher $\delta^{202}\text{Hg}$) (Zheng et al., in review-b). Therefore, the offsets in $\Delta^{199}\text{Hg}$ and $\delta^{202}\text{Hg}$ between lake water and precipitation are unlikely solely caused by in-lake processes, but may require additional Hg inputs to lake surface water other than direct atmospheric precipitation.

3.1.3. Necessary contribution of watershed MeHg

The above argument on additional Hg inputs is further supported by the $\Delta^{199}\text{Hg}/\Delta^{201}\text{Hg}$ linear regression slope across all Canadian lakes. Surface water samples of all Canadian lakes display the individual $\Delta^{199}\text{Hg}/\Delta^{201}\text{Hg}$ ratio ranges from 1.23 to 2.27 (Fig. 4 and Table 1), and a linear relationship between $\Delta^{199}\text{Hg}$ and $\Delta^{201}\text{Hg}$ with a slope of 3.32 ± 0.49 (1σ , $P < 0.02$, ANOVA model), despite the wide variation of lake characteristics (e.g., catchment area, pH, DOC, alkalinity, vegetation, etc.). The fact that this line intercepts the $\Delta^{199}\text{Hg}/\Delta^{201}\text{Hg}$ of 1:1 line at a $\Delta^{199}\text{Hg}$ of 0.50‰, the average value of local precipitation samples (Chen et al., 2012), may confirm again the precipitation as a main source to Hg in lake surface waters. The linear relationship between $\Delta^{199}\text{Hg}$ and $\Delta^{201}\text{Hg}$ has been widely used to identify the processes that control the odd-MIF. Experimental work has shown that photodemethylation of MeHg typically produces a $\Delta^{199}\text{Hg}/\Delta^{201}\text{Hg}$ slope of 1.36 ± 0.02 (Bergquist and Blum, 2007). Photoreduction of inorganic Hg(II) typically produces lower $\Delta^{199}\text{Hg}/\Delta^{201}\text{Hg}$ slopes from 1.0 to 1.3 depending on Hg/DOC ratios (Bergquist and Blum, 2007; Zheng and Hintelmann, 2009). Abiotic dark reduction of Hg(II), evaporation and equilibrium processes produce a typical slope of ~ 1.6 (Ghosh et al., 2005; Wiederhold et al., 2010; Zheng and Hintelmann, 2010b). Please note that with the current understanding on Hg isotope systematics and our current data, it is not possible to determine if the linear $\Delta^{199}\text{Hg}/\Delta^{201}\text{Hg}$ relationship across all lakes is just coincidental or actually a signature imparted by common processes or common Hg

sources to all lakes. However, since both the $\Delta^{199}\text{Hg}/\Delta^{201}\text{Hg}$ slope and individual $\Delta^{199}\text{Hg}/\Delta^{201}\text{Hg}$ ratios of lake water samples are higher than experimental values and those reported to date for most terrestrial and atmospheric samples (e.g., soils, plants, sediments, atmospheric Hg(0) and Hg(II)) (Bergquist and Blum, 2007; Biswas et al., 2008; Blum et al., 2014; Demers et al., 2013; Rolison et al., 2013; Sonke, 2011), we argue that the $\Delta^{199}\text{Hg}/\Delta^{201}\text{Hg}$ slope and individual ratios of lake water are unlikely caused by one single process or one single Hg source.

Although speculative, we hypothesize that the unusually high $\Delta^{199}\text{Hg}/\Delta^{201}\text{Hg}$ of Canadian lake water is caused by the mixing of different Hg pools with variable $\Delta^{199}\text{Hg}/\Delta^{201}\text{Hg}$ ratios (to explain the $\Delta^{199}\text{Hg}/\Delta^{201}\text{Hg}$ variation), of which Hg has undergone different types of photochemical processes. Based on the above discussion, we propose an isotopic binary mixing model between partially photoreduced Hg(II) (mainly from precipitation) and partially photodemethylated MeHg (the most possible contribution with positive odd-MIF and high $\Delta^{199}\text{Hg}/\Delta^{201}\text{Hg}$ ratio) as two end members to explain the high $\Delta^{199}\text{Hg}/\Delta^{201}\text{Hg}$ of Canadian lake water (Supplemental materials S2, Fig. 5). As demonstrated by Fig. 5, when the initial odd-MIF value (the starting point of the $\Delta^{199}\text{Hg}/\Delta^{201}\text{Hg}$ regression line) changes, the range of the mixed odd-MIF values between experimental $\Delta^{199}\text{Hg}/\Delta^{201}\text{Hg}$ lines of photoreduction and photodemethylation (the gray area in Fig. 5) also changes. For example, assuming a starting point with a $\Delta^{199}\text{Hg} = -0.60\text{‰}$ and $\Delta^{201}\text{Hg}/\Delta^{201}\text{Hg} = 1.0$ (the most common $\Delta^{199}\text{Hg}/\Delta^{201}\text{Hg}$ found in most natural abiotic samples), the mixed values between Hg(II) after partial photoreduction and MeHg after partial photodemethylation (gray area in Fig. 5) encompasses the data of most lake surface water samples (except Stony lake) (Fig. 5), suggesting that the mixing of Hg(II) and MeHg that have undergone different photochemical reactions is at least one probable explanation for the observed $\Delta^{199}\text{Hg}/\Delta^{201}\text{Hg}$ in Canadian lake waters. Though choosing the start point with a much lower initial $\Delta^{199}\text{Hg}$ value (e.g. -2.13‰) could also explain the Stony Lake data, we can't exclude the contribution from another unknown process/reaction with relatively high $\Delta^{199}\text{Hg}/\Delta^{201}\text{Hg}$ ratio.

The ensuing question is what are the sources of the partially photodemethylated MeHg? MeHg can be produced from Hg(II) in

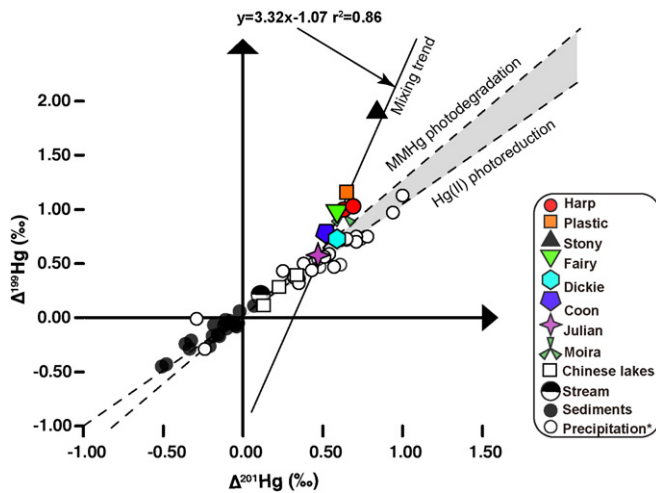


Fig. 4. Relationship between mass-independent fractionation of odd Hg isotopes in lake water, sediment and stream samples. While Chinese lake waters, Canadian lake sediments and stream sample plot on the line with a slope of 1:1, as defined by the local precipitation samples (Chen et al., 2012), all Canadian lake waters define a line with a relatively higher slope of 3.32, intercepting with the 1:1 line at an $\Delta^{199}\text{Hg}$ of about 0.50‰, the average $\Delta^{199}\text{Hg}$ of the local precipitation samples, indicating the important contribution of atmospheric precipitation to Hg in lake waters. The in-lake processes would induce $\Delta^{199}\text{Hg}/\Delta^{201}\text{Hg}$ ratios between 1 and 1.35, much lower than 3.32 and those of most Canadian lake samples. Watershed methylmercury (MeHg) is likely another source to explain Hg isotope data in Canadian lakes. Error bars are smaller than the symbols.

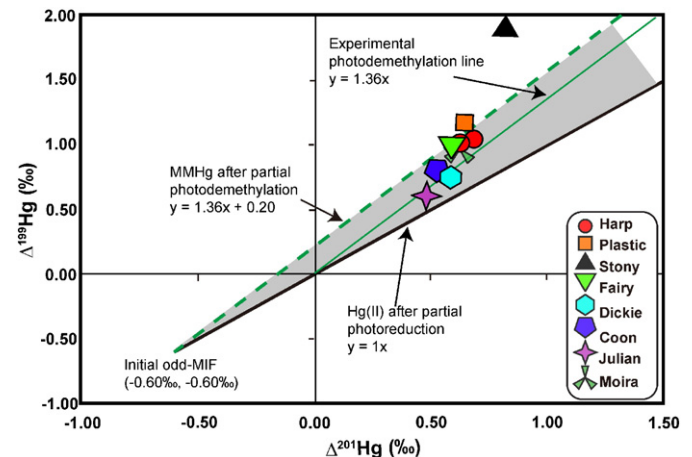


Fig. 5. Illustration of the mixing model for explaining $\Delta^{199}\text{Hg}/\Delta^{201}\text{Hg}$ relationship of lake surface waters in Canada. In addition to precipitation, watershed MeHg after partial photodemethylation (the green dashed line, see calculation in Supplemental materials S2) is likely an additional contributing source of Hg in Canadian lake waters. The typical value of -0.6‰ reported for terrestrial Hg such as soils, sediments and vegetation was chosen as the initial odd-MIF. The gray area that represents mixed values of partially photoreduced Hg(II) (black solid line) and partially photodemethylated MeHg (green dashed line) encompasses most surface water samples, suggesting that the MIF of these samples can be probably explained by the mixing model.

both water column (thus having positive odd-MIF) and sediment (with close to zero odd-MIF, see Section 3.2) (Eckley and Hintelmann, 2006; Krabbenhoft et al., 2002; Morel et al., 1998). However, according to our calculation (Supplemental materials S2), photodemethylation of these in-situ MeHg having positive or zero initial odd-MIF would not be able to produce the MeHg end member line of the mixing model, which requires negative initial odd-MIF for the MeHg end member. Therefore, in-situ MeHg would not explain the observed $\Delta^{199}\text{Hg}/\Delta^{201}\text{Hg}$ relationship of lake water samples, and external MeHg sources are needed. The direct atmospheric MeHg deposition is unlikely the major external MeHg source because it contributes only a small proportion to the total Hg budget (generally less than 5%) (Branfireun et al., 1996). Instead, we propose that MeHg produced in watersheds is likely the major source of the MeHg end member for the mixing model. The forested watersheds studied here are covered with different proportions of wetlands (Dillon and Molot, 1997b; Evans, 1986; Kwon et al., 2012; St. Louis et al., 1994), which are principal zones of MeHg production and are typically considered as important sources of MeHg to aquatic systems (up to 20% of total Hg export) due to the relatively high MeHg content (Bradley et al., 2012; Brown et al., 2007; Guentzel, 2009; Hall et al., 2008; Maruszczak et al., 2011; Selvendiran et al., 2008; Tjerngren et al., 2012; Tsui et al., 2013). Given the longer residence time for Hg species in the watershed (around 1 yr) compared to lake waters (several months) (Hines and Brezonik, 2007; Mason and Sullivan, 1997; Selvendiran et al., 2009), we can reasonably assume that MeHg produced in the watersheds could have undergone significant photodemethylation before exporting to lakes (Chandan et al., 2014; Hall et al., 2005; Tsui et al., 2013). Since photodemethylation has much higher fractionation factors of MIF than photoreduction (Bergquist and Blum, 2007), the MeHg from wetlands (and also upland forest) may contain a much higher odd-MIF signature than Hg(II) in lake waters. Thus, even a small contribution of watershed MeHg may largely increase the overall odd-MIF of Hg and thus modify the $\Delta^{199}\text{Hg}/\Delta^{201}\text{Hg}$ slope in lake waters.

It is interesting to note that the $\Delta^{199}\text{Hg}$ and $\Delta^{201}\text{Hg}$ of lake surface waters can only be encompassed by the mixing model when the initial odd-MIF of MeHg is significantly negative (i.e., $\sim -0.6\%$ according to our calculation) (Fig. 5). The negative initial odd-MIF suggests that the watershed MeHg was not synthesized directly from atmospheric precipitation (which has positive odd-MIF), but rather from other Hg pools with negative odd-MIF, such as atmospheric Hg(0) or terrestrial soils and vegetation (Biswas et al., 2008; Blum et al., 2014; Demers et al., 2013). A recent study on Hg isotopes in peat bogs showed that atmospheric Hg(0) is the dominant source (up to 80%) of Hg in sphagnum thus in such wetland (Enrico, 2015). This is likely the reason why the Northern Hemisphere peatlands are generally characterized by negative $\Delta^{199}\text{Hg}$ (down to -0.54%) (Enrico, 2015). Recent studies on Hg isotope compositions in North American forest systems have shown that soils and vegetation also display primarily negative $\Delta^{199}\text{Hg}$ (approximately -0.50% to 0.00%) as a result of dominant atmospheric Hg(0) input to forest and other surface ecosystems (Demers et al., 2013; Enrico, 2015; Zheng et al., in review-a). Hg of these materials may be methylated in wetland (Jeremiason et al., 2006) and the formed MeHg should have negative $\Delta^{199}\text{Hg}$ since no significant MIF was reported to be induced during methylation according to previous studies (Blum et al., 2014; Kritee et al., 2013). As a result, watershed MeHg would initially have negative odd-MIF, and MeHg from catchment wetland that experience partially photodemethylation is likely another contributing source to Hg in lake surface water. However, given the high even-MIF in lake water, this source may be not dominated (see above discussion).

Watersheds may also contribute inorganic Hg(II) to lake waters. These watershed Hg(II) may be derived from the atmospheric precipitation, the photodemethylation (direct Hg(II) product or possible re-oxidized Hg(0) product), or from other pools such as soil (and rock) weathering and vegetation release (Ethier et al., 2008; Demers et al., 2013; Jiskra et al., 2015; Mierle, 1990). Precipitation Hg(II) is expected

to have a similar $\Delta^{199}\text{Hg}/\Delta^{201}\text{Hg}$ pattern (1:1 ratio) as lake water Hg(II), since both are primarily subject to similar photoreduction processes. Although Hg(II) originated from the photodemethylation would have also a same $\Delta^{199}\text{Hg}/\Delta^{201}\text{Hg}$ of 1.36, the opposite fractionation (negative or comparably lower $\Delta^{199}\text{Hg}$) may indicate a limited contribution (see above discussion). According to the previous studies, Hg(II) derived from two other pools would be characterized by negative (foliage, litterfall) or close to zero (soil or rock weathering) $\Delta^{199}\text{Hg}$ values, and a $\Delta^{199}\text{Hg}/\Delta^{201}\text{Hg}$ ratio of about 1:1 (Blum et al., 2014; Demers et al., 2013; Jiskra et al., 2015). Therefore, these Hg(II) input could eventually contribute to lake water Hg budget (explaining the lower $\Delta^{199}\text{Hg}$ and $\Delta^{200}\text{Hg}$ values than precipitation), but could not explain the observed odd-MIF variation of lake waters (Supplemental materials S2). Considering all above discussion, the stream input Hg would be already a mixture of partially photoreduced Hg(II) and photodemethylated MeHg. The fact that the stream water collected on the Harp Lake catchment has relatively higher $\Delta^{199}\text{Hg}/\Delta^{201}\text{Hg}$ ratio (about 1.90, Table 1) confirms again the above conclusion, and the particular contribution of watershed MeHg.

We should mention here that, given the residence time (up to 6 months) of Hg in small to moderate lakes (Hines and Brezonik, 2007; Selvendiran et al., 2009), the result obtained here may be still valid for a relatively long period, as demonstrated by the similar Hg isotope composition in two Harp Lake samples collected at different dates (Table 1). We would like to highlight that this is the first study characterizing Hg isotopic compositions in dilute lake waters, though the above conclusion was obtained based on a limited number of samples and our current knowledge of the Hg isotope systematics. Future studies that include Hg isotopes and Hg speciation in watershed should be carried out to fully test the above hypothesis. Though isotopic composition of MeHg in watershed streams would give direct evidence for our mixing model, we are actually not able to measure specific isotopic composition of MeHg in water samples at this stage. The method developed by Janssen et al. (2015) for sediment can't be directly applied to water MeHg due to the very low concentration. Moreover, although we cannot exclude other terrestrial inputs to lake waters, these contributions are likely characterized by low or zero MIF of odd and even Hg isotopes (Demers et al., 2013; Jiskra et al., 2015), because they are strongly impacted by local geological background. For the same reason, these inputs are also deemed to be insignificant and were not considered as a major source of Hg to lake surface waters.

3.2. Sources of Hg to Canadian lake sediments

The MIF of Hg in lake sediments is decoupled from lake surface waters and the atmosphere (Table 2, Fig. 2). In all lakes, sediment samples including the sediment core samples from Fairy Lake display insignificant even-MIF ($\Delta^{200}\text{Hg}$ from -0.02% to 0.11% , Fig. 2) and mostly negative odd-MIF ($\Delta^{199}\text{Hg}$ from -0.45% to 0.11%). Both $\Delta^{200}\text{Hg}$ ($0.05 \pm 0.06\%$, 2SD, $n = 20$) and $\Delta^{199}\text{Hg}$ ($-0.14 \pm 0.29\%$, 2SD, $n = 20$) of sediment samples are statistically lower than those of lake water (ANOVA model, $P < 0.001$), indicating that lake sediments have different Hg sources from lake water (dissolved total Hg) that receives predominantly direct atmospheric precipitation. The lower $\Delta^{199}\text{Hg}$ values between sediments and lake waters is unlikely caused by in-lake fractionation processes because the principle reaction that produces odd-MIF in lake waters, photoreduction of Hg(II), normally result in more positive $\Delta^{199}\text{Hg}$ in residual Hg(II) that can be scavenged to sediments (Blum et al., 2014; Sonke, 2011; Zheng and Hintelmann, 2009). Moreover, dark reduction of Hg(II) occurring at the lake bottom also cannot explain the negative odd-MIF in sediments, because the $\Delta^{199}\text{Hg}/\Delta^{201}\text{Hg}$ slope defined by all sediments (close to 1, Fig. 4) is distinguishable from the slope (1.5 to 1.6) expected for abiotic dark reduction (Zheng and Hintelmann, 2010b). Given the contrasting odd and even MIF signatures between particles (as found in sediments) and surface waters, the impact of Hg released from sediments (having same MIF as

sediments) would be limited to the dissolved phase. Although the dissolved Hg would be partially adsorbed or incorporated into suspended particles, given the relatively high distribution coefficient K_d of Hg (approx. 4.8–5.7 in logarithm) in lakes (Chadwick et al., 2013; Harris et al., 2007; Mason and Sullivan, 1997; Rolffhus et al., 2003), the impact of dissolved Hg on the isotopic signature of sediments is expected to be very limited too.

Based on the comparison of isotope compositions between sediments and potential terrestrial Hg inputs (e.g., soils and vegetation) (Fig. S2), we propose that the dominant Hg source in surface sediments is most likely associated with the inflow particles from the catchment (e.g. soil weathering and erosion). North American forest soils and vegetation display primarily negative $\Delta^{199}\text{Hg}$ (from -0.58% to -0.16% , average $-0.24 \pm 0.16\%$, 2SD), near zero or slightly positive $\Delta^{200}\text{Hg}$ (from -0.13% to 0.16% , average $0.02 \pm 0.10\%$, 2SD) and negative $\delta^{202}\text{Hg}$ (from -2.53% to -0.74%) (Blum et al., 2014; Carignan et al., 2009; Demers et al., 2013, 2015; Estrade et al., 2010; Sonke, 2011; Zheng et al., in review-a). Both the even-MIF (average $0.05 \pm 0.06\%$) and odd-MIF (average $-0.14 \pm 0.29\%$) of our sediment samples are consistent with forest soils and vegetation (Fig. S2). Moreover, our recent study on Hg isotopes in a Chinese lake system confirms the catchment particles as a main source of Hg in lake sediments (Wang et al., in preparation). Unfortunately, direct catchment particle samples (e.g. soil, organic matters and stream solid) were not collected for this study. Mercury transported by particles is less reactive than Hg in the dissolved phase and thus is more likely to preserve the source isotope signatures (both MDF and MIF). Though more work is needed to investigate the exact proportions of variable sources to Hg in sediments, our study emphasizes the importance of stream particle input to Hg in sediment of lakes with large catchment.

4. Conclusions and implications

In this study, we report Hg isotope compositions in lake surface water across 8 Canadian lakes. We found significant even-MIF ($\Delta^{200}\text{Hg}$) in lake water that is similar to the even-MIF of atmospheric precipitation. Despite the discovery of even Hg isotope anomaly in atmospheric Hg species, even-MIF has rarely been observed in continental water reservoirs. Therefore, this study is the first to report even-MIF in lake systems and provides new isotopic evidence for the major contribution of atmospheric precipitation to Hg in lake surface waters. Moreover, we also observed more positive odd-MIF, more negative MDF ($\delta^{202}\text{Hg}$) and higher $\Delta^{199}\text{Hg}/\Delta^{201}\text{Hg}$ in lake water than in precipitation. These isotopic differences between lake water and atmospheric precipitation cannot be explained by in-lake transformations, but rather suggest that in addition to the major contribution of precipitation to Hg in lake water, catchment input especially MeHg from the watershed is most likely another important source of Hg in lake surface waters.

Mercury isotope compositions in surface sediments from the same lakes are decoupled from the lake waters and thus from the atmosphere. We observed negligible even-MIF and mostly negative odd-MIF in sediments, and attribute this decoupling to different Hg sources between surface sediment and lake waters. By comparing the isotopic signatures of sediment samples with potential terrestrial inputs (e.g., soils and vegetation), we suggest that sediment is dominated by terrestrial Hg inputs that are mainly transported in particulate form, whereas lake water is dominated by dissolved Hg input. This should be taken into account when using sediment cores to reconstruct the paleo-environment. Though the conclusions obtained here from a precise analysis of a limited number of samples need to be confirmed by further studies, our results demonstrate that Hg isotope compositions, particularly MIF, are a powerful tool for differentiating Hg sources and tracing its pathways in the environment.

Our study has potential implications in understanding the sources of MeHg in aquatic systems. MeHg can be produced from both water

column and sediment (Tsui et al., 2013). The different Hg sources and isotope signatures between lake water and sediment determined in this study suggests that MeHg produced in water column would likely have positive odd-MIF and significantly positive even-MIF because MeHg in water column is converted from inorganic Hg(II) whose isotopic signature is primarily imparted by atmospheric precipitation. In contrast, MeHg produced in the sediment may initially inherit the isotope signatures of the sediment with negative odd-MIF and negligible even-MIF. These different isotopic signatures may be transferred to the aquatic organism when these different pools of MeHg are bioaccumulated. This may have potential implication in distinguishing the sources of MeHg bioaccumulated in aquatic food webs, as demonstrated in a recent study (Kwon et al., 2015). However, the isotope compositions of MeHg in aquatic systems can be further modified by in-lake transformations such as photodemethylation and catchment inputs, which may obscure the isotopic differences between different pools of MeHg. Further studies on direct measurements of isotope compositions of MeHg in lake water, sediment and aquatic organisms are needed to test this hypothesis.

The contribution of photodegraded MeHg from watersheds to lake waters as revealed by our preliminary data may also have implications for the bioaccumulation of Hg in aquatic food webs. If our hypothesis about the contribution of watershed MeHg to Canadian lake waters were proven to be true, the wetland (peatland) area would be a critical factor controlling MeHg levels in aquatic organisms (Fig. 6). This may be one possible explanation for the fact that water from three Chinese lakes plot on the $\Delta^{199}\text{Hg}/\Delta^{201}\text{Hg} = 1.0$ line (as defined by the sediments and precipitation) in Fig. 4, clearly different from the Canadian lake water line, because these lakes are not forested lakes and wetlands are rarely present in their catchments (Supplemental materials S1). This may further, at least partially, explain the relatively lower Hg (mostly in MeHg, generally <500 ng/g of wwT of the Food and Agriculture Organization and the World Health Organization guideline) in wild fish in Chinese inland, coastal areas and even on the Tibetan Plateau than in western countries, despite the elevated Hg levels in the environment in China (Fitzgerald and Lamborg, 2003; Krabbenhoft et al., 2002; Lin et al., 2012; Lindqvist et al., 1991; Pan et al., 2014). However, due to the large effort required for sampling and isotope analysis, only a small number of Chinese lakes have been studied so far. Though the fact that, on a national scale, China has the lowest ratio (average 1.52) of natural wetland area to lake surface area compared to the USA (2.07, excluding the Great Lakes), Canada (3.03, excluding the Great Lakes) and Sweden (approximately 2) (Lehner and Doll, 2004, and references therein) coincidentally supports our suggestion, future work that involves nation-wide surveys on Hg isotope compositions in lake waters and aquatic biota is needed to confirm our speculation. Nevertheless, our current isotope data suggest that the watershed likely contributes an important source of MeHg to surface waters and also to aquatic food webs in lake systems and thus should be taken into account in future monitoring studies and for the policy setting with respect to environmental Hg toxicity.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <http://dx.doi.org/10.1016/j.chemgeo.2016.01.030>.

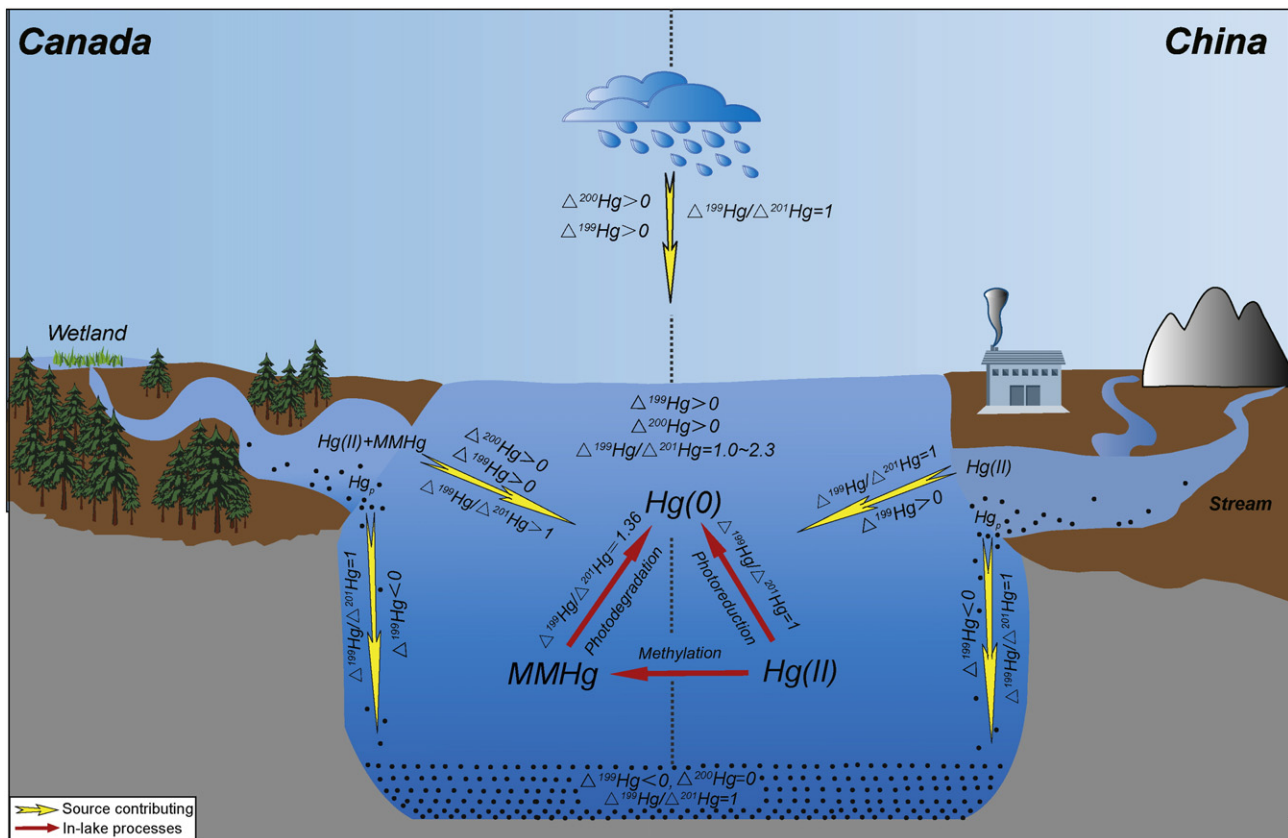


Fig. 6. Conceptual model of different pathways of Hg and its isotopes in Canadian lake systems compared to China. Except for the atmospheric contribution to Hg in lake water as demonstrated by anomalies of both odd ($\Delta^{199}\text{Hg}$) and even ($\Delta^{200}\text{Hg}$) Hg isotopes, the photodemethylated MeHg from the watershed wetland is likely another potential source of Hg in lake water and biota in Canada. The effect of in-lake processes such as photodegradation of MeHg and photoreduction of Hg(II) would be limited. The sediments are isotopically decoupled from the water column and the atmospheric precipitation, and are probably mainly derived from soil weathering products of the catchment. This model may explain, at least partially, why wild fish in China generally have lower Hg (MeHg) levels compared to those in Canada, USA and northern European countries.

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