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ORIGINAL PAPER

# Stratigraphic variations in the $\delta^{201}Hg/\delta^{199}Hg$ ratio of mercury in sediment cores as historical records of methylmercury production in lakes

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**Abstract** Total mercury (Hg) profiles of sediment cores from lakes serve as historical records of Hg pollution. They do not, however, provide information about temporal variations in the abundance of the toxic, preferentially bioaccumulated species methylmercury ($CH_3Hg^+$), whose production rate is largely a function of environmental variables that control the growth and activities of Hg-methylating and Hg-demethylating bacteria and the bioavailability of the inorganic Hg(II) from which $CH_3Hg^+$ is formed. Earlier studies showed that $CH_3Hg^+$ in freshwater food webs had anomalously high $\delta^{201}Hg/\delta^{199}Hg$ ratios and, similarly, that the $\delta^{201}Hg/\delta^{199}Hg$ ratio of Hg in a core from a severely Hg-polluted lake paralleled temporal changes in $CH_3Hg^+$ production. The present study was undertaken to test the hypothesis that variations in the $\delta^{201}Hg/\delta^{199}Hg$ ratios of sediment cores from lakes reflect historical variations in $CH_3Hg^+$ production in the lakes. Core profiles of $\delta^{201}Hg/\delta^{199}Hg$ ratios and total Hg concentrations from three widely separated, environmentally distinct temperate lakes polluted with Hg from different industrial sources, and one practically pristine Arctic lake, were examined, and changes attributable to known historical events were noted. Hg pollution led to increases in the $\delta^{201}Hg/\delta^{199}Hg$ ratio, suggesting enhanced production of $CH_3Hg^+$, but the lakes showed different patterns of variation over time, implying the influence of site-specific environmental and biotic factors. In one lake the $\delta^{201}Hg/\delta^{199}Hg$ ratio increased at the onset of each of three pollution episodes but peaked and then declined, suggesting a surge in methylation that was reversed by demethylation. In another lake, mercury pollution initiated a long-term upward trend in the isotope ratio, with secondary maxima and minima superimposed on it, implying a progressive increase in $CH_3Hg^+$, with successive shorter-term changes caused by fluctuations in methylation and demethylation rates. In the third lake, moderately elevated isotope ratios and one large maximum were associated with Hg contamination, but the maximum is attributable to accelerated eutrophication that intensified $CH_3Hg^+$ production. In the Arctic lake, the isotope ratio varied with climate change, decreasing during warming trends and increasing during cooling phases. These results constitute evidence that $\delta^{201}Hg/\delta^{199}Hg$ ratios of sediment cores from lakes record historical variations in the net rate of $CH_3Hg^+$ production.

**Keywords** Mercury isotopes · Methylmercury production · Lakes · Sediment cores · Stratigraphic records

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## Introduction

Total mercury (Hg) profiles in sediment cores from lakes serve as historical records of Hg pollution (Jackson 1997; Fitzgerald et al. 1998; Lockhart et al. 2000; Biester et al. 2007; Muir et al. 2009; Kirk et al. 2011; Hermanns and Biester 2013; Hermanns et al. 2013), but they do not provide information about temporal variations in the abundance and net production rate of the crucially important Hg species methylmercury ($CH_3Hg^+$), which is produced and decomposed by methylating and demethylating bacteria, respectively, in natural waters and sediments. $CH_3Hg^+$ is of particular concern from an ecological and public health point of view. It is highly toxic, is preferentially accumulated by aquatic food web organisms, and, unlike inorganic Hg(II), undergoes biomagnification from lower to higher trophic levels, comprising the principal form of Hg in the skeletal muscles of fish (Jackson 1998a). Thus, it renders the flesh of many fish, especially those at the upper end of the food web, unsafe for consumption by humans and wildlife.

$CH_3Hg^+$ is produced by methylation of inorganic Hg(II), which is the dominant form of both natural and anthropogenic Hg in sediments, and hence the principal component of the total Hg in core sections. Nevertheless, variations in the total Hg concentration in a sediment core cannot be used to track historical variations in the net rate of $CH_3Hg^+$ production, or even to estimate them, because the kinetics of $CH_3Hg^+$ formation depends not only on the supply of inorganic Hg(II), but also on a multitude of environmental and biotic variables that (1) determine the bioavailability of the inorganic Hg(II) (i.e. its availability for methylation) and (2) control the growth and activities of Hg-methylating and Hg-demethylating bacteria in the environment (Jackson 1998a). Although Hg pollution generally leads to an increase in $CH_3Hg^+$ production, the specific $CH_3Hg^+$ concentrations and rates of $CH_3Hg^+$ production in natural waters and sediments vary, in large part, as functions of factors such as the supply of organic nutrient substrates utilised by different species of Hg-transforming bacteria, ambient conditions (pH, Eh, dissolved $O_2$ concentration, etc.), and the abundances of biogenic sulphides and thiols, which lower the bioavailability of inorganic Hg(II) (Jackson and Woychuk 1980; Jackson 1986, 1988, 1991a, 1993a, b, 1998a, b, 2016; Lambertsson and Nilsson 2006; Meng et al. 2010). The abundance or production rate of $CH_3Hg^+$ in an aquatic or sedimentary environment at any particular time is the *net* effect of these physicochemical and biological factors, which may tend to cancel or reinforce one another's effects and are subject to temporal and spatial variation. Not surprisingly, therefore, $CH_3Hg^+$ concentrations often vary independently of total Hg or inorganic Hg(II) concentrations, and may even be correlated inversely with them, in Hg-polluted lakes and rivers (Jackson and Woychuk 1980; Jackson 1986, 1993a). In brief, the total Hg profile of a sediment core from a lake cannot be used as a record of historical variations in the abundance or production of $CH_3Hg^+$ in the lake. Furthermore, it is doubtful whether $CH_3Hg^+$ analyses of core sections would be helpful, as $CH_3Hg^+$ is labile and is subject to microbial decomposition.

Advances in the biogeochemistry of stable isotopes of Hg, however, have raised the possibility of using stratigraphic variations in the isotope composition of total Hg in sediment cores as proxies for historical changes in $CH_3Hg^+$ abundances and net production rates in aquatic environments. Utilisation of multicollector inductively coupled plasma mass spectrometry (MC-ICP-MS) has demonstrated that both biotic and abiotic processes may cause mass-dependent fractionation (MDF) or mass-independent fractionation (MIF) of Hg isotopes, thereby providing a wealth of information about the biogeochemical cycling of Hg in the environment. These phenomena and the literature documenting them were reviewed elsewhere (Buchachenko 2009a, b, 2018; Jackson and Muir 2012; Jackson et al. 2013; Bessinger 2014; Blum et al. 2014; Jackson 2015).

Research on Hg isotopes in lakes led to the discovery that the stable isotope composition of the Hg in the $CH_3Hg^+$ preferentially accumulated by fish and crustaceans in freshwater food webs is characterised by two distinctive anomalies: (1) selective enrichment in $^{199}Hg$ and $^{201}Hg$, i.e. the isotopes of odd mass number, relative to isotopes of even mass number and (2) enrichment in $^{201}Hg$ relative to $^{199}Hg$ (Jackson et al. 2006, 2008) (Fig. 1). The anomalous enrichment in $^{199}Hg$ and $^{201}Hg$ is a consequence of MIF, but the anomalously high proportion of $^{201}Hg$ to $^{199}Hg$, expressed as the ratio $\delta^{201}Hg/\delta^{199}Hg$ (see definition of δ-value in Materials and methods section, below), is attributable to the

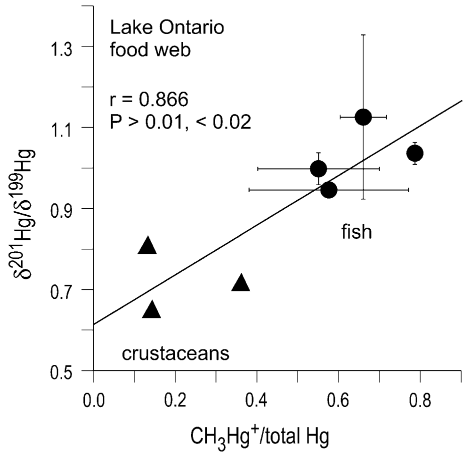

**Fig. 1** Relationship between the $\delta^{201}$Hg/$\delta^{199}$Hg and $CH_3Hg^+$/total Hg ratios of crustacean (Black triangle) and fish (Black circle) species of a food web in the Niagara Basin of Lake Ontario. The data represent planktonic and benthic crustaceans, forage fish that feed on them, and fish that prey on the forage fish. Single bulk samples of whole crustaceans and duplicate specimens of whole individual fish were analysed. $CH_3Hg^+$ and total Hg concentrations are expressed as ng Hg $g^{-1}$ dry weight. The crustacean samples were analysed only once, because there was a limited supply of sample materials. Error bar = mean ± standard error. Source of data: Jackson et al. (2008)

combined or mutually reinforcing effects of MIF and MDF rather than MIF alone (Jackson 2018)—specifically, enhancement of the stability of $^{201}$Hg–$CH_3$ bonds relative to $^{199}$Hg–$CH_3$ bonds owing to the higher nuclear spin and larger mass of $^{201}$Hg (Jackson 2016, 2018). These findings were applied to Hg in a sediment core from Clay Lake, a small riverine lake in the Wabigoon River system of northern Ontario, Canada. The lake had been severely polluted with Hg from a chlor-alkali plant, along with organic wastes from a pulp and paper mill, and had been affected by damming. The study yielded strong circumstantial evidence that temporal variations in the proportion of $^{201}$Hg to $^{199}$Hg reflect historical changes in the abundance of $CH_3Hg^+$ or net rate of $CH_3Hg^+$ production in the river–lake system (Jackson 2016).

The inferred relationship is consistent with analytical data that show greatly elevated concentrations of $CH_3Hg^+$ in the sediments, water, and biota of the Hg-polluted regions of the river–lake system (Jackson 2016); but it was confirmed in a particularly compelling manner by comparing the $\delta^{201}$Hg/$\delta^{199}$Hg ratio values for the years 1968–1997 with independently reported concentrations of Hg (mainly in the form of $CH_3Hg^+$) in the abdominal muscles of crayfish collected annually from Clay Lake during the same time span (Jackson 2016). The isotope ratio values of the core horizons and the $CH_3Hg^+$ content of the crayfish displayed temporal trends that closely paralleled one another, and similar trends were shown by total Hg (most of which was presumably in the form of $CH_3Hg^+$) in the muscle tissues of two species of fish (walleye and northern pike) at the upper end of the aquatic food web. The correspondence between these patterns of temporal variation was all the more impressive because a small peak superimposed on the trend for the isotope ratio coincided, within the bounds of analytical uncertainty, with a similar peak superimposed on the trends for the crayfish and walleye data. The marked similarity between the patterns of variation shown by the isotope data and the corresponding $CH_3Hg^+$ data raised the intriguing possibility that the $\delta^{201}$Hg/$\delta^{199}$Hg ratios of sediment cores can be used to track historical variations in bacterial $CH_3Hg^+$ production in aquatic environments. The research reported here was designed to pursue this promising line of inquiry by investigating temporal variations in the presumptive isotope signatures of $CH_3Hg^+$ in cores from an assortment of widely separated, environmentally different lakes.

Cores were collected from three temperate lakes polluted with Hg from different kinds of nearby industrial point sources and from one practically pristine Arctic lake contaminated only with diffuse background Hg from multiple distant sources. The objective of the research was to determine whether the inferences drawn from the previous research on Clay Lake are generally applicable to Hg in sediment cores from lakes—in particular, to test the hypothesis that variations in the $\delta^{201}$Hg/$\delta^{199}$Hg ratio of Hg in sediment cores can be used to track historical variations in $CH_3Hg^+$ abundance or production rate in freshwater environments. The premise that the isotope ratio is linked to the relative amount or net production rate of $CH_3Hg^+$ is based on previously published evidence (Jackson et al. 2006, 2008; Jackson 2016, 2018). Its applicability in the present case was assessed by relating changes in the $\delta^{201}$Hg/$\delta^{199}$Hg ratio to environmental and biotic factors that are likely to affect $CH_3Hg^+$ production (Hg pollution, eutrophication, climatic change, and pollution by toxic substances, such as heavy metals other than Hg), as indicated by chemical and geochronological data, independently documented historical events, and literature that reported effects of such factors on $CH_3Hg^+$ production.

## Materials and methods

Information about the field sites, background literature, procedures for sample collection and preservation, and analytical techniques, together with the analytical data (including the $\delta^{199}$Hg and $\delta^{201}$Hg values, but not the $\delta^{201}$Hg/$\delta^{199}$Hg ratios, which were calculated expressly for the present paper), was published elsewhere (Jackson and Muir 2012; Jackson 2013, 2015; Jackson et al. 2013, 2015a), but the essential facts are outlined briefly here:

- Lake Ontario, the easternmost of the North American Great Lakes, lies between southern Ontario (Canada) and New York State (USA). The Niagara Basin (i.e. western basin) of the lake is the receiving basin for the Niagara River and has been heavily polluted with an assortment of chemicals, including Hg, other heavy metals, and chlorinated hydrocarbons, from effluents of numerous industrial sites located on or near the river. The industrial pollution started in the 1890s and culminated in the mid-twentieth century. Most of the Hg emanated from Hg(0) electrodes employed in two chlor-alkali plants and was discharged into the Niagara River with plant effluents. One of the plants began operations in 1893 and the other in the early 1960s. Pollution abatement procedures were inaugurated at both plants in 1970, with the result that Hg concentrations in the sediments dropped considerably, although they tailed off at a level that stubbornly remained far above the pre-pollution background level. A core of fine-grained sediment was collected from the Niagara Basin in May 1999 and was cut into 1-cm sections, which were freeze-dried. Additional information is given by Jackson (2013).
- Moose Lake is a small boreal forest lake in northwestern Québec (Canada) that has been contaminated with airborne Hg and other heavy metals—notably copper (Cu) and zinc (Zn)—together with arsenic (As) and sulphate from the nearby Horne smelter at Rouyn-Noranda, Québec. A core of fine-grained sediment was collected in the winter of 1998 and cut into 1-cm sections, which were preserved by freezing. Additional information is given by Jackson et al. (2013).
- Wabamun Lake is a small, fairly eutrophic lake in the parkland region (the transition zone between prairie and boreal forest) in central Alberta, Canada. The lake has been contaminated with Hg, other heavy metals, and As from three coal-burning electric power plants that began operating in 1956, the 1970s, and 1983, respectively, and it underwent intensive eutrophication in the late twentieth century (Schindler et al. 2004). A core of fine-grained sediment was collected in August, 1999 and cut into 1-cm sections, which were freeze-dried. Additional information is given by Jackson and Muir (2012).
- Romulus Lake is a saline, oligotrophic, meromictic lake in the High Arctic desert of Ellesmere Island in Nunavut (Canada). It has not been polluted with Hg, except for trace quantities transported from distant sources by atmospheric circulation. A core of fine-grained sediment was collected in May, 2000 and cut into 1-cm sections, which were freeze-dried. Additional information is given by Jackson et al. (2004) and Jackson (2015).

Sediment cores from all the lakes except Moose Lake were subjected to radiometric dating using the $^{210}$Pb-$^{210}$Po technique and the Constant Rate of Supply model. The technique combined direct dating of selected core horizons with calculation of the ages of the other horizons by multiple regression analysis. The radiometric dates extend back as far as the 1890s. The year assigned to each core section represents the mean age of the section; it is not a specific year of deposition. For detailed information on the theory and practice of the method, see relevant literature cited by Jackson (2013, 2015) and Jackson and Muir (2012).

Total Hg concentrations were determined by digesting weighed portions of the core sections with hot $HNO_3$/HCl and $KMnO_4$, which converted all Hg to dissolved inorganic Hg(II), whereupon the Hg(II) was treated with $SnCl_2$ to reduce it to Hg(0) gas, which was then measured by cold vapour atomic absorption spectrophotometry. The total Hg concentrations were calculated on a dry weight basis.

Following the total Hg analyses, aliquots of the sample digests (adjusted to a total Hg range of 2–5 ng mL$^{-1}$), along with aliquots of a standard solution of Hg(II) in dilute $HNO_3$ (Inorganic Ventures, Inc.), were analysed for stable isotopes of Hg in the order standard-sample-standard. Dissolved Hg(II) was reduced to gaseous Hg(0) by treatment with $SnCl_2$, and the Hg(0) was stripped from the aqueous phase in a gas–liquid separator and analysed with a ThermoFinnigan Neptune MC-ICP-MS unit employing argon as the carrier gas and Faraday cups as the detectors. The solutions were automatically analysed 25 times in rapid succession, and the mean values of the isotope ratios $^{198}Hg/^{202}Hg$, $^{199}Hg/^{202}Hg$, $^{200}Hg/^{202}Hg$, and $^{201}Hg/^{202}Hg$, together with their standard deviations (SDs), were calculated. The reasons for normalising the isotope abundances with respect to $^{202}Hg$, the most abundant isotope of Hg, instead of the commonly used isotope $^{198}Hg$ are explained elsewhere (Jackson and Muir 2012; Jackson et al. 2013; Jackson 2015). The analytical error, expressed as the 2SD value for replicate analyses of the standard solution, an estimate of the 95% confidence interval about the mean, was usually $< 0.01\%$ of the mean, indicating a satisfactory degree of internal precision. The per mil (‰) deviation of the sample ratio from the mean ratio of the two standard solutions bracketing the sample solution (i.e. the δ-value) was calculated using the following equation:

$$\delta^{X}\mathrm{Hg} = \left[\left({}^{X}\mathrm{Hg}/{}^{202}\mathrm{Hg}\right)_{\mathrm{sample}} - \left({}^{X}\mathrm{Hg}/{}^{202}\mathrm{Hg}\right)_{\mathrm{standard}}\right] \times 10^{3}/\left({}^{X}\mathrm{Hg}/{}^{202}\mathrm{Hg}\right)_{\mathrm{standard}},$$

where X = 198, 199, 200, or 201.

The external precision for such analyses, based on the mean and standard error of δ-values for duplicate portions of selected core sections, is almost always satisfactory, as the standard error is usually much less than the mean (Jackson 2013, 2015; Jackson et al. 2013).

Note that $\delta^{199}Hg$ and $\delta^{201}Hg$ represent the combined effects of MDF and any MIF that took place when the isotope signature of the Hg was formed. Past experience with tissues of fish from Lake Ontario showed that the $\delta^{201}Hg/\delta^{199}Hg$ ratio is more useful as a proxy for the $CH_3Hg^+$ content of a sediment sample than the corresponding parameter based on the effects of MIF alone (the $\Delta^{201}Hg/\Delta^{199}Hg$ ratio), implying that the combined or interactive effects of MIF and MDF are of paramount importance (Jackson 2018).

## Results

### Lake Ontario

The total Hg profile of the Lake Ontario core (Fig. 2) shows uniformly low background concentrations of Hg in the unpolluted deepest (i.e. oldest) core strata, which span the depth range 30–22 cm. Starting at a depth of ~ 21–20 cm—at an unknown time, but probably in the mid-nineteenth century—total Hg jumps to a somewhat higher concentration and gradually increases over time, suggesting minor, though slowly worsening, Hg pollution from multiple diffuse sources. This probably reflects the impact of accelerating human activities, such as industrialisation, increasing population density, and increased burning of coal and wood. The core profile, however, is dominated by a pronounced bimodal maximum whose position on the radiometric age scale (Fig. 2) indicates that it was formed by severe Hg pollution from the two chlor-alkali plants, which started in 1893 and the early

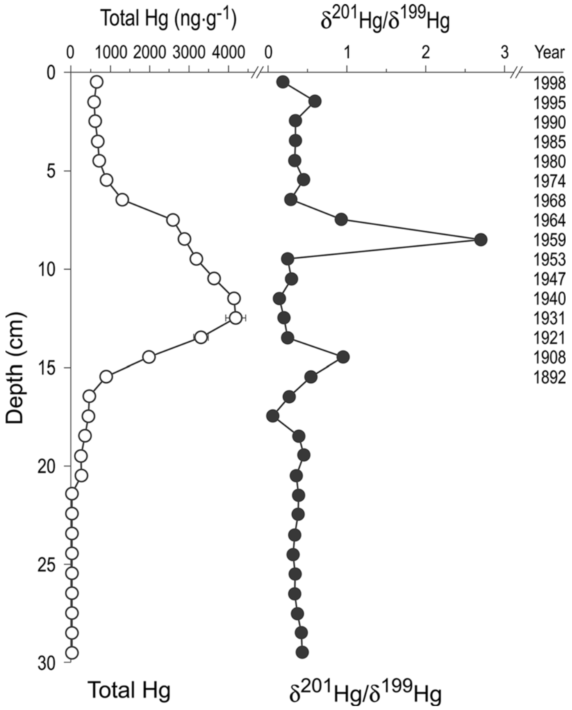

**Fig. 2** Variations in total Hg concentration, $\delta^{201}Hg/\delta^{199}Hg$ ratio, and radiometric age with depth in the core from the Niagara Basin of Lake Ontario. Error bar = mean of duplicate values ± standard error. Absence of an error bar means only a single analysis was done

1960s, respectively (Jackson 2013). The first of these two episodes of major pollution resulted in the highest Hg concentrations, which peaked in the early 1930s and then declined, possibly reflecting an adverse effect of the Great Depression on the chlor-alkali industry (Jackson 2016). The second episode is represented by a shoulder on the upper flank of the peak. The Hg concentration diminished sharply following the inauguration of pollution control measures in 1970 and, starting ca. 1990, levelled off at a mean concentration ~ 24 times the mean pre-pollution background value (Jackson 2013), indicating that the lake, though appreciably improved, is unlikely to return to its pristine condition any time in the foreseeable future.

The core profile of the $\delta^{201}$Hg/$\delta^{199}$Hg ratio (Fig. 2) displays a pattern of variation that is entirely different from that of total Hg; yet it is obviously linked to the episodes of Hg pollution, as shown by reference to the radiometric age scale and by comparison with the total Hg profile. As with the total Hg concentrations, the pre-pollution ratio values are uniformly low and show little variation over time, but at or just after the start of each phase of the Hg pollution the ratio rises to a maximum and then declines sharply to the baseline level. The onset of the minor pre-1893 Hg pollution is marked by a very small peak, whereas the onset of Hg pollution from each of the two chlor-alkali plants is accompanied by the rise of a much larger peak, the larger of which is the more recent one. Thus, the dominant features of the core profile are the two peaks associated with the onset of Hg pollution from the chlor-alkali plants. A few tiny peaks of unknown cause and doubtful significance also appear in the profile ca. 1947, 1974, and 1995.

The three peaks in the core profile of the $\delta^{201}$Hg/$\delta^{199}$Hg ratio suggest that each episode of Hg pollution, as expected, brought about a rise in the rate of Hg methylation in the lake, causing a marked increase in the abundance of $CH_3Hg^+$, but that the upward trend was soon reversed by demethylation. This implies that methylating bacteria were dominant at first owing to stimulation by the influx of Hg but were subsequently superseded by demethylating bacteria as a result of ecological succession in the microbial community in response to the buildup of $CH_3Hg^+$ in the sediment. Such patterns of variation have been observed repeatedly in experiments on bacterial production and decomposition of $CH_3Hg^+$ in lake sediments (Jackson 1989, 1991a, b). Note that the maximum in each case occurred only at or shortly after the onset of Hg pollution. Thus, there was no isotope ratio peak that coincided with the total Hg maximum in the early 1930s (Fig. 2). Assuming that the ratio does indeed represent the abundance and net production rate of $CH_3Hg^+$, this is an example of the fact that $CH_3Hg^+$ concentrations in sediments do not necessarily correlate with the corresponding total Hg or inorganic Hg concentrations, even though Hg pollution causes a general rise in the rate of $CH_3Hg^+$ production.

This interpretation is supported by the fact that the $\delta^{201}$Hg/$\delta^{199}$Hg ratio values of the Lake Ontario core show a pattern of variation that is distinctly different from that of the previously mentioned Clay Lake core (Jackson 2016), even though both lakes were polluted by Hg from fluvially transported chlor-alkali plant effluents. In Clay Lake the isotope ratio increased sharply to a maximum when Hg pollution from the chlor-alkali plant began, but instead of coming down rapidly to the baseline level, it declined gradually and tailed off asymptotically, remaining far above the background level and paralleling the trend shown by $CH_3Hg^+$ in fish and crayfish during the same time span (Jackson 2016). As both lakes were polluted with Hg in effluents discharged from point sources of the same kind (chlor-alkali plants employing Hg(0) electrodes) and conveyed to the basin of deposition by the same mechanism (fluvial transport), it follows that the differences between the patterns of variation in the cores from the two lakes are attributable to differences in physicochemical and biotic factors that affected biogeochemical reactions of Hg, notably methylation and demethylation, in the lacustrine environment. More research would be required to provide a more specific explanation of the contrast between profiles of the isotope ratio values of the cores from the two lakes. The contrast is not surprising, however, if only because the Niagara Basin of Lake Ontario is a large, deep body of water in a zone of deciduous Eastern woodland and carbonate bedrock in southern Ontario and northern New York State, whereas Clay Lake is a small riverine lake in the boreal forest zone on the Precambrian Shield of northern Ontario. Besides, no two lakes have identical properties and histories, even if they are in the same geographical and environmental setting.

### Moose Lake

The total Hg profile in the Moose Lake core (Fig. 3) shows uniformly low levels of pre-pollution background Hg and hardly any variation over time (i.e. upward in the core sequence). The region of background Hg spans the depth range 30–24 cm. Starting at a depth of ~ 24–23 cm the Hg concentrations gradually increase over time, indicating a period of minor but significant and continuous Hg pollution spanning the depth range 24–15 cm. Finally, a period of generally more intense but much more variable Hg pollution begins at a depth of ~ 15–14 cm and continues to the top of the core sequence. The Hg pollution was caused by emissions from the nearby base metal smelter, as shown by associated increases in the concentrations of Cu and Zn (Jackson et al. 2013).

As for the isotope data (Fig. 3), it is necessary to point out, to begin with, that the proportion of $\delta^{201}$Hg to $\delta^{199}$Hg in this particular case is expressed as the ratio ($\delta^{201}$Hg + 0.1)/($\delta^{199}$Hg + 0.1). The reason for this transformation of the data is that the $\delta^{201}$Hg values of the 24–23 and 23–22 cm core sections are negative (− 0.019 and − 0.026‰, respectively), whereas all other δ-values are positive (Jackson et al. 2013). As the comparative study of the ratio values for the purpose of understanding their pattern of temporal variation required that all δ-values have the same sign, the $\delta^{201}$Hg and $\delta^{199}$Hg values of the core horizons were each increased by 0.1 so that all the numbers used to calculate the ratio values would be positive. This has no bearing on the validity or meaning of the results, as the scientific information provided by the data depends solely on the pattern of variation, not on the absolute values of the ratio. The method used to calculate the isotope ratio altered the absolute values, but the shape of the core profile of the ratio was not affected.

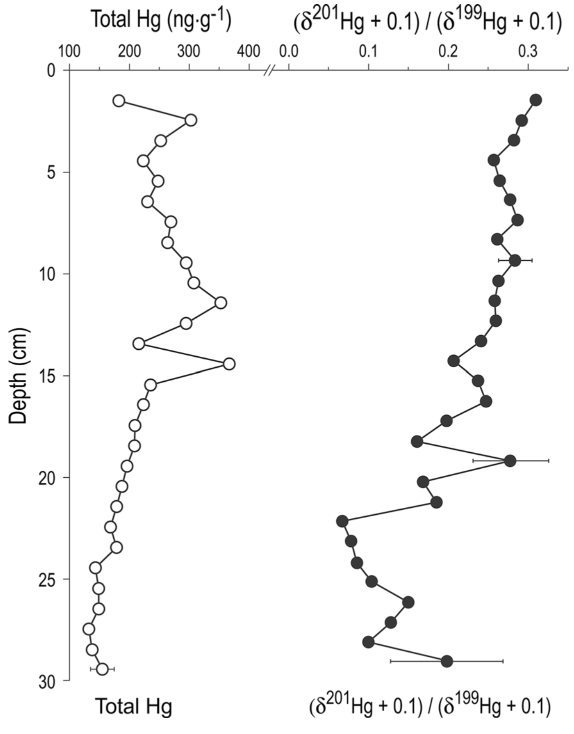

**Fig. 3** Variations in total Hg concentration and ($\delta^{201}$Hg + 0.1)/($\delta^{199}$Hg + 0.1) ratio with depth in the core from Moose Lake. Error bar = mean of duplicate values ± standard error. Absence of an error bar means only a single analysis was done

The core profile of the ($\delta^{201}$Hg + 0.1)/($\delta^{199}$Hg + 0.1) ratio (Fig. 3) is characterised by consistently higher values in the zones of minor and major Hg pollution than in any of the horizons in the zone of pre-pollution background Hg, except for the 30–29 cm horizon, whose mean ratio value, for unknown reasons, is relatively high. The isotope ratio values of the pre-pollution zone, though variable, tend to decrease over time, the trend being particularly consistent and well defined over the depth range 27–22 cm. This trend continues to the 23–22 cm horizon, at or just beyond the point where the minor pollution from the smelter begins (Jackson et al. 2013), whereupon the ratio rises abruptly to consistently much higher values and switches from a long-term decrease over time to a long-term tendency to *increase* over time from a depth of 22–21 cm to the top of the core sequence. Clearly the emissions from the smelter brought about a radical increase in the ratio values and a permanent tendency of the ratio to increase upward in the core sequence. The Hg, Cu, and Zn pollution from the smelter first become detectable at depths of 24–23, 23–22, and 21–20 cm, respectively (Jackson et al. 2013); this is consistent with the possibility that the shift in the magnitude and temporal trend of the ($\delta^{201}$Hg + 0.1)/($\delta^{199}$Hg + 0.1) ratio primarily represents a reaction of the microbial community to the increase in Cu concentration. It suggests inhibition of Cu-intolerant Hg-transforming bacterial species, allowing opportunistic growth of Cu-tolerant ones. The changes in the isotope ratio cannot be explained by the increase in total Hg concentration, which had started somewhat earlier.

Superimposed on the opposing long-term trends of the isotope ratio in the unpolluted and polluted zones of the core is a series of short-term maxima and minima, which form a “zigzag” pattern all the way up the core profile (Fig. 3). The upswings and downswings are largest in the zones of pre-pollution background Hg and minor Hg pollution, and are damped in the zone of most intense pollution, the overall result being a damped oscillation throughout the core profile, suggesting short-term fluctuations in the species composition of the microflora (see below).

The variations in the isotope ratio suggest that in Moose Lake, as in the Niagara Basin of Lake Ontario, Hg pollution brought about a marked increase in the abundance of $CH_3Hg^+$, implying an increased net rate of $CH_3Hg^+$ production. The pattern of temporal variation, however, was radically different from that in Lake Ontario, presumably because the two lakes differ greatly in their environmental and biotic properties, in the variations of these factors over time, and in their pollution history. Moose Lake is a small boreal forest lake on the Canadian Shield and has been polluted with heavy metals and other contaminants in fallout from a base metal smelter, whereas the Niagara Basin is a large, deep body of water further south in a region of deciduous woodland and carbonate bedrock, and has been polluted by a large assortment of organic and inorganic contaminants from different nearby industrial sources. Therefore, the contrast in patterns of variation in the Hg isotope data is not surprising, although additional research would be required to determine the reasons for it.

The highest isotope ratio values of the Lake Ontario core are an order of magnitude greater than those of the Moose Lake core, probably in large part because the concentrations of anthropogenic Hg are much lower in Moose Lake, as shown by the total Hg profiles (Figs. 2 and 3). Presumably the net rate of $CH_3Hg^+$ production, following the onset of Hg pollution, was lower in Moose Lake because the supply of inorganic Hg(II) was smaller, although environmental and biotic differences between the two lakes must have been involved as well. The principal conclusions to be drawn from comparison of the isotope data for the two lakes are that (1) the isotope ratio values reveal major site-specific differences in their patterns of temporal variation, (2) the patterns of variation reflect corresponding variations in environmental and biotic factors that control $CH_3Hg^+$ production rate and abundance, and (3) the differences between the patterns of variation that characterise the cores from the two lakes can be explained by differences in site-specific properties of the lakes and variations in these factors over time.

The $(\delta^{201}Hg + 0.1)/(\delta^{199}Hg + 0.1)$ ratio values of the Hg-contaminated horizons of Moose Lake suggest a long-term tendency of $CH_3Hg^+$ production to increase over time, possibly reflecting stimulation of the activities of methylating bacteria by the input of Hg and inorganic nutrients from the smelter. The alternating maxima and minima superimposed on this trend imply short-term fluctuations in the relative rates of methylation and demethylation, respectively, owing to changes in the species composition of the bacterial community as a result of ecological succession, or variations in the activities of particular Hg-transforming bacteria, in response to environmental variations. This applies to the zone of pre-pollution background Hg as well as the zones of Hg pollution. The damping of the oscillations in the ratio in the zone of maximum pollution suggests a reaction of bacterial population dynamics to fallout from the smelter (May 1981; Jackson 1991b; Jackson et al. 2013), although further research is needed to explain this phenomenon fully. One possible reason for the damping of the oscillations after the onset of the most intense pollution is that toxic pollutants, such as Cu and As, inhibited less tolerant bacterial species, including some of the Hg-transforming bacteria, thereby lowering the biodiversity of the microflora (Jackson 1991b; Jackson et al. 2015b). Experiments on the effects of heavy metals on bacterial $CH_3Hg^+$ production in lake sediments have shown pronounced oscillations in the abundance of $CH_3Hg^+$ with increasing concentrations of metals, including Cu, Zn, and Cd, in overlying water, and the variations were attributed to ecological succession among metal-sensitive and metal-tolerant bacteria in the microbial community (Jackson 1991b).

### Wabamun Lake

The total Hg profile of the Wabamun Lake core (Fig. 4) is characterised by consistently low Hg concentrations, and small short-term fluctuations, but no long-term temporal trend, in the pre-pollution (pre-1895) zone. Hg concentrations, however, jump to

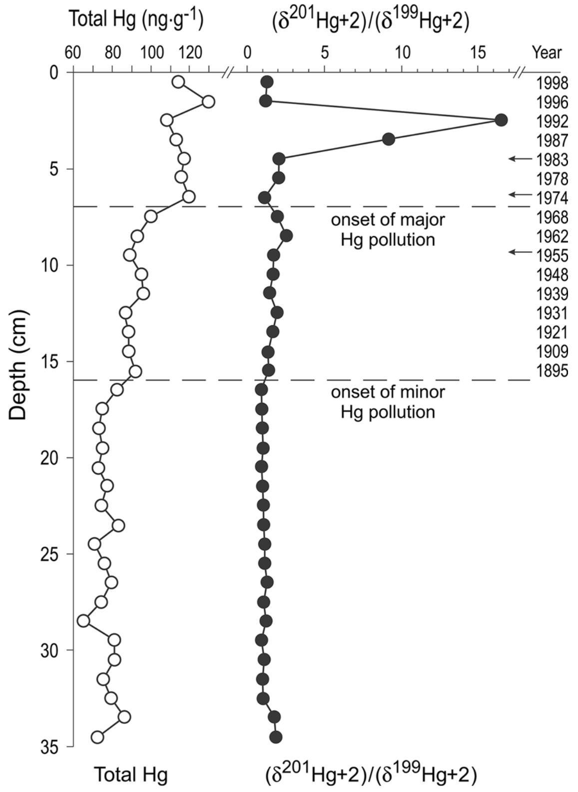

**Fig. 4** Variations in total Hg concentration, ($\delta^{201}$Hg + 2)/($\delta^{199}$Hg +2) ratio, and radiometric age with depth in the core from Wabamun Lake. Arrows mark the years in which power plants began operations. Each point in the plot represents a single analysis

consistently elevated values in the mid-1890s and then rapidly rise to considerably higher values starting in the mid-twentieth century, inaugurating periods of minor and major Hg pollution, respectively. The interval of minor pollution is attributable to an influx of settlers starting in 1896 and a concomitant increase in the domestic burning of coal, whereas the period of major pollution is attributable to emissions from the three coal-burning electric power plants built at different times in the second half of the twentieth century (Jackson and Muir 2012). The transition from "minor" to "major" Hg pollution began just after the first of the three power plants began operations, and the period of most intense pollution started at about the time the second power plant went online, but the third power plant did not increase the total Hg any further (Fig. 4).

Regarding the isotope data (Fig. 4), the proportion of $\delta^{201}$Hg to $\delta^{199}$Hg in this case is expressed as the ratio ($\delta^{201}$Hg + 2)/($\delta^{199}$Hg + 2). Because many of the $\delta^{199}$Hg and $\delta^{201}$Hg values were negative (Jackson and Muir 2012), the numerator and denominator were each increased by 2 so that all numbers would be positive. As with the comparable transformation of the Moose Lake isotope data, this has no bearing on the validity and meaning of the results, as the scientific information provided by the data depends solely on the pattern of temporal variation, which was not affected by the transformation, not on the absolute values of the ratio.

The ($\delta^{201}$Hg + 2)/($\delta^{199}$Hg + 2) ratio (Fig. 4) is consistently low in the pre-pollution (pre-1895) zone of the core profile, except for a very small peak, or shoulder, of unknown cause at the bottom of the profile, but jumps to consistently higher values in the zone of minor and major Hg pollution. The minor phase of Hg pollution preceding the construction of the power plants caused the ratio to be elevated only slightly, implying a small but significant acceleration of $CH_3Hg^+$ production. Just after each of the three power plants began operations, however, the ratio rose to a maximum and then declined, suggesting a rise in the methylation rate owing to the increased input of inorganic Hg(II), followed by a decrease in the net rate of $CH_3Hg^+$ production attributable to an upsurge in the rate of demethylation, as in Lake Ontario (Fig. 2). The peaks associated with the two power plants that went online earliest, in 1956 and the 1970s, are very small, but the peak associated with the power plant that went online most recently, in 1983, is an order of magnitude higher than the other two peaks and is far and away the dominant feature of the core profile (Fig. 4).

The uniquely large size of the youngest maximum in the core profile of the isotope ratio is not attributable to an increase in Hg deposition caused by emissions from the youngest power plant, as the total Hg profile does not show a corresponding peak in Hg deposition (Fig. 4). Indeed, total Hg concentrations show a gradual decline during the interval ~ 1974–1992, which brackets the onset of emissions from the youngest power plant and the rapid rise in isotope ratio values. The available evidence strongly suggests, instead, that environmental and biotic changes brought about by a documented major increase in eutrophication (Schindler et al. 2004) caused a large but short-lived upsurge in $CH_3Hg^+$ production, resulting in the exceptionally high peak in the isotope ratio profile. Core data reported by Schindler et al. (2004) show that the annual phosphorus flux to Wabamun Lake sediments, an index of the trophic status of the lake, was low in the second half of the nineteenth century but increased progressively throughout the twentieth century, starting with the influx of settlers in 1896 (Jackson and Muir 2012) and accelerating markedly from the 1970s to ca. 2000 owing to intensification of human activities in the vicinity of the lake. The rapid increase in eutrophication during the late twentieth century and consequent increase in the production of organic nutrient substrates available for utilisation by heterotrophic bacteria probably stimulated the growth of methylating bacteria. This, in turn, led to a substantial buildup of $CH_3Hg^+$, followed by a decline caused by the growth of demethylating bacteria, possibly accompanied by a decrease in methylating activity owing, at least in part, to increased bacterial production of Hg-binding substances such as sulphides and thiols that rendered inorganic Hg(II) less bioavailable. Such a sequence of events could account for the presumptive rise in the $CH_3Hg^+$ concentration to a maximum and the subsequent abrupt decline (Jackson 1986, 1988, 1991a, 1993a, b, 1998a, 2016; Lambertsson and Nilsson 2006; Meng et al. 2010). These processes could well explain the exceptionally large peak in the late twentieth century isotope data. Moreover, the moderately elevated isotope ratios during the interval of minor Hg pollution that began in the mid-1890s could have been caused by an associated moderate increase in eutrophication brought about by the documented increase in population density, as well as the increased input of Hg.

One other peculiarity of the core data deserves attention. Throughout the zones of Hg pollution there is a tendency for the isotope ratio to vary inversely with the total Hg concentration, as shown repeatedly in the short-term trends of the two variables (Fig. 4). For instance, just after the first power plant began its operation, total Hg increased steadily until about 1974, while the isotope ratio, except for a slight initial rise, decreased. Then, after the second power plant started up, total Hg declined gradually, while the isotope ratio increased. A possible explanation for this inverse correlation is that the heavy metals and As emitted along with the Hg during the combustion of coal (Jackson and Muir 2012) inhibited the more sensitive species of Hg-transforming bacteria, causing a net decrease in $CH_3Hg^+$ production by the microbial community (Jackson 1991b).

Finally, the relationship between the isotopes is further illustrated by a plot of $\delta^{201}Hg$ against $\delta^{199}Hg$ (Fig. 5). In this plot, the points that represent the zone of maximum Hg pollution and the zone of pre-pollution background Hg form distinct parallel regression lines, with the line for polluted sediments displaced upward from the line for unpolluted sediments, indicating that the polluted core horizons have anomalously high proportions of $^{201}Hg$ to $^{199}Hg$, as with $CH_3Hg^+$ in food web organisms (Fig. 1) (Jackson et al. 2008; Jackson 2018). There is less scatter, moreover, in the plot for polluted sediments, suggesting that toxic pollutants such as heavy metals and As reduced the biodiversity of the microbial community by suppressing less tolerant species, as inferred from the damped oscillations in the Moose Lake isotope ratio data (Fig. 3). The use of this method to illustrate the relationship between the two isotopes has two advantages: (1) it vividly demonstrates the characteristic isotopic anomaly of the Hg in polluted sediments relative to Hg in unpolluted ones; and (2) the sign of the δ-value does not matter. The usefulness of the method, however, is limited by the fact that it does not show variations in the proportion of $\delta^{201}Hg$ to $\delta^{199}Hg$ over the course of time.

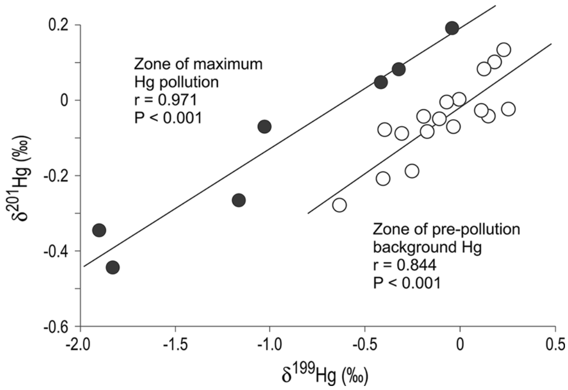

**Fig. 5** Relationships between the $\delta^{201}Hg$ and $\delta^{199}Hg$ values of Wabamun Lake core sections representing the zone of maximum Hg pollution (Black circle) and the zone of pre-pollution background Hg (White circle). Two horizons at the base of the pre-pollution zone (depth range 35–33 cm) were omitted, because their $\delta^{201}Hg$ values were, for unknown reasons, anomalously high relative to their $\delta^{199}Hg$ values. Each point in the plot represents a single analysis

### Romulus Lake

In contrast to the cores from the three severely polluted lakes, the core from Romulus Lake had consistently low total Hg concentrations, indicative of diffuse, low-level background Hg whose presence is attributable to long-range atmospheric transport from a variety of distant industrial and natural sources. Nevertheless, Hg concentrations in the sediment tended to increase over time throughout the twentieth century, reflecting a temporal increase in the emission and deposition of anthropogenic Hg (Fig. 6).

The core profile of the $\delta^{201}$Hg/$\delta^{199}$Hg ratio values (Fig. 6) appears to have been shaped primarily by a series of climate changes that are known to have occurred in the far North during the twentieth century. These variations in climate brought about characteristic changes in the isotope composition of Hg in Arctic and boreal forest lakes of Canada, apparently by altering the community structure of the phytoplankton, thereby altering the species composition, and hence the Hg isotope fractionating activities and other biogeochemical functions, of bacterial communities that decompose dead phytoplankton or colonise the surfaces of living phytoplankton (Jackson 2015). The ratio tended to be relatively high under cool conditions, but dropped to well-defined minima during warming trends. Specifically, the ratio was high during an interval of cool conditions in the 1890s and the first decade of the twentieth century, but declined progressively throughout a subsequent early twentieth century warming trend—gradually at first, but plunging steeply to a pronounced minimum at or near the end of the warming phase. Then a mid-twentieth century cooling trend set in, and the ratio increased over time until shortly after the onset of a second warming trend (the result of greenhouse gas emissions produced by human activities) in the late twentieth century, when, once again, the ratio dropped sharply to a minimum. In the 1990s the ratio, for unknown reasons, rebounded from this minimum and rose to a somewhat higher value ca. 1997. This increase, however, is based solely on data from a single core section and could represent a minor short-term fluctuation rather than a trend. The fact that both cool phases show the same tendency, whilst both warm phases show the opposite tendency, is compelling evidence that the apparent effects of climate change on the $\delta^{201}$Hg/$\delta^{199}$Hg ratio are real and consistent.

The climate-related pattern of variation shown by the $\delta^{201}$Hg/$\delta^{199}$Hg ratio strongly suggests that cool conditions lead to an increase in the net rate of $CH_3Hg^+$ production, whereas warmer temperatures tend to lower the rate, possibly owing to shifts in the relative rates of Hg methylation and demethylation. Such changes in the speciation of Hg are attributable to ecological succession in the bacterial community in response to changes in the community structure of the phytoplankton that provide the organic nutrient substrates on which the bacteria depend (Jackson 2015).

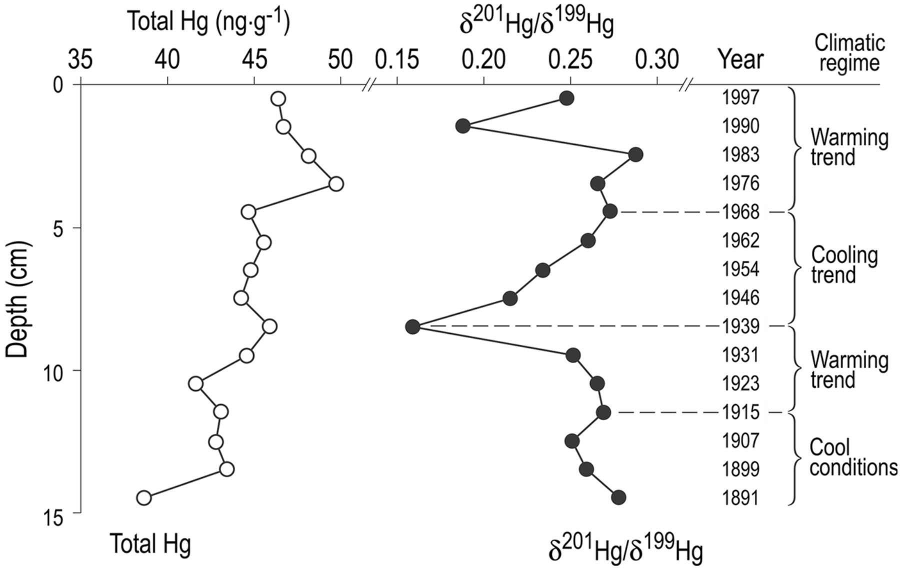

**Fig. 6** Variations in total Hg concentration, $\delta^{201}$Hg/$\delta^{199}$Hg ratio, and radiometric age with depth in the core from Romulus Lake. Data were grouped according to climate regime on the basis of climate information drawn from literature cited elsewhere (Jackson 2015). Each point in the plot represents a single analysis

This inference is consistent with published evidence demonstrating that certain phylogenetic groups of phytoplankton in eutrophic lakes, i.e. certain species of cyanobacteria, preferentially foster the activities of methylating bacteria, whereas certain other groups, i.e. diatoms and green algae, preferentially promote the activities of demethylating bacteria, even if those particular varieties of planktonic organisms are not the dominant members of the phytoplankton community (Jackson 1993b). Owing to a lack of micropaleontological data, this interpretation of the isotope data from the Romulus Lake core cannot be verified without further research. Nevertheless, cores from other northern lakes, in both the Arctic and the boreal forest zone, have shown well-defined relationships between the isotope composition of Hg and the abundances of particular phylogenetic groups of fossil phytoplankton, the values of biogeochemical variables associated with microbial activity, and the prevailing climatic conditions at the time when the sediments were deposited (Jackson 2015).

## Discussion

In all three Hg-polluted temperate lakes the $\delta^{201}$Hg/$\delta^{199}$Hg ratio of the sediment was low prior to the onset of Hg pollution but became higher when the pollution began, as observed previously in Clay Lake, strongly suggesting a concomitant increase in bacterial $CH_3Hg^+$ production in the lakes. The observed phenomenon appears to be a general effect of Hg pollution, regardless of the source of pollution and the particular lake environment or location, and regardless of whether the Hg came from effluents discharged directly into water or from atmospheric emissions. The pattern of temporal variation, however, differed greatly from one lake to another, each lake yielding its own characteristic core profile. In each case, moreover, the core profile of the isotope ratio was distinctly different from the corresponding total Hg profile, except that increases in total Hg concentration caused by pollution invariably initiated increases in the isotope ratio. These disparities imply that the patterns of variation in the isotope ratio over time were, for the most part, functions of site-specific environmental and biotic factors that controlled the rates of bacterial methylation and demethylation of Hg.

There is additional evidence for a predominant effect of environmental and biological variables. All of the cores showed peaks or zigzags in the isotope ratio, suggesting ecological succession in the Hg-transforming microbial populations, starting with stimulation of the growth and activity of methylating bacteria by the input of Hg, followed by the rise of demethylating bacteria to a position of dominance in the microbial community. In the case of Wabamun Lake the first two of the three peaks that mark the onset of Hg pollution events are dwarfed by the third one, whose exceptionally large size probably denotes intense amplification and subsequent decline of $CH_3Hg^+$ production because of a concurrent acceleration of primary productivity documented by others. Indeed, the initial modest increase in the isotope ratio in the mid-1890s, the time when there was an abrupt influx of settlers, may have been caused by a concomitant rise in the rate of eutrophication in addition to Hg contamination resulting from increased domestic consumption of coal. In Moose Lake the zigzags attributable to variations in the relative rates of Hg methylation and demethylation were damped after the onset of the period of the most severe pollution, suggesting inhibition of less tolerant methylating and demethylating bacterial species by the unrelenting input of large quantities of heavy metals and As.

In contrast to the Hg-polluted temperate lakes, the practically unpolluted Arctic lake yielded evidence that $CH_3Hg^+$ production was controlled primarily by variations in climate, i.e. alternation between cool and warm phases. This probably indicates that climate change altered the species composition of the phytoplankton community, thereby changing the nature of the organic nutrient substrates on which bacterial populations depended, which in turn led to ecological succession in the bacterial community. More research is needed to explain the observation that climate cooling increased the isotope ratio, implying an increase in the $CH_3Hg^+$ production, whereas climate warming decreased it.

Another point of interest is that the variations in isotope composition were manifested by the δ-values of $^{201}$Hg and $^{199}$Hg, implying combined effects of MIF and MDF rather than MIF alone, as observed in the $CH_3Hg^+$ of fish tissues. This is attributable to (1) the high nuclear spin of $^{201}$Hg (3/2) compared to that of $^{199}$Hg (1/2), and hence its higher nuclear magnetic moment, and (2) the greater mass of $^{201}$Hg. The results are consistent with the possibility that the isotope fractionation responsible for the anomaly occurred during either methylation or demethylation, as the effect of the stronger nuclear magnetic moment of $^{201}$Hg would be to strengthen the attraction of that isotope's nucleus for valence electrons penetrating the inner electron shells of the Hg, whilst the relatively large mass of the isotope would reinforce this effect by increasing the isotope's inertia, so that more energy would be required to dissociate it. Thus, both the high nuclear magnetic moment and the large mass of $^{201}$Hg would make $^{201}$Hg–C bonds of $CH_3Hg^+$ more stable and less readily broken than $^{199}$Hg–C bonds. In short, the mass-independent isotope effect was augmented by the mass-dependent effect.

The inferences drawn from the results of this study need, however, to be tested and verified by additional research. Future research efforts should include samples from a larger, more diverse assortment of natural waters and more detailed, refined, and powerful analyses to define and quantify the chemical species of Hg in sediments, to determine their isotope signatures, and to investigate further the mechanisms of isotope fractionation, with consideration of possible alternative explanations for observed variations in the $\delta^{201}$Hg/$\delta^{199}$Hg ratio. Chemical fractionation of sedimentary Hg, followed by isotopic analysis of the individual fractions ($CH_3Hg^+$ and inorganic Hg(II) species), could be useful in this regard.

In-depth research on the functions of bacterial activities and environmental variables in the fractionation of Hg isotopes during specific biogeochemical transformations of Hg in natural environments is also essential. Analysis of field samples should be complemented by controlled experiments, but experiments on the functions of bacteria should be performed on entire in situ natural microbial assemblages, i.e. microbial communities of fresh bulk sediments in their native state, using culture-independent methods for determining the phylogenetic composition and biogeochemical activities of the microflora. In particular, it would be useful to monitor variations in community structure during specific experimental treatments using different culture-independent methods, including ribosomal ribonucleic acid (rRNA) analysis, while concurrently monitoring $CH_3Hg^+$ production and decomposition, changes in Hg isotope ratios, and other biogeochemical processes, such as oxidation–reduction reactions mediated by bacteria. Experiments performed on pure cultures of individual bacterial species isolated and grown in artificial media have their uses, but by themselves they are of limited value in research on microbial ecology and biogeochemistry. Indeed, they can be misleading in the light of the vast number of bacterial species that coexist and interact in various ways in natural microbial communities, the fact that few of them can be cultured, and the fact that pure cultures provide no information about interactions between species.

Nevertheless, information obtained by culture-dependent methods could be used to complement or supplement information yielded by culture-independent techniques. Thus, if experiments employing culture-independent methods produce data suggesting involvement of a particular taxonomic group of bacteria in the chemical and isotopic transformations of Hg, then additional information can conceivably be obtained by further experimentation using enrichment culture techniques or isolated microbial species cultured in artificial media. Nonetheless, experiments that employ culture-independent methods applied to in situ microbial communities in their native state are of primary importance and must come first.

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