Historical Mercury Releases from Commercial Products: Global Environmental Implications

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S Supporting Information

ABSTRACT: The intentional use of mercury (Hg) in products and processes ("commercial Hg") has contributed a large and previously unquantified anthropogenic source of Hg to the global environment over the industrial era, with major implications for Hg accumulation in environmental reservoirs. We present a global inventory of commercial Hg uses and releases to the atmosphere, water, soil, and landfills from 1850 to 2010. Previous inventories of anthropogenic Hg releases have focused almost exclusively on atmospheric emissions from "byproduct" sectors (e.g., fossil fuel combustion). Cumulative anthropogenic atmospheric Hg emissions since 1850 have recently been estimated at 215 Gg (only including commercial Hg releases from chlor-alkali production, waste incineration, and mining). We find that other

Global Hg Releases

Additional releases from commercial Hg

Previously estimated Hg emissions*

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commercial Hg uses and nonatmospheric releases from chlor-alkali and mining result in an additional 540 Gg of Hg released to the global environment since 1850 (air: 20%; water: 30%; soil: 30%; landfills: 20%). Some of this release has been sequestered in landfills and benthic sediments, but 310 Gg actively cycles among geochemical reservoirs and contributes to elevated present-day environmental Hg concentrations. Commercial Hg use peaked in 1970 and has declined sharply since. We use our inventory of historical environmental releases to force a global biogeochemical model that includes new estimates of the global burial in ocean margin sediments. Accounting for commercial Hg releases improves model consistency with observed atmospheric concentrations and associated historical trends.
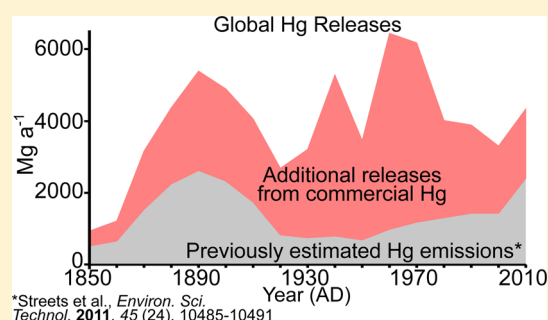
INTRODUCTION

Methylmercury, a neurotoxin formed from inorganic mercury (Hg), bioaccumulates in aquatic food chains and adversely affects human health on a global scale through fish consumption.[1,2] Hg has been mined since antiquity and extensively used in many commercial products,[3] leading to its eventual release to the environment upon disposal. Hg cycles rapidly between air, water, and soil reservoirs so that releases to any of these reservoirs can contribute to oceanic Hg levels.[4] Background levels of Hg in the environment have increased ~3-fold since preindustrial times[5] and may be 5−10 times above natural levels.[4,6] This has been conventionally attributed to atmospheric emissions from mining and combustion.[7,8] Here, we show that releases of commercial Hg to air, water, and soil have contributed a large, previously unquantified source of Hg to the global environment over the industrial era, with major implications for historical and present-day conditions.

Hg is transferred from its stable lithospheric reservoir to surface environmental reservoirs by natural geological processes, fossil fuel combustion, and mining (including for commercial products). It then is exchanged between the atmosphere, surface ocean, and terrestrial ecosystems on time scales of years to decades.[4] The atmospheric lifetime of gaseous elemental Hg is of the order of a year, allowing transport and deposition on a global scale.[9] Hg is eventually transferred to long-lived soil and deep-ocean pools over hundreds of years and returns to the lithosphere to close the cycle on a time scale of thousands of years.[10] The lasting environmental legacy of Hg released to surface reservoirs mandates a historical perspective for understanding present-day environmental burdens and for evaluating the effectiveness of regulatory actions such as the Minamata Convention.[11]

While an estimated 112 Gg of Hg has been emitted directly to the atmosphere since 1850 from byproduct sources (fuel combustion, cement production, metals smelting, large-scale gold mining with non-Hg methods), 720 Gg of Hg was mined during the same period for commercial use.[12] This "commercial

Hg" includes Hg-containing products (e.g., batteries) and manufacturing processes that involve Hg (e.g., vinyl chloride monomer production). Commercial Hg enters the environment either during use or following product disposal. Previous studies have estimated present-day environmental releases of Hg from commercial products and processes only for a subset of uses and fate pathways, with a predominant focus on atmospheric emissions.[13−23] Streets et al.[12] estimate that 103 Gg was emitted to the atmosphere from chlor-alkali production, mining of silver and gold using Hg amalgamation, and waste incineration from the 720 Gg of Hg mined for commercial use since 1850, leaving unresolved the fate of the remaining 617 Gg.

Commercial Hg can enter the environment by various pathways. For example, Hg in paint rapidly volatilizes to the atmosphere.[24] The chemical manufacturing industry historically discharged large amounts of Hg directly into waterways, reflected by legacy contamination in many estuaries today.[25−28] Hg-containing agricultural fungicides and pesticides were applied to soil in large quantities for much of the 20th century.[29] Discarded Hg-containing batteries have generally been incinerated or landfilled.[30,31] More recently, many industries have made progress toward recycling Hg in commercial products or phasing out its use.[32]

Here, we quantify the global time-dependent historical releases of commercial Hg to different environmental reservoirs (air, water, soil, landfills) and include these in a global biogeochemical model[4] to investigate their impact on historical and present-day global Hg accumulation. Water releases include effluent discharges to both estuaries and inland freshwater systems, and soil releases are deposited to soil or vegetation. A current conundrum that we try to resolve is the apparent inconsistency between anthropogenic atmospheric emission inventories, which indicate rising or flat emissions over the past decades,[12,20] and environmental archives, which often imply a peak in atmospheric Hg deposition in the 1970s.[33−36] Atmospheric observations also indicate a ~20% to 50% decrease in total gaseous mercury in the Northern Hemisphere since 1995,[37,38] which Soerensen et al.[38] attributed to declining ocean evasion driven by changes in seawater concentrations. Commercial use of Hg peaked in the 1970s and has declined dramatically since,[12,39] and we investigate the role of the related decline in commercial Hg releases in driving environmental trends.

■ METHODS

We present a global, historical analysis tracking Hg from when it is mined, through all intentional uses and fate pathways, to its final time-dependent releases to different environmental reservoirs. Commercial Hg uses are grouped by similar environmental release patterns for a total of 14 use categories (Table 1). We estimate global environmental releases of Hg and track recycled and landfilled quantities from each use category on a decadal scale between 1850 and 2010. We first estimate the quantity of Hg consumed in each use category constrained by the total amount of Hg mined globally. We then distribute commercial Hg to environmental reservoirs following a simplified substance flow analysis approach that aims to quantify each transfer of Hg over its life cycle (e.g., Barr Engineering[14]). Finally, we investigate the environmental impacts of these global time-dependent releases using a seven-box biogeochemical Hg model.

Table 1. Intentional Uses of Hg in Products and Processes

category name	description
chlor-alkali plants	electrochemical production of caustic soda and chlorine with Hg cathode
silver and large-scale gold mining	extraction from ore by Hg amalgamation
artisanal and small-scale gold mining (ASGM)	Hg amalgamation by individual miners
vinyl chloride monomer (VCM) and other chemical	production of chemicals with Hg catalysts, felt hat manufacturing, and laboratory uses
paint	Hg fungicide in marine antifouling paint, interior and exterior latex paint
lamps	all types of Hg-containing lightbulbs (fluorescent, high intensity discharge, etc.)
batteries	button cells and cylinders using Hg as cathode or to prevent corrosion
wiring devices and industrial measuring devices	switches and relays, thermostats, barometers, manometers
medical devices	thermometers and sphygmomanometers (blood pressure meters)
pharmaceuticals and personal care products	vaccines and medicines, soaps, cosmetics
dental amalgam	cavity fillings with Hg/silver/tin/copper amalgam
dyes/vermilion	pigments containing Hg compounds
pesticides and fertilizer	fungicides used in agriculture and pulp and paper
explosives/weapons	munitions, blasting caps, fireworks
other	ritual, cultural, and miscellaneous uses

Global Commercial Hg Consumption Patterns, 1850−2010. We assume that significant Hg release from nonmining commercial Hg uses began in 1850. Anthropogenic releases prior to 1850 were mainly from mining.[12] Overall decadal estimates of the magnitude of Hg used throughout the industrial era are constrained by global primary production of Hg from mining between 1850 and 1980[12,39] combined with changes in the Hg supply available for consumption due to government stockpiling[40] (Figure 1). We assume that primary
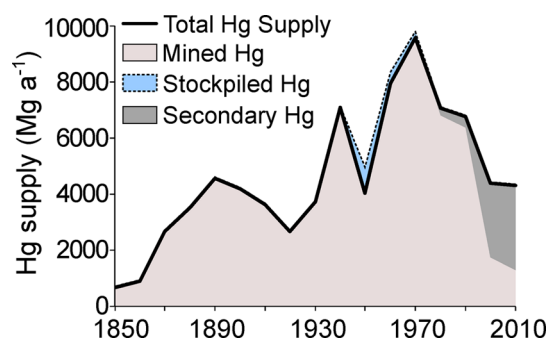

Figure 1. Historical global supply of Hg for commercial uses. This supply includes primary mined Hg (1850−2008 data from Streets et al.[12]), minus the amount stockpiled by the United States between 1945 and 1970, and is augmented by secondary Hg including that recycled, recovered as a byproduct, and released from stockpiles after 1980.

mined Hg that is not stockpiled is used in products and processes within a decade. Secondary Hg sources (releases from strategic stockpiles, recovery from mining and smelting, and recycling of Hg-containing products) became significant after 1980.[13,32,41] Therefore, for 1990−2010, we use total Hg consumption from Wilson et al.[20] that includes both primary mining and secondary sources. Wilson et al.[20] do not fully

account for Hg consumption in liquid crystal display (LCD) screens (and potentially other specific uses), so total Hg consumption in recent decades may be underestimated.[42]

We then partition the global total Hg supply into individual uses. Methods used to estimate Hg consumption for each category vary depending on data availability. We divide countries into two groups, developed countries (North America, OECD/EU Europe, Oceania) and developing countries including economies in transition (rest of world), based on similarities in environmental regulations and control technologies within each group that lead to differences in Hg use and release patterns. Data from Streets et al.[12] are used to constrain total Hg consumed globally for the chlor-alkali industry between 1850 and 1930 and silver and gold mining between 1850 and 1990, including artisanal and small-scale gold mining (ASGM). Decadal use patterns available for the United States[43,44] are used to estimate global consumption of Hg by the remaining uses for 1850−1960. During this period, the US consumed ∼25% of total Hg mined globally and its Hg use data is the most complete. This may underestimate the fraction of Hg used by the chlor-alkali industry, historically more important in Western Europe than in the US.[45] However, using available data from Sweden[46] for Hg consumption patterns instead of the US does not affect significantly our estimate of all-time environmental releases and model results (see the Supporting Information).

The ca. 1970 onset of environmental regulations targeting Hg releases in developed countries resulted in major changes in Hg consumption patterns.[25] We therefore estimate Hg consumption separately for developing countries from 1970 to the present. For 1970 and 1980, we divide the global total Hg supply between the developed and developing world by the fraction of global GDP held by each group of countries.[47] Consumption patterns for the developed world are assumed to follow those of the US in 1970 and 1980.[48] Consumption patterns for the developing world in 1970 and 1980 are assumed to be similar to those of the US in 1960, when Hg use was unregulated. For 1990−2000, we use regionally resolved Hg consumption data from Wilson et al.[20] For 2010, we use annual consumption data from AMAP/UNEP[22] for the uses available and extrapolate the 2000−2005 trend from Wilson et al.[20] for the remaining uses.

Environmental Releases of Commercial Hg. Figure 2 shows a generic diagram of our simplified substance flow analysis that tracks the fate of commercial Hg for each decade and use category (Table 1) to its eventual release in different environmental reservoirs. First, the Hg consumed in each use category is divided among direct releases to air, water, and soil, recycling, and disposal to solid waste or wastewater treatment ("Tier 1" distribution factors). Certain use categories have additional disposal pathways with environmental fates that are distinct from general solid waste or wastewater disposal. Hg entering the three waste disposal pathways is divided further ("Tier 2" distribution factors). Solid waste is split between disposal in landfills, incineration, and direct release to air and to soil (representing open burning and dumping of waste). Wastewater is partially captured in sewage sludge, and the rest is released to water. "Other Disposal" is distributed between air, land, and landfills. A third tier of distribution factors is needed to characterize environmental releases for solid waste incineration (emitted to air or captured in ash and then deposited to soil or in landfills) and sewage sludge (incinerated and emitted to air, applied to soil, or disposed of in landfills).
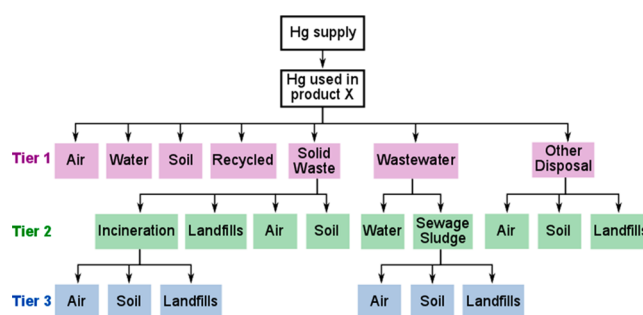

Figure 2. Generic substance flow analysis diagram for commercial Hg. Each arrow is a distribution factor quantified in this work (Table S3, Supporting Information). This diagram applies to all intentional use categories with the exception of dental amalgam, which has additional pathways (see Methods and Figure S2, Supporting Information). "Other disposal" refers to medical waste incineration (for Medical Devices and Dental use categories) and iron and steel recycling (for Wiring Devices and Industrial Measuring Devices use category).

Historical waste incineration emissions are estimated in Streets et al.[12] using a population-based method and total waste activity data, but here, we generate a different estimate that involves tracking the Hg content in products that are incinerated (see Figure S1 and discussion in the Supporting Information). Dental amalgam Hg may be released to air, water, and soil upon cremation and has unique fate pathways not represented in Figure 2 (see Figure S2, Supporting Information). Hg in teeth is assumed to be permanently sequestered during burial as there is no evidence of release to cemetery soil.[49]

Distribution factors for each use category were estimated from a variety of sources (Tables S1 and S2, Supporting Information). Distribution factors are applied globally for 1850−1960 and separately for the developed and developing world between 1970 and 2010. We use previous decadal estimates from Streets et al.[12] for global atmospheric emissions from chlor-alkali plants, silver and large-scale gold mining, and ASGM, except for 2010 ASGM emissions that are based on AMAP/UNEP[22] estimates.

Temporal variability in distribution factors is governed by the availability of evidence that releases have changed from one decade to another due to regulatory controls and other factors. Global distribution factors are held constant in time through 1950, with variation in 1960 for three use categories (VCM and Other Chemical, Paint, and Pesticides and Fertilizer). This reflects significant changes in consumption patterns (a change from chemicals to laboratory uses, marine antifouling paint to home interior/exterior latex paint, and agricultural to pulp and paper fungicides, respectively). Different distribution factors in the developed world are applied for each decade between 1970 and 2010. Developing world distribution factors are assumed constant for 1970−2010. The "Other" category in Table 1 (9% of 1850−2010 global consumption) encompasses a diverse set of uses with an unknown distribution, and we assume for this category the average fate of all other categories.

Releases to different environmental reservoirs are calculated on a global scale by multiplying the Hg consumed in each use category and decade by the corresponding distribution factors. The only exceptions are for Wiring Devices and Industrial Measuring Devices and Dental use categories, for which we estimate delayed releases based on the long lifetime of Hg in these products after the original consumption of Hg. Most products are disposed of and enter the environment within the

decade when they were produced, and manufacturing processes generally consume and release Hg within a year.[13,15,16,30,50−53] Our inventory has a decadal resolution; thus, delays of less than a decade between production and release can be ignored. Products in the Wiring Devices and Industrial Measuring Devices category are often in use for 20−50 years before disposal.[13−15,30,52] For these products, we follow the methods of Jasinski[13] and Cain et al.[16] and assume that 10% is discarded after 10 years, 40% after 30 years, and the remaining 50% after 50 years. Dental amalgams generally remain in living teeth for 10 to 30 years or more. We estimate excretion and exhalation releases from dental amalgam to air and water during this time and track the remaining Hg that will be released through cremation pathways or permanently stored through burial after 30 to 50 years, depending on average life expectancy[54] and ages of individuals receiving fillings.[16]

Recycled Hg is estimated separately for (1) internal reuse of Hg in chemicals manufacturing and large-scale mining[30,55,56] and (2) external recycling of products like batteries that returns Hg to the global Hg supply for future use.[56] External recycling did not become widespread until 1990.[13] We do not tie our estimates of recycled Hg to global Hg supply and instead use estimated total Hg consumption from Wilson et al.[20] that includes secondary sources for 1990−present. Following UNEP methods,[56] we assume that no Hg is released to the environment during the recycling process.

Implications for the Biogeochemical Hg Cycle and Atmospheric Trends. We use the fully coupled global biogeochemical Hg box model from Amos et al.[4,57] to track the fate of commercial Hg after it has been released to the environment. The model includes seven reservoirs that represent the atmosphere, ocean (surface, subsurface, deep), and terrestrial pools (fast, slow, armored). Fluxes between reservoirs are determined by first-order rate coefficients applied to the inventory of the exporting reservoir (Table S3, Supporting Information). Riverine rate coefficients have been updated by Amos et al.[57] to include the permanent removal of Hg to benthic sediment at ocean margins. Primary anthropogenic and geogenic emissions are treated as external forcings.

We added a landfill reservoir to this model. Landfills can emit Hg into the atmosphere through vent pipes and diffusion from cover soil and from the "working face" where waste is exposed and actively dumped.[31] They can also release Hg into groundwater and soils through the base of the landfill, but this appears to be negligible.[58] Data available on Hg emissions for managed landfills in China,[31,59] the United States,[60] and Korea[61] indicate very low values. We estimate a mean lifetime of 20 000 years for Hg in landfills by combining emissions values for each site with estimated Hg reservoirs inferred from the waste content and disposal magnitudes. Landfills can therefore effectively be viewed as a permanent sink on centurial time scales.

Commercial Hg enters the biogeochemical cycle as an external forcing factor to the atmosphere, water, soil, and landfills. Hg releases to soil are distributed among the three terrestrial reservoirs of the model in the same manner as atmospherically deposited Hg.[4] Hg releases to water are distributed to inland freshwater systems (90%) and to estuaries (10%) based on the locations of present-day point sources.[57,62] We assume that 75% of the Hg input to inland freshwater systems is sequestered permanently in sediments and 25% evades to the atmosphere, based on models for a variety of lakes and rivers.[63] On the basis of previous work, we assume

that 50% of the Hg directly released to estuaries is transported to the surface ocean, 10% evades to the atmosphere, and 40% is sequestered permanently in coastal sediments.[64,65] In this manner, we estimate that 70% of Hg released to water is permanently sequestered, 23% enters the atmosphere, and 7% enters the surface ocean.

We apply the box model to time-dependent simulations from 2000 BC to 2010 following the methods described in Amos et al.[4] We simulate 1850−2010 with anthropogenic atmospheric emissions from Streets et al.[12] plus the releases from commercial Hg quantified in this study. We evaluate the model with three global observational constraints, following Amos et al.:[4] (1) the present-day atmospheric inventory (best estimate of 5000 Mg, range of 4600−5600 Mg), (2) the present-day mean concentration in the upper (0−1500 m) ocean (best estimate of 1.0 pM, range of 0.5−1.5 pM), and (3) the relative anthropogenic enrichment factor (AEF) in atmospheric deposition between preindustrial and present-day (best estimate of 3, range of 2 to 5). We define AEF as the ratio of 1985−2000 deposition to 1760−1880 deposition.[66,67]

■ RESULTS AND DISCUSSION

Global Commercial Hg Consumption Patterns, 1850−2010. Figure 3 shows the global commercial use of Hg since 1850 for all categories in Table 1 and is partitioned between the developed and developing world after 1970. Prior to 1900, almost all mined Hg was used in silver and gold mining. Hg uses diversified greatly in the 20th century. Consumption in large-scale mining declined following the end of the gold rush and as extraction methods that did not require Hg became widespread. The 1940s peak in Figure 3 is driven by chemicals production for munitions during WWII. The 1970s peak represents the height of Hg use in consumer products like paint and batteries and in chlor-alkali plants. Total consumption declined after the 1970s when many developed countries implemented regulations on Hg uses and environmental releases. Since 1990, the developing world has dominated global Hg consumption. ASGM in developing countries is presently the largest use of Hg globally and is increasing.[22,68]

Environmental Releases of Commercial Hg. Figure 4 compares the historical atmospheric emissions inventory of Streets et al.[12] (including sources from fuel combustion, cement production, metals smelting, mining, chlor-alkali plants, and some waste incineration) with our best estimate of additional releases to air, water, soil, and landfills from commercial Hg. Streets et al.[12] estimate total emissions to air of 215 Gg since 1850. We estimate additional environmental releases over the same period of 540 Gg. Of these, 230 Gg is permanently sequestered in landfills or in benthic sediments of freshwater and estuarine systems. The remaining 310 Gg (including 110 Gg emitted to air) cycles between biogeochemical reservoirs and represents a larger anthropogenic perturbation to the global Hg cycle than the 215 Gg of Streets et al.[12] Commercial Hg thus represents a major, previously unquantified source of Hg to the global environment. The temporal pattern of anthropogenic Hg releases is also affected. Whereas Streets et al.[12] indicate rising emissions since 1950, our estimate shows a decline in total releases from 1970 to 2000.

Figure 5 presents the historical contributions of individual commercial use categories to global environmental releases to air, water, soil, and landfills. Releases to air, water, and soil all show similar enhancements from late 19th-century mining. Differences are attributable to changes in the fate of commercial
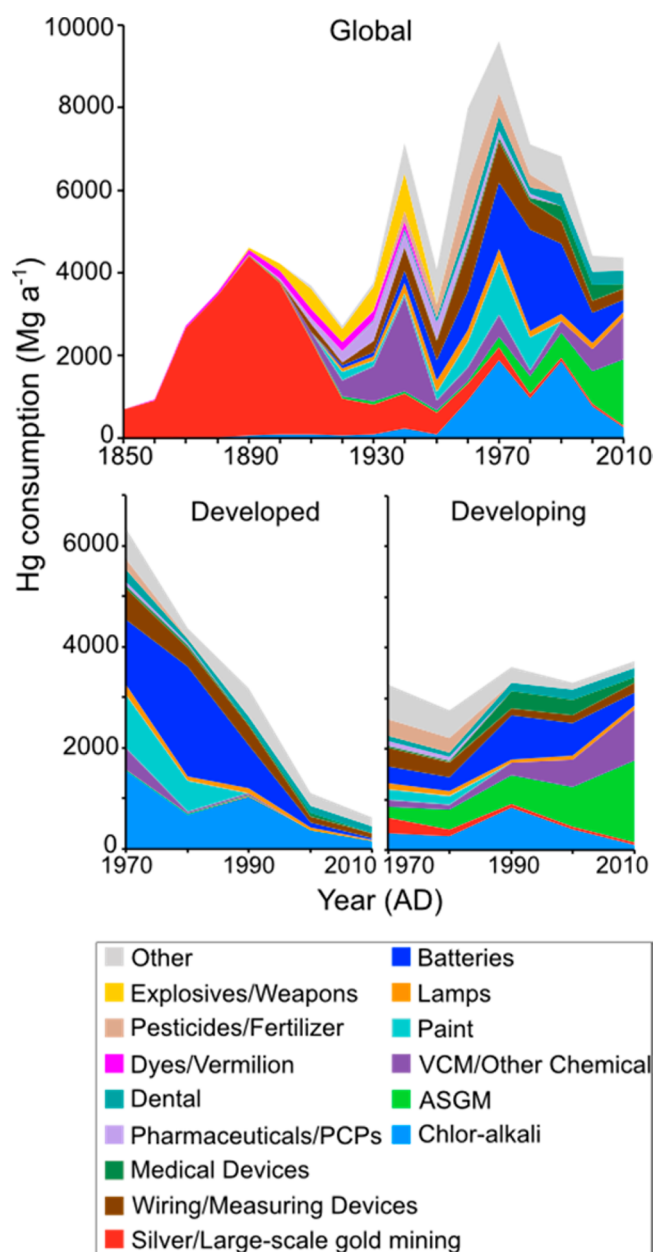
Figure 3. Global historical Hg consumption in commercial products. Consumption is partitioned for each decade between the different use categories of Table 1 and further partitioned between developed countries and developing countries after 1970.

Figure 4. Historical global releases of Hg to the environment. The Streets et al.[12] inventory includes atmospheric releases from combustion, smelting, mining, and chlor-alkali plants. Additional air, soil, water, and landfill releases shown are associated with commercial Hg products as quantified in this work.

Hg over time. Emissions to air peak in 1970, mainly due to paint volatilization and incineration of batteries. Although Hg use in batteries increased from 1970 to 1980, open-air waste burning at landfills was eliminated in developed countries like the US during this period following solid waste regulations.[69,70] Use of explosives and weapons was a major emitter to air during 1900−1950 with a peak in WWII.

Water releases also exhibit a peak during WWII, due to laboratory uses and chemicals manufacturing. The overall maximum occurs in 1960, with a steep subsequent decline following implementation of chlor-alkali liquid effluent regulations in the early 1970s in North America and Europe.[71,72] Implementation of wastewater treatment from the 1980s onward led to even greater declines in water releases[73] but contributes a small amount to soils due to
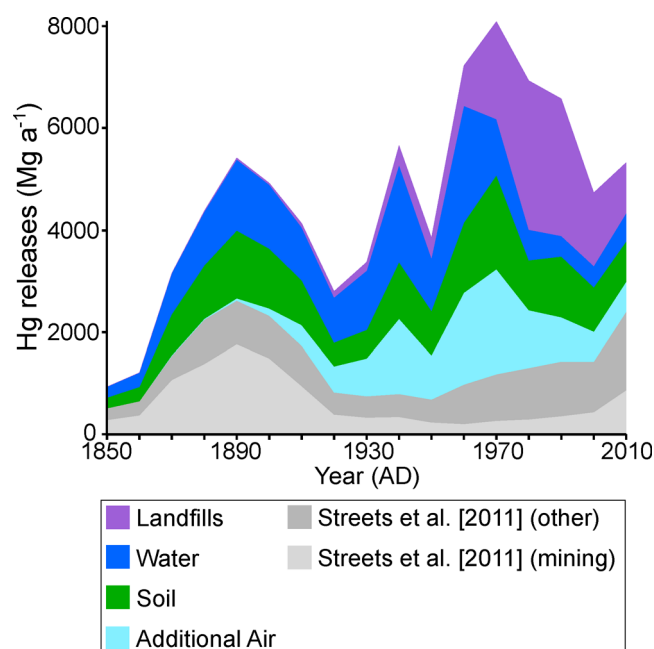
application of Hg-containing sludges.[16,56] Similarly, chlor-alkali plants began capturing Hg in sludges in the 1970s, which were subsequently dumped on land or landfilled on-site.[72] The 1970 peak in soil releases is driven by Hg used in chlor-alkali plants and Hg-containing pesticides and fertilizer that were applied directly to land.

Implications for the Biogeochemical Hg Cycle and Atmospheric Trends. Figure 6 shows simulated atmospheric Hg from 1850 to the present after adding our historical inventory of commercial Hg emissions and releases to the global biogeochemical Hg model described previously. Figure S3, Supporting Information, gives present-day reservoirs and flows. Our simulated present-day atmospheric reservoir is 5800 Mg; the mean Hg concentration in the upper ocean is 1.5 pM, and the AEF for atmospheric deposition is 4.4. The original Amos et al.[4] simulation not including commercial Hg yielded a present-day atmosphere of 5300 Mg but did not account for burial of Hg in ocean margin sediments.[57] Accounting for burial without commercial Hg results in an atmosphere that is too low (2700 Mg). Conversely, including commercial Hg in the original Amos et al.[4] simulation without burial of riverine Hg would yield a present-day atmospheric reservoir of 10 000 Mg, much higher than that observed.

Our simulated present-day atmospheric reservoir of 5800 Mg is slightly higher than the observational range (4600−5600 Mg), but this could be accommodated by uncertainty in Hg re-emission from soils.[74,75] The atmospheric increase over the past decade (Figure 6) is driven by rising anthropogenic emissions in the Streets et al.[12] inventory (primarily from coal burning in Asia) and rising releases from ASGM[22] (Figures 3 and 4). However, Wilson et al.[20] and AMAP/UNEP[22] suggest that global total anthropogenic emissions have in fact remained constant since 2000. AMAP/UNEP estimate that coal combustion emissions specifically have remained constant since at least 2005, as increased energy production efficiency
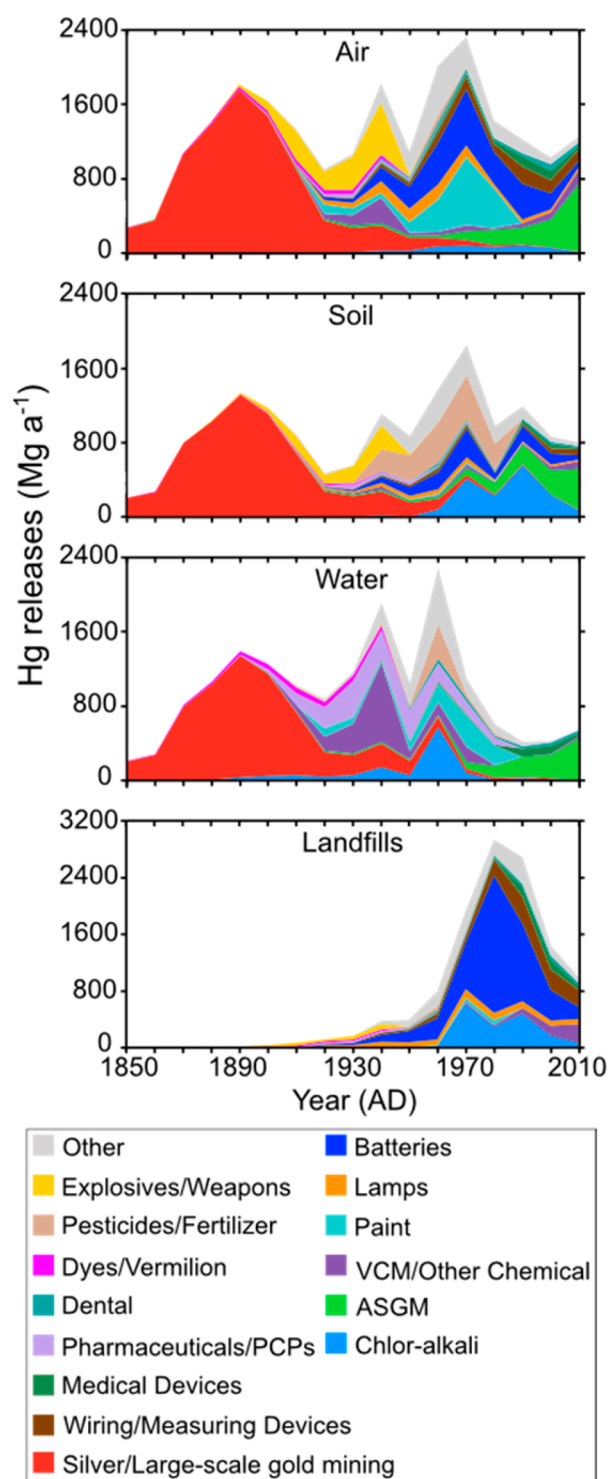
Figure 5. Global historical releases of commercial Hg to environmental reservoirs by use category.

Figure 6. Trend in simulated atmospheric Hg from 1850 to 2010. Results for mass (left axis) and implied mean tropospheric concentration (right axis) are shown for the updated biogeochemical model including historical commercial Hg releases. The dashed line shows results from a sensitivity simulation with Streets et al.[12] anthropogenic atmospheric emissions held constant from 2000 to 2010 (see text).

Inclusion of commercial Hg releases in the global biogeochemical model improves model consistency with archival records of atmospheric deposition. Lake sediments and ombrotrophic peat bogs generally indicate a gradual rise over the industrial era with a peak in the 1970s.[33−36] Figure 6 indicates a 1970s peak in simulated atmospheric Hg and a muted 19th century mining signal. Without the inclusion of commercial Hg, model deposition increases from 1970 to the present and there is a prominent 19th century peak.[4] Our inventory also helps to explain the observed 1990 to the present declines in atmospheric Hg over North America and Europe.[37,38] The model increase from 2000 to 2010 is driven by increasing global anthropogenic atmospheric emissions in the Streets et al.[12] inventory, but holding these constant as another emissions inventory suggests[20,22] results in a relatively flat global trend (see previous paragraph and Figure 6).

Our work shows that environmental releases of commercial Hg to air, water, and soil over the industrial period have represented a major and previously unquantified perturbation to Hg in the global environment. The legacy of this source in oceanic and terrestrial reservoirs has important implications for future ecosystem responses to changes in emissions. Addressing the impact of commercial Hg on regional-scale environmental Hg loadings and atmospheric trends requires better information on the geographical distribution of commercial Hg releases. Better understanding of the role of soils for long-term storage of anthropogenic Hg is also critically needed.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Additional information on data sources used to estimate distribution factors (Table S1), distribution factors used in this study (Table S2), model rate coefficients (Table S3), waste incineration emissions estimates (Figure S1), release pathways for dental amalgam Hg (Figure S2), present-day reservoirs and flows in the global biogeochemical model (Figure S3), and results from sensitivity studies on the uncertainty in chlor-alkali

and control technologies have compensated for increases in fuel burned.[22] Moreover, the ASGM increase since 2005 may be an artifact of improved reporting.[22] We conducted a sensitivity simulation holding constant anthropogenic atmospheric emissions for the 2000−2010 period, and results are shown as the dashed line in Figure 6. We obtain in that simulation an atmospheric reservoir of 5100 Mg, more consistent with observations, and an unchanged upper ocean concentration of 1.5 pM and AEF of 4.4.
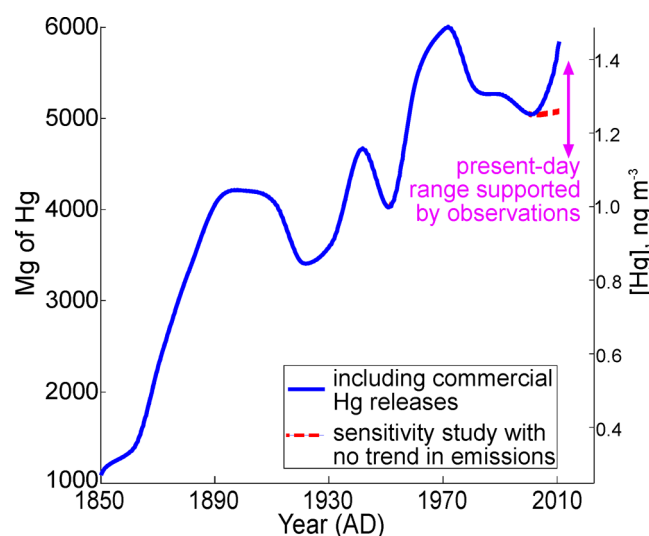
Hg consumption. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes
The authors declare no competing financial interest.

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■ REFERENCES

(1) Mahaffey, K. R.; Sunderland, E. M.; Chan, H. M.; Choi, A. L.; Grandjean, P.; Marien, K.; Oken, E.; Sakamoto, M.; Schoeny, R.; Weihe, P.; Yan, C. H.; Yasutake, A. Balancing the benefits of n-3 polyunsaturated fatty acids and the risks of methylmercury exposure from fish consumption. *Nutr. Rev.* **2011**, *69* (9), 493−508.

(2) Karagas, M. R.; Choi, A. L.; Oken, E.; Horvat, M.; Schoeny, R.; Kamai, E.; Cowell, W.; Grandjean, P.; Korrick, S. Evidence on the human health effects of low-level methylmercury exposure. *Environ. Health Perspect.* **2012**, *120* (6), 799−806.

(3) Nriagu, J. O. Production and uses of mercury. In *The biogeochemistry of mercury in the environment*; Nriagu, J. O., Ed.; Elsevier/North-Holland Biomedial Press: Amsterdam, the Netherlands, 1979; pp 23−40.

(4) 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* (2), 410−421.

(5) 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), 1−7.

(6) Serrano, O.; Martinez-Cortizas, A.; Mateo, M. A.; Biester, H.; Bindler, R. Millennial scale impact on the marine biogeochemical cycle of mercury from early mining on the Iberian Peninsula. *Global Biogeochem. Cycles* **2013**, *27* (1), 21−30.

(7) Mason, R. P.; Fitzgerald, W. F.; Morel, F. M. M. The biogeochemical cycling of elemental mercury: Anthropogenic influences. *Geochim. Cosmochim. Acta* **1994**, *58* (15), 3191−3198.

(8) Selin, N. E.; Jacob, D. J.; Yantosca, R. M.; Strode, S.; Jaegle, 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*, 2.

(9) Slemr, F.; Schuster, G.; Seiler, W. Distribution, speciation, and budget of atmospheric mercury. *J. Atmos Chem.* **1985**, *3* (4), 407−434.

(10) Andren, M. O.; Nriagu, J. O. The global cycle of mercury. In *The biogeochemistry of mercury in the environment*; Nriagu, J. O., Ed.; Elsevier/North-Holland Biomedial Press: Amsterdam, the Netherlands, 1979; pp 1−15.

(11) *Minamata Convention on Mercury: Text and Annexes*; United Nations Environment Programme: Geneva, 2013; http://www.mercuryconvention.org/Portals/11/documents/Booklets/Minamata%20Convention%20on%20Mercury_booklet_English.pdf.

(12) 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* (24), 10485−10491.

(13) Jasinski, S. M. *The materials flow of mercury in the United States*; Bureau of Mines Information Circular IC 9412; U.S. Department of the Interior: Washington, DC, 1994.

(14) *Substance Flow Analysis of Mercury in Products*; Barr Engineering: Minneapolis, MN, August 15, 2001.

(15) *Assessment of Mercury Releases from the Russian Federation*; Arctic Council Action Plan to Eliminate Pollution of the Arctic (ACAP), Russian Federal Service for Environmental, Technological and Atomic Supervision and Danish Environmental Protection Agency: Copenhagen, Denmark, 2005.

(16) Cain, A.; Disch, S.; Twaroski, C.; Reindl, J.; Case, C. R. Substance flow analysis of mercury intentionally used in products in the United States. *J. Ind. Ecol.* **2007**, *11* (3), 61−75.

(17) Kindbom, K.; Munthe, J. *Product-related emissions of mercury to air in the European Union*; IVL Swedish Environmental Research Institute Ltd.: Göteborg, Sweden, 2007.

(18) Pacyna, E. G.; Pacyna, J. M.; Sundseth, K.; Munthe, J.; Kindbom, K.; Wilson, S.; Steenhuisen, F.; Maxson, P. Global emission of mercury to the atmosphere from anthropogenic sources in 2005 and projections to 2020. *Atmos. Environ.* **2010**, *44* (20), 2487−2499.

(19) Pirrone, N.; Cinnirella, S.; Feng, X.; Finkelman, R. B.; Friedli, H. R.; Leaner, J.; Mason, R.; Mukherjee, A. B.; Stracher, G. B.; Streets, D. G.; Telmer, K. Global mercury emissions to the atmosphere from anthropogenic and natural sources. *Atmos. Chem. Phys.* **2010**, *10* (13), 5951−5964.

(20) Wilson, S.; Munthe, J.; Sundseth, K.; Kindbom, K.; Maxson, P.; Pacyna, J. M.; Steenhuisen, F. *Updating Historical Global Inventories of Anthropogenic Mercury Emissions to Air*; Arctic Monitoring and Assessment Program (AMAP): Oslo, Norway, 2010.

(21) Sundseth, K.; Pacyna, J.; Pacyna, E.; Panasiuk, D. Substance flow analysis of mercury affecting water quality in the European Union. *Water, Air, Soil Pollut.* **2011**, 1−14.

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

(23) Chakraborty, L. B.; Qureshi, A.; Vadenbo, C.; Hellweg, S. Anthropogenic mercury flows in India and impacts of emission controls. *Environ. Sci. Technol.* **2013**, *47* (15), 8105−8113.

(24) Taylor, C. G. The loss of mercury from fungicidal paints. *J. Appl. Chem.* **1965**, 232−236.

(25) D'Itri, P. A.; D'Itri, F. M. *Mercury Contamination: A Human Tragedy*; John Wiley & Sons: New York, 1977.

(26) Rudd, J. W. M.; Turner, M. A.; Furutani, A.; Swick, A. L.; Townsend, B. E. The English Wabigoon River System 0.1. A synthesis of recent research with a view towards mercury amelioration. *Can. J. Fish. Aquat. Sci.* **1983**, *40* (12), 2206−2217.

(27) Gill, G. A.; Bloom, N. S.; Cappellino, S.; Driscoll, C. T.; Dobbs, C.; McShea, L.; Mason, R.; Rudd, J. W. M. Sediment-water fluxes of mercury in Lavaca Bay, Texas. *Environ. Sci. Technol.* **1999**, *33* (5), 663−669.

(28) Kocman, D.; Horvat, M.; Pirrone, N.; Cinnirella, S. Contribution of contaminated sites to the global mercury budget. *Environ. Res.* **2013**, *125*, 160−170.

(29) Rissanen, K.; Miettinen, J. K. Use of mercury compounds in agriculture and its implications. In *Mercury contamination in man and his environment: A joint undertaking by the International Labor Organisation, Food and Agriculture Organization of the United Nations, The World Health Organization and the International Atomic Energy Agency*; International Atomic Energy Agency: Vienna, Austria, 1972.

(30) *Characterization of Products Containing Mercury in Muncipal Solid Waste in the United States, 1970 to 2000*; U.S. Environmental Protection Agency, Office of Solid Waste, Municipal and Industrial Solid Waste Division: Washington, DC, 1992.

(31) Li, Z. G.; Feng, X.; Li, P.; Liang, L.; Tang, S. L.; Wang, S. F.; Fu, X. W.; Qiu, G. L.; Shang, L. H. Emissions of air-borne mercury from five municipal solid waste landfills in Guiyang and Wuhan, China. *Atmos. Chem. Phys.* **2010**, *10* (7), 3353−3364.

(32) Brooks, W. E.; Matos, G. R. Mercury recycling in the United States in 2000. In *Flow studies for recycling metal commodities in the United States*; U.S. Geological Survey Circular 1196-U; Sibley, S. F., comp., Ed.; USGS: Reston, VA, 2005; p 21.

(33) Kamman, N. C.; Engstrom, D. R. Historical and present fluxes of mercury to Vermont and New Hampshire lakes inferred from Pb-210 dated sediment cores. *Atmos. Environ.* **2002**, *36* (10), 1599−1609.

(34) Engstrom, D. R.; Balogh, S. J.; Swain, E. B. History of mercury inputs to Minnesota lakes: Influences of watershed disturbance and localized atmospheric deposition. *Limnol. Oceanogr.* **2007**, *52* (6), 2467−2483.

(35) Fain, X.; Ferrari, C. P.; Dommergue, A.; Albert, M. R.; Battle, M.; Severinghaus, J.; Arnaud, L.; Barnola, J. M.; Cairns, W.; Barbante, C.; Boutron, C. Polar firn air reveals large-scale impact of anthropogenic mercury emissions during the 1970s. *Proc. Natl. Acad. Sci. U.S.A.* **2009**, *106* (38), 16114−16119.

(36) Allan, M.; Le Roux, G.; Sonke, J. E.; Piotrowska, N.; Streel, M.; Fagel, N. Reconstructing historical atmospheric mercury deposition in Western Europe using: Misten peat bog cores, Belgium. *Sci. Total Environ.* **2013**, *442*, 290−301.

(37) Slemr, F.; Brunke, E. G.; Ebinghaus, R.; Kuss, J. Worldwide trend of atmospheric mercury since 1995. *Atmos. Chem. Phys.* **2011**, *11* (10), 4779−4787.

(38) Soerensen, A. L.; Jacob, D. J.; Streets, D. G.; Witt, M. L. I.; Ebinghaus, R.; Mason, R. P.; Andersson, M.; Sunderland, E. M. Multidecadal decline of mercury in the North Atlantic atmosphere explained by changing subsurface seawater concentrations. *Geophys. Res. Lett.* **2012**, *39*, DOI: 10.1029/2012GL053736.

(39) Hylander, L. D.; Meili, M. 500 years of mercury production: Global annual inventory by region until 2000 and associated emissions. *Sci. Total Environ.* **2003**, *304* (1−3), 13−27.

(40) Kelly, T. D.; Matos, G. R., Eds. Mercury statistics. In *Historical statistics for mineral and material commodities in the United States*; U.S. Geological Survey Data Series 140, USGS: Reston, VA, 2012; accessed September 25, 2013, at http://minerals.usgs.gov/ds/2005/140/.

(41) Maxson, P. *Mercury flows in Europe and the world: The impact of decommissioned chlor-alkali plants*; Concorde East/West Sprl for the European Commission Environment Directorate-General: Brussels, Belgium, February, 2004.

(42) *Technical Background Report to the Global Atmospheric Mercury Assessment*; Arctic Monitoring and Assessment Programme/UNEP Chemicals Branch: Geneva, Switzerland, 2008.

(43) *Mineral Resources of the United States*; U.S. Geological Survey/Bureau of Mines, US Department of the Interior, Government Printing Office: Washington, D.C., 1882−1929.

(44) *Minerals Yearbook*; US Bureau of Mines, US Department of the Interior, Government Printing Office: Washington, D.C., 1941−1968.

(45) Emerson, D. G. The industrial uses of mercury. In *I congreso internacional del mercurio*, Barcelona, Spain, 6−10 May, 1974; Fabrica Nacional de Moneda y Timbre: Barcelona, Spain, 1974; pp 29−37.

(46) Hylander, L. D.; Meili, M. The rise and fall of mercury: Converting a resource to refuse after 500 years of mining and pollution. *Crit. Rev. Environ. Sci. Technol.* **2005**, *35* (1), 1−36.

(47) GDP and its breakdown at constant 2005 prices in US dollars - All countries and regions/subregions (totals) for all years. In *National Accounts Main Aggregates Database*; United Nations Statistics Division: New York, 2012.

(48) *Metal statistics*; American Metal Mart: New York, 1960−1995.

(49) Arenholt-Bindslev, D. Environmental aspects of dental filling materials. *Eur. J. Oral Sci.* **1998**, *106* (2), 713−720.

(50) *Mercury Study Report to Congress Vol. II: An Inventory of Anthropogenic Mercury Emissions in the United States*; Office of Air Quality Planning & Standards and Office of Research and Development, U.S. Environmental Protection Agency: Washington, DC, December, 1997.

(51) Floyd, P.; Zarogiannis, P.; Crane, M.; Tarkowski, S.; Bencko, V. *Risks to health and the environment related to the use of mercury products*; Risk & Policy Analysts for the European Commission, DG Enterprise: Norfolk, UK, 2002.

(52) Hagreen, L. A.; Lourie, B. A. Canadian mercury inventories: The missing pieces. *Environ. Res.* **2004**, *95* (3), 272−281.

(53) *Report on the major mercury-containing products and processes, their substitutes and experience in switching to mercury-free products and processes*; UNEP(DTIE)/Hg/OEWG.2/7/Add.1; United Nations Environment Programme (UNEP): Geneva, Switzerland, 2008.

(54) *World Population Prospects: The 2010 Revision, Vol. I: Comprehensive Tables*; ST/ESA/SER.A/313; United Nations Department of Economic and Social Affairs Population Division: New York, 2011.

(55) *NRDC submission to UNEP in response to March 2006 request for information on mercury supply, demand, and trade*; National Resources Defense Council (NRDC): Washington, DC, May, 2006.

(56) *Toolkit for Identification and Quantification of Mercury Sources, Reference Report and Guideline for Inventory Level 2, Version 1.2, April 2013*; UNEP Chemicals Branch: Geneva, Switzerland, 2013.

(57) 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.

(58) Li, Z.; Feng, X. *Balance of Mercury in a Modern Municipal Solid Waste Landfill in China*. In Air and Waste Management Association International Specialty Conference, Xi'an, China, May 10−14, 2010.

(59) Zhu, W.; Li, Z. G.; Chai, X. L.; Hao, Y. X.; Lin, C. J.; Sommar, J.; Feng, X. B. Emission characteristics and air-surface exchange of gaseous mercury at the largest active landfill in Asia. *Atmos. Environ.* **2013**, *79*, 188−197.

(60) Lindberg, S. E.; Southworth, G. R.; Bogle, M. A.; Blasing, T. J.; Owens, J.; Roy, K.; Zhang, H.; Kuiken, T.; Price, J.; Reinhart, D.; Sfeir, H. Airborne emissions of mercury from municipal solid waste. I: New measurements from six operating landfills in Florida. *J. Air Waste Manage. Assoc.* **2005**, *55* (7), 859−869.

(61) Kim, S.; Karl, T.; Guenther, A.; Tyndall, G.; Orlando, J.; Harley, P.; Rasmussen, R.; Apel, E. Emissions and ambient distributions of biogenic volatile organic compounds (BVOC) in a ponderosa pine ecosystem: Interpretation of PTR-MS mass spectra. *Atmos. Chem. Phys.* **2010**, *10* (4), 1759−1771.

(62) Kocman, D.; Horvat, M.; et al. *A Global Inventory of Present-Day Mercury Releases to Aquatic Environments*, to be submitted for publication.

(63) Knightes, C. D.; Sunderland, E. M.; Barber, M. C.; Johnston, J. M.; Ambrose, R. B. Application of ecosystem-scale fate and bioaccumulation models to predict fish mercury response times to changes in atmospheric deposition. *Environ. Toxicol. Chem.* **2009**, *28* (4), 881−893.

(64) Mason, R. P.; Lawson, N. M.; Lawrence, A. L.; Leaner, J. J.; Lee, J. G.; Sheu, G. R. Mercury in the Chesapeake Bay. *Mar. Chem.* **1999**, *65* (1−2), 77−96.

(65) Sunderland, E. M.; Dalziel, J.; Heyes, A.; Branfireun, B. A.; Krabbenhoft, D. P.; Gobas, F. A. P. C. Response of a macrotidal estuary to changes in anthropogenic mercury loading between 1850 and 2000. *Environ. Sci. Technol.* **2010**, *44* (5), 1698−1704.

(66) Sonke, J. E. GET-Observatoire Midi-Pyrénées, CNRS, Université de Toulouse III, Toulouse, France. Personal communication, 2014.

(67) Amos, H. M.; Sunderland, E.; Corbitt, E. S.; Hedgecock, I.; Kocman, D.; Krabbenhoft, D.; Lamborg, C. H.; Obrist, D.; Pirrone, N.; Sonke, J. E.; Witt, M. L. I.; Horowitz, H. M. *Estimating global anthropogenic enrichment of mercury: A critical review.* In preparation.

(68) Telmer, K. M.; Veiga, M. M. World emissions of mercury from artisanal and small scale gold mining. In *Mercury Fate and Transport in the Global Atmosphere*; Springer: New York, 2009; pp 131−172.

(69) *Municipal Solid Waste in the United States: 2001 Facts and Figures*; EPA530-R-03-011; U.S. Environmental Protection Agency, Office of Solid Waste and Emergency Response: Washington, DC, 2003.

(70) *Modern Landfills: A Far Cry from the Past*; National Solid Wastes Management Association: Washington, DC, 2008.

(71) Flewelling, F. J. Loss of mercury to the environment from chlor-alkali plants. In *Special symposium on mercury in man's environment*, Ottawa, Canada, February 15−16, 1971; Watkin, J. E., Ed.; National Research Council of Canada: Ottawa, Canada, 1971.

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dx.doi.org/10.1021/es501337j | *Environ. Sci. Technol.* 2014, 48, 10242−10250

(72) Trip, L.; Thorleifson, M. *The Canadian Mercury Cell Chlor-Alkali Industry: Mercury Emissions and Status of Facilities 1935−1996*; Environment Canada, Transboundary Air Issues Branch: Quebec, Canada, April, 1998.

(73) *Materials balance and technology assessment of mercury and its compounds on national and regional bases*; EPA 560/3-75-007; U.S. Environmental Protection Agency Office of Toxic Substances: Washington, D.C., October, 1975.

(74) Obrist, D.; Pokharel, A. K.; Moore, C. Vertical profile measurements of soil air suggest immobilization of gaseous elemental mercury in mineral soil. *Environ. Sci. Technol.* **2014**, *48* (4), 2242−2252.

(75) Krabbenhoft, D. Understanding the Propagation of Atmospheric Mercury through Terrestrial Landscapes: After Twenty Five Years of Research does the Story Make Sense? Presented at *11th International Conference on Mercury as a Global Pollutant*, Edinburgh, Scotland, 2013.