

Mercury Profiles in Sediments of the Arctic Ocean Basins

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Total Hg distributions have been measured for seven sediment cores collected from the major basins of the Arctic Ocean during the Arctic Ocean Section in 1994. Hg determinations were performed on the top 10 cm of the sectioned cores using gold amalgamation atomic fluorescence spectroscopy. In five cores, Hg concentrations decrease downward from 34 to 116 ng g⁻¹ at the sediment surface to 10–65 ng g⁻¹ at 5 cm depth and then remain almost constant with increasing depth. In the other two cores, the Hg decrease with depth is interrupted by a maximum (96–107 ng g⁻¹) at 7–8 cm. The obvious inference—pervasive Hg contamination from anthropogenic sources even at the North Pole—is discounted after a careful evaluation of sediment geochemistry. The evidence suggests that these Hg profiles have been produced by Hg redistribution during diagenesis. In all seven cores, strong similarities are observed between the Hg and the reactive Fe profiles, implying that a portion of the total Hg deposited is recycled along with Fe during redox changes. Intense redox processing in these cores is demonstrated by sharp decreases in organic content with depth and by vertical profiles showing surface enrichments for Mn and Fe. The crucial factors governing surface Hg enrichments in Arctic basin sediments are the low sedimentation rates (<1 cm ka⁻¹) and sediment mixing rates (<0.03 cm² yr⁻¹) that permit even minor Hg fluxes to have a significant cumulative effect.

Introduction

Human activities have increased global Hg cycling by 2–3 times the natural, pre-industrial rates (1). This enhanced cycling has produced a parallel concentration increase in the upper ocean and, of greater concern, has probably led to a similar increase in the Hg burden of aquatic biota (2). Because Hg shares many of the properties of the organochlorines (volatile, persistent, bioaccumulative), the Arctic marine food web is especially vulnerable to an increase in global Hg cycling (3). Furthermore, human exposure to Hg

via the global cycle is likely to be greatest in the Arctic where natives depend on freshwater and marine fish and marine mammals for much of their diet (4). Despite these concerns, we have few data from which to infer with confidence recent Hg trends in the Arctic (5).

Sediments from the deep ocean are poor locations to evaluate modern contaminant trends because of the very low sedimentation rates. Nevertheless, metal enrichments in surface sediments of the pelagic ocean can result from human activities as clearly demonstrated for Pb (6, 7). For Hg enrichments in surface sediments to be attributed to modern contamination, it is necessary that Hg have a strong affinity for particles and that, once sedimented, it does not undergo migration by remobilization during diagenesis (8). The specter of postdepositional movement producing distorted vertical profiles in lakes and coastal environments leading to incorrectly deduced Hg trends has been discussed by Rasmussen (9). Countering Rasmussen's arguments, Fitzgerald et al. (10) provide compelling evidence that many sediment cores do, indeed, faithfully reflect atmospheric trends and fluxes in their Hg profiles. These two papers, however, agree on one point—sedimentary records of Hg should only be interpreted after "careful scrutiny" of the data, which must include an evaluation of the importance of diagenesis.

Here, we will join the debate on the influence of diagenesis on the distribution of Hg in marine sediments. Vertical profiles of Hg will be shown for 7 box cores collected from the major basins of the Arctic Ocean. Biomixing and diagenesis will be evaluated for each core using ²¹⁰Pb, Fe, Mn, and organic C as geochemical markers. The relative importance of diagenesis versus potential contaminant input will be evaluated for these sediments specifically and for marine environments distinguished by extremely low sedimentation and mixing rates in general.

Methods

Sediment cores were collected at depths of 2265–4230 m (Figure 1) from the CCGS Louis St. Laurent during the Canada/U.S. Arctic Ocean Section (AOS) in 1994 (11). The regions sampled include the Canadian Basin (stations 11 and 18), the Makarov Basin (station 26), the Nansen Basin (station 35), the Amundsen Basin (stations 36 and 37), and the Greenland Sea Basin (station 39). The box corer used for the sampling had a collection area of 600 cm². All cores were immediately sectioned horizontally in 1 cm thick slices from the surface to 10 cm depth using a fine-scale subsampling strategy (12). The outer 3 cm of the sediment layers that had been in contact with the core liner was discarded. Sediments were stored in plastic bags and kept frozen for later chemical analysis.

In the laboratory, sediment aliquots were dried at 60 °C and homogenized by grinding, and a known amount (~0.2 g) of the sample was digested in a Teflon tube for 2 h at 90 °C in a mixture of nitric (1 mL), hydrochloric (0.3 mL), and hydrofluoric acids (4 mL). The solution was diluted to 27 mL while adding 2 g of suprapur boric acid (13). The Hg concentration was then determined using gold amalgamation atomic fluorescence spectroscopy after reduction with stannous chloride (14). Saturated Hg vapor has been used for the calibration. The procedure allows complete recovery of the Hg content (92 ± 9 ng g⁻¹) of the National Research Council of Canada sediment standard BEST-1. The precision, expressed as the coefficient of variation of replicate analyses ($n = 19$) of this reference material, was 4.1%. The accuracy was 2.6%.

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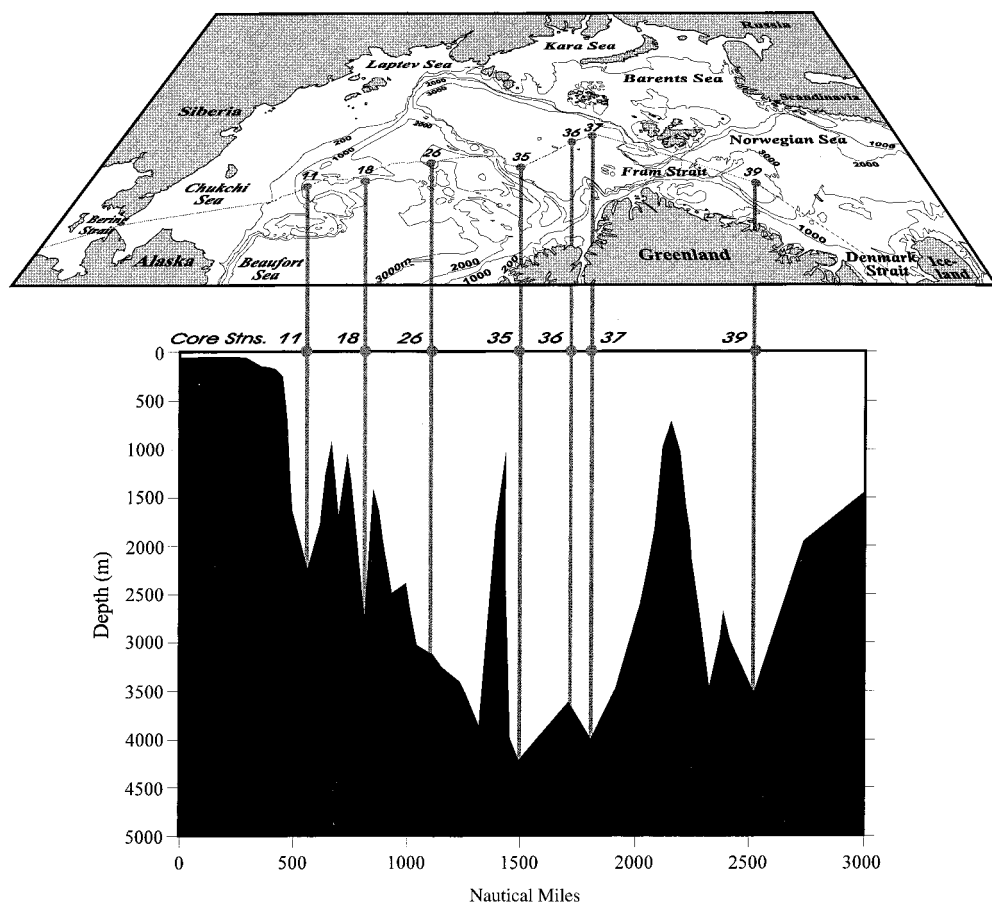


FIGURE 1. Map showing the sampling locations in the major basins of the Arctic Ocean.

Manganese and iron, extracted from 0.5 g of dried sediments during 12 h with 25 mL of a 1 N hydrochloric acid solution, were determined by atomic absorption spectroscopy with an air-acetylene flame. This extraction removes from the sediments "reactive" authigenic phases such as manganese and iron oxyhydroxides, while liberating only minor amounts of the metals associated with silicate minerals (15). The reproducibility of the measurements was better than 10%. Total aluminum was determined by flame atomic absorption spectroscopy using an acetylene-nitrous oxide flame after complete digestion of the sediment with a mixture of hydrofluoric, nitric, hydrochloric, and perchloric acids (16). The precision and accuracy were within 10%. Organic carbon was determined using an automated CHN analyzer following the procedure that includes an aqueous acidification step described by Hedges and Stern (17). The precision and accuracy, estimated by replicate analysis ($n = 8$) of the certified sediment standard BCSS-1, were respectively 5% and 3%. Total ^{210}Pb was determined by α -counting of ^{210}Po electrodeposited onto nickel disks (18). Supported ^{210}Pb was determined by the measurement of ^{226}Ra on air-sealed sediment samples using a 50% low background, hyperpure Ge well detector.

Results and Discussion

The mercury content in all cores decreases from the sediment surface to a depth of 10 cm (Figure 2). In five cores, the mercury shows a relatively smooth exponential-like decrease whereas at stations 18 and 36 this smooth decrease is interrupted by a well-defined subsurface maximum at about 7–9 cm. Surface enrichment factors, defined as the Hg concentration at the core top divided by its concentration at 10 cm depth, vary from 1.3 to 6.2 with an average of 2.6. At first glance, the profiles in Figure 2 and the enrichment

factors seem consistent with a history of increasing Hg fluxes (cf. 19–22). Assigning the increasing Hg fluxes to long-range transport of atmospheric Hg leads inevitably to the conclusion that the Arctic Ocean basins now show pervasive Hg contamination. However, in view of the significance of such a finding, careful scrutiny of the geochemical context of the sediments is warranted.

The first indication that these Hg profiles do not simply reflect recent contaminant histories comes from the average basin sedimentation rates, which have been measured at less than 0.3 cm ka^{-1} and perhaps as low as 0.02 cm ka^{-1} (23, 24). Taking the slightly faster post-glacial sedimentation rates of $0.4\text{--}0.7 \text{ cm ka}^{-1}$, determined by Darby et al. (23) at four sites along the Arctic Ocean transect, the Hg concentration gradients shown in Figure 2 clearly span more than 5000 yr. We must therefore consider other contributing factors in order to explain these profiles. Four distinct types of processes could produce the observed profiles: (i) textural changes in sedimenting particles or variations in natural Hg input occurring within the period spanned by the core could lead to a change in the concentration of Hg with depth; (ii) a decreasing sedimentation rate coupled with little or no change in Hg flux; (iii) bioturbation could have redistributed a recent (i.e., post-industrial) Hg input signal into deeper layers of the sediment; and (iv) diagenesis, in particular redox-mediated reactions, could have redistributed the Hg through a sequence of remobilization, diffusion, and scavenging processes. We will evaluate the potential for each of these processes to produce the Hg profiles shown in Figure 2.

It is unlikely that the depth variations in the Hg content are caused by changes in grain-size distribution as inferred by Al content since the latter varies by only 10% as compared to at least 100% for Hg. As a result, vertical profiles of Hg normalized to Al (cf. ref 25) have practically an identical shape

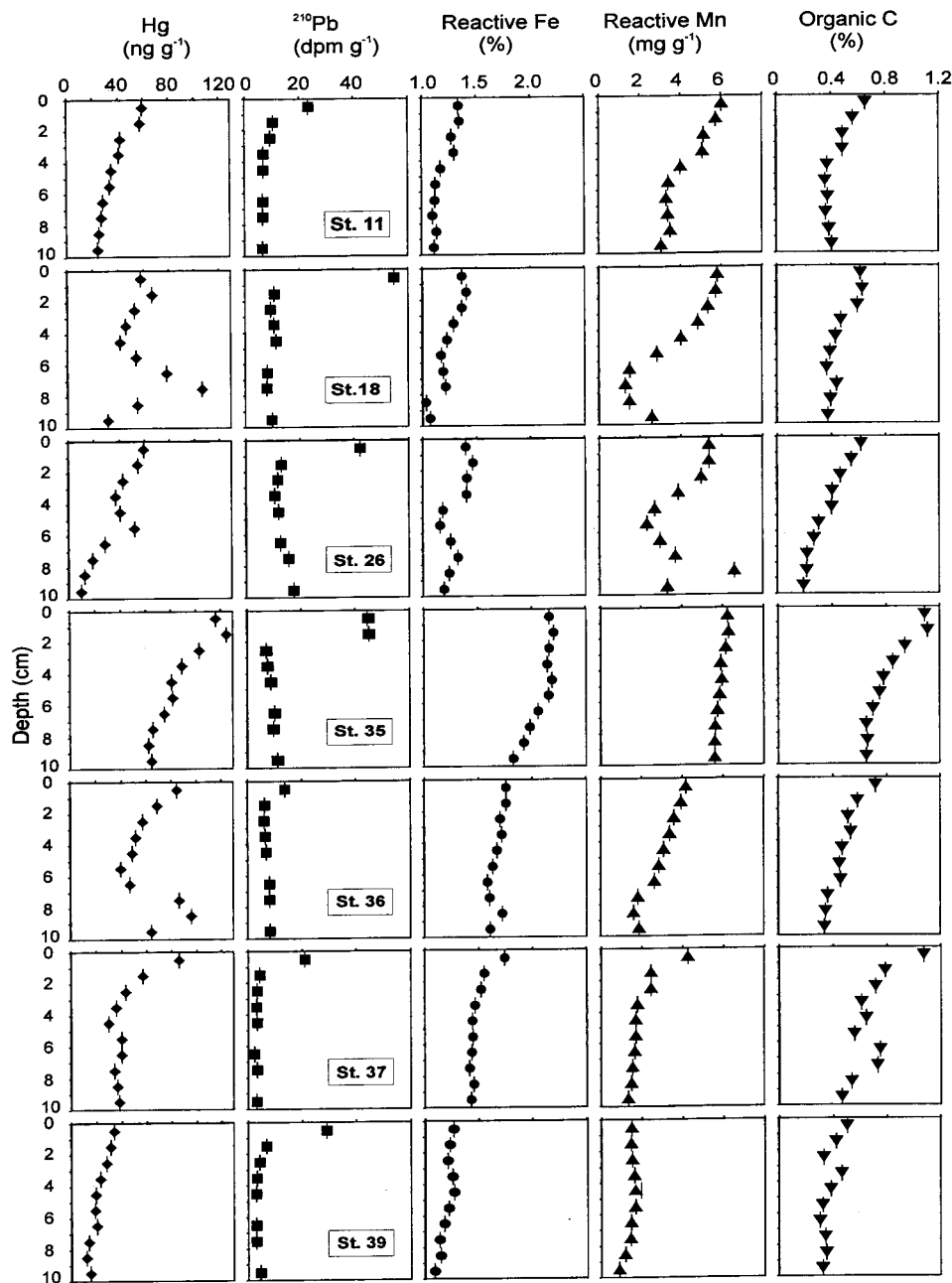


FIGURE 2. Vertical distributions of Hg, ^{210}Pb , reactive Fe and Mn, and organic C in sediment cores at the sampling locations shown in Figure 1. All exhibit elevated concentrations at the sediment surface.

to those shown in Figure 2. Furthermore, it is hard to imagine a textural change occurring throughout the Arctic basin sediments such that parallel Hg enrichments, both in depth of penetration and shape of profile, are produced everywhere. The influence of an increase in the natural Hg input within the period spanned by the core is probably minimal considering that the Hg profiles in cores 18 and 26 are very similar despite differences of a factor of 2 in the sedimentation rate at these stations (24).

A decreasing sedimentation rate during the past 5000 yr together with constant Hg fluxes would produce Hg sediment profiles that increase in concentration toward the surface. While we cannot with certainty discount this mechanism to explain the mercury profiles in Figure 2, it seems an improbable explanation. First, the sedimentation rates would have to have decreased everywhere throughout the basins over the past 5000 yr, a phenomenon that has not been observed in previous sedimentation rate studies of AOS cores

(23, 24). Second, the rates of decrease at each site would have to have occurred in concert so as to produce similar Hg enrichments in the top 4–8 cm of all cores despite intercore variations in sedimentation rate. Third, a correlation between Hg and Fe would also have to have been maintained (Figure 3).

Biomixing has long been known for its potential to produce a surface mixed layer (SML) and to reshape contaminant pulses in sediments (26). In particular, mixing spreads a contaminant pulse over a wider sediment interval and distributes the contaminant deeper into the sediments, giving a false impression that it entered the sediments earlier than was actually the case. The dating bias inherent in mixing is exacerbated by both a deeper SML and a slower sedimentation rate. With a half-life ($t_{1/2}$) of 22.3 yr, excess ^{210}Pb (i.e., ^{210}Pb supplied to the sediments in the particle rain as opposed to supported ^{210}Pb produced within the sediments by the ^{226}Ra decay series) has proven particularly useful as a marker

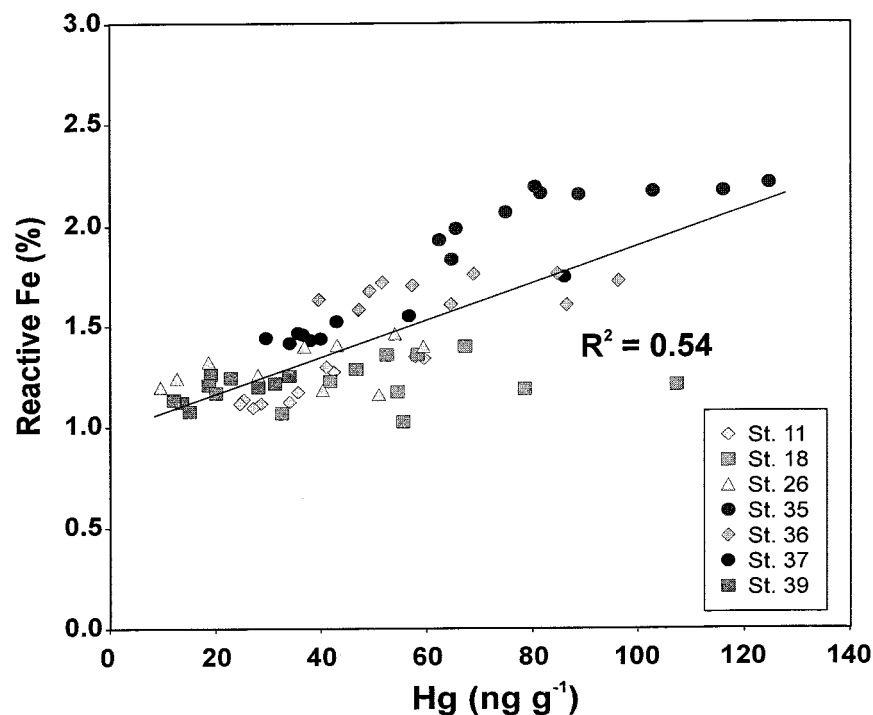


FIGURE 3. Covariance of total Hg with reactive Fe in the entire suite of sediment samples collected in the Arctic basins is indicative of a mechanism driven by redox cycling.

for the post-industrial era of the past 100–150 yr. However, at the slow sediment accumulation rates in the Arctic basins (approximately 1 mm/100 yr), excess ^{210}Pb provides little insight into the sedimentation rate, but instead becomes an ideal indicator of sediment mixing (27). Clearly, excess ^{210}Pb above the supported ^{210}Pb background is confined to the uppermost 3 cm in all cores (Figure 2). We therefore conclude that the SML is likewise confined to this very shallow layer in the sediments. A similar result was reported by Clough et al. (28) from ^{210}Pb measurements on a series of sediment cores collected from the USCGC *Polar Sea* during AOS at locations close to those in the present study.

Particle mixing rates (D_b) can be estimated from the excess ^{210}Pb profiles (Figure 2) by assuming steady-state conditions, a negligible change in sediment solids density, and sedimentation rates $< 1 \text{ cm ka}^{-1}$. Under these conditions, excess ^{210}Pb will decrease exponentially with depth, and a plot of \ln ^{210}Pb activity versus sediment depth (cm) will have a slope equal to $-(0.693/t_{1/2}D_b)^{1/2}$ where D_b is the mixing coefficient ($\text{cm}^2 \text{ yr}^{-1}$). Values of D_b estimated from the ^{210}Pb profiles lie in the range of $0.01\text{--}0.03 \text{ cm}^2 \text{ yr}^{-1}$, in agreement with the results of Clough et al. (28), and are at the low end of the range ($0.03\text{--}0.2 \text{ cm}^2 \text{ yr}^{-1}$) of values measured in abyssal sediments from the Pacific and Atlantic Oceans (27, 29).

Most of the contaminant Hg has entered the global biogeochemical cycle during the past 100 yr (1). Therefore, like excess ^{210}Pb , contaminant Hg burdens if they are present ought to be found predominantly within the top 2–3 cm of the sediment cores, and Hg trends deeper than this cannot be explained by human activities. For our Arctic basin cores, Hg concentrations are always higher in the SML than in the underlying sediments (Figure 2). However, elevated Hg levels persist well below the SML in all of the cores. For instance, at station 35, where the SML is clearly confined to the top 2 cm, the Hg concentration progressively diminishes from the sediment surface down to 10 cm. This continuous, coherent decrease of Hg concentration with depth indicates that modern contamination is not the major explanation for elevated Hg in these sediments.

If the Hg profiles in our sediments are not produced by textural or sedimentation rate changes and cannot be

explained by sediment mixing, what then is the cause for the ubiquitous Hg enrichments toward the surface of arctic basin sediments? The similarity between Hg profiles in all cores implies a common cause while the close relation between Hg and Fe profiles implicates redox cycling (Figure 3). Several studies have shown that not only may Hg be recycled during diagenesis but also that it does so in concert with Fe (30–32), although one cannot exclude the possibility that some Hg is also released to pore water as organic matter decay and taken up again by freshly deposited organic material (33). Redox processes are delineated in all of our cores by sharp decreases in organic carbon concentrations with depth and by significant Fe and Mn enrichments in the vicinity of the sediment–water interface (Figure 2).

The anomalous peaks in Hg observed at a depth of 7–9 cm in sediment cores at stations 18 and 36 provide further evidence of a causal mechanism linking Hg and Fe concentrations since peaks for both elements appear at the same depth in each core. The occurrence of subsurface peaks of Fe (and Mn) in sediments has been previously attributed to episodic changes in the deposition of organic matter that could occur, for example, as a result of periods of high production or turbidity flows (cf. ref 34 and references therein).

Evidence for the diagenetic remobilization of Hg comes from studies showing the following: (i) Hg concentrations in sediment pore water several times higher than those measured in the overlying water (30–32, 35, 36); (ii) significant production of methylmercury forms in anoxic sediments (31, 37); (iii) Hg associated with recycled Fe in partial chemical extractions of sediments (28, 30, 35); and (iv) elevated fluxes of dissolved Hg out of sediments measured using benthic chambers (33). The remobilization mechanisms for Hg are apparently related to organic carbon both by initial direct association and, indirectly, by Hg release and scavenging as part of the Fe diagenetic cycle, which is itself fed by carbon metabolism.

If we accept that Hg can be remobilized under favorable diagenetic conditions, the important question becomes whether such a process can produce significant Hg redistribution in sediments. This question, which is at the heart

of the debate over whether observed surface Hg enrichments in sediment cores collected from remote locations reflect atmospheric depositional trends or diagenetic redistribution (8–10), can be resolved only by considering the burial time scale (sedimentation rate) and the redistribution rate (pore water diffusion). In the case of the Arctic basin cores, sedimentation rates of about 0.5 cm ka⁻¹ and surface Hg concentrations of 50–100 ng g⁻¹ imply a downward flux of about 0.01–0.02 ng cm⁻² yr⁻¹. The principal criterion for the production and maintenance of the profiles in Figure 2 is that the upward flux of Hg in pore waters must equal or exceed the downward flux. Although there is no Arctic basin sediment pore water data for Hg with which to make direct comparisons, dissolved Hg gradients at 2 cm depth in pore water of coastal marine sediments can support an upward flux of approximately 1 ng cm⁻² yr⁻¹ (30). This flux was measured in coastal sediments having Hg concentrations of 200–350 ng g⁻¹, which is about twice that measured in the North Pole core. Gobeil and Cossa (30) concluded that the magnitude of Hg redistribution in the coastal sediments was only a small fraction of the total Hg deposited at the sediment surface. In contrast, a Hg flux of 1 ng cm⁻² yr⁻¹ in the Arctic basin cores would meet the above criterion and could lead to the observed surface enrichments. Indeed, even were the flux 100 times lower, it would still generate measurably elevated concentrations at the sediment surface. The contrast between Hg enrichment mechanisms for the basin and coastal sites derives primarily from the large differences in sedimentation and mixing rates.

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