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Historical mercury releases from commercial products: global environmental implications

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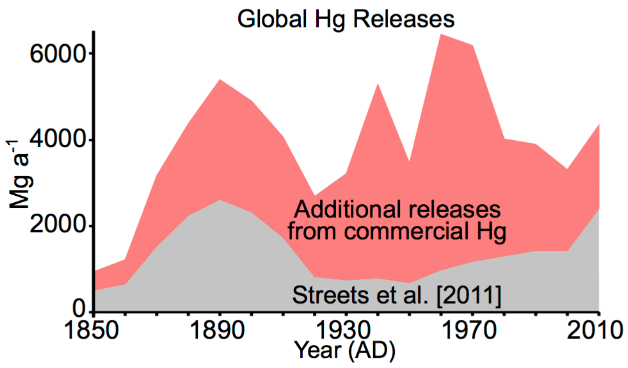

ABSTRACT

Use and disposal of commercial products has contributed a large and previously unquantified anthropogenic source of mercury (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. Cumulative anthropogenic Hg emissions since 1850 have recently been estimated at 220 Gg. We find that commercial use of Hg released an additional 540 Gg to the global environment since 1850 (20% to air, 30% to water, 30% to soil, 20% to landfills). 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. Using our inventory to force a global biogeochemical model improves model consistency with observed (1) changes in atmospheric deposition recorded in many remote lake sediments and ombrotrophic peat bogs over the industrial era, and (2) declines in atmospheric Hg concentrations since the 1990s.

INTRODUCTION

Methylmercury, a toxin formed from inorganic 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 pre-industrial 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 timescale 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 215 Gg of Hg have been emitted directly to the atmosphere since 1850 from fuel combustion, metals smelting, mining, and chlor-alkali plants, an additional 616

Gg have been mined during the same period for numerous commercial uses.[12] These include 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] The environmental fate of most of the mined Hg has not yet been quantified.

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 land or vegetation. Previous work has had difficulty reconciling the temporal trend of anthropogenic emissions with archival records of historical atmospheric Hg deposition, many of which show a peak in the 1970s.[33-36] Atmospheric observations indicate a ~20% to 50% decrease in total gaseous mercury in the Northern Hemisphere since 1995,[37, 38] at odds with atmospheric emission inventories that estimate increased or flat emissions over this period.[12, 20] Soerensen et al.[38] suggested that the observed atmospheric trend could be explained by declining oceanic evasion to the atmosphere due to decreased seawater concentrations. Commercial use of Hg peaked in the 1970s and has declined dramatically since,[12, 39] and we investigate how the related changes in historical commercial Hg releases may play a role in reconciling these trends.

METHODS

We present a global, historical analysis tracking Hg from when it is mined, through all known 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 apply a series of distribution factors that vary temporally and by economic development status of different countries to distribute commercial Hg to its final environmental releases following a simplified substance flow analysis (e.g. Barr Engineering[14]). Finally, we investigate the impacts of these global, time-dependent releases on accumulation and cycling among environmental reservoirs using a seven-box biogeochemical Hg model.

Global Commercial Hg Consumption Patterns, 1850 – 2010

We assume that significant Hg release from non-mining 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 Hg production 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 mined Hg that is not stockpiled is incorporated into products 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] which includes both primary mining and secondary sources.

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 between them. 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[42, 43] are used to estimate global consumption of Hg in 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.

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 on. 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.[44] Consumption patterns for the developed world are assumed to follow those of the US in 1970 and 1980.[45] 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 substance flow analysis diagram 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 disposal to soil, wastewater is partially captured in sewage sludge and the rest is released to water, and ‘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). Dental amalgam has unique fate pathways not represented in Figure 2. Some Hg in teeth is permanently stored during burial[46] or partially released to air, water, and soil upon cremation.

Distribution factors for each use category were estimated from a variety of sources (Tables S1 and S2). 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 for which we use 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 anti-fouling 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. 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, 47-50] Products in the Wiring Devices and Industrial Measuring Devices category are often in use for 20-50 years before disposal.[13-15, 30, 49] For these products we follow the methods of

Jasinski et al.[13] and Cain et al.[16] and assume that 10% are 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[51] and ages of individuals receiving fillings.[16]

Recycled Hg is estimated separately for internal reuse of Hg in chemicals manufacturing and large-scale mining[30, 52, 53] and external recycling of Hg in products like batteries that returns Hg to the global Hg supply for future use.[53] 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 supply from Wilson et al.[20] which includes all secondary sources for 1990 – present. We assume that no Hg is released to the environment during the recycling process, based on available data suggesting releases are negligible.[53]

Implications for the Biogeochemical Hg Cycle and Atmospheric Trends

We use the fully-coupled global biogeochemical Hg box model from Amos et al.[4] 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, and deep), and terrestrial pools (fast, slow, and armored). Fluxes between reservoirs are determined by first-order rate coefficients applied to the inventory of the exporting reservoir. Atmospheric rate coefficients are from Holmes et al.[54] and oceanic rate coefficients are from Soerensen et al.[55] and Sunderland and Mason[56] (for a full list, see Table S3). Riverine rate coefficients have been updated following Amos et al.[57] to include the settling of particle-bound Hg to benthic estuarine and shelf sediments. This effectively adds a permanent sink from the terrestrial pools. 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, 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] the United States,[59] and Korea[60] indicate low values. We find 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 as defined here can therefore effectively be viewed as a permanent sink.

Commercial Hg enters the biogeochemical cycle via 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 in Amos et al.[4] Hg releases to water are distributed as 90% to inland freshwater systems and 10% to estuaries based on the distribution of present-day point sources.[57, 61] 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.[62] Based on 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.[63, 64] 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 4600 – 5600 Mg), (2) the present-day mean upper (0 to 1500 m) ocean concentration (best estimate of 1.0 pM, range 0.5-1.5 pM), and (3) the relative anthropogenic enrichment factor (AEF) in atmospheric deposition between pre-industrial and present-day (best estimate of 3, range 2 to 5). We define our model AEF as the ratio of average 1985-2000 deposition to average 1760-1880 deposition.[65, 66] These two time intervals are empirically determined from the compilation of lake sediments described in Biester et al.[67] to provide a more consistent comparison between models and observations.[65]

RESULTS AND DISCUSSION

Global Commercial Hg Consumption Patterns, 1850 – 2010

Figure 3 shows the global commercial use of Hg since 1850 for all categories described in Table 1, and partitioned between the developed and developing world after 1970. Prior to 1900, almost all mined Hg was used in silver and gold mining. In the 20th century, Hg uses diversified greatly. Hg use 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. 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 combustion, metals smelting, mining, and chlor-alkali plants) 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. Additional releases in our inventory over the same period total 540 Gg. Of these, 230 Gg are permanently sequestered in landfills or in benthic sediments of freshwater and estuarine systems. The remaining 310 Gg (including 110 Gg emitted to air) cycle between biogeochemical reservoirs and represent 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 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 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, 53] 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-present after adding our inventory of commercial Hg releases to the updated global biogeochemical Hg model, which includes burial of riverine Hg in benthic sediments of coastal marine systems from Amos et al.[57] and an additional reservoir representing landfills. 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 riverine Hg. 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 would yield a present-day atmospheric reservoir of 10,000 Mg, much higher than observed.

Our simulated present-day atmospheric reservoir of 5800 Mg is still slightly higher than the observational range (4600-5600 Mg). This is due to the increase over the past decade (Figure

6) driven by rising anthropogenic atmospheric 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] suggest that global anthropogenic emissions have in fact remained relatively constant since 2000, and AMAP/UNEP[22] suggest that the ASGM increase since 2000 may be an artifact of improved reporting. We conducted a sensitivity simulation holding constant anthropogenic atmospheric emissions and ASGM releases 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 5000 Mg, more consistent with observations, and unchanged upper ocean concentration of 1.5 pM and AEF of 4.4. Alternatively, the atmospheric reservoir could be reduced within the range of observational constraints if the efficacy of Hg re-emission from soils were decreased, a change supported by recent observational evidence.[74, 75]

Inclusion of commercial Hg releases in our 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 present and there is a prominent 19th century peak.[4] Our inventory also helps to explain the observed 1990-present declines in atmospheric Hg over North America and Europe.[37, 38]

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 policy. Future work should examine the geographical distribution of commercial Hg releases and its impact on regional-scale environmental Hg loadings and atmospheric trends. Better understanding of the role of soils for long-term storage of anthropogenic Hg is also critically needed.

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SUPPORTING INFORMATION. Additional information on data sources used to estimate distribution factors (Table S1), distribution factors used in this study (Table S2), and model rate coefficients (Table S3). This material is available free of charge via the Internet at http://pubs.acs.org.

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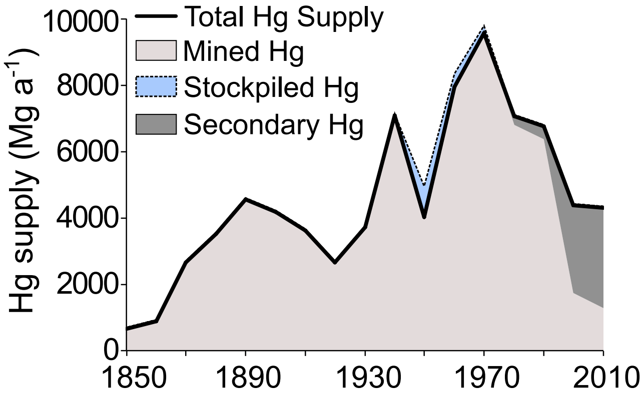

Figure 1. Historical global supply of Hg for commercial uses. This supply includes primary mined Hg (1850 – 2008 data from Streets et al.[10]), minus the amount stockpiled by the United States between 1945 and 1970, and augmented by secondary Hg including recycled, recovered as a byproduct, and released from stockpiles after 1980.

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 anti-fouling 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

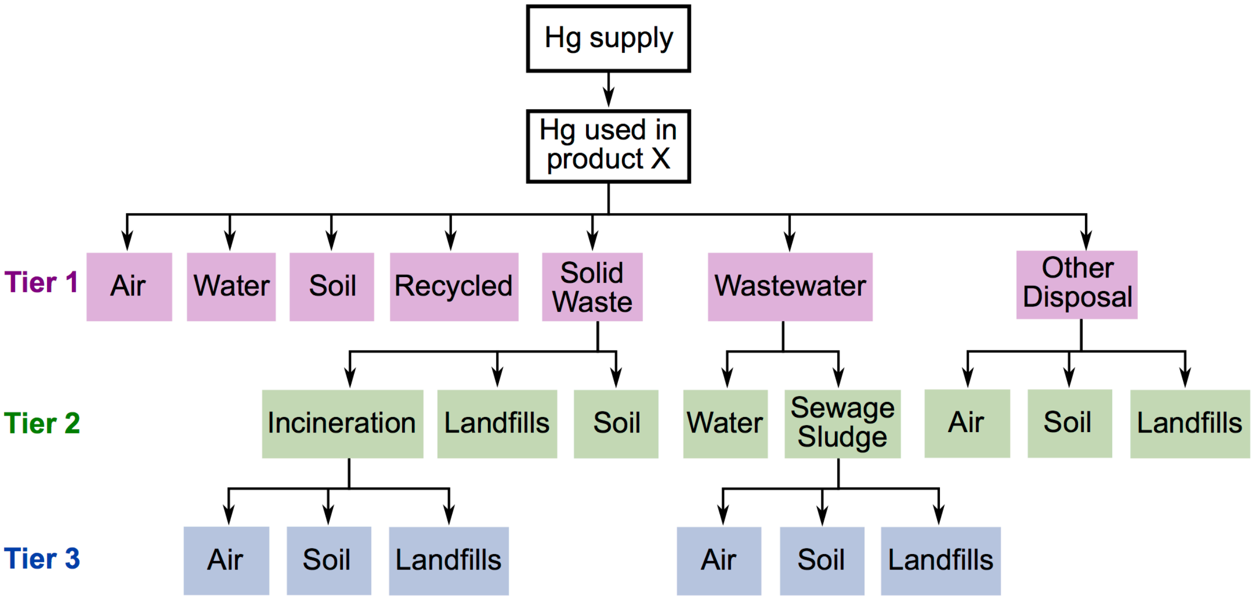

Figure 2. Generic substance flow analysis diagram for commercial Hg. Each arrow is a distribution factor quantified in this work (Table S3). This diagram applies to all intentional use categories with the exception of dental amalgam, which has additional pathways (see Methods). “Other disposal” refers 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).

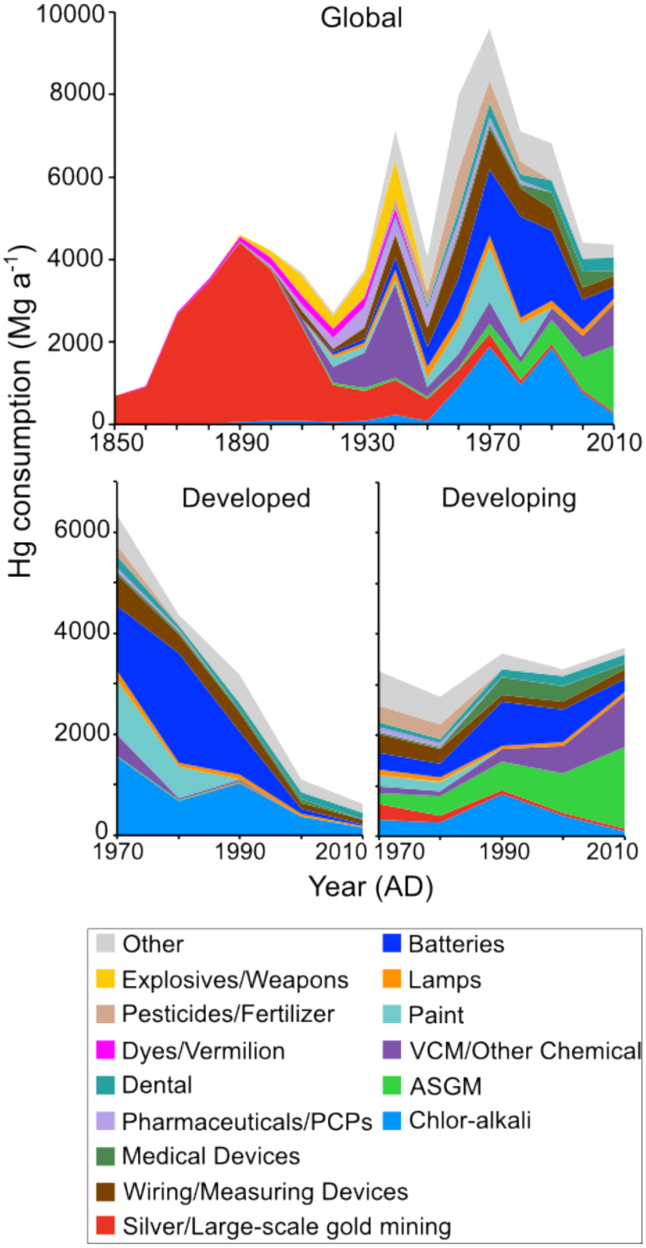

Figure 3. Global historical Hg consumption in commercial products. Consumption is partitioned for each decade between the different use categories of Table 1, and further partitioned between developed countries and developing countries after 1970.

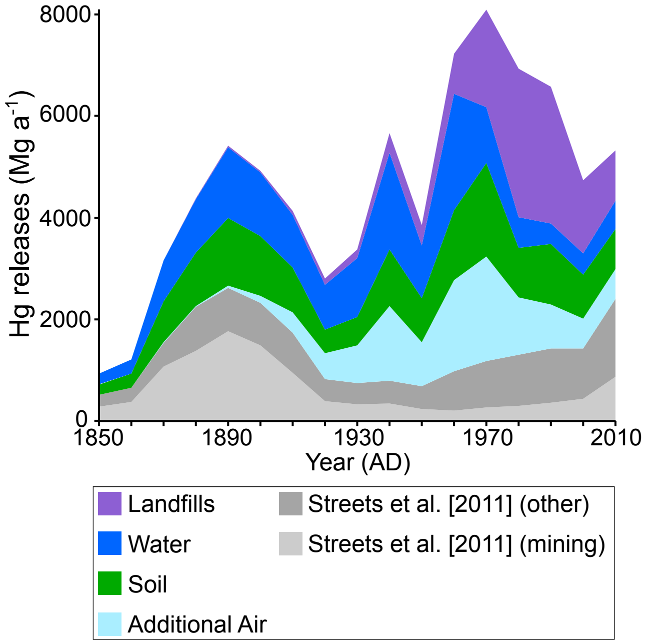

Figure 4. Historical global releases of Hg to the environment. The Streets et al.[10] inventory includes atmospheric releases from combustion, smelting, mining, and chlor-alkali plants. Additional air, soil, water, and landfill releases shown are associated with commercial Hg products as quantified in this work.

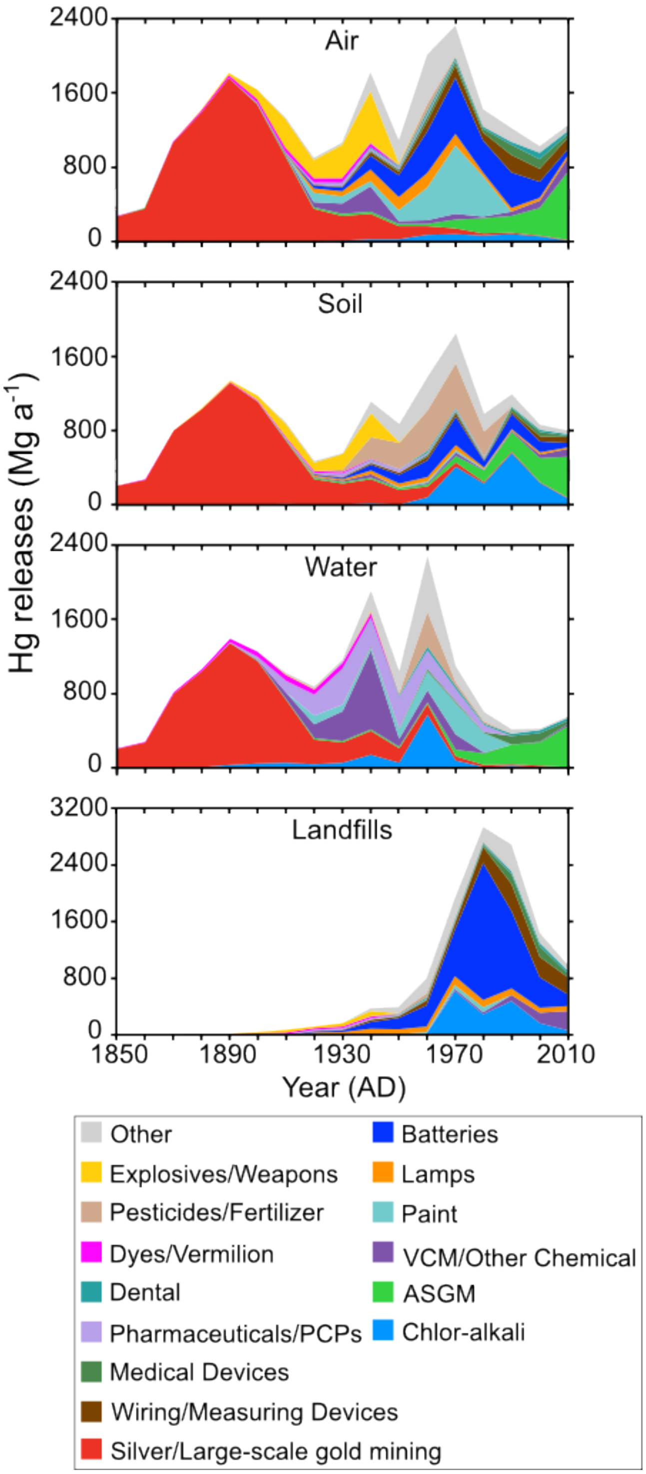

Figure 5. Global historical releases of commercial Hg to environmental reservoirs by use category.

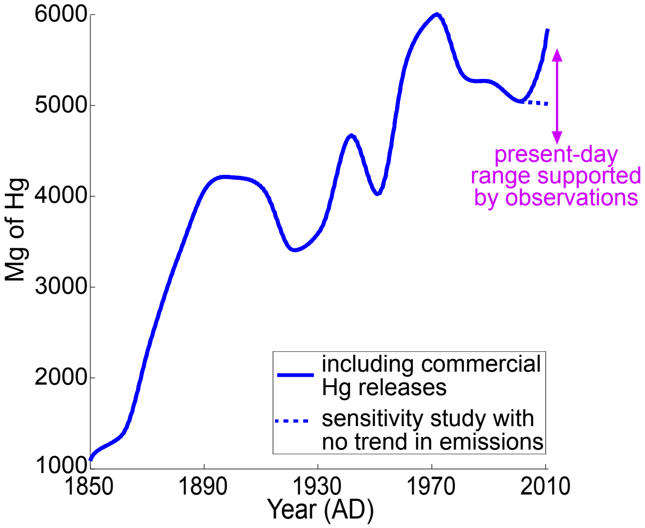

Figure 6. Trend in simulated atmospheric Hg mass from 1850 to 2010. Results shown using the updated biogeochemical model described in the text, including additional commercial Hg releases (blue) and a sensitivity simulation with ASGM releases and Streets et al.[10] anthropogenic atmospheric emissions held constant from 2000-2010 (dotted blue line).