Environmental Science & Technology
Critical Review
Cite This: Environ. Sci. Technol. 2018, 52, 11466−11477
pubs.acs.org/est

Updated Global and Oceanic Mercury Budgets for the United Nations Global Mercury Assessment 2018

P. M. Outridge,*,†,‡ R. P. Mason,§ F. Wang,‡ S. Guerrero,// and L. E. Heimbürger-Boavida⊥

†Geological Survey of Canada, Natural Resources Canada, 601 Booth St., Ottawa, Ontario K1A 0E8, Canada

‡Center for Earth Observation Science and Department of Environment and Geography, University of Manitoba, Winnipeg, Manitoba R3T 2N2, Canada

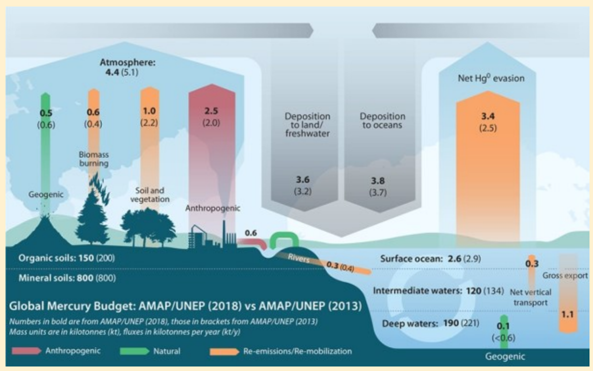
§Department of Marine Sciences, University of Connecticut, 1080 Shennecossett Road, Groton, Connecticut 06340, United States

//Universidad Metropolitana, Autopista Caracas Guarenas, Caracas 1073, Venezuela

⊥Aix Marseille Université, CNRS/INSU, Université de Toulon, IRD, Mediterranean Institute of Oceanography (MIO) UM 110, 13288, Marseille, France

Supporting Information

ABSTRACT: In support of international efforts to reduce mercury (Hg) exposure in humans and wildlife, this paper reviews the literature concerning global Hg emissions, cycling and fate, and presents revised global and oceanic Hg budgets for the 2018 United Nations Global Mercury Assessment. We assessed two competing scenarios about the impacts of 16th − late 19th century New World silver (Ag) mining, which may be the largest human source of atmospheric Hg in history. Consideration of Ag ore geochemistry, historical documents on Hg use, and comparison of the scenarios against atmospheric Hg patterns in environmental archives, strongly support a "low mining emission" scenario. Building upon this scenario and other published work, the revised global budget estimates human activities including recycled legacy emissions have increased current atmospheric Hg concentrations by about 450% above natural levels (prevailing before 1450 AD). Current anthropogenic emissions to air are 2.5 ± 0.5 kt/y. The increase in atmospheric Hg concentrations has driven a ~ 300% average increase in deposition, and a 230% increase in surface marine waters. Deeper marine waters show increases of only 12−25%. The overall increase in Hg in surface organic soils (~15%) is small due to the large mass of natural Hg already present from rock weathering, but this figure varies regionally. Specific research recommendations are made to reduce uncertainties, particularly through improved understanding of fundamental processes of the Hg cycle, and continued improvements in emissions inventories from large natural and anthropogenic sources.



INTRODUCTION

Mercury (Hg) is released into the environment as a result of human activities, as well as by natural sources and processes such as volcanoes and rock weathering.[1,2] Following its release, Hg is transported and recycled among the major environmental compartments—air, soils and waters—until it is eventually removed from the surface system through burial in coastal and deep ocean sediments, lake sediments, and subsurface soils.[2,3] However, owing to its long residence times in the oceans and soils, current concentrations of Hg in the environment are well above those that can be explained by current releases. Therefore, consideration of historical emissions from natural and anthropogenic sources, and the ongoing recycling of this "legacy" Hg, is an important part of understanding the current global Hg budget.[4−7] A small fraction on average of the Hg in global aquatic environments is present as monomethylmercury—the only Hg form that biomagnifies in food chains—although it can be a larger fraction in some ocean regions and specific water masses.[2] For the sake of simplicity, monomethylmercury is referred to by its generic name, methylmercury (MeHg). Many of the processes involved in Hg methylation, or influencing MeHg uptake into food chains, are still inadequately understood,[8,9] which contributes to the difficulties in precisely predicting the effects of regulatory action on wildlife and human Hg exposure.

To address the global problem of Hg pollution, the Minamata Convention was adopted by the United Nations in 2013 (www.mercuryconvention.org) and entered into force in August 2017. As part of efforts to support the Convention, the United Nations Environment Programme (UNEP) is undertaking regular assessments of the scientific literature on Hg at five-year intervals.

Received: March 6, 2018
Revised: September 13, 2018
Accepted: September 18, 2018
Published: September 18, 2018

DOI: 10.1021/acs.est.8b01246
Environ. Sci. Technol. 2018, 52, 11466−11477

An improved quantitative understanding of the global Hg cycle is important for our capacity to predict how regulatory actions to reduce emissions will affect Hg concentrations in different environmental compartments, biota and humans. Given its scale and biogeochemical complexity, and the lack of detailed information for many of its aspects, the planetary Hg cycle is best described using budgets derived from global-scale models and literature compilations. This review presents a synthesis of recent advances since the 2013 Global Mercury Assessment (GMA) report[1] in our understanding of the global Hg cycle, including an evaluation of the influence of historical emissions on current anthropogenic Hg levels in the biosphere, and provides updated global and oceanic total Hg budgets that are incorporated into the 2018 GMA.[10]

A GENERAL OVERVIEW OF RECENT ADVANCES

In the technical background report to the 2013 GMA,[1] based on a global budget developed by Mason et al.,[11] it was estimated that human activities had increased atmospheric Hg concentrations by 300−500% since about the end of the 19th century. Mercury concentrations in surface ocean waters less than 200 m deep had increased on average by ~200% over the past century, whereas deeper waters exhibited smaller increases (11−25%) because of the century- to millennium-scale residence times of these slowly overturning water masses. The average Hg increase in surface organic soils was estimated at ~20% and was negligible in mineral soils.

Recent studies[4,7,12,13] have emphasized the point that the end of the 19th century, or even the last few centuries of the so-called "pre-industrial period", are not a suitable natural or "pre-anthropogenic" reference point from which to gauge the full impact of human activities on the current global Hg cycle. Studies of Hg consumption and production during New World precious metal and cinnabar (Hg ore) mining from the 16th century onward,[14,15] and re-examination of the atmospheric Hg fluxes recorded in long lake sediment and peat cores covering most of the last millennium,[7] indicate that significant amounts of Hg were emitted by human activities in the period after the 16th century, and before the mid-19th century when the "pre-industrial period" is often regarded as having ended (e.g., refs 16 and 17). There are different definitions of a time that represents truly natural or "preanthropogenic" conditions: for example, 2000 BC,[13] 3000 BC to 1550 AD,[7] or prior to 1450 AD.[18] For the purposes of this review we adopted Zhang et al.'s[5] definition of 1450 AD as the end of the preanthropogenic era.

As with almost all global trace metal budgets, uncertainties exist regarding the amounts of anthropogenic and natural Hg "stored" in different environmental compartments, the fluxes between them, and the rates of removal of Hg from the biosphere.[1] Major ongoing efforts have been mounted to reduce these uncertainties. Since 2011, additional measurements of Hg concentrations and fluxes in oceans, atmosphere, and soils have led to suggested refinements of global budgets and models.[4−7,12,13,18−20] Major uncertainties persist, however, especially in estimates of the amount of anthropogenic Hg in the oceans (cf., refs 5 and 13).

Despite differences in definition of the "natural" period in Hg contamination history, the two most comprehensive, recent global Hg budgets generally agree that human activities have increased atmospheric Hg concentrations by a similar range: 450%[5] to 660%,[13] such that total atmospheric concentrations today are 5.5- to 7.6-fold higher than natural levels, respectively. These estimates include revolatilized legacy Hg. There are greater differences in the budgets' estimates of atmospheric Hg deposition increases. Zhang et al.[5] calculated that there had been an average 4.8-fold increase in deposition to oceans and a 7.8-fold increase to land. However, Amos et al.,[13] by modeling various emission scenarios and comparing these trends with a re-evaluation of long peat and lake sediment cores, and the Hg concentration in surface reservoirs, proposed substantially higher increases. Median increases in Hg accumulation rates between the preanthropogenic period and the 20th century peak were a factor of ~26 in peat bogs and ~14 in lake sediments, with both archive types showing increases of about 5-fold between the preanthropogenic and the preindustrial (i.e., 1760−1880) periods. By analyzing Hg isotopes in Pyrenean peat cores, Enrico et al.[21] reported that maximum 20th century concentrations of gaseous elemental Hg (Hg(0); GEM) were 15 ± 4 times higher than in the early- to mid-Holocene. These increases are several times higher than other, sediment-based literature had indicated, of a ~3-fold increase due to anthropogenic activities.[2,16,22] Amos et al.[7] attributed the lower estimates to an erroneous selection of natural deposition values that were too high, because they were based on 18th and early 19th century sediment samples that were already contaminated with mining-emitted Hg. Thus, studies since about 2012 indicate that the true impact of anthropogenic emissions on atmospheric Hg deposition, based on a comparison to preanthropogenic values, is greater than previous comparisons to the 19th century had suggested. But there is considerable variation in the estimates of the degree of that impact.

The differences between the two most recent global budgets[5,13] are most apparent in their estimates of the amount of anthropogenic Hg in today's oceans. The primary cause is their varying estimates of the amount and environmental fate of atmospheric emissions from historical silver (Ag), cinnabar (HgS), and gold (Au) mining in the Americas between the 16th and late 19th centuries, and to differences in the estimated amount of natural Hg originally present in the oceans. Both studies based their global budget calculations on Streets et al.'s[4] all-time emission inventory, with Zhang et al.[5] reducing the emissions from Ag mining by 3-fold. For convenience, we will refer to these two emissions scenarios as "low mining emissions" and "high mining emissions", represented by Zhang et al.[5] and Amos et al.,[13] respectively, although each of these papers is underpinned by a wealth of supporting literature published before and since their respective publication. Overall, the chemical rate constants used for modeling circulation processes within and between oceanic, atmospheric and terrestrial compartments are a secondary factor differentiating the two scenarios.

Considerable Hg releases to land, freshwaters and air are known to have occurred from the mining and production of Ag (as well as Hg and Au) in South/Central America during the Spanish colonial period (about 1520−1850 AD), and later from North American artisanal and small-scale mining during the "Gold Rush" era (roughly 1850−1920).[15,23−25] It is generally agreed that some fraction of the Hg from both historical periods is still circulating within the global biosphere, and that this has had an effect on present-day environmental Hg levels. But quantification of that effect is uncertain. Thus, before revising the global and oceanic budgets, evidence for the impact of historic mining on the global environment and

DOI: 10.1021/acs.est.8b01246
Environ. Sci. Technol. 2018, 52, 11466−11477

its relative importance in the different scenarios must be evaluated.

INFLUENCE OF HISTORIC AG MINING ON ANTHROPOGENIC HG EMISSION INVENTORIES

The total amount of Hg currently in the environment reflects a mixture of sources: historical anthropogenic releases to air, land, and waters; historical natural inputs; and present-day anthropogenic and natural releases. Streets et al.'s[12] updated inventory of all-time Hg emissions concluded that historic Ag mining and production was the largest single source of anthropogenic Hg to the environment, contributing several-times more Hg to the atmosphere (146 kt, 31% of total emissions) than combined industrial and artisanal Au production (55.4 kt) or coal combustion (26.4 kt). Mercury production, much of which was destined for use with small-scale Ag and Au mining, contributed the second highest amount, 91.7 kt. Most of the Ag mining-related Hg releases to air occurred before 1920.

A historical analysis of elemental Hg importation and consumption in the 16th to 19th centuries, in what is today Mexico, Peru, and Bolivia, indicated that large quantities of liquid Hg were indeed used during Spanish colonial Ag production.[14] Mercury was also refined from cinnabar at two major sites in the Spanish New World, as well as in California, and at Idrija and Almaden in Europe.[15] During the 250 years after ~1560, records indicate that over 120 kt of liquid Hg (average of at least 0.48 kt/y) was imported from Europe into the New World or produced in the region, and virtually all of this was lost to the regional environment.[26] Given the likely large scale of contraband Hg involved in mining, this amount may be considerably underestimated. Because of the importance of legacy Hg in the modern environment, a correct interpretation of the impact of historic Ag mining emissions on the current global Hg budget is particularly critical.[5,7,27]

Streets et al.'s[4,12] inventories assumed emission factors of 52% and 40%, respectively, to calculate atmospheric Hg emissions from historic Ag mining, based on Ag metal production data. These factors represent the putative fraction of the Hg utilized in Ag mining that was ultimately emitted to the atmosphere, and were adapted from Nriagu's estimates[23,24] based on artisanal Au mining. This form of small-scale Au mining commonly used direct amalgamation of Au with elemental Hg (a physical process), which was then heated to recover the Au. In contrast, the nature of Ag ore geochemistry, and different Ag production practices, meant atmospheric Hg emissions were much lower per unit of historic Ag metal production than from artisanal Au.[14,15,27] Unlike Au, the Ag in economic ores mostly does not occur in its elemental form. Smelting (without any Hg involvement) was applied to Ag-rich galena (PbS) or copper ores, producing about half of all global Ag production up to 1900.[27,28] Thus, Hg emissions from this industry must have come only from the nonsmelted half, using other ore types. Many other Ag-rich ore bodies, including those in the New World, are predominantly silver sulfide (acanthite, Ag_2S) with silver chloride in varying proportions.[15,29] Historic refining of these ores used Hg, and involved two distinct but concurrent chemical reactions: an oxidative chloride leach to convert silver sulfide to silver chloride, and a redox reaction with Hg to produce metallic silver from silver chloride, followed by amalgamation of the Ag with excess Hg.[30] The Ag-Hg amalgam was then heated to remove the Hg. These Spanish colonial practices were later employed during the 19th century North American Gold Rush, except that iron was added to the chemical slurry to minimize Hg loss to insoluble calomel (Hg_2Cl_2).[27] In the refining process, the major cause of Hg loss was calomel formation, with minimal volatile emissions even during the heating stage.[27,30] Mercury was carefully controlled during these reactions and during heating, and was recycled as much as possible because Hg was expensive relative to Ag, unlike the current situation where Hg is cheap relative to Au. The calomel reaction in the Hg treatment of Ag ores has been confirmed by laboratory experiments.[31] The waste rock tailings were typically disposed of with the calomel, thereby burying it in soils and sediments, although its long-term fate in the environment has not yet been studied.

In contrast to the use of emission factors with Ag production data to estimate Hg releases, Guerrero[14] used importation statistics and consumption records on Hg itself, from Spanish colonial government and independent observers. His calculations suggested that no more than 7−34% of the Hg used during Ag production was physically lost through volatilization, ground spills and in wastewater, with 66−93% of the consumed Hg chemically transformed into calomel. Volatilization was thus a small fraction (<34%) of total Hg consumption. During the 19th century, numerous sources reported Hg losses to air of less than 1% of the Hg consumed by refining,[15,27,30] owing to improvements in the equipment used to recapture and condense gaseous Hg after amalgamation and heating. Thus, the putative 40−52% emission factors for Ag mining appear to be inconsistent with newly available historical and chemical information. Recognition of the importance of history and chemistry in resolving the role of Ag mining is an important recent advance, and represents a fundamental difference between the low and high mining emission scenarios discussed in this review.

The 2013 GMA[1] used an emission factor of 45% for Hg emissions from artisanal and small-scale gold mining (ASGM) in the present-day. That estimate is not affected by the new evidence concerning Ag mining. The Au amalgamation process with Hg does not involve calomel formation, and thus historic Hg losses from Ag mining are not representative of those from ASGM,[30] which are likely to be higher as there is little attempt to recover Hg during heating of the amalgam.

EVIDENCE FROM NATURAL ARCHIVES

Based on Guerrero,[14] Zhang et al.[5] adopted a low emission factor of 17% for Hg from Spanish colonial and 19th century Gold Rush Ag mining. The resulting all-time cumulative anthropogenic emissions to air (190 kt[5]) were just over half those estimated by Streets et al.[4] of 351 kt, decidedly lower releases during the Spanish colonial and Gold Rush periods (Supporting Information (SI) Figure S1a). Modeling of Hg deposition based on the low mining emission scenario predicted fluxes markedly closer to measured values in 120 widely dispersed lake sediments around the world, compared to those based on another model with the high emission scenario (see SI Figure S1b, c, d). A more recent estimate for all-time anthropogenic releases to air at 472 kt[12] was even higher than Streets et al.,[4] because of added commercial product emissions after the late 19thcentury,[6] but this addition would not affect the high emission scenario prediction concerning historical Ag mining.

Support for the low mining emission scenario came from an independent analysis by Engstrom et al.[22] of another large global set of lake sediment Hg profiles separate from those

DOI: 10.1021/acs.est.8b01246
Environ. Sci. Technol. 2018, 52, 11466−11477

in Zhang et al.[5] Although atmospheric Hg deposition was substantially increased during the Spanish colonial period in one South American lake (Laguna Negrilla) near the major cinnabar mining and Hg production site of Huancavelica, Peru, there was little evidence of increased deposition at this time in sediment cores from many remote North American, Arctic, or African lakes, suggesting that the contamination from Ag-, Hg-, and Au-mining was, at most, limited to surrounding terrestrial, freshwater, and coastal ecosystems in western South/Central America.[22]

Similarly, there is little evidence in natural archives to support a major atmospheric Hg impact from late 19th century North American Gold Rush mining. Streets et al.'s[4] results suggested a bimodal pattern of total anthropogenic Hg emissions to air and modeled atmospheric concentrations from 1850 onward, with values in the 1890s that were as high or higher than in the mid- to late 20th century, due to a 450% increase in primary emissions mostly from Gold Rush Ag mining. A revision to include Hg releases from commercial products from the late 1800s onward[6] did not substantially diminish the late 19th century peak in emissions and atmopheric concentrations (see[12]). Although increases in Hg accumulation occurred in remote lake sediments at this time, they were small relative to those observed later in the 20th century in the same core profiles.[5,22,25] Thus, the worldwide lake sediment record appears to suggest a negligible global impact from Ag, Hg and Au production during the 16th to early 20th centuries. Coincident increases in atmospheric emissions from other sources such as coal combustion and commercial Hg uses[12,32] may have contributed to the steady increase of Hg in worldwide deposition (see above) and in Arctic marine biota[33] that started in the latter half of the 19th century.

Amos et al.[7] discounted the lake sediment evidence by arguing that sediments in general respond relatively slowly and insensitively to changes in atmospheric Hg deposition compared with peat bogs. Amos et al.[7] also proposed that the Guerrero[14] volatilization estimate was unrealistically low because it omitted Hg losses during reprocessing of Hg-containing Ag and Au products, and revolatilization from solid mining wastes including calomel. There is some evidence that calomel may disproportionate to Hg(0) and Hg(II) under ambient environmental temperatures and sunlight,[34] but the extent of such disproportionation has not yet been studied under realistic controlled conditions. Evaluation of alternative global model scenarios by Amos et al.[7] suggested that the low emission scenario was inconsistent with Hg measurements in present-day environmental matrices, as well as with the magnitude of Hg enrichment in peat and some lake sediment archives. However, examination of the published outputs in Amos et al.[7] showed that the "mining reduced 3x" scenario actually gave better agreement with observed upper ocean total Hg concentrations and net oceanic evasion rates than the high emission scenario based on Streets et al.,[4] with similar estimates for present-day soil Hg concentrations and net terrestrial flux (see Figure 3d,g,f,h, respectively, in ref 7). Furthermore, the lake sediment-based interpretations (above) of Strode et al.,[25] Engstrom et al.[22] and Zhang et al.[5] were supported by peat bog studies from the Faroe Islands,[35] Maine,[36] Swiss Jura Mountains,[37] and the Pyrenees[21] that all showed relatively muted Hg increases prior to 1900, and with 20th century accumulation rates substantially higher than in the late 19th century. Recently published high-resolution marine sediment cores from a remote region in the Southern Ocean,[38] and off New England, U.S.A.,[39] also provide no evidence of significant global dispersion of emissions from historic Ag, Hg, and Au mining.

Additional independent evidence supporting the low emission scenario, and the sediment and peat bog patterns, was provided by recent studies of glacier ice cores (Figure 1). In contrast to the modeled 450% increase in global primary Hg emissions between 1850 and 1890,[12] three ice cores displayed increases in Hg accumulation between 1840 and 60 and 1880−1900 of 40−150% (reanalysis of data from refs 40−42). All three studies indicated that Hg accumulation rates were substantially greater after 1950 than in the late 1800s, in contrast to the high emission scenario prediction (see SI Figure S1). Furthermore, in a core from Mount Logan, Yukon, the peak periods of Spanish colonial mining (~1600−1850) and the North American Gold Rush (1850−1900) represented only 8% and 14%, respectively, of total anthropogenic Hg deposition in the core, with 78% occurring during the 20th century.[40] Finally, it should be noted that the Freemont Glacier ice core, that has been cited as evidence to support significant emissions from the North American Gold Rush, has had its chronology revised. With this new dating, the Hg profile is now in good agreement with the other ice core studies, and shows little evidence for Hg emissions during the Gold Rush.[43]

Thus, the weight of natural archive evidence, as well as new historical and chemical information, supports the low mining emission scenario, and suggests that any atmospheric Hg emissions produced by historical Ag, Au, and Hg production were restricted to areas around some mining operations. Other studies have shown marked local contamination by nearby historic Ag, cinnabar and Au mining,[17,44] although these effects are not seen everywhere (e.g., ref 43).

REVISED GLOBAL AND OCEANIC TOTAL HG BUDGETS

Here we present the updated budgets included in the 2018 GMA,[10] explain how they were developed, and specify how the two main contrasting views of the world's historical emissions[5,7,13] compare with each other in terms of the current budget. In general, the revised global Hg budget (Figure 2) was constructed by updating the previous version[1,11] with results from Zhang et al.'s model[5] and after consideration of much of the new information and mass and flux estimates published by different groups since 2012 (see SI Table S1).

Estimates of the amounts of natural and anthropogenic Hg in the atmosphere by Amos et al.[13] and Zhang et al.[5] agreed to within about 30% of the estimates in the 2013 GMA budget[1] (Table 1). We accepted Zhang et al.'s[5] estimate that human activities have increased current atmospheric Hg concentrations by about 450% above natural levels (defined as those prevailing before 1450 AD). This represents an increase of 3.6 kt in atmospheric Hg mass above the natural value of 0.8 kt, for a total of 4.4 kt. We calculated that the increase in atmospheric Hg concentrations has driven a ~300% average increase in deposition, which is the largest source of Hg (~90%) entering the surface ocean.[11] Surface marine waters have shown an average 230% increase in Hg concentrations above natural levels, showing some lag with atmospheric changes given the longer residence time of Hg in surface waters. Deeper marine waters in our budget show increases of only 12−25% owing to the slow rate of penetration of anthropogenic Hg into the large deep-water reservoir, which is again consistent with the literature,[18−20] and estimates of deep ocean Hg sediment accumulation. However, our estimate for ocean accumulation

DOI: 10.1021/acs.est.8b01246
Environ. Sci. Technol. 2018, 52, 11466−11477

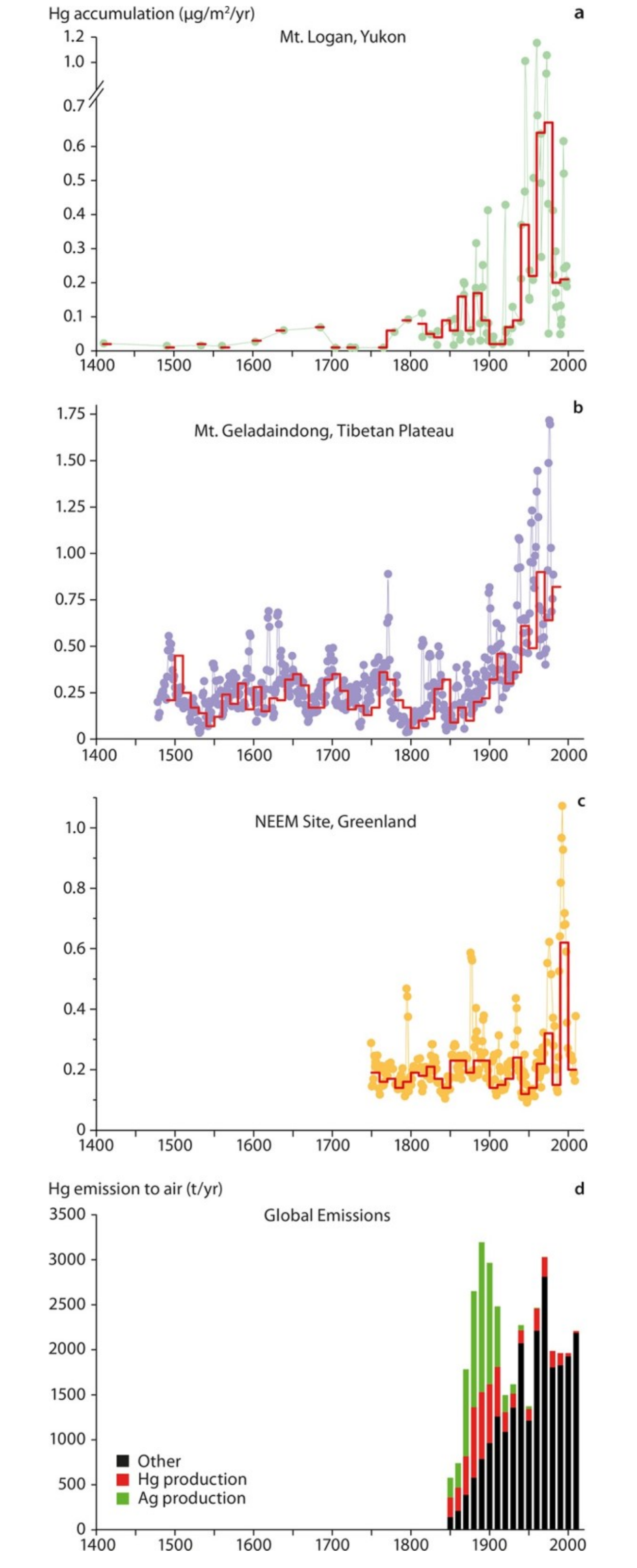


Figure 1. Glacial ice core records of atmospheric Hg deposition from (a) Mount Logan, Yukon, Canada,[40] (b) Mount Geladaindong, Tibetan Plateau, China,[42] and (c) the NEEM site, Greenland,[41] compared with (d) the global atmospheric emission history since 1850 AD.[12] Ice core Hg data are displayed: in (a) as mean ± SD values; in (b) and (c) as 3-point running averages. In all ice core plots, the solid red lines indicate decadal median values calculated from raw data. In (d), atmospheric emissions from Hg (cinnabar) refining and Ag mining operations are shown separately from all other anthropogenic sources ("other").

(see Figure 3), while consistent with prior literature and modeling, is lower than and not consistent with Zaferani et al.'s[38] recent Holocene-long marine sediment core study from remote Antarctica, in a region of high sediment accumulation. More research is clearly needed to further constrain the magnitude of deep ocean net burial. The overall increase in Hg in surface organic soils (~15%) is small due to the large mass of natural Hg already present from rock weathering, but this figure varies regionally because of variations in natural features and processes such as vegetation cover and soil organic matter, as well as anthropogenic inputs.[45]

The new terrestrial reservoir and flux estimates (see Table 1 and Figure 2) were updated from Driscoll et al.[19] and Amos et al.[7] Specific fluxes were also adopted from Pacyna et al.[46] and Cohen et al.,[47] who advocated for particular values from biomass burning, soil and vegetation emissions, and geogenic sources. The revised soil plus vegetation emissions are lower than the 2013 GMA[1] value, but for most of the remaining fluxes, the changes are relatively small (<30%) compared to the previous estimates. Both Amos et al.[13] and Zhang et al.[5] suggested that soils globally contain more anthropogenic Hg than was stated in the 2013 GMA,[1] and these more recent values were considered in our reanalysis. The relative anthropogenic:natural balance in riverine fluxes in Figures 2 and 3 was revised considering the estimates of Zhang et al.,[5] Liu et al.,[48] and Kocman et al.[49]

Fluxes between the atmosphere and terrestrial and oceanic reservoirs were modified in accordance with our best estimate for global atmospheric anthropogenic emissions (2.5 kt/yr), which is 25% higher than in the 2013 GMA,[1] and using the relative anthropogenic:natural flux estimates from Zhang et al.[5] The higher emissions value reflects the fact that the documented emission inventory presented in the 2018 GMA (2.15 kt/yr for 2015[10]) acknowledges that emissions for several sectors cannot be reliably quantified and so are omitted. Provisionally, these sectors, which include agricultural waste burning and municipal and industrial waste disposal, can be expected to contribute tens to hundreds of additional tonnes of atmospheric Hg. The 2.5 kt/yr value adopted here is therefore considered to be a conservative estimate for use in a contemporary global budget calculation. This estimate contains several acknowledged uncertainties (especially for emissions from ASGM, and waste combustion) and so a relatively wide uncertainty of ±0.5kt/yr is included. Similarly, there is a large range in estimates for ocean evasion, and the value adopted here represents the lower evasion estimates from recent high-resolution measurements (e.g.,[50]). A new estimate for total anthropogenic releases from point sources to freshwaters, of 0.6kt/yr,[10] is included based on recent literature.[7,49] An estimate for oil and gas releases to marine systems (0.015 kt/yr[10]) was insignificant compared with the other fluxes and so is not included in Figure 2. No reliable estimates of natural terrestrial Hg fluxes to freshwaters at a global scale were available, and thus this pathway was not quantified. Riverine fluxes into the open ocean are reduced by particule scavenging and sedimentation in estuaries and coastal seas, and the estimate used here is the lowest of those in recent models[3,5,7]. Kocman et al.'s[49] compilation and evaluation of global freshwater Hg contamination suggested that Liu et al.'s[48] measurements of Chinese riverine Hg fluxes were consistent with their data, and were more reliable and significantly lower than Amos et al.'s[3] (2014) modeling study. Kocman et al.[49] advocated for a relatively low global riverine flux value similar

DOI: 10.1021/acs.est.8b01246
Environ. Sci. Technol. 2018, 52, 11466−11477

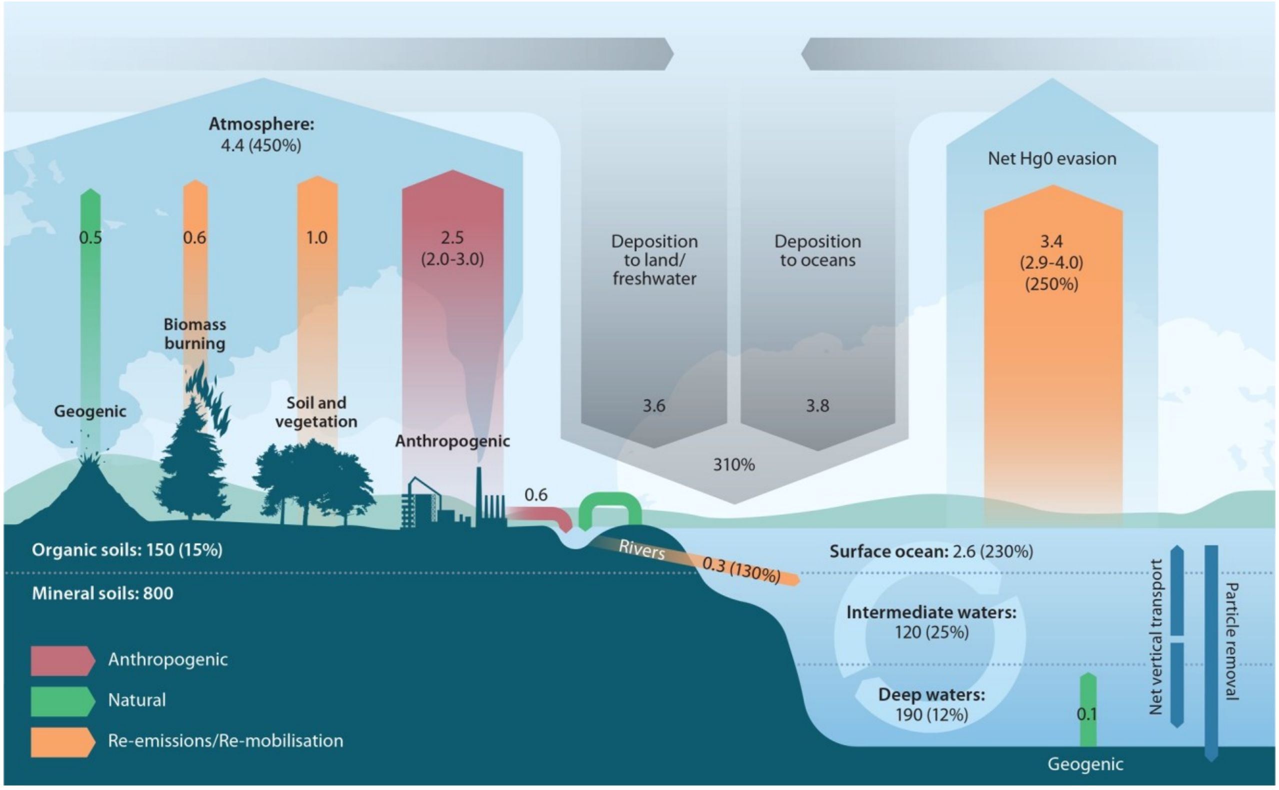


Figure 2. Updated global Hg budget showing the anthropogenic impact on the Hg cycle since the preanthropogenic period (prior to 1450 AD). (Ranges (where available) are given in brackets after the best estimate values; percentages in brackets represent the estimated increase in mass or flux due to human activities since the preanthropogenic period. Mass units in kilotonnes (kt), fluxes in kilotonnes per year (kt/y)).

to that of Sunderland and Mason.[51] The anthropogenic fraction in the freshwater flux entering oceans is increased by upstream urban/industrial point sources so that the anthropogenic:natural ratio is higher than the small anthropogenic fraction in organic soils (~15%) would suggest. Overall, flux uncertainties in the budget should each be regarded as spanning a range of at least ±20%, and subject to future revision. The mass budget is balanced to within 5%.

A recent paper by Schuster et al.[52] suggested that thawing of permafrost in the Arctic could be a globally significant additional source of soil Hg to the atmosphere and aquatic systems in future. A major reason for discrepancies between that paper and other estimates of the soil Hg reservoir is the depth of Hg concentration data integration. Mason et al.[53] and most subsequent modeling and budget estimates reported the amount of Hg in a surface active soil layer of a certain thickness (e.g., 10 cm) or reflected a specific soil pool (e.g., the fast recycling pool in many models; ~4% of the total soil reservoir). Schuster et al.[52] integrated to a depth of several meters, but then compared their values to the previous estimates for surface pools. Such comparisons can lead to incorrect conclusions, and so for the soil reservoir the integration depth is a critical parameter. Here we use the amount of Hg in the actively recycling soil pool (i.e., with an average depth of 10 cm).

With respect to the world's oceans, there are significant differences between recent papers concerning the quantity of anthropogenic Hg presently circulating in seawater.[5,7,13,20] Up to 2012, published estimates of the oceanic anthropogenic Hg mass ranged over more than an order of magnitude, from 7.2 to 263 kt.[4,11,51,53−57] Since then, Amos et al.[13] derived another estimate (222 kt) near the upper end of this range based on the historical mining-influenced high emission scenario. As described above, additional evidence published since 2012, and considerations of Ag ore geochemistry and production techniques, strongly support Zhang et al.'s[5] suggestion that the high emissions scenario is too high.

Even with the low mining emissions scenario, Zhang et al.'s[5] calculations indicated that the cumulative impact of those emissions over four centuries has been substantial, with 67% of the increase in oceanic Hg mass above natural levels occurring prior to 1920, and mostly ascribed to Ag mining-related airborne contamination. The total anthropogenic mass in today's oceans (66 kt) estimated by Zhang et al.[5] is in good agreement with another recent estimate (58 ± 16 kt[20]) derived using a different methodology based on seawater Hg concentration profiles combined with anthropogenic CO_2 and remineralized phosphate as proxies for oceanic Hg distribution. That the two studies, using different approaches, arrived at similar estimates increases confidence in the robustness of their conclusions. Both recent estimates fall within the lower half of the previous range of values and are close to the Mason et al.[11] estimate of 53 kt used in the 2013 GMA[1] (see Table 1).

Based on this revised global budget, the Hg budget in the world's oceans, as represented in Zhang et al.[5] was updated in light of the mass balance fluxes and reservoirs in Figure 2, and is presented in greater detail in Figure 3. The ratios of natural to anthropogenic Hg reported by Zhang et al.[5] were retained for most of the reservoirs and fluxes, although their relative increase in oceanic Hg mass due to anthropogenic inputs is higher than in other publications. This difference was taken into account in updating and revising their budget for this paper. In Figure 3, each reservoir and flux term includes both

DOI: 10.1021/acs.est.8b01246
Environ. Sci. Technol. 2018, 52, 11466−11477

Table 1. Recent Estimates of Total, Anthropogenic and "Natural"[a] Hg Masses in Global Air, Soils, and Oceans (data in kilotonnes)

	Mason et al.;[11] UNEP[1]	et al.[13]	Zhang et al.[5]	et al.[20]	study[b]
Atmospheric Hg					
total	5.1	5.3	4.4	n/a	4.4
anthropogenic	3.4−4.1	4.6	3.6	n/a	3.6
natural	1.0−1.7	0.7	0.8	n/a	0.8
Soil Hg (Organic Layers)					
total	201	271	n/a	n/a	150
anthropogenic	40	89	92	n/a	20
natural	161	182	n/a	n/a	130
Oceanic Hg					
total	358	343	257	316	313
anthropogenic	53	222	66 (38−106)[c]	58 ± 16[d]	55
natural	305	122	191	258[e]	258

[a]The time point for designation of the "natural" Hg state, and thus the quantification of "natural" and "anthropogenic" Hg masses, differed between studies: 2000 BC in the "preanthropogenic period";[13] prior to 1450 AD[5,18] which preceded New World Ag, Au and Hg production; and about 1840 AD[20] which was prior to the North American Gold Rush and the expansion of coal-fired combustion sources. The anthropogenic Hg values from Mason et al.[11] and Lamborg et al.[20] are based on increases over the past ~100 to 150 years, and thus their "natural" Hg masses may be overestimated and the anthropogenic masses underestimated compared with the other studies. [b]Estimates for this assessment modified from Zhang et al.[5] as described in text, and thus the anthropogenic values represent the impact of human activities since 1450 AD. [c]Uncertainty range shown in brackets. [d]Based on an oceanic anthropogenic Hg:anthropogenic CO_2 ratio for 1994; a more recent (higher) oceanic CO_2 Estimate gave an anthropogenic Hg estimate of 76 kt Hg.[20] [e]Calculated by subtraction. n/a = not available.

the natural and anthropogenic contribution. The graphic also shows the cycling of Hg in the ocean through scavenging by particulate organic matter, which is a major mechanism for transport of Hg between surface waters and deep ocean (e.g., see ref 38). In this graphic, the intermediate and deep waters are combined, whereas they are treated separately in the global budget in Figure 2.

In addition to differences in the amount of anthropogenic Hg in the world's oceans, the balance of anthropogenic Hg distribution between global soils and oceans differs between budgets, with oceans holding either about as much anthropogenic Hg mass as the actively recycling soils[1,5] or substantially less.[13] The difference between outcomes may be partly due to our lack of understanding of some of the basic processes governing Hg transport and fate in the terrestrial environment. For example, recent studies on atmospheric Hg dynamics under a range of different plant communities—from tundra plants to temperate forests—continue to demonstrate that the direct uptake of GEM through the stomata of plant leaves is much more significant than previously thought.[58−63] Globally, litterfall containing GEM and throughfall, and not direct wet and dry deposition of oxidized Hg species, may represent the largest net flux of atmospheric Hg to terrestrial ecosystems, with estimates in the range of 1−2 kt/yr.[59,60,64]

The inconsistencies that remain in the evidence concerning the actual rates of historical mining emissions that affected the global atmosphere, soils and oceans, also impact the evidence supporting these revised estimates of oceanic and global Hg cycling. The 3-fold reduction in Ag mining emissions by Zhang et al.[5] brought their modeled emission and deposition history closer to the worldwide lake sediment pattern (compared with the Streets et al.[4,12] emission inventories and atmospheric con-

modeled deposition during the late 19th and early 20th centuries is unlike the steadily increasing trend in lake sediment, peat, and glacial ice Hg deposition (see Figure 1 and SI Figure S1), as well as in Arctic marine biota[33] during the same period. A further reduction in the mass of volatilized Hg from historical Ag and Hg production, which would not be inconsistent with the evidence discussed above, would bring the low emission scenario, and the natural archival records, into even closer agreement. There is recent evidence that further reductions may be justified. Guerrero's[27] analysis of reports from all global Ag mining jurisdictions between 1590 and 1895 suggested a total global Hg release to air from Ag mining of just 6 kt. By comparison, Zhang et al.[5] and Streets et al.[12] estimated this release at 48 kt and 146 kt (most before 1920), respectively.

they have significant potential implications for our understanding of the anthropogenic component of the modern global Hg cycle and budget. If implemented in future models, the additional reductions would reduce the estimated amount of anthropogenic Hg in modern oceans and soils.

THE RATE OF CLEARANCE OF ANTHROPOGENIC HG FROM THE WORLD'S OCEANS

The differences between the alternate emission scenarios are associated with significant differences in the implied response times of the oceans to current emission reductions. All global ocean-atmosphere models predict that Hg clearance rates from most ocean basins will be slow relative to the rate of emission reductions in future, such that removal of anthropogenic Hg from the world's oceans will take many decades to centuries depending on the specific ocean basin and depth interval of the water mass in question, as well as the trajectory of emission controls.[5,7,11,20] But, according to Selin[65] and Engstrom et al.,[22] the high emission scenario predicts much slower and delayed reductions in environmental Hg levels following emission curbs than the low emissions scenario, because of the higher cumulative anthropogenic Hg totals in the environment, especially the oceans. Even at current global emission levels, there is a general scientific consensus that seawater and marine food chain Hg levels are likely to substantially increase over time, because of the slow clearance rate of Hg from the world's oceans coupled with additional legacy anthropogenic Hg released from soil and abandoned urban/industrial sources into rivers and revolatilized into the air.[66]

Until significant deficiencies in our current understanding of marine Hg cycling are resolved, especially for net ocean sediment burial rates and transformation rates between Hg species that influence the major sinks for seawater Hg (evasion to the atmosphere and burial in sediments), and greater consistency is achieved in the interpretation of natural archives of atmospheric Hg deposition, the prediction of the timeline and effects of global emission reductions will remain uncertain. It is clear, however, that irrespective of these scientific uncertainties, emissions reductions are required to reverse the trend in oceanic anthropogenic Hg back toward natural levels, owing to the long response time of the subsurface ocean to changes in inputs.[22,65,66]

DOI: 10.1021/acs.est.8b01246
Environ. Sci. Technol. 2018, 52, 11466−11477

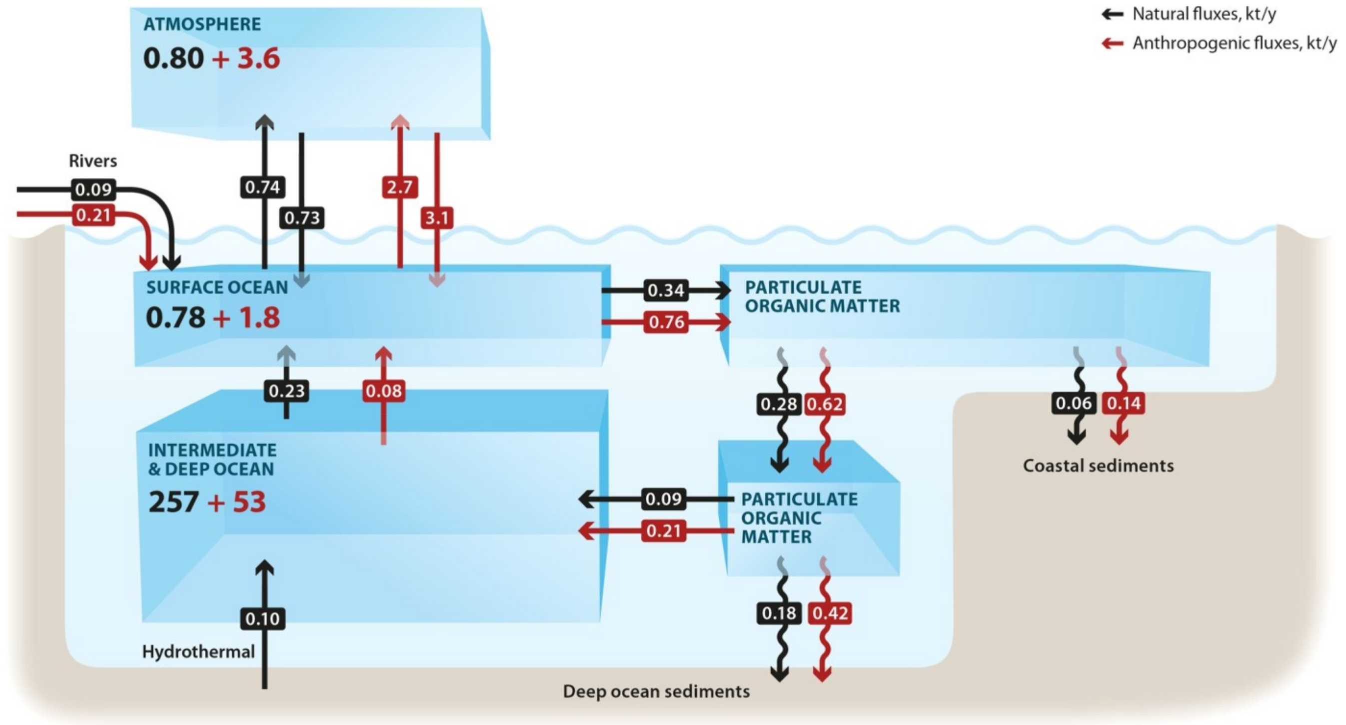


Figure 3. Natural and anthropogenic Hg fluxes and masses in the world's oceans. (Masses in kilotonnes (kt), and fluxes in (kt/y). Data adapted and revised from Zhang et al.,[5] based on the revised global budget shown in Figure 2. Natural fluxes and masses in black, anthropogenic in red).

THE MAIN UNCERTAINTIES IN GLOBAL HG MODELS AND BUDGETS

In this section, we summarize knowledge gaps and recommendations for further research stated in or developed from recent papers.[5,9,13,20,22,67−70] Recommendations were selected on the basis of their relevance to global or oceanic models and budgets. Scientific uncertainties can be grouped under two headings: natural inputs and processes, and anthropogenic emissions.

Uncertainties in Natural Inputs and Processes. Net removal rates of anthropogenic Hg from the surface ocean are the result of competition between three simultaneously occurring natural processes: the particulate flux from the surface to the deep ocean (the "biological pump", involving particle scavenging, remineralization and sedimentation); the mixing of surface and deep-ocean waters; and the net reduction of inorganic Hg(II) and subsequent evasion of Hg(0) back into the atmosphere.[11,51] Some of the evaded Hg(0) is rapidly photo-oxidized in the lower troposphere and redeposited to the ocean surface. Additional coupled ocean-atmosphere measurement studies are needed to comprehensively measure the concentrations of various Hg species spatially and temporally, and to better understand the transport and transformation rates of these co-occurring processes. The need is particularly acute in the Southern Hemisphere open oceans, as well as in regions where elevated anthropogenic Hg concentrations can be expected, such as the eastern equatorial Atlantic, eastern equatorial and high latitude Pacific, and northern Indian Oceans.

Uncertainties in the robustness of measurements of atmospheric and seawater Hg concentrations are exacerbated by relatively large interlaboratory comparison errors, and so there is a particular need to improve the overall reliability of atmospheric and seawater Hg concentration and speciation measurements. Few intercomparison efforts have been mounted (see a review of atmospheric Hg determinations[71]). Past intercalibration exercises for seawater have only addressed total Hg, and the results have indicated significant discrepancies among the participating laboratories.[72] Future exercises should continue the effort of attaining reliable data, and should be extended to include all Hg species, even unstable species such as dimethyl Hg and dissolved Hg(0). The development of suitable seawater reference materials is encouraged.

The role of natural inputs in the global Hg budget is poorly constrained by measurements but potentially of major importance. If the actual rate of emissions from natural sources such as volcanoes, geothermal systems and marine hydrothermal vents is markedly higher or lower than currently thought, this would affect assumptions about the absolute amounts of, and relative balance between, natural and anthropogenic sources which are fundamental to our understanding of the global Hg cycle. Published estimates of global volcanic Hg emissions to air range over 4 orders of magnitude (0.1−1000 t/yr),[73−77] with a recent summation of the literature estimating 76 ± 30 t/yr from quiescent volcanic degassing, not including effusions or eruptions.[77] For oceans, the 2013 GMA[1] estimated <0.6 kt/yr total Hg input from hydrothermal vents, which was based on few data and no systematic studies. Two recent GEOTRACES cruises in the North Atlantic and equatorial Pacific Oceans[78,79] found conflicting evidence of an effect from vents on seawater Hg concentrations. Some shallow vents may release a substantial fraction of their emisisons at the surface as gas bubbles containing GEM.[80] More direct observations of focused and diffuse-flow vent fluids, gases and hydrothermal plumes are needed to better constrain the Hg flux, and its contribution to the global Hg cycle.[81] Submarine groundwater discharges (SGDs) are also likely to bring important amounts of Hg into the ocean, but there are as yet insufficient data to quantify their

DOI: 10.1021/acs.est.8b01246
Environ. Sci. Technol. 2018, 52, 11466−11477

inputs globally.[82] Several recent papers indicate that SGD inputs of Hg may be locally as important as atmospheric inputs, at least in some coastal environments.[85−87] Additionally, the recent findings of Zaferani et al.[38] that sediment burial fluxes of Hg in a region of high opal accumulation in Antarctica are much higher than the average values used in our budget and in recent models points to the need to obtain better information on net Hg burial rates in ocean sediments, both in the coastal and deep oceans.

Given the importance of terrestrial soils as possibly the largest reservoir of natural and legacy anthropogenic Hg, global budget calculations will benefit from a better understanding of terrestrial Hg cycling.[62] The lack of knowledge on the actual reservoir size that may be interacting with other parts of the biosphere has been highlighted by Schuster et al.,[52] who suggested that Arctic permafrost soils are an under-appreciated major repository of Hg. Although permafrost Hg is mainly natural in origin, it could become an important part of the global Hg cycle in future. There is little understanding of precisely how much and how rapidly Hg releases from this source may grow with future climate warming, but they are expected to increase. Export of the stored Hg and organic matter could lead to greater MeHg production in northern aquatic ecosystems.[88] Other research priorities in this area include more measurements of the evasion rates of Hg from soils and the release rates of Hg to water following degradation of soil organic matter, as well as improvements in defining the foliar uptake Hg(0) pathway in global models.

Uncertainties in Anthropogenic Emissions. The absolute amounts in historical emission inventories, and especially the role of Ag metal mining, have been questioned in recent work comparing model outputs with past Hg deposition rates, as reconstructed from natural archives of atmospheric deposition (see above). Some of the uncertainty lies with the natural archives. For example, a recent paper has shown that the Hg accumulation rates in a Tibetan Plateau glacier ice core were 1−2 orders of magnitude lower than in a nearby lake sediment, yet both archives yielded remarkably similar trends.[42] Similarly, the sediment, peat, and ice core literature reviewed above displays similar Hg deposition trends over time, but different absolute fluxes, with ice cores exhibiting the lowest values of all possibly because of Hg photoreduction of deposited Hg(II) to Hg(0) and its revolatilization from snow surfaces.[89] Given the apparent importance of historical deposition to current world Hg budgets and to future emission reduction scenarios, a concerted effort to understand the reasons for the different findings from peat, lake sediment, and glacial ice archives is called for that would build upon earlier work.[7,54,90,91] Arriving at an agreed historical emission amount from precious metal mining would eliminate much of the uncertainty surrounding current anthropogenic Hg inventories in soils and the oceans.

The accuracy of the recent atmospheric emission inventories, including that of the 2013 GMA,[1] has also been questioned in the literature, in part due to the inconsistency between the recent trends in primary industrial emissions, which are flat or rising, and the large (~30−40%) decreases in atmospheric GEM concentrations and wet deposition at background Northern Hemisphere monitoring stations since 1990.[22,69] Zhang et al.[69] found that primary industrial emissions and GEM trends were brought into closer agreement by accounting for the decline in Hg release from commercial products over this period, by reducing the assumed volatilization rate of Hg from present-day ASGM, and by accounting for the shift in Hg(0)/Hg(II) speciation of emissions from coal-fired utilities after implementation of gaseous pollutant control measures. Because the emission inventories are the basis of global modeling efforts, resolving this discrepancy should improve the accuracy of global budgets and future trend scenarios. ASGM emissions were the largest anthropogenic source of atmospheric Hg in recent years, according to the 2013 GMA,[1] but this finding has been disputed.[22,69] Verifiable and higher quality emission data from ASGM operations are therefore a priority need. Studies of the speciation and distribution of the Hg released into air, land, and waters from present day ASGM operations are also called for.

The identified uncertainties and knowledge gaps described above should not be construed as undermining the rationale for the Minamata Convention on Mercury. All model and budget studies are in agreement that current levels of anthropogenic Hg emissions are likely to lead to increased environmental exposure of wildlife and humans (albeit of varying magnitude in different species and settings), and that reducing these emissions is a necessity for reducing their negative environmental and health impacts. The uncertainties and knowledge gaps mainly affect our capability to predict where, when, and by how much, rather than if, the environment will respond to reduced emissions.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.8b01246.

Figure S1 presents the two contrasting estimates of global anthropogenic Hg emissions to air, and associated atmospheric deposition to lakes through history as discussed in this review. Table S1 contains Supporting Information relevant to the development of the global and ocean budgets (PDF)

AUTHOR INFORMATION

Corresponding Author

*E-mail: peter.outridge@canada.ca.

ORCID

P. M. Outridge: 0000-0002-5240-589X

F. Wang: 0000-0001-5297-0859

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This paper was prepared as a contribution to the United Nations Environment Programme's 2018 Global Mercury Assessment, and we thank all of our colleauges who participated in this process, particularly G. Futsaeter and E. Toda (UNEP), S. Wilson (AMAP) and J. Munthe (IVL Swedish Environmental Research Institute). The work was financially supported by UNEP, and by support from the Geological Survey of Canada (G. Cotteret and B. Vigneault) to P.M.O. P.M.O. was hosted by the Department of Geoscience, Aarhus University, during preparation of this paper. R.P.M.'s involvement was supported by NSF Chemical Oceanography Grant No. 1634048, and F.W.'s involvement by the Canada Research Chairs program. S. Duckworth prepared the figures and C. Symon was copy editor. We kindly thank the following for access to their raw data: E. Beal, S. Kang, D. Streets, C. Zdanowicz, Y. Zhang, and J. Zheng.

REFERENCES

(1) AMAP/UNEP Technical Background Report for the Global Mercury Assessment 2013; Arctic Monitoring and Assessment Programme, Oslo, Norway/UNEP Chemicals Branch: Geneva, Switzerland, 2013; p 263.

(2) Fitzgerald, W. F.; Lamborg, C. H., Geochemistry of mercury in the environment. In Treatise on Geochemistry, 2nd Ed, Elsevier: 2014.

(3) Amos, H. M.; Jacob, D. J.; Kocman, D.; Horowitz, H. M.; Zhang, Y.; Dutkiewicz, S.; Horvat, M.; Corbitt, E. S.; Krabbenhoft, D. P.; Sunderland, E. M. Global biogeochemical implications of mercury discharges from rivers and sediment burial. Environ. Sci. Technol. 2014, 48, 9514−9522.

(4) Streets, D. G.; Devane, M. K.; Lu, Z.; Bond, T. C.; Sunderland, E. M.; Jacob, D. J. All-time releases of mercury to the atmosphere from human activities. Environ. Sci. Technol. 2011, 45, 10485−10491.

(5) Zhang, Y.; Jaeglé, L.; Thompson, L.; Streets, D. G. Six centuries of changing oceanic mercury. Global Biogeochem. Cycles 2014, 28, 1251−1261.

(6) Horowitz, H. M.; Jacob, D. J.; Amos, H. M.; Streets, D. G.; Sunderland, E. M. Historical mercury releases from commercial products: Global environmental implications. Environ. Sci. Technol. 2014, 48, 10242−10250.

(7) Amos, H. M.; Sonke, J. E.; Obrist, D.; Robins, N.; Hagan, N.; Horowitz, H. M.; Mason, R. P.; Witt, M.; Hedgecock, I. M.; Corbitt, E. S.; Sunderland, E. M. Observational and modeling constraints on global anthropogenic enrichment of mercury. Environ. Sci. Technol. 2015, 49, 4036−4047.

(8) Paranjape, A. R.; Hall, B. D. Recent advances in the study of mercury methylation in aquatic systems. Facets 2017, 2, 85−119.

(9) Sonke, J. E.; Heimbürger, L.-E.; Dommergue, A. Mercury biogeochemistry: Paradigm shifts, outstanding issues and research needs. C. R. Geosci. 2013, 345, 213−224.

(10) AMAP/UNEP Technical Background Assessment for the 2018 Global Mercury Assessment; United Nations Environment Programme: Geneva, Switzerland, 2018; (in press).

(11) Mason, R. P.; Choi, A. L.; Fitzgerald, W. F.; Hammerschmidt, C. R.; Lamborg, C. H.; Soerensen, A. L.; Sunderland, E. M. Mercury biogeochemical cycling in the ocean and policy implications. Environ. Res. 2012, 119, 101−117.

(12) Streets, D. G.; Horowitz, H. M.; Jacob, D. J.; Lu, Z.; Levin, L.; ter Schure, A. F. H.; Sunderland, E. M. Total mercury released to the environment by human activities. Environ. Sci. Technol. 2017, 51, 5969−5977.

(13) Amos, H. M.; Jacob, D. J.; Streets, D. G.; Sunderland, E. M. Legacy impacts of all-time anthropogenic emissions on the global mercury cycle. Global Biogeochem. Cycles 2013, 27, 410−421.

(14) Guerrero, S. Chemistry as a tool for historical research: Identifying paths of historical mercury pollution in the Hispanic New World. Bull. Hist. Chem. 2012, 37, 61−70.

(15) Guerrero, S. The history of silver refining in New Spain, 16C to 18C: back to the basics. Hist. Technol. 2016, 32, 2−32.

(16) Fitzgerald, W. F.; Engstrom, D. R.; Mason, R. P.; Nater, E. A. The case for atmospheric mercury contamination in remote areas. Environ. Sci. Technol. 1998, 32, 1−7.

(17) Correla, J. P.; Valero-Garces, B. L.; Wang, F.; Martínez-Cortizas, A.; Cuevas, C. A.; Saiz-Lopez, A. 700 years reconstruction of mercury and lead atmospheric deposition in the Pyrenees (NE Spain). Atmos. Environ. 2017, 155, 97−107.

(18) Zhang, Y.; Jaeglé, L.; Thompson, L. Natural biogeochemical cycle of mercury in a global three-dimensional ocean tracer model. Global Biogeochem. Cycles 2014, 28, 553−570.

(19) Driscoll, C. T.; Mason, R. P.; Chan, H. M.; Jacob, D. J.; Pirrone, N. Mercury as a global pollutant: sources, pathways, and effects. Environ. Sci. Technol. 2013, 47, 4967−4983.

(20) Lamborg, C. H.; Hammerschmidt, C. R.; Bowman, K. L.; Swarr, G. J.; Munson, K. M.; Ohnemus, D. C.; Lam, P. J.; Heimbürger, L.-E.; Rijkenberg, M. J. A.; Saito, M. A. A global ocean inventory of anthropogenic mercury based on water column measurements. Nature 2014, 512, 65−68.

(21) Enrico, M.; Le Roux, G.; Heimburger, L. E.; Van Beek, P.; Souhaut, M.; Chmeleff, J.; Sonke, J. E. Holocene atmospheric mercury levels reconstructed from peat bog mercury stable isotopes. Environ. Sci. Technol. 2017, 51, 5899−5906.

(22) Engstrom, D. R.; Fitzgerald, W. F.; Cooke, C. A.; Lamborg, C. H.; Drevnick, P. E.; Swain, E. B.; Balogh, S. J.; Balcom, P. H. Atmospheric Hg emissions from preindustrial gold and silver extraction in the Americas: A reevaluation from lake-sediment archives. Environ. Sci. Technol. 2014, 48, 6533−6543.

(23) Nriagu, J. O. Legacy of mercury pollution. Nature 1993, 363, 589.

(24) Nriagu, J. O. Mercury pollution from the past mining of gold and silver in the Americas. Sci. Total Environ. 1994, 149, 167−181.

(25) Strode, S.; Jaegle, L.; Selin, N. E. Impact of mercury emissions from historic gold and silver mining: Global modeling. Atmos. Environ. 2009, 43, 2012−2017.

(26) TePaske, J. J.; Brown, K. W. A New World of Gold and Silver. Brill: Leiden, 2010.

(27) Guerrero, S. The environmental history of silver production, and its impact on the United Nations Minimata Convention on mercury; Extended Abstract, Session on Global Production and Distribution of Silver, World Economic History Congress, Boston, USA, July 29 - August 3, 2018. Available at: http://wehc2018.org/wp-content/uploads/2018/04/WEHCguerreroMinamata-2.pdf.

(28) Director of U.S. Mint. Annual Report of the Director of the U.S. Mint for the Fiscal Year Ended June 1944, including Report on the Production of Precious Metals During the Calendar Year 1943; Treasury Dept. Doc. 3133, U.S. Govt. Printing Office: WA, 1945; p 101.

(29) Sillitoe, R., Supergene silver enrichment reassessed. In Supergene Environments, Processes, and Products. Spec. Publ. 14, Titley, S. R., Ed.; Society of Economic Geologists, 2009; pp 15−32.

(30) Guerrero, S. Silver by Fire, Silver by Mercury: A Chemical History of Silver Refining in New Spain and Mexico, 16th to 19th Centuries; Brill: Leiden, the Netherlands, 2017.

(31) Johnson, D. A.; Whittle, K. The chemistry of the Hispanic-American amalgamation process. J. Chem. Soc., Dalton Trans. 1999, 4239−4243.

(32) Streets, D. G.; Lu, Z.; Levin, L.; ter Schure, A. F. H.; Sunderland, E. M. Historical releases of mercury to air, land, and water from coal combustion. Sci. Total Environ. 2018, 615, 131−140.

(33) Dietz, R.; Outridge, P. M.; Hobson, K. A. Anthropogenic contributions to mercury levels in present day Arctic animals - A review. Sci. Total Environ. 2009, 407, 6120−6131.

(34) Copan, L.; Fowles, J.; Barreau, T.; McGee, N. Mercury toxicity and contamination of households from the use of skin creams adulterated with mercurous chloride (calomel). Int. J. Environ. Res. Public Health 2015, 12, 10943−10954.

(35) Shotyk, W.; Goodsite, M. E.; Roos-Barraclough, F.; Givelet, N.; Le Roux, G.; Weiss, D.; Cheburkin, A. K.; Knudsen, K.; Heinmeier, J.; van Der Knaap, W. O.; Norton, S. A.; Lohse, C. Accumulation rates and predominant atmospheric sources of naturla and anthropogenic Hg and Pb on the Faroe Islands. Geochim. Cosmochim. Acta 2005, 69, 1−17.

(36) Roos-Barraclough, F.; Givelet, N.; Cheburkin, A. K.; Shotyk, W.; Norton, S. A. Use of Br and Se in peat to reconstruct the natural and anthropogenic fluxes of atmospheric Hg: a 10, 000-year record from Caribou Bog, Maine. Environ. Sci. Technol. 2006, 40, 3188−3194.

(37) Roos-Barraclough, F.; Shotyk, W. Millennial-scale records of atmospheric mercury deposition obtained from ombrotrophic and minerotrophic peatlands in the Swiss Jura Mountains. Environ. Sci. Technol. 2003, 37, 235−244.

(38) Zaferani, S.; Perez-Rodríguez, M.; Biester, H. Diatom ooze − a large marine mercury sink. Science 2018, 361, 797.

(39) Fitzgerald, W. F.; Engstrom, D. R.; Hammerschmidt, C. R.; Lamborg, C. H.; Balcom, P. H.; Lima-Braun, A. L.; Bothner, M. H.;

DOI: 10.1021/acs.est.8b01246
Environ. Sci. Technol. 2018, 52, 11466−11477

Reddy, C. M. Global and local sources of mercury deposition in coastal New England reconstructed from a multiproxy, high-resolution estuarine sediment record. Environ. Sci. Technol. 2018, 52, 7614−7620.

(40) Beal, S. A.; Osterberg, E. C.; Zdanowicz, C. M.; Fisher, D. A. Ice core perspective on mercury pollution during the past 600 years. Environ. Sci. Technol. 2015, 49, 7641−7647.

(41) Zheng, J. Archives of total mercury reconstructed with ice and snow from Greenland and the Canadian High Arctic. Sci. Total Environ. 2015, 509−510, 133−144.

(42) Kang, S.; Huang, J.; Wang, F.; Zhang, Q.; Zhang, Y.; Li, C.; Wang, L.; Chen, P.; Sharma, C.; Li, Q.; Sillanpää, M.; Hou, J.; Xu, B.; Guo, J. Atmospheric mercury depositional chronology reconstructed from lake sediment and ice cores in the Himalayas and Tibetan Plateau. Environ. Sci. Technol. 2016, 50, 2859−2869.

(43) Chellman, N.; McConnell, J. R.; Arienzo, M.; Pederson, G. T.; Aarons, S. M.; Csank, A. Reassessment of the Upper Fremont Glacier ice-core chronologies by synchronizing of ice-core-water isotopes to a nearby tree-ring chronology. Environ. Sci. Technol. 2017, 51, 4230−4238.

(44) Cooke, C. A.; Hintelmann, H.; Ague, J. J.; Burger, R.; Biester, H.; Sachs, J. P.; Engstrom, D. R. Use and legacy of mercury in the Andes. Environ. Sci. Technol. 2013, 47, 4181−4188.

(45) Obrist, D.; Pearson, C.; Webster, J.; Kane, K.; Lin, C. J.; Aiken, G. R.; Alpers, C. N. A synthesis of terrestrial mercury in the western United States: Spatial distribution defined by land cover and plant productivity. Sci. Total Environ. 2016, 568, 522−535.

(46) Pacyna, J. M.; Travnikov, O.; De Simone, F.; Hedgecock, I. M.; Sundseth, K.; Pacyna, E. G.; Steenhuisen, F.; Pirrone, N.; Munthe, J.; Kindbom, K. Current and future levels of mercury atmospheric pollution on a global scale. Atmos. Chem. Phys. 2016, 16, 12495−12511.

(47) Cohen, M. D.; Draxler, R. R.; Artz, R. S.; Blanchard, P.; Gustin, M. S.; Han, Y.-J.; Holsen, T. M.; Jaffe, D. A.; Kelley, P.; Lei, H.; Loughner, C. P.; Luke, W. T.; Lyman, S. N.; Niemi, D.; Pacyna, J. M.; Pilote, M.; Poissant, L.; Ratte, D.; Ren, X.; Steenhuisen, F.; Steffen, A.; Tordon, R.; S.J, W. Modeling the global atmospheric transport and deposition of mercury to the Great Lakes. Elementa 2016, 4, 000118.

(48) Liu, M.; Chen, L.; Wang, X.; Zhang, W.; Tong, Y.; Ou, L.; Xie, H.; Shen, H.; Ye, X.; Deng, C.; Wang, H. Mercury export from mainland China to adjacent seas and its influence on the marine mercury balance. Environ. Sci. Technol. 2016, 50, 6224−6232.

(49) Kocman, D.; Wilson, S. J.; Amos, H. A.; Telmer, K. H.; Steenhuisen, F.; Sunderland, E. M.; Mason, R. P.; Outridge, P.; Horvat, M., Toward an assessment of the global inventory of present-day mercury releases to freshwater environments. Int. J. Environ. Res. Public Health 2017, 14, 138.

(50) Mason, R. P.; Hammerschmidt, C. R.; Lamborg, C. H.; Bowman, K. L.; Swarr, G. J.; Shelley, R. U. The air-sea exchange of mercury in the low latitude Pacific and Atlantic Oceans. Deep Sea Res., Part I 2017, 122, 17−28.

(51) Sunderland, E. M.; Mason, R. P., Human impacts on open ocean mercury concentrations. Global Biogeochem. Cycles 2007, 21, .

(52) Schuster, P. F.; Schaefer, K. M.; Aiken, G. R.; Antweier, R. C.; Dewild, J. F.; Gryziec, J. D.; Gusmeroli, A.; Hugelius, G.; Jafarov, E.; Krabbenhoft, D. L.; Liu, L.; Herman-Mercer, N.; Mu, C.; Roth, D. A.; Schaefer, T.; Striegal, R. G.; Wickland, K. P.; Zhan, T., Permafrost stores a globally significant amount of mercury. Geophys. Res. Lett. 2018, 45, 1463.

(53) Mason, R. P.; Fitzgerald, W. F.; Morel, F. M. M. The biogeochemical cycling of elemental mercury: Anthropogenic influences. Geochim. Cosmochim. Acta 1994, 58, 3191−3198.

(54) Lamborg, C. H.; Fitzgerald, W. F.; O'Donnell, J.; Torgerson, T. A non-steady-state compartmental model of global-scale mercury biogeochemistry with interhemispheric gradients. Geochim. Cosmochim. Acta 2002, 66, 1105−1118.

(55) Selin, N. E.; Jacob, D. J.; Yantosca, R. M.; Strode, S.; Jaeglé, L.; Sunderland, E. M. Global 3-D land-ocean-atmosphere model for mercury: present day versus preindustrial cycles and anthropogenic enrichment factors for deposition. Global Biogeochem. Cycles 2008, 22, GB2011.

(56) Soerensen, A. L.; Sunderland, E. M.; Holmes, C. D.; Jacob, D. J.; Yantosca, R. M.; Skov, H.; Christensen, J. H.; Strode, S. A.; Mason, R. P. An improved global model for air-sea exchange of mercury: High concentrations over the North Atlantic. Environ. Sci. Technol. 2010, 44, 8574−8580.

(57) Strode, S.; Jaegle, L.; Emerson, S. Vertical transport of anthropogenic mercury in the ocean. Global Biogeochem. Cycles 2010, 24, GB4014.

(58) Enrico, M.; Le Roux, G.; Marusczak, N.; Heimburger, L. E.; Claustres, A.; Fu, X.; Sun, R.; Sonke, J. E. Atmospheric mercury transfer to peat bogs dominated by gaseous elemental mercury dry deposition. Environ. Sci. Technol. 2016, 50, 2405−2412.

(59) Fu, X.; Zhu, W.; Zhang, H.; Sommar, J.; Yu, B.; Yang, X.; Wang, X.; Lin, C.-J.; Feng, X. Depletion of atmospheric gaseous elemental mercury by plant uptake at Mt. Changbai, Northeast China. Atmos. Chem. Phys. 2016, 16, 12861−12873.

(60) Wang, X.; Bao, Z.; Lin, C. J.; Yuan, W.; Feng, X. Assessment of global mercury deposition through litterfall. Environ. Sci. Technol. 2016, 50, 8548−8557.

(61) Obrist, D.; Agnan, Y.; Jiskra, M.; Olson, C. L.; Colegrove, D. P.; Hueber, J.; Moore, C. W.; Sonke, J. E.; Helmig, D. Tundra uptake of atmospheric elemental mercury drives Arctic mercury pollution. Nature 2017, 547, 201−204.

(62) Obrist, D.; Kirk, J. L.; Zhang, L.; Sunderland, E. M.; Jiskra, M.; Selin, N. E. A review of global environmental mercury processes in response to human and natural perturbations: Changes of emissions, climate, and land use. Ambio 2018, 47, 116−140.

(63) Risch, M. R.; De Wild, J. F.; Gay, D. A.; Zhang, L.; Boyer, E. W.; Krabbenhoft, D. P. Atmospheric mercury deposition to forests in the eastern USA. Environ. Pollut. 2017, 228, 8−18.

(64) Jiskra, M.; Sonke, J. E.; Obrist, D.; Bieser, J.; Ebinghaus, R.; Myhre, C. L.; Pfaffhuber, K. A.; Wangberg, I.; Kyllönen, K.; Worthy, D.; Martin, L. G.; Labuschagne, C.; Mkololo, T.; Ramonet, M.; Magand, O.; Dommergue, A. A vegetation control on seasonal variations in global atmospheric mercury concentrations. Nat. Geosci. 2018, 11, 244−250.

(65) Selin, N. E. Global change and mercury cycling: Challenges for implementing a global mercury treaty. Environ. Toxicol. Chem. 2014, 33, 1202−1210.

(66) Sunderland, E. M.; Selin, N. E., Future trends in environmental mercury concentrations: implications for prevention strategies. Environ. Health 2013, 12. DOI: 10.1186/1476-069X-12-2

(67) Lamborg, C. H.; Hammerschmidt, C. R.; Bowman, K. L. An examination of the role of particles in oceanic mercury cycling. Philos. Trans. R. Soc., A 2016, 374, 2081.

(68) Song, S.; Selin, N. E.; Soerensen, A. L.; Angot, H.; Artz, R.; Brooks, S.; Brunke, E.; Conley, G.; Dommergue, A.; Ebinghaus, R.; Holsen, T.; Kang, S.; Kelley, P.; Luke, W.; Magand, O.; Marumoto, K.; Pfaffhuber, K. A.; Ren, X.; Zhang, Q. Top-down constraints on atmospheric mercury emissions and implications for global biogeochemical cycling. Atmos. Chem. Phys. 2015, 15, 7103−7125.

(69) Zhang, Y.; Jacob, D. J.; Horowitz, H. M.; Chen, L.; Amos, H. M.; Krabbenhoft, D. P.; Slemr, F.; St. Louis, V. L.; Sunderland, E. M. Observed decrease in atmospheric mercury explained by global decline in atmospheric emissions. Proc. Natl. Acad. Sci. U. S. A. 2016, 113, 201516312.

(70) Kwon, S. Y.; Selin, N. E. Uncertainties in atmospheric mercury modeling for policy evaluation. Current Pollut. Rep. 2016, 2, 103−114.

(71) Gustin, M. S.; Amos, H. M.; Huang, J.; Miller, M. B.; Heidecorn, K. Measuring and modeling mercury in the atmosphere: a critical review. Atmos. Chem. Phys. 2015, 15, 5697−5713.

(72) Lamborg, C. H.; Hammerschmidt, C. R.; Gill, G. A.; Mason, R. P.; Gichuki, S. An intercomparison of procedures for the determination of total mercury in seawater and recommendations regarding mercury speciation during GEOTRACES cruises. Limnol. Oceanogr.: Methods 2012, 10, 90−100.

DOI: 10.1021/acs.est.8b01246
Environ. Sci. Technol. 2018, 52, 11466−11477

(73) Nriagu, J. O. A global assessment of natural sources of atmospheric trace metals. Nature 1989, 338, 47−49.
(74) Nriagu, J.; Becker, C. Volcanic emissions of mercury to the atmosphere: global and regional inventories. Sci. Total Environ. 2003, 304, 3−12.
(75) Ferrara, R.; Mazzolai, B.; Lanzillotta, E.; Nucaro, E.; Pirrone, N. Volcanoes as emission sources of atmospheric mercury in the Mediterranean basin. Sci. Total Environ. 2000, 259, 115−121.
(76) Pyle, D. M.; Mather, T. A. The importance of volcanic emissions for the global atmospheric mercury cycle. Atmos. Environ. 2003, 37, 5115−5124.
(77) Bagnato, E.; Tamburello, G.; Avard, G.; Martinez-Cruz, M.; Enrico, M.; Fu, X.; Sprovieri, M.; Sonke, J. E., Mercury fluxes from volcanic and geothermal sources: an update. In The Role of Volatiles in the Genesis, Evolution and Eruption of Arc Magmas; Zellmer, G. F.; Edmonds, M.; Straub, S. M., Eds.; Geological Society: London, 2015; Vol. Special Publications, 410, p doi: DOI: 10.1144/SP410.2.
(78) Bowman, K. L.; Hammerschmidt, C. R.; Lamborg, C. H.; Swarr, G. J. Mercury in the North Atlantic Ocean: The U.S. GEOTRACES zonal and meridional sections. Deep Sea Res., Part II 2015, 116, 251−261.
(79) Bowman, K. L.; Hammerschmidt, C. R.; Lamborg, C. H.; Swarr, G. J.; Agather, A. M. Distribution of mercury species across a zonal section of the eastern tropical South Pacific Ocean (U.S. GEOTRACES GP16). Mar. Chem. 2016, 186, 156−166.
(80) Astakhov, A. S.; Ivanov, M. V.; Li, B. Y. Hydrochemical and atmochemical mercury dispersion zones over hydrothermal vents of the submarine Piip Volcano in the Bering Sea. Oceanology 2011, 51, 826−835.
(81) German, C. R.; Casciotti, K. A.; Dutay, J. C.; Heimbürger, L. E.; Jenkins, W. J.; Measures, C. I.; Mills, R. A.; Obata, H.; Schlitzer, R.; Tagliabue, A.; Turner, D. R.; Whitby, H. Hydrothermal impacts on trace element and isotope ocean biogeochemistry. Philos. Trans. R. Soc., A 2016, 374, 2081.
(82) Moore, W. S. The effect of submarine groundwater discharge on the ocean. Annu. Rev. Mar. Sci. 2010, 2, 59−88.
(83) Bone, S. E.; Charette, M. A.; Lamborg, C. H.; Gonneea, M. E. Has submarine groundwater discharge been overlooked as a source of mercury to coastal waters? Environ. Sci. Technol. 2007, 41, 3090−3095.
(84) Black, F. J.; Paytan, A.; Knee, K. L.; De Sieyes, N. R.; Ganguli, P. M.; Gary, E.; Flegal, A. R. Submarine groundwater discharge of total mercury and monomethylmercury to central California coastal waters. Environ. Sci. Technol. 2009, 43, 5652−5659.
(85) Ganguli, P. M.; Conaway, C. H.; Swarzenski, P. W.; Izbicki, J. A.; Flegal, A. R. Mercury speciation and transport via submarine groundwater discharge at a southern California coastal lagoon system. Environ. Sci. Technol. 2012, 42, 1480−1488.
(86) Lee, Y.-G.; Rahman, M. D. M.; Kim, G.; Han, S. Mass balance of total mercury and monomethylmercury in coastal embayments of a volcanic island: significance of submarine groundwater discharge. Environ. Sci. Technol. 2011, 45, 9891−9900.
(87) Laurier, F. J. G.; Cossa, D.; Beucher, C.; Breviere, E. The impact of groundwater discharges on mercury partitioning, speciation and bioavailability to mussels in a coastal zone. Mar. Chem. 2007, 104, 143−155.
(88) Stern, G. A.; Macdonald, R. W.; Outridge, P. M.; Wilson, S.; Chetelat, J.; Cole, A.; Hintelmann, H.; Loseto, L. L.; Steffen, A.; Wang, F.; Zdanowicz, C. How does climate change influence arctic mercury? Sci. Total Environ. 2012, 414, 22−42.
(89) Douglas, T. A.; Loseto, L. L.; Macdonald, R. W.; Outridge, P.; Dommergue, A.; Poulain, A.; Amyot, M.; Barkay, T.; Berg, T.; Chetelat, J.; Constant, P.; Evans, M.; Ferrari, C.; Gantner, N.; Johnson, M. S.; Kirk, J.; Kroer, N.; Larose, C.; Lean, D.; Nielsen, T. G.; Poissant, L.; Rognerud, S.; Skov, H.; Sorensen, S.; Wang, F.; Wilson, S.; Zdanowicz, C. M. The fate of mercury in Arctic terrestrial and aquatic ecosystems, a review. Environ. Chem. 2012, 9, 321−355.
(90) Biester, H.; Bindler, R.; Martinez-Cortizas, A.; Engstrom, D. R. Modeling the past atmospheric deposition of mercury using natural archives. Environ. Sci. Technol. 2007, 41, 4851−4860.
(91) Outridge, P. M.; Rausch, N.; Percival, J. B.; Shotyk, W.; McNeely, R. Comparison of mercury and zinc profiles in peat and lake sediment archives with historical changes in emissions from the Flin Flon metal smelter, Manitoba, Canada. Sci. Total Environ. 2011, 409, 548−563.

DOI: 10.1021/acs.est.8b01246
Environ. Sci. Technol. 2018, 52, 11466−11477