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Variations in the Isotope composition of mercury in a sediment core and food web

By:

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Abstract

Analysis of a sediment core and food-web animals from the Niagara Basin of Lake Ontario yielded the first recorded evidence for systematic variations in the stable-isotope composition of mercury (Hg) in natural environments on Earth. The sediments comprised younger strata enriched in Hg by recent pollution overlying order strata containing background Hg only. Several Hg isotope ratios, including $^{199}Hg/^{201}Hg$, $^{201}Hg/^{204}Hg$, and $^{202}Hg/^{204}Hg$, varied significantly with the Mn/Fe ratio of the extractable readily reduced oxyhydroxide fraction of the sediment and with the concentrations of extractable Mn or Fe fractions, or both, in the sediment, and the zone of recent Hg pollution gave strikingly different results that the zone of background Hg. Food-web animals displayed a progressive increase in the $^{202}Hg/^{204}Hg$ ratio from lower to higher trophic levels in the order crustaceans < forage fish < trout; but super imposed on this trend were secondary trends owing to systematic decreases in the ratio from planktonic to benthic crustaceans and, correspondingly, from plankton-eating to benthos-eating forage fish. The results of the research suggest fractionation of Hg isotopes by natural processes, including Hg methylation, with effects linked to temporal variations in the oxidation-reduction potential of the sediments. These findings show that Hg isotopes could provide valuable but as yet untapped information about the sources and biogeochemical cycling of natural and anthropogenic Hg.

Résumé

L'analyse d'une carotte sédimentaire et l'étude des animaux du réseau trophique du basin Niagara, dans le lac Ontario, on mis pour la première fois en évidence des variations systématiques de la composition des isotopes stables du mercure (Hg) dans les milieux naturels de la Terre. Les sédiments se composaient de strates jeunes enrichies en Hg par la pollution récente, qui recouvraient des strates plus anciennes présentant seulement une concentration de fond de Hg. Plusieurs rapports des isotopes de Hg, notamment $^{199}Hg/^{201}Hg$, $^{201}Hg/^{204}Hg$, et $^{202}Hg/^{204}Hg$, variaient de façon significative avec le rapport Mn/Fe de la fraction oxyhydroxide extractible et facilement réduite du sédiment, et avec les concentrations des fractions extractibles de Mn ou de Fe, ou avec les deux, dans le sédiment, et la zone présentant une pollution récente par Hg donnait des résultats remarquablement différents des ceux de la zone ne présentant qu'une concentration de fond de Hg. Les animaux du réseau trophiques les plus bas aux niveaux les plus hauts dans l'ordre crustacés < poissons fourrage < truite; mais à cette tendance venaient se superposer des tendances secondaires liées aux baisses systématiques du rapport des crustacés planctoniques aux crustacés benthiques et, en parallèle, des poissons fourrage planctivores aux poissons benthivores. Les résultats de la recherche permettent de penser que les isotopes de Hg sont fractionnés par des processus naturels, notamment la méthylation, et ont des effets liés aux variations temporelles dans le potentiel oxydoréducteur des sédiments. Ces constats montrent que les isotopes de hg pourraient fournier une information

précieuse mais encore inexploitée sur les sources et le cycle biogéochimique du Hg naturel et anthropique.

Variations in the isotope composition of mercury in a freshwater sediment sequence and food web

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Résumé : L'analyse d'une carotte sédimentaire et l'étude des animaux du réseau trophique du bassin Niagara, dans le lac Ontario, ont mis pour la première fois en évidence des variations systématiques de la composition des isotopes stables du mercure (Hg) dans les milieux naturels de la Terre. Les sédiments se composaient de strates jeunes enrichies en Hg par la pollution récente, qui recouvraient des strates plus anciennes présentant seulement une concentration de fond de Hg. Plusieurs rapports des isotopes de Hg, notamment $^{199}Hg/^{201}Hg$, $^{201}Hg/^{204}Hg$ et $^{202}Hg/^{204}Hg$, variaient de façon significative avec le rapport Mn/Fe de la fraction oxyhydroxide extractible et facilement réduite du sédiment, et avec les concentrations des fractions extractibles de Mn ou de Fe, ou avec les deux, dans le sédiment, et la zone présentant une pollution récente par Hg donnait des résultats remarquablement différents de ceux de la zone ne présentant qu'une concentration de fond de Hg. Les animaux du réseau trophique présentaient une augmentation progressive du rapport $^{202}Hg/^{204}Hg$ lorsqu'on passait des niveaux trophiques les plus bas aux niveaux les plus hauts dans l'ordre crustacés < poissons fourrage < truite; mais à cette tendance venaient se superposer des tendances secondaires liées aux baisses systématiques du rapport des crustacés planctoniques aux crustacés benthiques et, en parallèle, des poissons fourrage planctivores aux poissons benthivores. Les résultats de la recherche permettent de penser que les isotopes de Hg sont fractionnés par des processus naturels, notamment la méthylation, et ont des effets liés aux variations temporelles dans le potentiel oxydoréducteur des sédiments. Ces constats montrent que les isotopes de Hg pourraient fournir une information précieuse mais encore inexploitée sur les sources et le cycle biogéochimique du Hg naturel et anthropique.

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Introduction

Mercury in the environment

The contamination of ecosystems with mercury (Hg) is a serious, widespread problem (Jackson 1997, 1998a; Fitzgerald et al. 1998). In aquatic environments, Hg, mostly in the form of inorganic Hg(II), is concentrated in fine-grained sed-

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iments and is partly converted to the highly toxic, relatively bioavailable species methyl Hg (CH_3Hg^+) by microorganisms. CH_3Hg^+ is readily accumulated by organisms and, unlike inorganic Hg(II), it undergoes biomagnification from lower to higher trophic levels, becoming preferentially concentrated in fish.

Since the onset of industrialisation, Hg introduced into the environment from various sources of pollution has greatly augmented the Hg released from natural sources (Jackson 1997, 1998a, 1998b). Some of this Hg is discharged directly into natural waters (usually rivers) and may be transported to lakes or the sea by fluvial action. Major quantities of Hg are also released into the atmosphere and are transported by winds to ecosystems up to several thousand kilometres away

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(Jackson 1997; Fitzgerald et al. 1998). Consequently, cores of continuous undisturbed sequences of fine-grained lake sediments, which provide historical records of Hg deposition, commonly show Hg enrichment in the upper (younger) strata, with lower Hg concentrations in the lower (older) strata. This tendency, accompanied by anomalously high CH_3Hg^+ levels in fish under conditions particularly favourable for the production and bioaccumulation of CH_3Hg^+, is found in virtually pristine lakes far from known sources of pollution, as well as in lakes polluted with Hg from local sources. Typically, the Hg concentration increases progressively upward to the sediment–water interface, implying that the rate of anthropogenic Hg deposition has been rising unchecked over time, or else increases to a maximum and then declines, indicating the occurrence of Hg pollution followed by abatement of the pollution (Engstrom and Swain 1997; Jackson 1997). Although there is general agreement on the broad features of the biogeochemical cycle of Hg and on the interpretation of Hg profiles in cores, the Hg cycle is somewhat clouded by uncertainties, owing to its complexity and, in contaminated ecosystems far from the sources of contamination, the difficulty of identifying and quantifying contributions from specific sources. Natural and anthropogenic Hg from a variety of primary and secondary sources undergo mixing, cycling, and recycling in the environment. Once Hg has been dispersed in the environment, attempts to differentiate between the effects of different sources and to disentangle the separate histories of the different Hg atoms brought together at a particular locality are rather problematic, except in the vicinity of a known point source, although in remote regions, where the uncertainty is greatest, reasonable inferences may be drawn from various lines of evidence, such as spatial and temporal trends (Jackson 1997; Fitzgerald et al. 1998). Variations in the stable-isotope composition of Hg could conceivably provide important but hitherto unknown information on the sources and biogeochemistry of Hg in natural environments. The purpose of the author's research was to investigate this possibility.

Stable isotopes of Hg and other elements

Owing to their different atomic and molecular weights, the stable isotopes of an element and simple compounds of these isotopes, respectively, differ somewhat in their physicochemical properties (e.g., rates of evaporation, reaction rates, and binding energies), and these isotope effects are influenced by environmental variables, such as temperature and pH (Rankama 1956, 1963; Hoefs 1973). The differences in properties, though generally small, may lead to isotope fractionation by physicochemical and biological processes. Separation of isotopes in complex natural environments is apt to be the net effect of several different processes. Some of these phenomena may have additive effects, while others may tend to cancel each other's effects, and the overall result may be hard to predict or interpret (Rankama 1956, 1963). Natural fractionation of isotopes has provided important information about the sources, biogeochemical cycling, and geological history of various elements, in particular the lighter ones, such as C, H, O, N, and S (Rankama 1956, 1963; Hoefs 1973). The tendency of stable isotopes to be separated by natural processes decreases sharply, however, with increasing atomic mass and is thought to be negligible for the heavier elements, such as Hg, be-

cause the isotopes differ so little from one another in mass (Rankama 1956; Hoefs 1973). Nevertheless, measurable systematic variations in the isotope composition of relatively heavy elements are theoretically possible, especially since a series of small effects can lead to a greatly amplified overall effect in nature (Rankama 1956).
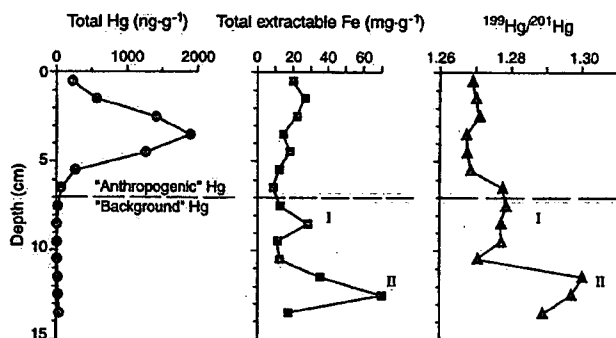
Hg has seven stable isotopes, the atomic weights and conventional percent abundances of which are ^{196}Hg (0.146%), ^{198}Hg (10.02%), ^{199}Hg (16.84%), ^{200}Hg (23.13%), ^{201}Hg (13.22%), ^{202}Hg (29.80%), and ^{204}Hg (6.85%) (Bainbridge and Nier 1950; Rankama 1956). Appreciable separation of Hg isotopes has been achieved experimentally by evaporation and distillation, by effusion, and by the action of an electric current (Brönsted and von Hevesy 1921; Mulliken and Harkins 1922; Haeffner 1953). This implies that certain natural and industrial processes may lead to the fractionation of Hg isotopes and that the isotope composition of Hg could depend to some extent on the source of the Hg (Rankama 1956, 1963). In theory, fractionation of Hg isotopes at sources of contamination and in the environment could give rise to small systematic spatial and temporal variations in the isotope composition of Hg in natural environments. If so, measurements of Hg isotope ratios performed with sufficiently precise and sensitive instruments could be used to distinguish between different sources and biogeochemical pathways of Hg in ecosystems. However, with the exception of several papers on the supposed occurrence of Hg isotope anomalies in meteorites and moon rocks (Jovanovic and Reed 1990; Kumar and Goel 1992a, 1992b) and an early report of an unsuccessful attempt to detect differences in the isotope content of Hg ore samples from different deposits (Brönsted and von Hevesy 1922), there appears to be no published evidence for or against the occurrence of significant variations in Hg isotope ratios in nature, nor any mention of attempts to obtain such information. Here, evidently for the first time, systematic variations in the stable-isotope composition of Hg in a sediment sequence and associated food web are demonstrated. The abstract of an oral presentation on this work has been published elsewhere (Jackson 1999).

Materials and methods

The Niagara Basin of Lake Ontario was selected for study because it is polluted with Hg from industrial point sources along the Niagara River, which flows into the basin (Mudroch 1983; Thomas 1983; Whittle and Fitzsimons 1983). A mini box core of fine-grained profundal sediment was collected from the basin in August 1996. From this, a second core was taken by hand, stored at 4°C, and, in the spring of 1998, cut into 1-cm sections and analyzed.

Portions of the core sections were analysed in duplicate for total Hg by extraction with H_2SO_4/HNO_3 (2:1, v/v) at 60°C, addition of $KMnO_4$, $K_2S_2O_8$, and H_2SO_4, reduction of Hg(II) to Hg(0) by $SnCl_2$, and determination of the Hg(0) by cold vapour atomic absorption spectrophotometry (AAS). The Hg isotope content of each extract was then determined in triplicate by the reduction of Hg(II) to Hg(0) with $SnCl_2$, and analysis of the Hg(0) by inductively coupled plasma quadrupole mass spectrometry (ICP-MS), using a VG Elemental PQ2+ ICP-MS system, with argon as the carrier gas. Thus, a total of six replicate sets of data were obtained for each core section. The isotopes ^{198}Hg, ^{199}Hg, ^{200}Hg, ^{201}Hg, ^{202}Hg, and ^{204}Hg were determined, but ^{196}Hg was omitted, because it was not abundant enough to be measured with sufficient accuracy and precision. Hg isotope composition was expressed as a series of simple

Fig. 1. The vertical profiles of total Hg, total extractable Fe, and the ^{199}Hg/^{201}Hg ratio in the sediment core from the Niagara Basin of Lake Ontario.

Table 1. The total Hg concentrations and ^{210}Pb dates of consecutive 1-cm sections of the core from the Niagara Basin of Lake Ontario; the Hg concentrations are based on dry weight.

Depth (cm)	Total Hg (ng·g^{-1}) Mean	Range	^{210}Pb date
0–1	239.34	198.49–280.19	1989±16
1–2	566.68	496.18–637.18	1976±11
2–3	1420.785	1375.56–1466.01	1963±14
3–4	1886.65	1882.29–1891.01	1949±14
4–5	1264.1	1258.73–1269.4	1933±17
5–6	274.92	219.7–330.14	1916±18
6–7	70.01	61.77–78.25	1898±18
7–8	16.3	13.89–18.8	—
8–9	10.6	9.86–11.39	—
9–10	9.67	9.43–9.91	—
10–11	11.55	9.77–13.33	—
11–12	12.89	12.17–13.61	—
12–13	11.685	11.59–11.78	—
13–14	28.9	21.84–35.9	—

isotope ratios. A solution of high-purity Hg(0) (99.98% source purity) (High Purity Standards, Charleston, South Carolina) was used to calibrate the system and to correct the data for any inherent mass bias effect, on the assumption that the proportions of the isotopes in the pure metal were the same as those reported in the literature (Bainbridge and Nier 1950; Rankama 1956). The precision of each isotope ratio was calculated from replicate measurements of the concentration ratios of the standard; the relative standard deviation and 99% confidence limits can be provided on request. A standard solution of Hg(II) was analysed at intervals throughout the course of the sample analyses, to check for possible systematic errors caused by drift of the readings in a preferred direction over time.

In addition, duplicate subsamples of the core sections were extracted sequentially with $NH_2OH \cdot HCl/HNO_3$, $H_2O_2/HNO_3/NH_4$ acetate (Ac), and citrate/dithionite, in that order, to isolate the easily reduced "amorphous" (short-range order) oxyhydroxides, organically bound species, and less easily reduced "crystalline" (long-range order) oxyhydroxides, respectively, of Fe and Mn (Gupta and Chen 1975). The extracts were then analysed for Fe and Mn by AAS and for Hg by cold vapour AAS. The core sections were also subjected to radiometric dating, employing the ^{210}Pb method (Eakins and Morrison 1978; Turner 1990).

The biological samples consisted of planktonic and benthic crustaceans, forage fish that feed on these invertebrates, and trout, which prey on the forage fish. The specimens were collected from the Niagara Basin in August and September 1998, whereupon they were frozen, homogenised, and analysed for total Hg and Hg isotope content by the techniques used for analysis of the sediments. Single samples of the crustaceans and duplicate samples of the fish were each analysed in duplicate. As with the core sections, a standard solution of Hg(II) was analysed at intervals during the course of the isotope analyses.

Ten replicate portions of a sample of pulverised cinnabar from the Almaden Hg mine in Spain were analysed as well, for the purpose of estimating the precision of the techniques used to measure the Hg isotope ratios and for the sake of obtaining reference data for comparison with the data for the core sections and biological samples.

In all plots and regression analyses involving sediment data, the average values of the Hg isotope ratios for each core section were expressed as medians rather than means, to minimise distortion due to extreme values. Averages for biological samples, however, were expressed as means, because three of a total of seven specimens were analysed in duplicate only. Similarly, all chemical data had to be expressed as mean values, because the analyses were done in duplicate.

Results and discussion

The sediment core

Analysis of the core sections revealed striking systematic vertical variations in the total Hg and total extractable Fe content and the ^{199}Hg/^{201}Hg ratio of the sediment (Fig. 1; Tables 1–3) (total extractable Fe being defined as the sum of the three solvent-extractable Fe fractions, of which citrate/dithionite-extractable Fe was the most abundant (Table 3)). The ^{199}Hg/^{201}Hg ratio of the Hg standard solution (T.A. Jackson, unpublished data) showed only minor random fluctuation about a vertical line, demonstrating that there were no systematic errors caused by deviation in a preferred direction during the course of the sample analyses. Moreover, the ^{210}Pb measurements (Table 1) imply that the core data comprise an unbroken historical record. Thus, the ^{210}Pb ages increase progressively with depth, and the correlation of age with depth is highly significant ($r = 0.998$; $P < 0.001$), indicating continuous deposition at a virtually constant annual rate and the absence of postdepositional disturbance.

The total-Hg profile shows a large buried maximum representing Hg pollution from local sources, with consistently low background values below this zone of anthropogenic Hg enrichment (Fig. 1). The pollution began around 1898, became progressively worse until some time between 1949 and 1963, and then abated (Table 1). For convenience, the region of Hg enrichment and the underlying Hg-poor region are herewith designated as the zones of "anthropogenic" and "background" Hg, respectively (although this is an oversimplification, as the anthropogenic Hg of local origin is presumably mixed with background Hg comprising trace amounts of natural and anthropogenic Hg from various primary and secondary sources (Jackson 1997, 1998a)). The ^{199}Hg/^{201}Hg ratio is independent of total Hg, but its core profile parallels that of the total extractable Fe and citrate/dithionite-extractable Fe to a remarkable degree (Fig. 1; Tables 2 and 3). The ^{199}Hg/^{201}Hg ratio and Fe show little variation with depth in the zone of anthropogenic Hg but, in the zone of background

Table 2. The $^{199}Hg/^{201}Hg$, $^{201}Hg/^{204}Hg$, $^{202}Hg/^{204}Hg$, $^{200}Hg/^{202}Hg$, and $^{198}Hg/^{204}Hg$ ratios of consecutive 1-cm sections of the core from

Depth (cm)	$^{199}Hg/^{201}Hg$				$^{201}Hg/^{204}Hg$			
	Median	Mean	SD	Range	Median	Mean	SD	Range
0–1	1.269	1.269	0.005574	1.264–1.276	1.945	1.946	0.01145	1.932–1.962
1–2	1.270	1.268	0.006802	1.259–1.276	1.9255	1.9265	0.005010	1.921–1.933
2–3	1.271	1.273	0.005279	1.269–1.281	1.9305	1.928	0.006306	1.916–1.933
3–4	1.2675	1.270	0.006831	1.262–1.278	1.949	1.948	0.007062	1.938–1.956
4–5	1.2675	1.267	0.003615	1.263–1.273	1.938	1.9375	0.003209	1.932–1.941
5–6	1.2685	1.268	0.005115	1.259–1.273	1.929	1.932	0.01665	1.914–1.958
6–7	1.2775	1.277	0.005879	1.270–1.284	1.930	1.930	0.009131	1.917–1.943
7–8	1.2785	1.277	0.01611	1.257–1.297	1.879	1.886	0.02165	1.861–1.919
8–9	1.277	1.279	0.01867	1.257–1.306	1.9105	1.917	0.02544	1.887–1.962
9–10	1.277	1.270	0.02049	1.234–1.289	1.9205	1.922	0.03744	1.874–1.974
10–11	1.2705	1.278	0.02283	1.258–1.316	1.9385	1.924	0.04636	1.843–1.969
11–12	1.300	1.303	0.01765	1.283–1.329	1.8895	1.895	0.03327	1.863–1.946
12–13	1.297	1.293	0.01374	1.273–1.311	1.876	1.8955	0.03939	1.864–1.952
13–14	1.284	1.286	0.008501	1.278–1.299	1.9115	1.921	0.02703	1.901–1.974

Note: The data are based on the results of six replicate analyses per core section (more precisely, triplicate analyses of duplicate extracts). SD is the

Hg (together with the lowest anthropogenic horizon (the 6- to 7-cm section), which borders it), they are each characterised by a small maximum overlying a much larger maximum (called peaks I and II, respectively). Unlike the other core sections, which were grey to brownish grey, the sections represented by peak I and, to a far greater extent, peak II were distinguished by a conspicuous yellowish brown colour, reflecting an anomalous abundance of Fe oxyhydroxide, as confirmed by the analytical data (Table 3).

As would be expected from the variations revealed in Fig. 1, the $^{199}Hg/^{201}Hg$ ratio of the background zone (combined with the adjacent basal section of the anthropogenic zone) gave a significant positive correlation with total extractable Fe ($r = 0.790$; $P > 0.01$, < 0.02); the anthropogenic zone, too, gave a positive correlation, although a much weaker one ($r = 0.696$; $P > 0.1$). However, a plot of the $^{199}Hg/^{201}Hg$ ratio against the Mn/Fe ratio of the $NH_2OH \cdot HCl/HNO_3$-extractable oxyhydroxide fraction yielded more significant and instructive results (Fig. 2; Tables 2 and 3). The Mn/Fe ratio of the $NH_2OH \cdot HCl/HNO_3$-extractable fraction of lake sediment tends to increase with the oxidation–reduction potential (Eh) of the sediment and the degree of aeration of the overlying water (Jackson 1988; Jackson and Bistricki 1995), reflecting the fact that, at any given pH, MnOOH precipitates at a higher Eh or dissolved O_2 concentration than does FeOOH (Degens 1965). The Mn/Fe ratio, therefore, is a useful index of sediment Eh at the time of deposition.

The plot of the $^{199}Hg/^{201}Hg$ ratio against the Mn/Fe ratio (Fig. 2) resolves itself into three highly significant trends representing the three principal regions of the core as defined thus far: the anthropogenic zone and the peak I and peak II segments of the background zone. Not surprisingly, the base of the anthropogenic zone (the 6- to 7-cm section), which has the lowest proportion of anthropogenic Hg to background Hg, falls on the peak I curve; it has, therefore, been treated as part of the peak I sequence of core sections. The two sets of background data yielded inverse correlations with separate but converging regression lines, and the point where the trends are joined represents, appropriately, the physical boundary between peaks I and II (the 10- to 11-cm section). In contrast, the anthropogenic zone gave a positive

correlation, and the slope of the regression line is relatively low. Moreover, the regression line for the anthropogenic zone lies below both of the regression lines for the background zone. Thus the anthropogenic Hg is isotopically heavier than the background Hg, insofar as the $^{199}Hg/^{201}Hg$ ratio is concerned, with the sole exception of the 6- to 7-cm section and possibly the 10- to 11-cm section, which is a borderline case. Also note that the four oldest anthropogenic sections, which record the temporal increase in the severity of Hg pollution up to its maximum, have much lower Mn/Fe ratios than the three youngest sections, which record the subsequent decrease in the severity of Hg pollution over time (Fig. 2). This contrast in sediment chemistry suggests that these two regions of the anthropogenic zone represent quite different environmental conditions owing to their differences in pollution history.

For all three regions of the core, the Mn/Fe ratio of the $NH_2OH \cdot HCl/HNO_3$-extractable fraction gave much higher correlation coefficients (r values) and significance probabilities (P values) than the Mn or Fe concentration alone. Thus, P values for the Mn/Fe ratios range from <0.001 to >0.001, <0.01 (Fig. 2), but the values for Fe and Mn alone range from >0.02, <0.05 to $>>0.1$. This implies that the causes of the variations in Hg isotope composition are related to the environmental factors that determined the proportion of MnOOH to FeOOH at the time of deposition, whereas the abundance of MnOOH or FeOOH, in itself, is not necessarily important or even relevant. More specifically, the isotope ratio is probably a function of certain biogeochemical processes (possibly microbial activities) directly or indirectly linked to Eh. However, the marked differences between the three curves in Fig. 2 suggest that several different factors, which varied from one environment of deposition to another, determined the overall relationship between isotope ratio and Eh. Evidently each of the three zones in the sediment sequence represents a distinct environmental and biogeochemical regime with its own specific relationship between isotope ratio and Eh.

The radical differences between the results for the anthropogenic zone as a whole and the background zone as a whole might be supposed, at first glance, to result from the

the Niagara Basin of Lake Ontario.

$^{202}Hg/^{204}Hg$				$^{200}Hg/^{202}Hg$				$^{198}Hg/^{204}Hg$			
Median	Mean	SD	Range	Median	Mean	SD	Range	Median	Mean	SD	Range
4.350	4.351	0.02209	4.325–4.384	0.7735	0.775	0.00327	0.771–0.780	1.4705	1.470	0.01009	1.454–1.480
4.302	4.300	0.01247	4.283–4.316	0.770	0.770	0.00151	0.768–0.771	1.4535	1.453	0.003327	1.448–1.458
4.343	4.340	0.01879	4.307–4.357	0.7655	0.765	0.00306	0.761–0.770	1.4435	1.4445	0.006535	1.434–1.452
4.381	4.386	0.01736	4.363–4.407	0.780	0.786	0.0241	0.763–0.820	1.4535	1.450	0.005317	1.443–1.454
4.345	4.343	0.01411	4.325–4.365	0.7635	0.763	0.00279	0.759–0.766	1.4425	1.444	0.004875	1.439–1.450
4.315	4.318	0.04436	4.261–4.369	0.774	0.774	0.00367	0.770–0.777	1.4555	1.457	0.01790	1.436–1.477
4.337	4.341	0.03686	4.290–4.401	0.7755	0.7755	0.00351	0.770–0.779	1.471	1.469	0.01280	1.452–1.487
4.262	4.269	0.03574	4.223–4.314	0.772	0.770	0.00728	0.758–0.779	1.437	1.440	0.01828	1.421–1.472
4.2865	4.303	0.07375	4.227–4.431	0.771	0.772	0.00769	0.762–0.783	1.4425	1.436	0.01898	1.407–1.455
4.313	4.335	0.09592	4.232–4.482	0.7735	0.775	0.0105	0.763–0.789	1.4425	1.449	0.02549	1.418–1.480
4.327	4.330	0.07582	4.212–4.427	0.7665	0.768	0.0116	0.756–0.785	1.461	1.454	0.03791	1.387–1.500
4.302	4.299	0.03801	4.252–4.352	0.7645	0.764	0.00739	0.754–0.774	1.4545	1.456	0.02911	1.416–1.494
4.297	4.306	0.07212	4.193–4.403	0.7665	0.766	0.00564	0.757–0.774	1.4265	1.433	0.02579	1.403–1.467
4.329	4.343	0.05223	4.284–4.439	0.7665	0.766	0.00542	0.758–0.772	1.453	1.455	0.02132	1.429–1.488

standard deviation.

occurrence of contrasting isotope signatures for different sources of Hg. This idea is negated, however, by the fact that the isotope ratios in the zone of anthropogenic Hg are unrelated to the total Hg concentration and, hence, are independent of variations in the proportion of Hg from local sources of pollution to background Hg from other sources. The fact that the $^{199}Hg/^{201}Hg$ ratio shows little variation within the sediment sequence overlying the basal section of this zone, despite enormous variation in total Hg content due to increases and decreases in the severity of pollution, and is covariant with the Mn/Fe ratio but independent of total Hg concentration, constitutes strong evidence that isotope composition was determined by certain physicochemical and biological processes characteristic of the sedimentary environment and bears no discernible imprint of the original isotope composition of the Hg. The abrupt and drastic change in the behaviour of Hg on going from the background zone to the anthropogenic zone, along with the fact that the isotope ratios consistently conform to the same distinctive pattern of variation throughout the anthropogenic zone (not counting the basal section), despite large variations in the proportion of anthropogenic Hg of local origin to diffuse background Hg, suggests the influence of environmental changes caused by human activities that occurred contemporaneously with Hg pollution and continued over the entire time interval in which the sediments of the anthropogenic zone were laid down. However, some influence of the source of the Hg cannot be ruled out altogether; nor do the data for Lake Ontario preclude the possible existence of source-related isotopic signatures elsewhere.

One possible reason for the inverse correlation of the $^{199}Hg/^{201}Hg$ ratio with the Mn/Fe ratio in the background zone is that the activities of microbes which convert Hg(II) to Hg(0) increased with increasing aeration (Jackson 1998a), causing the sediment to be preferentially depleted in the lighter isotope, owing to the escape of isotopically light gaseous Hg(0) into the atmosphere. It is likely, though, that many different isotope-fractionating processes were responsible for the observed overall effect (Rankama 1956, 1963). In the anthropogenic zone, alteration of the environmental regime by pollutants (including pollutants other than Hg) may

have brought about a profound change in the nature of the microbial community, leading to an entirely different relationship between Hg isotope fractionation and sediment Eh.

Moving on to other Hg isotope ratios, we find that a plot of the $^{201}Hg/^{204}Hg$ ratio against the Mn/Fe ratio of the $NH_2OH\cdot HCl/HNO_3$ extract (Fig. 3; Tables 2 and 3) also resolves itself into a family of significant regression lines: two converging curves representing the peak I (7- to 8-cm to 10- to 11-cm) and peak II (10- to 11-cm to 13- to 14-cm) regions of the background zone, and a separate but roughly parallel curve for the 3- to 4-cm to 6- to 7-cm sections of the anthropogenic zone (the region showing temporal increase in total Hg to a maximum). But in this case, all three of the curves represent positive correlations, and the curve for the anthropogenic zone lies above the two curves for the background zone. Moreover, the 0- to 1-cm to 2- to 3-cm sections of the anthropogenic zone (the region representing pollution abatement) are highly anomalous with respect to the 3- to 4-cm to 6- to 7-cm sections. Another noteworthy feature is that, in Fig. 3 and in the other plots that follow (see below), the lowest anthropogenic horizon (the 6- to 7-cm section) falls in line with the other parts of the 3- to 4-cm to 6- to 7-cm region of the anthropogenic zone. Also note that the trends shown by the $^{201}Hg/^{204}Hg$ ratio (Fig. 3) are essentially the inverse of the trends shown by the $^{199}Hg/^{201}Hg$ ratio (Fig. 2). Probably the reason is that ^{201}Hg is the numerator of the one ratio and the denominator of the other. In other words, the two ratios are not entirely independent of each other and, therefore, display partial self-correlation. Nonetheless, a comparison of Figs. 2 and 3 is instructive, because Fig. 3, unlike Fig. 2, reveals (i) a profound difference between the regions of increasing and decreasing pollution in the zone of anthropogenic Hg, (ii) essential similarity between all three regression lines, and (iii) conformity of the 6- to 7-cm section to the other parts of the region of increasing pollution in the anthropogenic zone. The contrast between the upper and lower regions of the anthropogenic zone suggests an important difference in sedimentary environment, as implied by their radically different Mn/Fe ratios, and, correspondingly, in the nature of the sedimentary microflora. Another point worth mentioning is that, in the 7- to

Table 3. Solvent extractable Mn and Fe fractions in consecutive 1-cm sections of the core from the Niagara Basin of Lake Ontario.

| Depth (cm) | NH$_2$OH·HCl/HNO$_3$-extractable fractions | | | | Mn/Fe (wt./wt.) | | Citrate/dithionite-extractable Fe (mg·g^{-1}) | | Total extractable Fe (mg·g^{-1}) | |
| | Mn (µg·g^{-1}) | | Fe (µg·g^{-1}) | | | | | | | |
	Mean	Range	Mean	Range	Mean	Range	Mean	Range	Mean	Range
0–1	286.425	284.79–288.06	63.12	59.68–66.56	4.550	4.328–4.772	20.14	19.70–20.58	20.309	19.862–20.756
1–2	316.33	315.63–317.03	42.54	38.63–46.45	7.498	6.825–8.171	26.855	22.28–31.43	26.989	22.424–31.555
2–3	276.795	265.62–287.97	33.455	32.53–34.38	8.289	7.726–8.852	22.125	20.46–23.79	22.250	20.579–23.9205
3–4	242.565	241.78–243.35	261.46	244.43–278.49	0.93149	0.87382–0.98916	14.055	13.27–14.84	14.585	13.737–15.434
4–5	228.28	218.59–237.97	354.18	266.44–441.92	0.67945	0.53849–0.82041	16.995	10.58–23.41	18.269	11.849–24.689
5–6	231.445	227.05–235.84	484.99	480.53–489.45	0.47734	0.46389–0.49079	10.28	10.08–10.48	11.916	11.782–12.0495
6–7	243.80	242.32–245.28	612.37	581.58–643.16	0.399015	0.38137–0.41666	7.48	6.91–8.05	8.830	8.230–9.430
7–8	218.735	214.79–222.68	740.45	731.51–749.39	0.295515	0.28662–0.30441	10.925	7.26–14.59	12.483	8.681–16.284
8–9	249.085	242.34–255.83	462.97	348.22–577.72	0.569385	0.44283–0.69594	27.56	25.86–29.26	28.8655	27.083–30.648
9–10	257.58	255.89–259.27	331.47	315.05–347.89	0.77925	0.73555–0.82295	9.965	9.61–10.32	11.044	10.751–11.336
10–11	288.585	288.29–288.88	171.875	117.91–225.84	1.86205	1.2791–2.4450	11.585	11.54–11.63	12.415	12.222–12.608
11–12	306.255	303.64–308.87	455.61	342.50–568.72	0.717855	0.53390–0.90181	34.105	27.44–40.77	35.566	29.093–42.040
12–13	275.00	263.72–286.28	472.515	299.54–645.49	0.682145	0.40856–0.95573	68.74	58.94–78.54	69.909	60.253–79.5645
13–14	272.435	271.34–273.53	217.965	217.73–218.20	1.2499	1.2462–1.2536	16.295	14.94–17.65	16.860	15.556–18.163

Note: "Total extractable Fe" is Fe extracted sequentially with NH$_2$OH·HCl/HNO$_3$, H$_2$O$_2$/NH$_3$Ac/HNO$_3$, and citrate/dithionite. The Fe and Mn concentrations are expressed on the basis of the unit dry weight of the sediment.

8-cm to 10- to 11-cm region of the background zone, the ^{201}Hg/^{204}Hg ratio gave a less significant correlation with the Mn/Fe ratio ($P > 0.02$, < 0.05) (Fig. 3) than with Mn alone ($r = 0.992$; $P > 0.001$, < 0.01) or Fe alone ($r = -0.998$; $P > 0.001$, < 0.01), although the opposite is true for the other two regions of the core (the P values for Mn and Fe ranging from >0.02, <0.05 to $>>0.1$). Nevertheless, only the Mn/Fe ratio gave significant correlation coefficients for all three of the curves in Fig. 3. In any case, the curves in Fig. 3, as with those in Fig. 2, are subject to interpretation in terms of the biogeochemical processes related directly or indirectly to sediment Eh, and different effects were produced in the three regions of the core owing to environmental differences at the time of deposition.

The ^{202}Hg/^{204}Hg ratio of the background zone gave an extremely significant positive correlation with the Mn/Fe ratio of the NH$_2$OH·HCl/HNO$_3$ extract and an even stronger inverse correlation with NH$_2$OH·HCl/HNO$_3$-extractable Fe ($P < 0.001$ for both plots) (Fig. 4; Tables 2 and 3), but only a weak correlation with NH$_2$OH·HCl/HNO$_3$-extractable Mn ($r = 0.674$; $P > 0.05$, < 0.1). In Fig. 4, unlike Figs. 2 and 3, all seven sections of the background zone conform to the same trends, and there is remarkably little scatter. In contrast, the isotope ratios of the anthropogenic zone as a whole are virtually independent of the Mn/Fe and Fe data as well as the Mn data (all three P values being $>>0.1$). The isotope ratios of the 3- to 4-cm to 6- to 7-cm region of the anthropogenic zone lie above the curves for the background zone and tend to parallel them (Fig. 4), but the trend is weak (P ranging from >0.05, <0.1 in Fig. 4a to >0.1 in Fig. 4b).

Obviously, the strong correlation between the ^{202}H/^{204}Hg and Mn/Fe ratios (Fig. 4a) is due chiefly to Fe (Fig. 4b). Insofar as this particular isotope ratio is concerned, therefore, the relationship between isotope composition and sediment Eh is not as clear-cut as with the ^{199}Hg/^{201}Hg ratio. Possibly the ^{202}Hg/^{204}Hg ratio was largely determined by some process or complex of processes, or a set of environmental conditions, that was linked directly or indirectly to the precipitation of FeOOH (e.g., certain microbial activities) or to direct interaction between Hg and FeOOH (e.g., preferential sorption of the heavier isotope by FeOOH and preferential desorption of the lighter isotope (Rankama 1956; Hoefs 1973)). Perhaps the most puzzling feature of the ^{202}Hg/^{204}Hg data is that the variations of this ratio with respect to Mn, Fe, and the Mn/Fe ratio are so radically different from those of the ^{199}Hg/^{201}Hg ratio (in particular, compare Figs. 2 and 4a). Intuitively, one would expect the two isotope ratios to yield similar patterns of variation, because each of them represents a lighter isotope of Hg divided by a heavier one, besides which the difference in mass between ^{199}Hg and ^{201}Hg is the same as the difference in mass between ^{202}Hg and ^{204}Hg. In this case, the contrast cannot be explained by the occurrence of a common simple variable in each of the two compound variables, as with the ^{199}Hg/^{201}Hg and ^{201}Hg/^{204}Hg ratios (see above). Further research is required to explain this mystery. Perhaps it reflects the fact that the fractionation of Hg isotopes in nature is a complex process involving many different reactions occurring simultaneously or in succession at different rates and as functions—possibly nonlinear functions—of many physicochemical and biological factors, all of which are subject to spatial and temporal variation. Under the circum-

Fig. 2. Variations in the $^{199}Hg/^{201}Hg$ ratio of the sediment as functions of the Mn/Fe ratio of the $NH_2OH\cdot HCl/HNO_3$-extractable fraction of the sediment in the zones of anthropogenic and background Hg in the core from the Niagara Basin of Lake Ontario. Symbols: (*i*) zone of anthropogenic Hg: 0- to 1-cm to 2- to 3-cm sections (region of decreasing pollution), □; 3- to 4-cm to 5- to 6-cm sections (region in which pollution is increasing to a maximum, excluding the 6- to 7-cm section), △; 6- to 7-cm section (base of the zone), ▲; (*ii*) zone of background Hg: 7- to 8-cm to 9- to 10-cm sections (peak I region), ●; 10- to 11-cm section (boundary between the peak I and peak II regions), ◆; 11- to 12-cm to 13- to 14-cm sections (peak II region), ■.
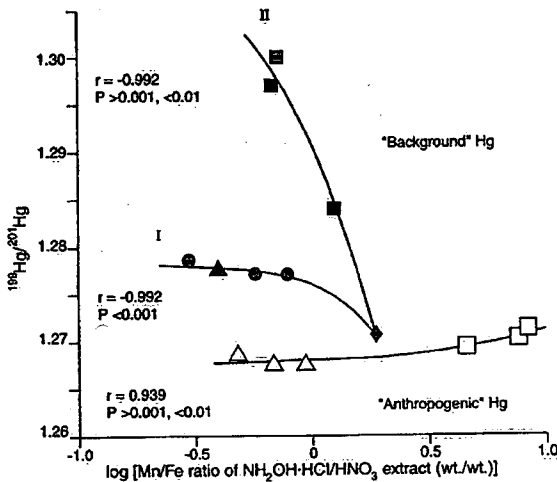

Fig. 3. Variations of the $^{201}Hg/^{204}Hg$ ratio of the sediment as functions of the Mn/Fe ratio of the $NH_2OH\cdot HCl/HNO_3$ extract of the sediment in the zones of anthropogenic and background Hg in the core from the Niagara Basin of Lake Ontario. Symbols: (*i*) zone of anthropogenic Hg: 0- to 1-cm to 2- to 3-cm sections (region of decreasing pollution), □; 3- to 4-cm to 6- to 7-cm sections (region in which pollution is increasing to a maximum), △; (*ii*) zone of background Hg: 7- to 8-cm to 9- to 10-cm sections (peak I region), ●; 10- to 11-cm section (boundary between peak I and peak II regions), ◆; 11- to 12-cm to 13- to 14-cm sections (peak II region), ■.
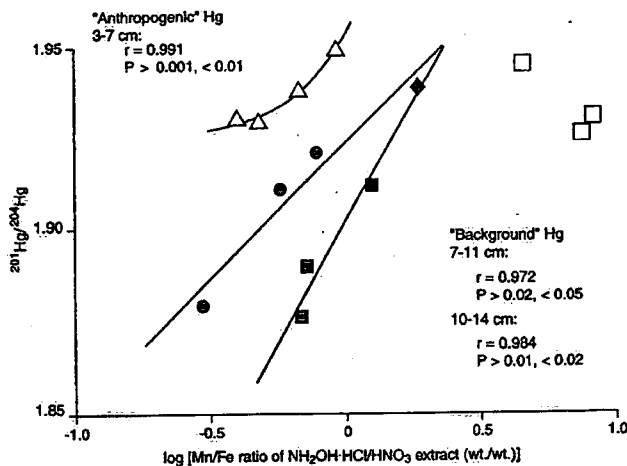
Fig. 4. Variations of the $^{202}Hg/^{204}Hg$ ratio of the sediment with respect to the Mn/Fe ratio of the $NH_2OH\cdot HCl/HNO_3$ extract (*a*) and the $NH_2OH\cdot HCl/HNO_3$-extractable Fe content (*b*) of the sediment in the Niagara Basin of Lake Ontario. Symbols: (*i*) zone of anthropogenic Hg: 0- to 1-cm to 2- to 3-cm sections (region of decreasing pollution), □; 3- to 4-cm to 6- to 7-cm sections (region in which pollution is increasing to a maximum), △; (*ii*) zone of background Hg: 7- to 8-cm to 9- to 10-cm sections (peak I region), ●; 10- to 11-cm section (boundary between peak I and peak II regions), ◆; 11- to 12-cm to 13- to 14-cm sections (peak II region), ■.
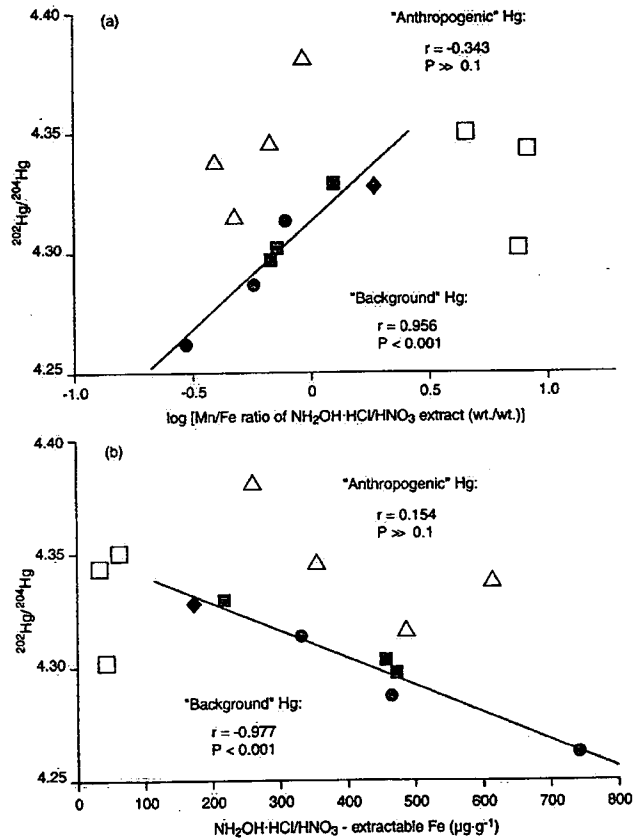

stances, some isotope ratios could conceivably give quite different results than others.

Although the $^{202}Hg/^{204}Hg$ ratio correlates strongly with $NH_2OH\cdot HCl/HNO_3$-extractable Fe but weakly with $NH_2OH\cdot HCl/HNO_3$-extractable Mn, the opposite is true of the $^{200}Hg/^{202}Hg$ ratio (the ratio of the two most abundant Hg isotopes (Bainbridge and Nier 1950; Rankama 1956)) (Fig. 5; Tables 2 and 3). The $^{200}Hg/^{202}Hg$ ratio gave a significant inverse correlation with $NH_2OH\cdot HCl/HNO_3$-extractable Mn ($P > 0.01, < 0.02$) (Fig. 5) but highly insignificant correlations with $NH_2OH\cdot HCl/HNO_3$-extractable Fe ($r = 0.381; P >> 0.1$) and the Mn/Fe ratio of the $NH_2OH\cdot HCl/HNO_3$ extract ($r = -0.518; P >> 0.1$). These relationships suggest that the variation in the $^{200}Hg/^{202}Hg$ ratio is linked specifically to the formation of MnOOH, either because both were functions of certain environmental factors and microbial processes or because MnOOH preferentially bound the heavier isotope and released the lighter one (Rankama 1956; Hoefs 1973).

Fig. 5. Variation of the $^{200}Hg/^{202}Hg$ ratio as a function of the $NH_2OH\cdot HCl/HNO_3$-extractable Mn concentration in the zone of background Hg in the sediment core from the Niagara Basin of Lake Ontario. Symbols: 7- to 8-cm to 9- to 10-cm sections (peak I region), ●; 10- to 11-cm section (boundary between peak I and peak II regions), ◆; 11- to 12-cm to 13- to 14-cm sections (peak II region), ■.
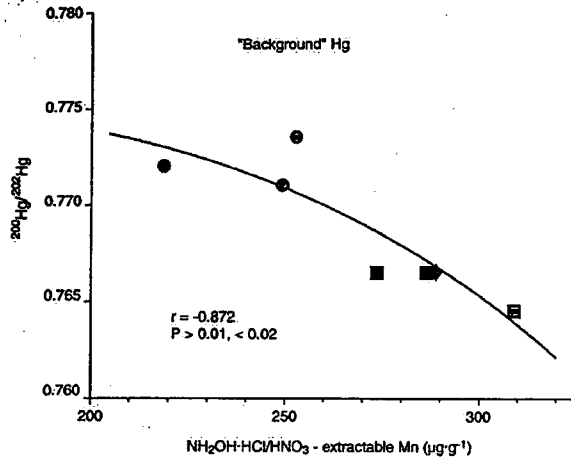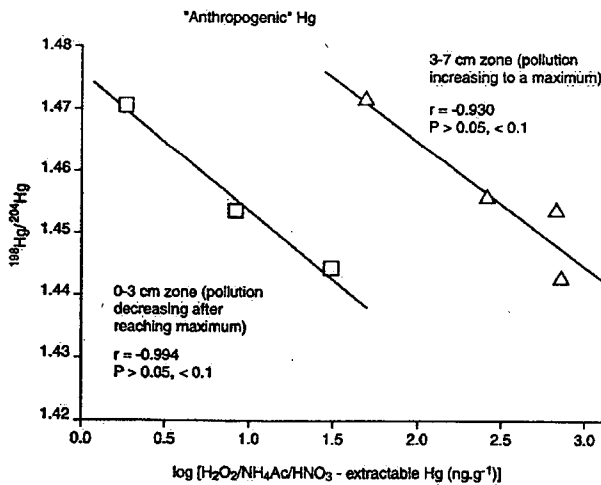

Fig. 6. Variations of the $^{198}Hg/^{204}Hg$ ratio with respect to $H_2O_2/NH_4Ac/HNO_3$-extractable Hg in the zone of anthropogenic Hg in the core from the Niagara Basin of Lake Ontario. Symbols: 0- to 1-cm to 2- to 3-cm sections (region of decreasing pollution), □; 3- to 4-cm to 6- to 7-cm sections (region in which pollution is increasing to a maximum), △.

Nevertheless, the difference between the results for the $^{202}Hg/^{204}Hg$ and $^{200}Hg/^{202}Hg$ ratios is probably due, in part, to the fact that ^{202}Hg is the numerator of the former but the denominator of the latter.

Finally, we come to the $^{198}Hg/^{204}Hg$ ratio, which is of interest because it is the ratio of the lightest isotope (not counting ^{196}Hg) to the heaviest. The results are unlike any of the others. The $^{198}Hg/^{204}Hg$ ratios of the 0- to 1-cm to 2- to 3-cm and 3- to 4-cm to 6- to 7-cm regions of the anthropogenic zone vary inversely with the $H_2O_2/NH_4Ac/HNO_3$-extractable (organically bound) Hg content of the sediment, but the two

Table 4. Concentrations of $H_2O_2/NH_4Ac/HNO_3$-extractable Hg in consecutive 1-cm sections of the core from the Niagara Basin of Lake Ontario.

| Depth (cm) | $H_2O_2/NH_4Ac/HNO_3$-extractable Hg (ng·g^{-1}) | |
	Mean	Range
0–1	1.845	1.56–2.13
1–2	8.265	8.26–8.27
2–3	30.85	27.60–34.10
3–4	670.91	666.03–675.79
4–5	716.925	693.46–740.39
5–6	257.14	253.59–260.69
6–7	49.05	46.15–51.95
7–8	20.265	18.63–21.90
8–9	15.115	14.59–15.64
9–10	13.375	12.16–14.59
10–11	12.32	11.55–13.09
11–12	18.05	17.00–19.10
12–13	13.695	12.28–15.11
13–14	13.65	13.57–13.73

Note: The Hg concentrations are based on the unit dry weight of the sediment.

Fig. 7. Variations in the $^{202}Hg/^{204}Hg$ ratios of food-web animals from the Niagara Basin of Lake Ontario. Organisms at the same trophic level are represented by points surrounded by a dashed line, and the large arrows point from lower to higher trophic levels.
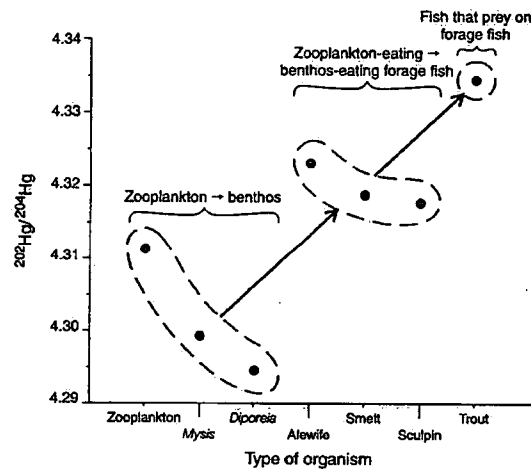
regions show separate, though nearly parallel, trends covering different ranges of $H_2O_2/NH_4Ac/HNO_3$-extractable Hg concentrations (Fig. 6; Tables 2 and 4). Although the correlations are not very strong ($P > 0.05, < 0.1$), the regularity of the two trends and their similarity to each other suggest that the relationships are real. The sharp separation of the curves constitutes further evidence that the two regions of the anthropogenic zone represent different environmental conditions and, hence, different isotope-fractionating effects. Isotope fractionation could have resulted from preferential binding of the heavier isotope and release of the lighter one by organic matter (Rankama 1956; Hoefs 1973). The $^{198}Hg/^{204}Hg$ ratios of the background Hg zone, however, vary independently of $H_2O_2/NH_4Ac/HNO_3$-extractable Hg ($r = -0.205$; $P \gg 0.1$), possibly because the background Hg was associ-

Table 5. The ^{202}Hg/^{204}Hg, ^{199}Hg/^{204}Hg, ^{198}Hg/^{199}Hg, ^{201}Hg/^{204}Hg, ^{198}Hg/^{204}Hg, and ^{200}Hg/^{202}Hg ratios of the food-web animals from the Niagara Basin of Lake Ontario. (Table 5 is concluded on pages 194 and 195.)

Type of organism	N	^{202}Hg/^{204}Hg				^{199}Hg/^{204}Hg			
		Median	Mean	SD	Range	Median	Mean	SD	Range
Zooplankton (mostly cladocerans)	2	4.311	4.311	0.02760	4.292–4.331	2.430	2.430	0.01980	2.416–2.444
Mysis relicta	2	4.299	4.299	0.005228	4.296–4.303	2.427	2.427	0.005657	2.423–2.431
Diporeia hoyi	2	4.295	4.295	0.01435	4.284–4.305	2.4255	2.4255	0.01061	2.418–2.433
Alewife (Alosa pseudoharengus)	4	4.326	4.323	0.01277	4.305–4.335	2.442	2.441	0.008869	2.430–2.450
Rainbow smelt (Osmerus mordax)	4	4.322	4.319	0.01532	4.299–4.333	2.442	2.440	0.01103	2.425–2.450
Slimy sculpin (Cottus cognatus)	4	4.320	4.318	0.009372	4.305–4.327	2.445	2.442	0.008717	2.434–2.450
Lake trout (Salvelinus namaycush)	4	4.337	4.335	0.01201	4.320–4.348	2.451	2.4505	0.005508	2.444–2.456

Note: N is the number of replicate analyses (= two for single samples analysed in duplicate and four for duplicate samples analysed in duplicate); SD is the standard deviation.

ated mainly with oxyhydroxides rather than with organic matter.

The food-web animals

Among the biological specimens, the ^{202}Hg/^{204}Hg ratio varies systematically with respect to trophic level, habitat, and diet (Fig. 7; Table 5), and the data for the Hg standard solution fluctuate randomly about a vertical line, demonstrating the absence of bogus trends due to systematic drift in the readings during analysis (T.A. Jackson, unpublished data). The ^{199}Hg/^{204}Hg, ^{201}Hg/^{204}Hg, ^{198}Hg/^{199}Hg, ^{198}Hg/^{204}Hg, and ^{200}Hg/^{202}Hg ratios (Table 5) show weaker, less-consistent relationships with trophic level and the other biological factors, and the ^{199}Hg/^{201}Hg ratio (T.A. Jackson, unpublished data) shows no apparent relationship at all.

The ^{202}Hg/^{204}Hg ratio increases progressively from lower to higher trophic levels, i.e., in the sequence crustaceans < forage fish < lake trout (Salvelinus namaycush). But superimposed on this trend are two secondary trends parallel to each other, one for the crustaceans and the other for the forage fish. Among the crustaceans, the isotope ratio decreases in the order zooplankton (a 153 μm net sample composed mostly of cladocerans) > Mysis relicta (a mysid that is both planktonic and benthic) > Diporeia hoyi (a benthic amphipod). This sequence demonstrates that Hg in planktonic crustaceans tends to be isotopically lighter than Hg in benthic ones; the tendency is especially convincing, because the ^{202}Hg/^{204}Hg ratio of M. relicta, which is both planktonic and benthic, is intermediate between the ^{202}Hg/^{204}Hg ratios of the purely planktonic and purely benthic species. Among forage fish, the ^{202}Hg/^{204}Hg ratio decreases in the order alewife (Alosa pseudoharengus) > rainbow smelt (Osmerus mordax) > slimy sculpin (Cottus cognatus). This trend corresponds perfectly to the trend observed in the crustaceans on which the fish feed: Alewife eat comparable amounts of zooplankton and Mysis (with minor quantities of Diporeia), smelt feed mainly on Mysis (with smaller amounts of Diporeia), and sculpin feed primarily on Diporeia (with smaller amounts of Mysis). Thus, the variation in Hg isotope composition seen in the fish reflects the feeding habits of the fish. Evidently the isotope composition of a forage fish is determined largely by the isotope composition of its food, resulting in modification of the overall tendency toward higher isotope ratios at higher trophic levels. This conclusion is consistent with radioactive-tracer data indicating that, in slimy sculpin and lake trout at least, direct absorption of Hg from

water is not a major pathway of Hg uptake, implying that food is the principal vehicle for uptake (Klaverkamp et al. 1983; Harrison et al. 1990). The importance of dietary sources of Hg is widely recognised (Spry and Wiener 1991; Rodgers 1994).

Although more research is needed to explain these results, all available information supports the hypothesis that the ^{202}Hg/^{204}Hg ratios of the animals increase with the proportion of CH$_3$Hg$^+$ to unmethylated Hg in their tissues, suggesting that CH$_3$Hg$^+$ tends to have a higher ^{202}Hg/^{204}Hg ratio than the inorganic Hg(II) from which it is formed. This inference is based on the well-established fact that concentrations of CH$_3$Hg$^+$ (but not inorganic Hg(II)) in aquatic organisms generally increase from lower to higher trophic levels (Jackson 1991, 1998a; Spry and Wiener 1991) and on indirect evidence that plankton and plankton-eating fish have higher proportions of CH$_3$Hg$^+$ to unmethylated Hg than benthic invertebrates and benthos-eating fish, respectively, in at least some cases (Jackson 1991). The specimens were not analysed for CH$_3$Hg$^+$, but their total Hg content is consistent with the author's interpretation, as it is highest at the highest trophic level, where we would expect to find the greatest abundance of Hg, most of it in the form of CH$_3$Hg$^+$. Thus, the mean Hg content of lake trout was 175 ng·g^{-1} wet weight (with a range of 146–197 ng·g^{-1}), whereas the Hg levels in the other organisms were mostly on the order of several tens of nanograms per gram (with a total range of 3–139 ng·g^{-1}). It seems likely, then, that the fractionation of Hg isotopes occurred during microbial methylation of Hg in the environment, although other factors, such as the preferential release of isotopically lighter CH$_3$Hg$^+$ molecules from sediments into the overlying water and the preferential uptake of isotopically lighter CH$_3$Hg$^+$ by the organisms, could have been involved.

Another observation worth noting is that the ^{202}Hg/^{204}Hg ratio of the surface sediment, as represented by the 0- to 1-cm section of the core (4.350) (Table 2), is higher than the ^{202}Hg/^{204}Hg ratios of the biota (4.295–4.335) (Table 5). The mean value for the 0- to 3-cm region of the core is 4.330, which is slightly lower than the value for lake trout (4.335) but higher than any of the values for the other animals (which fall in the range 4.295–4.323). The mean ratio value for a depth of 0–5 cm is 4.344 and the mean value for a depth of 0–7 cm (i.e., the entire zone of anthropogenic Hg) is 4.340; both of these values are higher than the value for lake trout. In brief, the Hg-polluted upper horizons of the sediment

Table 5 *(concluded).*

Type of organism	$^{198}Hg/^{199}Hg$				$^{201}Hg/^{204}Hg$			
	Median	Mean	SD	Range	Median	Mean	SD	Range
Zooplankton (mostly cladocerans)	0.5962	0.5962	0.005515	0.5923–0.6001	1.904	1.904	0.01980	1.890–1.918
Mysis relicta	0.59825	0.59825	0.001061	0.5975–0.5990	1.898	1.898	0.001414	1.897–1.899
Diporeia hoyi	0.5969	0.5969	0.003536	0.5944–0.5994	1.901	1.901	0.001414	1.900–1.902
Alewife (*Alosa pseudoharengus*)	0.5929	0.5929	0.001098	0.5919–0.5939	1.9125	1.911	0.004349	1.905–1.915
Rainbow smelt (*Osmerus mordax*)	0.59615	0.5959	0.003255	0.5920–0.5994	1.9125	1.9115	0.006245	1.903–1.918
Slimy sculpin (*Cottus cognatus*)	0.5935	0.59335	0.001328	0.5918–0.5946	1.908	1.909	0.004646	1.904–1.915
Lake trout (*Salvelinus namaycush*)	0.59285	0.5929	0.001928	0.5910–0.5950	1.919	1.9195	0.007767	1.911–1.929

have isotopically lighter Hg than the food-web animals, insofar as the $^{202}Hg/^{204}Hg$ ratio is concerned. These results suggest that the processes responsible for the Hg isotope fractionation seen in food-web organisms differ appreciably from the isotope-fractionating processes that prevail in the associated sediments. Further work, of course, is needed to explain why the $^{202}Hg/^{204}Hg$ ratio showed more pronounced and consistent correlations with trophic level and other biological factors than the other isotope ratios did. As with the sediment data, a possible reason is that Hg isotope fractionation is a complex process involving many individual reactions and is controlled by a number of different environmental and biological factors, the observed result being the net effect of all these diverse phenomena. The kinetics of the reactions could be appreciably different for different isotopes of Hg, resulting in the observed difference in the relationships between Hg isotope ratios and biological factors such as trophic level, habitat, and diet.

The cinnabar reference sample

Statistical data for the $^{199}Hg/^{201}Hg$, $^{202}Hg/^{204}Hg$, $^{198}Hg/^{204}Hg$, and $^{200}Hg/^{202}Hg$ ratios of the cinnabar sample from the Almaden Hg mine are shown in Table 6. Comparison with the equivalent results for the core sections (Table 2) and biological specimens (Table 5) revealed systematic differences. For the most part, the cinnabar was isotopically lighter than the sediments and organisms. Thus, the $^{199}Hg/^{201}Hg$, $^{202}Hg/^{204}Hg$, $^{198}Hg/^{204}Hg$, and $^{200}Hg/^{202}Hg$ ratios are higher in the cinnabar than in most of the core sections. Insofar as the $^{202}Hg/^{204}Hg$ and $^{198}Hg/^{204}Hg$ ratios are concerned, the cinnabar is isotopically lighter than any of the organisms, although the $^{200}Hg/^{202}Hg$ ratios for the organisms are mostly similar to the value for cinnabar and seem not to differ systematically from it.

The systematic differences in Hg isotope composition between the cinnabar sample and the core sections and biological specimens are further indications that fractionation of Hg isotopes occurs in nature. The fact that the cinnabar shows the same general tendency with respect to two such unlike materials as the sediments and biota, which tend to differ from each other in isotope composition, suggests that the formation of the cinnabar involved appreciable separation of Hg isotopes. This hypothesis is consistent with both the general theory of isotope fractionation and the results of experimental separation of Hg isotopes (see Introduction). As the cinnabar precipitated from hydrothermal solutions of relatively low temperature migrating upward through the Earth's crust from a body of magma below the surface (Bateman 1950), there could well have been a tendency toward

preferential movement of the lighter isotopes, resulting in concentration of these isotopes in the precipitate. The comparatively low temperatures of the hydrothermal solutions make isotope separation during migration of the Hg from its source to the site of deposition in the host rock all the more likely (Hoefs 1973).

The standard deviations for all four of the isotope ratios of the cinnabar fall within the range of standard deviations for the Lake Ontario core samples (Table 2), indicating a comparable degree of dispersion, even though fewer replicate analyses were done in the case of the core sections. However, there is some ambiguity here, because the standard deviations for the core tend to be higher in the zone of background Hg than in the zone of anthropogenic Hg, as might have been predicted from the fact that the total Hg levels are lower in the background zone: Presumably the random analytical error was greatest where the Hg content was lowest. Perhaps it would be more meaningful to say that the standard deviations for the cinnabar specimen are comparable with the low to intermediate standard deviations of the core sections.

One peculiarity of the standard deviations that is immediately apparent from inspection is that the values for the $^{202}Hg/^{204}Hg$ ratios of both the cinnabar and the core sections are aberrantly high with respect to the standard deviations of the other isotope ratios of these materials (Tables 2 and 6). Possibly the abnormally high degree of scatter implied by the data for this ratio is related to the fact that ^{202}Hg and ^{204}Hg are the most abundant and least abundant isotopes, respectively (Bainbridge and Nier 1950; Rankama 1956). The observation that anomalously high standard deviations are characteristic of this particular isotope ratio, irrespective of whether the sample material is cinnabar or sediment and despite homogenisation of the samples prior to analysis, is consistent with the possibility that the high values are artifacts of the analytical technique rather than peculiarities of the samples. Yet this interpretation would seem to be incompatible with the fact that the plots of the median $^{202}Hg/^{204}Hg$ values for the core sections against the Mn/Fe ratio of the $NH_2OH \cdot HCl/HNO_3$ extract and the concentration of $NH_2OH \cdot HCl/HNO_3$-extractable Fe gave highly significant trends with very little scatter (Fig. 4). More research is needed to explain this apparent inconsistency.

As with the core sections, the standard deviations of the $^{198}Hg/^{204}Hg$ and $^{200}Hg/^{202}Hg$ ratios of the cinnabar (Table 6) fall within the ranges of corresponding values for the biological specimens (Table 5). The standard deviations for the $^{200}Hg/^{202}Hg$ ratio, however, are anomalous, as the value for cinnabar is higher than the values for any of the organisms

$^{198}\text{Hg}/^{204}\text{Hg}$				$^{200}\text{Hg}/^{202}\text{Hg}$			
Median	Mean	SD	Range	Median	Mean	SD	Range
1.4485	1.4485	0.002121	1.447–1.450	0.7782	0.7782	0.0009899	0.7775–0.7789
1.4525	1.4525	0.0007071	1.452–1.453	0.77875	0.77875	0.001626	0.7776–0.7799
1.4475	1.4475	0.01485	1.437–1.458	0.7761	0.7761	0.001556	0.7750–0.7772
1.447	1.447	0.004425	1.443–1.452	0.77855	0.7779	0.001578	0.7756–0.7790
1.454	1.454	0.002449	1.451–1.457	0.77785	0.7780	0.001124	0.7769–0.7793
1.4485	1.450	0.004967	1.446–1.457	0.77715	0.7773	0.001682	0.7757–0.7791
1.4535	1.453	0.007616	1.445–1.460	0.77505	0.7745	0.004957	0.7680–0.7800

Table 6. Values of the statistical parameters for Hg isotope data obtained by analysis of 10 replicate portions of a cinnabar sample from the Almaden mercury mine, Spain.

Parameter	$^{199}\text{Hg}/^{201}\text{Hg}$	$^{202}\text{Hg}/^{204}\text{Hg}$	$^{198}\text{Hg}/^{204}\text{Hg}$	$^{200}\text{Hg}/^{202}\text{Hg}$
Mean	1.284	4.352	1.4645	0.7772
Median	1.286	4.361	1.4625	0.7781
SD	0.007009	0.03800	0.007337	0.003540
SEM	0.002216	0.01202	0.002320	0.001119
Range	1.268–1.292	4.263–4.392	1.455–1.478	0.7703–0.7816

Note: SD is the standard deviation; SEM is the standard error of the mean.

except lake trout (Tables 5 and 6). But the most extreme and intriguing anomaly emerged from the data for the $^{202}\text{Hg}/^{204}\text{Hg}$ ratio. In this case, the standard deviation for the cinnabar (0.03800) is higher than the standard deviations of any of the food-web animals (0.005228–0.02760) (Tables 5 and 6), even though the number of replicate analyses of the organisms was smaller than those of the cinnabar and despite homogenisation of the samples prior to analysis. By the same token, the range of values for the $^{202}\text{Hg}/^{204}\text{Hg}$ ratio (the highest value minus the lowest) was much higher for the cinnabar (0.129) than for any of the organisms (0.007–0.039). Moreover, the standard deviations of the $^{202}\text{Hg}/^{204}\text{Hg}$ ratios of the core sections tend to be higher than those of the organisms, although the ranges of the two sets of measurements overlap (Tables 2 and 5). In short, the $^{202}\text{Hg}/^{204}\text{Hg}$ ratios show much less random variation in the organisms than in the sediments and, in particular, than in the cinnabar. The uniqueness of the biological data in this regard suggests that the processes responsible for the discrimination between different Hg isotopes by the organisms are characterised by a higher degree of efficiency, selectivity, and consistency than the processes that determined the isotope composition of the sediments and cinnabar.

Summary of results, inferences, and implications, with suggestions for future research

Briefly, the principal results and interpretations are as follows. (i) The stable-isotope ratios of Hg in the sediment sequence varied with the Mn and Fe oxyhydroxide content of the sediments and the Mn/Fe ratio of the oxyhydroxide fraction. These systematic variations are attributable to isotope fractionation in the environment, and the processes responsible for the observed effects were probably linked to the Eh of the sediment at the time of deposition. The data showed major fundamental differences between the zone of recent pollution and the underlying older zone of background Hg (and between different regions within each zone), probably owing to differences in sedimentary environment and micro-

bial activities. The results provide no evidence that the Hg from the sources of recent pollution is characterised by a specific isotopic signature. However, this does not rule out the possibility of discovering source-related isotopic signatures, as well as quite different environmental and biologically mediated effects, elsewhere. (Note that preliminary investigation of a core from a small lake contaminated with Hg from a nearby smelter revealed Hg isotope variations that differ radically from the variations observed in the Lake Ontario core (Jackson 1999).) (ii) The isotope composition of Hg in food-web animals varied progressively from lower to higher trophic levels, and also from planktonic to benthic crustaceans and, correspondingly, from zooplankton-eating to benthos-eating fish, probably reflecting variations in the abundance of CH_3Hg^+ in relation to unmethylated Hg. (iii) The reference specimen of cinnabar showed a marked tendency to be isotopically lighter than the sediments and biota, providing further evidence of Hg isotope fractionation in nature.

These findings imply that systematic variations in the stable-isotope composition of Hg in the environment may provide an as yet untapped and previously unsuspected supply of valuable information about the sources and biogeochemical cycling of natural and anthropogenic Hg. Further research is needed, however, to confirm, extend, and explain the results. More precise and sensitive methods of mass spectrometry (e.g., multicollector ICP-MS) should be used in any future work, and an effort should be made to detect and eliminate possible artifacts, such as false results arising from inadvertent fractionation of Hg isotopes during the extraction and analysis of samples. Sediments representing different environments and different pollution histories, along with a wider variety of organisms, should be compared, and data for field samples should be compared with results of relevant controlled experiments on the fractionation of Hg isotopes by abiotic and biological processes in model environments. One very useful approach would be to compare samples collected along environmental gradients and at different distances from sources of contamination. Another would be to compare data

for Hg from different sources and from different *kinds* of sources.

Acknowledgements

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