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Diatom ooze—A large marine mercury sink

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The role of algae for sequestration of atmospheric mercury in the ocean is largely unknown due to the lack of marine sediment data. We estimated Holocene global mercury accumulation in biogenic siliceous sediments (diatom ooze) based on high resolution cores from marine Antarctica. Diatom ooze exhibits the highest mercury accumulation rates ever reported for the marine environment and provided a large sink of anthropogenic mercury, surpassing existing model estimates up to seven fold. Anthropogenic pollution of the Southern Ocean began ~150 years ago and up to 20% of anthropogenic mercury emitted to the atmosphere may have been stored in diatom ooze. These findings reveal the crucial role of diatoms as a fast vector for mercury sequestration and diatom ooze as a large marine mercury sink.

Due to the scarcity of archive data from the marine environment the role of primary production and biogenic sediments for natural and anthropogenic mercury (Hg) sequestration in the oceans is poorly understood. In the open ocean most Hg is received by atmospheric deposition and to a minor extent by discharge from rivers and most atmospheric Hg is thought to be reemitted (*1, 2*). Available data on global Hg burial in marine sediments are based on model estimates (*1, 3*). These studies estimate that the amount of Hg buried in open ocean sediments is relatively low (190–200 Mg yr⁻¹ (*2, 4*)). Several studies indicate that the marine Hg cycle is closely related to biological productivity and that Hg scavenging by organic particles is an important vector for Hg burial in sediments (*5–7*). However, the contribution of these processes to the accumulation of Hg in marine sediments and the overall marine Hg mass balance in the oceans is not known.

Diatoms are a major group of microalgae, and their remains make up pelagic sediments called diatom ooze (DO), which cover ~11% of the ocean floor (*8*) and show highest accumulation in the Southern Ocean (*9, 10*). Up to now, no high resolution (<50 years) Hg record from ocean sediment is available, which allows calculation of global marine Hg sequestration and data on Hg in the ocean is limited to water column measurements (*7*).

Here we show high resolution Holocene Hg records from diatom ooze sediment cores taken at three basins around Antarctica: Adélie Basin (AB) (IODP318-U1357), Prydz Bay (PrB) (ODP119-740) and Palmer Basin (PB) (ODP178-1098) (Fig. 1). From these cores and modeled marine biogenic silica (BSi) sequestration we evaluated the role of diatom ooze as a Holocene Hg sink and estimated the global amount of Hg accumulated in diatom ooze. In addition, we reconstructed the chronology of Hg accumulation and anthropogenic atmospheric Hg pollution during the past 8600 years from annually

laminated Adélie Basin sediments at a resolution of 10–20 and 200 years.

Composition of the sediment at the three locations is similar (Fig. 2) showing high SiO₂ concentrations of 53% (PB), 66% (PrB) and 70% (AB), respectively, which identifies the sediments as diatom ooze (*11–13*). Principal component analyses reveal that Hg generally shows low or no positive covariance with lithogenic elements (e.g., Al, Ti, Zr (fig. S1)). This indicates that binding of atmospheric derived Hg to microalgae particles is the dominant process of Hg accumulation in these sediments and that terrestrial influences are negligible. The upper core sections contain median Hg concentrations between 55.6 and 70.9 ng g⁻¹ and, thereby, exceed the median background (lower core section) concentrations between 32.1 and 36.0 ng g⁻¹ by a factor of 2.2 (Fig. 3). Maximum concentrations reached 73.0 (PB), 84.5 (AB) and 86.6 ng g⁻¹ (PrB). This strong increase in Hg concentrations in the upper core sections likely results from the 2–5-fold increase in global atmospheric Hg loads due to industrial Hg emissions in the past two centuries (*14*). These concentrations are similar to those found in other marine sediments (*15*). In the lower core sections Hg concentrations vary little only (Fig. 3), but exhibit dilution effects at higher silica concentrations (see Si-normalized Hg concentrations in fig. S2). Similar Hg concentrations in the three cores taken at locations separated thousands of kilometers indicate the absence of strong local effects and suggest that Hg concentrations in diatom ooze are related to concentrations of dissolved Hg in seawater, which are controlled by atmospheric Hg deposition and the Henry's Law constant as well as scavenging and mineralization processes of sinking particles.

Due to the consistency in Hg concentrations, the different sedimentation rates of the three cores control the large differences in Hg accumulation rates (Hg_{AR}). The extremely high

sedimentation rates ($\sim 2 \text{ cm yr}^{-1}$) of AB sediments lead to Hg_{AR} that are the highest ever reported from remote marine areas (median rates of 576 and 1200 $\mu\text{g m}^{-2} \text{ yr}^{-1}$ for the pre-industrial and industrial (after 1850) period, respectively) (Fig. 3). These values even exceed those reported from estuaries and shelf areas (60–700 $\mu\text{g m}^{-2} \text{ yr}^{-1}$) (16), which have hitherto been ranked as the largest marine Hg sink (17). The lower sedimentation rates of the PrB and PB cores produce lower Hg_{AR} (PrB median: 16.8 and 33.3 $\mu\text{g m}^{-2} \text{ yr}^{-1}$; PB median: 124 and 192 $\mu\text{g m}^{-2} \text{ yr}^{-1}$ for the lower section and upper section of the cores, respectively), although still high relative to previously reported values indicating areas with high accumulation of diatom ooze as large Hg sinks.

To quantify the role of diatom ooze sediments for Hg sequestration in the oceans, we used the estimated total area of pelagic diatom ooze sediments of 23.3 – 31.1 Mio km^2 (10, 18). Due to the high sedimentation rates of our Antarctic cores, which may lead to large overestimation of global Hg_{AR} in diatom ooze (DOHg_{AR}), we applied two independent approaches for DOHg_{AR} calculation. For calculation 1 (Calc.1) we used the diatom ooze sedimentation rates suggested for the Southern Ocean (0.75 mm yr^{-1} (19)) (dry mass accumulation rate of 0.68 $\text{kg m}^{-2} \text{ yr}^{-1}$) in combination with median Hg concentrations (pre-industrial and industrial period) derived from our Antarctic cores. For calculation 2 (Calc. 2), we used published estimates of global annual BSi accumulation rates and different diatom preservation rates (30%, 60%, 80%) combined with median Si/Hg ratios from our cores for the pre-industrial and industrial period, respectively (Table 1).

Average DOHg_{AR} for the industrial period range between 850 and 1166 Mg yr^{-1} (Table 1), which is by a factor of ~ 4.5 and 6.1 higher than estimates of existing model approaches (190 Mg yr^{-1}) (1, 3) for burial of Hg in deep ocean sediments indicating that Hg sequestration in biogenic marine sediments appear to have been hitherto largely underestimated. Pre-industrial DOHg_{AR} range between 497 and 689 Mg yr^{-1} , which is by a factor of 1.7 lower than those calculated for the industrial period. Although diatom ooze sedimentation and preservation in the Southern Ocean is known to be generally high ($>86\%$) (20), we additionally calculated two conservative approaches using the lowest reported diatom ooze sedimentation rate ($\sim 0.01 \text{ mm yr}^{-1}$) (21, 22) and the lowest published BSi preservation rate (3%) (23). This calculations reveal DOHg_{AR} of 18 and 38 Mg yr^{-1} which still account for 9 and 20% of the model estimate (190 Mg yr^{-1}), respectively (1, 3) and underlines the importance of Hg sequestration in diatom ooze in particular and the role of marine primary production in general. However, the amount of data used for these calculations is still small and may exhibit large uncertainties.

Streets *et al.* (24) estimated that about 1130 Gg of Hg were released from anthropogenic sources to the environment between 1850 and 2010 and 336 Gg of which were emitted

directly to the atmosphere. Based on the minimum and maximum DOHg_{AR} obtained from Calc.1 and 2 (397–1322 Mg yr^{-1}), the total amount of Hg accumulated in diatom ooze in the past 150 years amounts to 22 to 84 Gg. This is about 6.5 to 25% of all Hg emitted to the atmosphere and 2.0 to 7.4% of all Hg released to through anthropogenic emissions in the past 150 years. The remote location and large distance of most diatom ooze sediments from coastlines indicate atmospheric fluxes as the predominant Hg source. Under this assumption, roughly 20% of the anthropogenic Hg emitted to the atmosphere since 1850 may have been buried in diatom ooze alone. This amount may have been even higher taking into account that DOHg_{AR} in areas such as Adélie Basin largely exceeds the rates used in our calculation. The unequal distribution of atmospheric Hg concentrations during the industrial period as well as that of diatom ooze sediments between the hemispheres suggest that Hg sequestration by diatom ooze might be more important in the Southern than in the Northern Hemisphere, which might reduce the amount of anthropogenic Hg accumulated in diatom ooze. It is further unknown to what extent the 1 to 5.5 Gg yr^{-1} of global river discharge of Hg, mainly released to the Northern Ocean (25), contribute to Hg burial in diatom ooze. However, recent studies indicate that most of this Hg is buried in estuaries and on the continental shelf (17).

The high Hg accumulation rates in diatom ooze, which largely surpass the reported Hg deposition rates to the oceans (1), might be partly explained by increased Hg fluxes from the atmosphere into the seawater. Similar to CO_2 , such increased atmospheric Hg fluxes could be caused by a permanent shift of the dissolution equilibrium (based on Henry's Law constant) toward the dissolved phase if the dissolved phase is permanently removed through Hg scavenging by the large amount of algae during blooms. We assume that scavenging of water phase Hg by sinking diatom-organic matter rather than active uptake (see (26) for Hg uptake by algae) is the dominant process of Hg binding in diatom ooze. Furthermore, dissolved Hg in the water column will provide a large Hg pool for scavenging by sinking particles, which could explain the high observed Hg sedimentation rates (see SI for further discussion). Previous mass-balance models estimated that 96% ($\sim 1300 \text{ Mg yr}^{-1}$) of the atmospheric Hg flux to the ocean ($\sim 1350 \text{ Mg yr}^{-1}$) is re-emitted (1). Even the conservative Hg accumulation rates in diatom ooze suggest that these high re-emission fluxes are likely overestimated if used on a global scale. A recent model approach on Hg mass-balance changes during eutrophication in the Baltic Sea estimated a 30–40% decrease in Hg evasion during diatom blooms (27) attributed to Hg sedimentation by algae organic matter. This is in line with findings of Hg concentrations in settling organic particulate matter in the Atlantic Ocean which suggest that Hg partitioning to particles is up to 1000 times greater than

suggested by models resulting in decreasing Hg availability for evasion (28), emphasizing the important role of the marine biological pump for the global Hg cycle.

The undisturbed 170 m long annually laminated sediments of Adélie Basin offer an ultra-high resolution ($\sim 2 \text{ cm yr}^{-1}$) record of Hg accumulation in the oceans spanning large parts of the Holocene (Fig. 3) (13). Hg concentrations in AB sediments show a median of 32.1 ng g^{-1} between ~ 8600 years and ~ 1850 and Hg accumulation rates largely follow the Hg concentration record with a median value of $556 \text{ } \mu\text{g m}^{-2} \text{ yr}^{-1}$. Since 1850, Hg concentrations and accumulation rates increase by a factor of ~ 2.2 to median values of 70.9 ng g^{-1} and $1296 \text{ } \mu\text{g m}^{-2} \text{ yr}^{-1}$, with local peaks around 1890, 1950, and 1990, and highest values of 84.5 ng g^{-1} and $1830 \text{ } \mu\text{g m}^{-2} \text{ yr}^{-1}$ in ~ 1990 . The increase in Hg accumulation is coincident with the onset of the industrial period and intense coal burning which has been the most important anthropogenic source of Hg emissions to the atmosphere and global Hg dispersion. The local peaks in Hg accumulation during 1900–1920 and 1950–1970 (Fig. 3) correspond to emission peaks calculated based on global Hg production and consumption rates (24, 29). An indication of a global influence of Hg emissions from gold and silver mining in the Americas during 1850 and 1910, as estimated in recent models (29), which nearly reach or even surpass levels of those found at times of maximum Hg emissions during the 20th century, was not found in our cores. Moreover, no anthropogenic influence prior to ~ 1850 that could be linked to Hg emissions from colonial gold mining in South America as suggested by model estimates could be detected (16). The amount of Hg emitted to the atmosphere by colonial gold mining was probably too low to be detectable in remote Antarctica. Similar, the increase in global atmospheric Hg loads, as revealed by our Antarctic marine sediment cores, attributed to all time anthropogenic activities is only about a factor of 2.2, which is slightly lower than in most Hg records from terrestrial archives (14, 30–32), but distinctly lower than current model predictions. This might be due to the fact that most anthropogenic Hg has been emitted in the Northern Hemisphere so that a larger Hg portion is sequestered there. However, the Southern Ocean is one of the most productive areas on earth and due to the link between primary production and Hg sequestration likely a large sink for global atmospheric Hg.

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SUPPLEMENTARY MATERIALS

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Materials and Methods

Supplementary Text

Figs. S1 to S4

Tables S1 to S14

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Fig. 1. Map of core sites. Locations of the investigated cores in Antarctica: Prydz Bay core, ODP Expedition 119 site 740; Palmer Basin core, ODP Expedition 178 Site 1098; and Adélie Basin core, IODP Expedition 318 Site U1357.

ANTARCTICA IMAGE SOURCE: © BRITISH ANTARCTIC SURVEY

Fig. 2. Silicon concentrations in diatom ooze sediments. Down-core records of silicon (Si) concentrations in Adélie Basin (AB), Palmer Basin (PB) and Prydz Bay (PrB) sediments (Note the difference in the length of the cores).

Fig. 3. Mercury concentration and accumulation rate in diatom ooze sediments. (A to C) Down core records of mercury (Hg) concentrations in Adélie Basin (AB), Palmer Basin (PB) and Prydz Bay (PrB), and mercury accumulation rates (Hg_{AR}) in AB sediments. The shaded section in panel A, represents the industrial period. Average sedimentation rate of 2 cm yr⁻¹ was used for chronology construction of AB (13). Median background Hg concentration equal 32.1, 34.5 and 36.0 ng g⁻¹ with median absolute deviation of 2.74, 2.21 and 1.20 for AB, PB and PrB, respectively (note the difference in the length of the cores).

Table 1. Global annual mercury accumulation and total accumulated mercury in diatom ooze sediments. Global annual Hg accumulation and total accumulated Hg in diatom ooze sediments (DOHg_{AR}) for the industrial (after 1850) and the pre-industrial (before 1850) period calculated from Calc.1: a diatom ooze area of 23.3 – 31.1 Mio km² (10, 18) and a sedimentation rate of 0.75 mm yr⁻¹ as suggested for Antarctic diatom ooze (19) and average Hg concentrations for the pre-industrial and the industrial period derived from AB, PrB and PB cores, and Calc.2: based on the annual accumulation of biogenic silica (BSi) in the world's oceans (23) assuming BSi preservation of 30, 60 and 80% and the average Si/Hg ratios for the pre-industrial and the industrial period derived from AB, PrB and PB cores.

Calculation	DOHg_{AR} pre-industrial (Mg yr⁻¹)	DOHg_{AR} industrial period (Mg yr⁻¹)	Enrichment factor	DO-stored pollution Hg since ~1850 (Gg)
Calc. 1	574/765	992/1322	1.7	63/84
Calc. 2	230/460/613	397/758/1010	1.6	22/45/60
Average Calc. 1 and 2 (range based on 2)	497/613/689	850/1040/1166	1.7	53/64/72