

Total Mercury Released to the Environment by Human Activities

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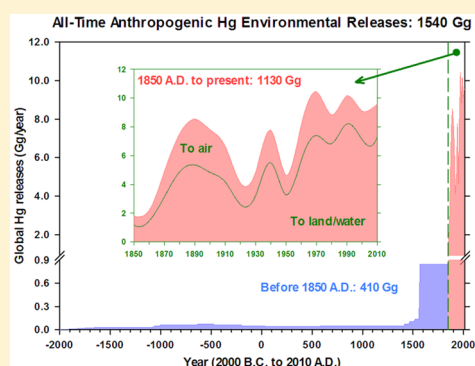
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ABSTRACT: We estimate that a cumulative total of 1540 (1060–2800) Gg (gigagrams, 10⁹ grams or thousand tonnes) of mercury (Hg) have been released by human activities up to 2010, 73% of which was released after 1850. Of this liberated Hg, 470 Gg were emitted directly into the atmosphere, and 74% of the air emissions were elemental Hg. Cumulatively, about 1070 Gg were released to land and water bodies. Though annual releases of Hg have been relatively stable since 1880 at 8 ± 2 Gg, except for wartime, the distributions of those releases among source types, world regions, and environmental media have changed dramatically. Production of Hg accounts for 27% of cumulative Hg releases to the environment, followed by silver production (24%) and chemicals manufacturing (12%). North America (30%), Europe (27%), and Asia (16%) have experienced the largest releases. Biogeochemical modeling shows a 3.2-fold increase in the atmospheric burden relative to 1850 and a contemporary atmospheric reservoir of 4.57 Gg, both of which agree well with observational constraints. We find that approximately 40% (390 Gg) of the Hg discarded to land and water must be sequestered at contaminated sites to maintain consistency with recent declines in atmospheric Hg concentrations.



INTRODUCTION

Mercury (Hg) is a natural element found everywhere in Earth's crust. It is released by a number of natural processes, principally the weathering of Hg-containing rocks, geothermal activity, and volcanism. Present-day anthropogenic Hg emissions of about 2 Gg yr⁻¹ are more than an order of magnitude higher than natural emissions.^{1,2} Archives of atmospheric deposition recorded in remote peat and lake sediments consistently indicate a 3-to-5-fold enrichment in atmospheric deposition of Hg relative to 1850 (taken to be the start of the Industrial Era) due to anthropogenic releases.^{3,4} Global biogeochemical models suggest that this 1850 baseline was in turn enhanced by pre-1850 anthropogenic emissions, so that the actual enrichment above natural levels may be larger.^{5,6} Such inferences rely on an accurate knowledge of all-time Hg emissions from human activity, the estimation of which is the goal of this study.

About 4000 years ago humans began extracting gold, silver, copper, zinc, lead, coal, and other materials—all of which contained Hg as an impurity. Mercury itself became an important element, mined for its intrinsic qualities, initially mostly of an alchemical nature, and for its use in extracting gold and silver through the process of amalgamation.⁷ Since those ancient days, ever larger amounts of minerals and fuels have been extracted, refined, and used, and large quantities of Hg have been liberated in the process. Some of that Hg was

emitted directly into the atmosphere, while the remainder was released to the land or nearby water bodies. The atmospheric lifetime of Hg against removal, via both deposition and recycling, is ~6 months,^{8,9} allowing transport on a hemispheric-to-global scale. Mercury released to land can be transported into rivers and find its way into lakes and oceans.^{10,11} Atmospherically deposited Hg cycles through the surface environment in oceans, lakes, rivers, and soils and can be re-emitted to the atmosphere. Thus, considerable mobilization and redistribution of Hg occurs over time.⁶ Eventually, Hg is buried mainly in estuarine or deep ocean sediment or stable terrestrial reservoirs, and the time scale for this sequestration ranges from decades to millennia.^{6,10,12,13} Thus, Hg accumulates in the global environment, redistributing itself spatially and among different media, with continuous augmentation from human activities. Because of this persistence in the environment, it is important to know how much anthropogenic Hg has been liberated and what has been its fate. Only then can we explain observed concentrations in the environment, estimate health impacts, design efficient and effective mitigation measures, and assess the benefits of these measures.^{5,14}

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Table 1. Cumulative Manmade Releases of Hg to Air, Land, and Water Up to 2010

process	releases to air (Gg) ^a	fraction of Hg ⁰ in air releases	releases to land and water (Gg)	ratio of air to land/water releases	total releases (Gg)
copper smelting	4.91	0.64	12.6	0.39	17.5
zinc smelting	10.5	0.73	25.3	0.42	35.8
lead smelting	6.04	0.74	8.57	0.71	14.6
ironmaking	1.2	0.40	1.45	0.83	2.65
steelmaking	0.41	0.45	2.41	0.17	2.82
mercury production	91.7	0.80	321	0.29	413
gold, large-scale production	21.0	0.80	114	0.18	135
gold, artisanal production	34.4	1.00	51.6	0.67	86.0
silver production	146	0.80	219	0.67	365
cement production	3.29	0.51	3.47	0.95	6.76
caustic soda production	8.80	1.00	63.6	0.14	72.4
coal combustion	26.4	0.53	11.4	2.32	37.8
oil combustion	0.77	0.50	0	—	0.77
municipal waste incineration	34.6	0.22	0	—	34.6
other waste burning	27.8	0.20	0	—	27.8
electrical and measuring equipment	5.52	0.71	97.7	0.06	103
chemicals manufacturing	47.5	1.00	131	0.36	179
dental	1.06	0.71	5.69	0.19	6.75
total	472	0.74	1070	0.44	1540

^a1 Gg = 10⁹ grams = 1000 tonnes.

This paper quantifies for the first time the total amount of Hg released to the environment over the entire period of human activity. In previous work, we reported on emissions just to the atmosphere (but not to land/water) from the major smelting and combustion source types for the period 1850–2008¹⁵ and emissions from the commercial use of Hg to all three media for 1850–2010.¹⁶ Decadal estimates were made in detail for the period since 1850, and less-detailed estimates were made for emissions before 1850.^{5,6} In this paper, we combine the results of our previous work, extend it to 2010, regionally resolve commercial Hg releases since 1850, include media that were not calculated previously, and update selected emission factors using the most recent literature. We thus obtain a complete and consistent quantification of total Hg releases from the beginning of human activity up to the year 2010, characterized by releases to different media, from different source types, and in different world regions.

DATA AND METHODS

We estimate the total amount of Hg released into the global environment (to air, water bodies, and land surfaces) by human activities up to the year 2010. For the period 1850–2010, we present decadal estimates for 18 source types (Table 1). We calculate emissions for 17 world regions and summarize them for seven larger regions.¹⁵ The same methodologies as described in previous papers^{5,6,15,16} are followed, incorporating updates to emission factors and some new estimation methods described below. The major addition to the previous work is that emissions to land/water for coal combustion and metals smelting are estimated for the first time.

Figure 1 presents a conceptual diagram of the methodology that is used to estimate the time variation of total Hg emissions to the environment for source types that involve combustion or metal-extraction techniques. The total Hg that is released in the combustion of a ton of coal or the production of a ton of silver, for example, is constrained by the Hg content of the raw coal or the silver ore. The relationship between these parameters

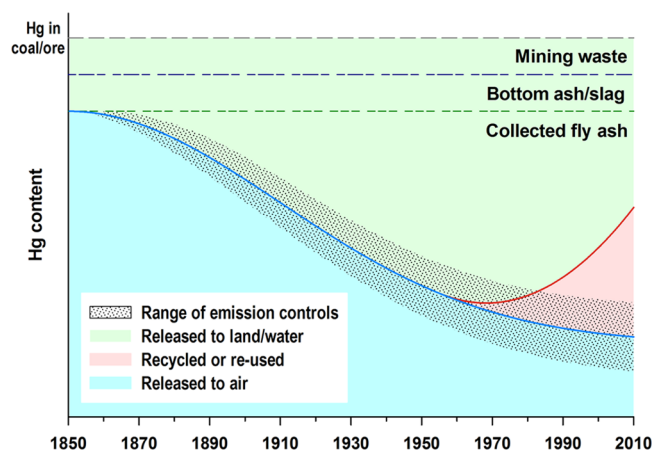


Figure 1. Conceptual diagram of the methodology used to estimate the time-varying composition of Hg releases to air and land/water per unit of fuel combusted or metal produced, as a function of the Hg content of the raw material (gray dashed line), increased penetration of emission control technologies and waste treatment systems over time (solid blue line), and recent trend toward capturing and reusing Hg (solid red line).

determines an upper bound on the amount of Hg that can have been released in the all-time combustion of coal and production of silver. The partitioning of emissions between air, land, and water is driven largely by the implementation of emission control technology. Before 1900, there were few attempts to limit air pollution, and so the release of Hg to the air was at a maximum per unit of activity. As time went on, there was a transition from old, small-scale, uncontrolled processes to modern, large-scale industrial processes with emission controls, and therefore, the air emissions per unit of coal combusted or silver produced declined (Figure 1). Consequently, more Hg was released to land and water. The production of desirable materials has increased continuously. At the same time, process technology has improved and pollution controls have been

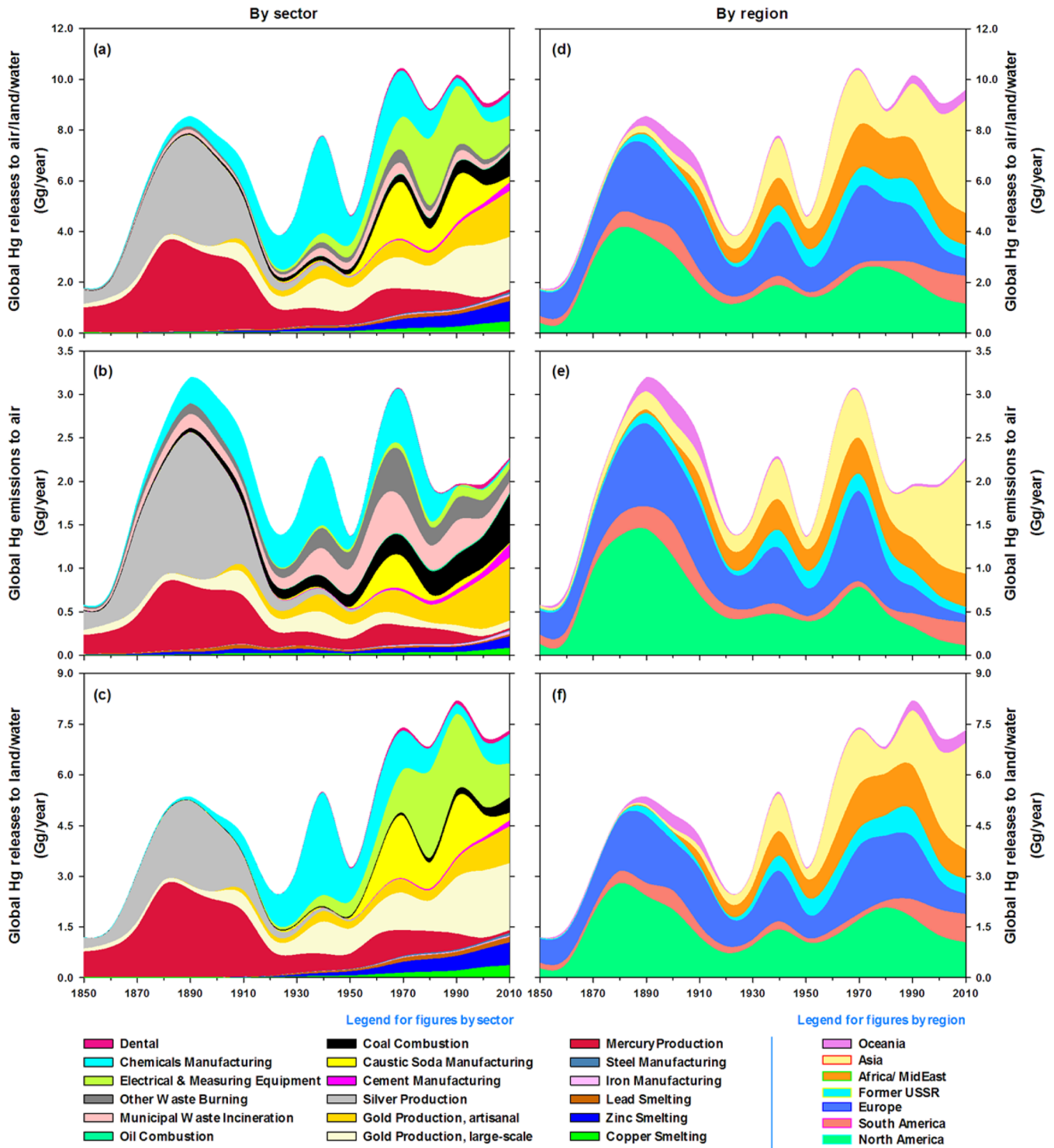


Figure 2. Global Hg release trends, 1850–2010, by sector (a,b,c, left) and world region (d,e,f, right) and by air, land, and water combined (a,d, upper), air only (b,e, center), and land/water only (c,f, lower). Note that the vertical axes are on different scales.

adopted, so the resulting level of Hg releases at any given time is determined by competition between production growth and technology improvement. The partitioning between air and land/water is similarly determined.

As in our previous work,¹⁵ we use the following transformed normal distribution function to estimate the change in air emission factors over time and hence the boundary between air and land/water emissions, as shown in Figure 1

$$y_{r,p,t} = (a_{r,p} - b_{r,p})e^{(-t^2/2s_{r,p}^2)} + b_{r,p}$$

where $y_{r,p,t}$ = air emission factor in region r for process p in year t (g Mg^{-1}); $a_{r,p}$ = pre-1850 emission factor (g Mg^{-1}) in region r for process p ; $b_{r,p}$ = best emission factor achieved in region r for process p today (g Mg^{-1}); $s_{r,p}$ = shape parameter of the curve for region r and process p .

The use of such sigmoid curves to simulate the dynamics of technology change has been previously applied to energy and

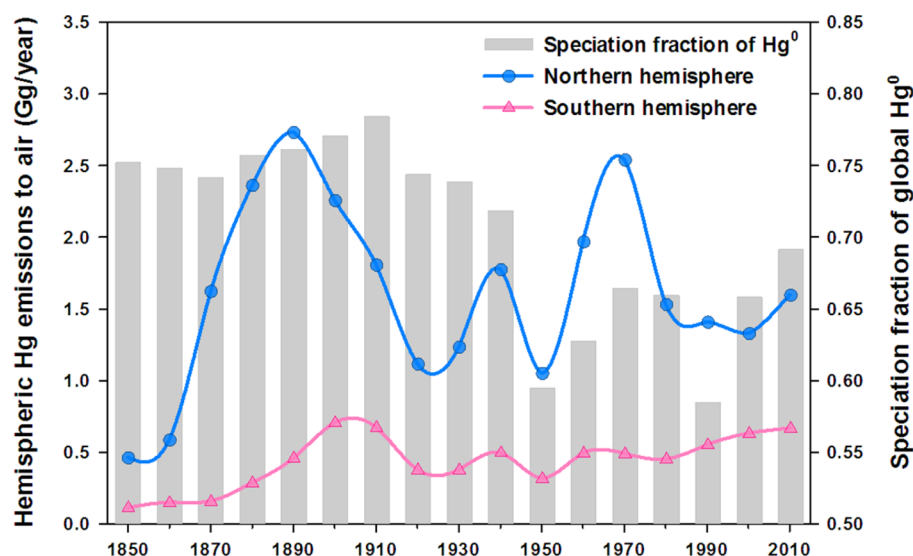


Figure 3. Trends in emissions of Hg to air, 1850–2010: speciation fraction of Hg^0 (gray bars) and hemispheric distribution (Northern hemisphere, blue line; Southern hemisphere, red line).

emission control technology,¹⁷ carbon sequestration,¹⁸ and automobile technology.¹⁹ We have demonstrated the use of this technique in estimating both historical¹⁵ and future²⁰ emissions. By selecting values of the parameters a , b , and s to correspond to the known or inferred time development pathway of relevant technologies, we can estimate the value of emission factor y at any point in time. Speciation profiles are developed at the same level of detail as the Hg emission factors.

Figure 1 shows that Hg not directly released to air is composed of Hg remaining in the waste left over from the extraction and processing of the raw coal or ore, Hg left in discarded bottom ash and slag during the combustion/smelting process, and Hg contained in fly ash that is collected at the facility. Historically, and still today to some extent, these waste products have accumulated at sites contaminated by Hg such as waste piles, storage ponds, and adjacent rivers.²¹ In recent years, greater efforts have been taken to secure these wastes in controlled landfills, to recycle the Hg,^{16,22,23} and to reuse the collected wastes^{24,25} (in products such as cement, gypsum, and sulfuric acid), as indicated in Figure 1 and discussed later. The total Hg released to land/water can be calculated by subtraction of the air emissions from the total Hg content of the raw or processed material, by direct calculation of the amount of collected fly ash, or by the ratio of air to land/water releases.

Emission factors used for each source type are the same as in previous work,^{15,16} with selected updates to incorporate experimental measurements made since the previous analysis was published and to establish ratios of releases to different media (nonferrous metal smelters,^{26,27} mercury production,^{21,28,29} large-scale gold production,³⁰ and other waste burning³¹), in addition to data from the UNEP Global Mercury Assessment (GMA)^{1,2} for all source types. For artisanal and small-scale gold mining (ASGM), activity levels reported in the GMA were adopted as anchor points for each country, and activity levels for other years were then established using the method of Muntean et al.³² The review by Zhang et al.³³ was valuable in establishing speciation factors for many source types. Because of a reassessment of China's coal use in recent years,³⁴ and its implications for Hg released during coal combustion, we updated all global coal use data using the latest International Energy Agency (IEA) data from summer 2016.³⁵

RESULTS AND DISCUSSION

Estimates of global Hg releases by sector and world region are presented in Table 1 and Figure 2. Table 1 shows cumulative anthropogenic releases for all-time, whereas Figure 2 shows decadal estimates for the main study period of 1850–2010. Cumulative releases to air over all time are estimated to have been 472 Gg, with 336 Gg (71%) occurring in the 1850–2010 time period. The largest contributing source category to total cumulative air emissions is silver production (146 Gg, 31%), followed by Hg production (92 Gg, 19%) and chemicals manufacturing (48 Gg, 10%). Figure 2(b) shows that 19th century releases to air were dominated by silver production and the production of the Hg needed to extract that silver through amalgamation, peaking in 1890 at 3.2 Gg yr^{-1} . This contribution has disappeared over time and been replaced by a variety of source types, led by ASGM and coal combustion. Air emissions show a second peak in 1970 of 3.0 Gg yr^{-1} , followed by a rapid decline due primarily to the phase-out of Hg products and elimination of Hg from caustic soda manufacturing. Geographically, it is shown in Figure 2(e) that the 19th century Hg releases to air occurred mainly in Europe and North America, whereas present-day releases are primarily in Asia, Africa, and South America.

The fraction of total, cumulative Hg emissions to air that were in the form of elemental mercury (Hg^0) is 0.74. Figure 3 shows that the Hg^0 speciation fraction has tended to decline over time from about 0.75 in the 19th century to 0.6–0.7 in modern times. The variation is not smooth, however, because of the continually changing mix of contributing source types over time. Additionally, the relative contribution of the two hemispheres to air emissions has a temporal pattern. Over the whole period 1850–2010, 79% of anthropogenic Hg emitted to air was from sources in the Northern Hemisphere and 21% was from sources in the Southern Hemisphere. However, Figure 3 shows that the relative distribution has changed over time with a gradual shift from north to south. In 1870, for example, the Northern Hemisphere contribution was 91%, whereas in 2010 it was 71%. Changes in both the speciation fraction and the hemispheric distribution of air emissions have important implications for Hg cycling, air concentrations, and deposition.

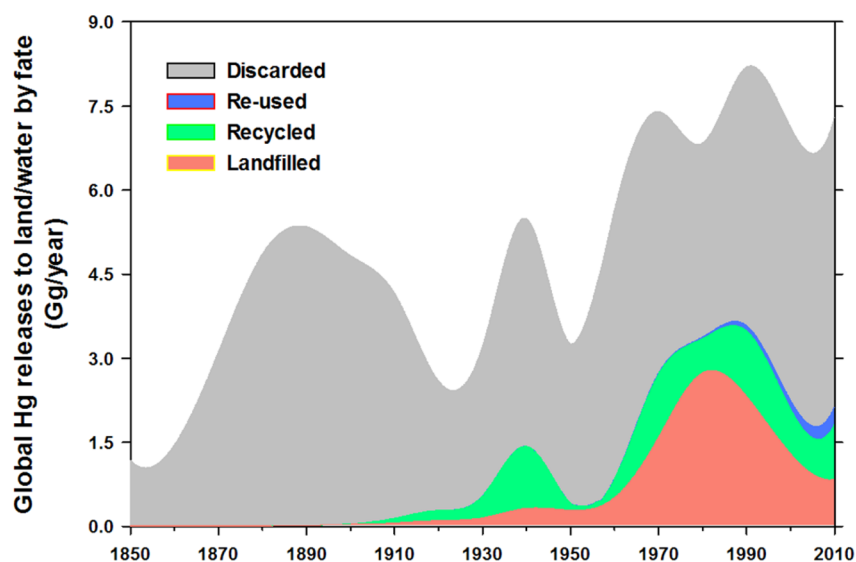


Figure 4. Fate of Hg releases to land/water, 1850–2010.

For example, the directionality of the speciation shift means that local sources have greater importance when the fraction of Hg^{II} is high, and global sources have greater importance when the fraction of Hg^0 is high. Similarly, the shift in origin of the emissions implies that local signatures of deposition are now moving to the Southern Hemisphere.

Cumulative releases to land and water over all time are estimated to have been 1070 Gg, about 2.3 times the amount released to air (Table 1). In this work, we present combined releases to land and water. We do not believe it is possible to separate the releases between land and water *a priori* because industrial facilities, power plants, waste disposers, etc., have never made public how they disposed of their waste products, and statistics are lacking. Biogeochemical cycling model results may be the best way to further investigate the likely fate of nonair releases.¹⁶ We estimate that 74% of the releases to land and water, 790 Gg, occurred in the 1850–2010 time frame. Hg production is the largest contributing source category to total cumulative land/water emissions (321 Gg, 30%), followed by silver production (219 Gg, 21%) and chemicals manufacturing (131 Gg, 12%). In contrast to the air emissions shown in Figure 2(b), Figure 2(c) shows that there has been a general trend of increasing releases to land and water over time, particularly since the mid-20th century, reaching 7–8 Gg yr^{-1} today. Releases to land/water follow a similar regional pattern to that of air emissions, with the exception that industrialized countries continue to have a significant share today because of environmentally driven capture of Hg, as shown in Figure 2(f).

Overall, we estimate that total releases of Hg to the environment as a result of human activities have been 1540 Gg up to 2010. About 73% (1120 Gg) of this amount was released after 1850. As shown in Figure 2(a), the 1890 peak value was 8.5 Gg yr^{-1} , and the 1970 peak was 10.4 Gg yr^{-1} , after which the releases began to slowly decline. Surprisingly, we find that total releases of Hg into the environment have been relatively stable since 1880 at about $8 \pm 2 \text{ Gg yr}^{-1}$, except for the periods of the two World Wars when levels fell to roughly half this value. However, as shown in Figures 2(a) and (d), the distributions of those releases among source types, world regions, and environmental media have altered dramatically. Mercury production has accounted for the

greatest contribution of total Hg releases to the environment (413 Gg, 27%), followed by silver production (365 Gg, 24%) and chemicals manufacturing (179 Gg, 12%). North America (30%), Europe (27%), and Asia (16%) have experienced the largest cumulative releases of Hg to the environment since 1850, as depicted in Figure 2(d). Information about the distribution of releases before 1850 is based on the work of Amos et al.,^{5,6} in which it was estimated that 81% of the pre-1850 releases occurred in association with silver production in Spanish America.

We conclude from this analysis that the total amount of Hg released to the environment by human activities has been very large. On the basis of the primary release estimate for geogenic sources from Amos et al. of 90 Mg yr^{-1} (excluding re-emission of previously deposited Hg),^{5,6} we estimate that total anthropogenic inputs since 1850 (1120 Gg) have been 78 times the total geogenic inputs of 14.4 Gg, and the presence of such large amounts of anthropogenic Hg in the environment has led to widespread pollution of land and water bodies, in general, and severe contamination of specific sites where Hg was produced or used for metals extraction. We see a shifting trend from direct air emissions to land/water releases over time. For example, the ratio of air to land/water releases declined from 42% at the start of the modern industrial era in 1950 to 31% in 2010. Part of this trend can be attributed to the capture and containment of air pollutant emissions, including the Hg it contains, in solid and liquid wastes. For a source category like coal combustion, where pollution controls are now commonplace, this effect is even more pronounced, with a ratio decreasing from 3.2 to 1.2, including Hg in both ash and FGD waste. We estimate that in 2010, 55% of coal waste was discarded to land and water, with 45% used as fill. However, over all time, 84% of the Hg in nonair waste from all source types was simply discarded onto the land or into convenient water bodies. As shown in Figure 4, the remaining 16% of this Hg has either been landfilled, recycled into “new” Hg which then re-enters the Hg use chain, or reused in the sense of being contained in other products such as ash for fill, cement, or sulfuric acid (from controlled metal smelters).

We performed an uncertainty analysis for these results, following the method initially developed for China³⁶ and

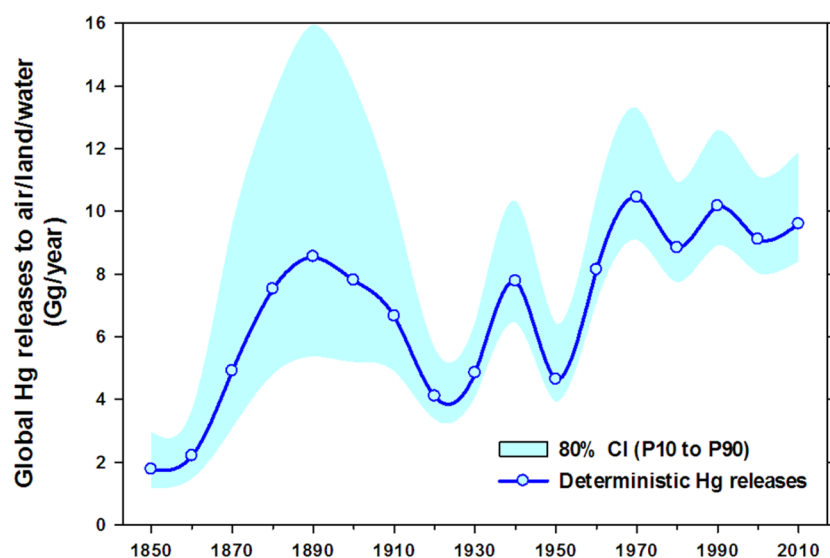


Figure 5. Uncertainty bounds of total Hg release estimates, 1850–2010, showing 80% confidence intervals (CI) on the estimates of total releases.

subsequently expanded for global emissions¹⁵ that uses a Monte Carlo framework of 10,000 simulations and uncertainty estimates for all emission factors and activity levels. Figure 5 shows the uncertainty bounds for total Hg releases in this work, expressed as 80% confidence intervals (C.I.) surrounding the central estimate. This means that the probability of releases being outside the calculated range is 20% or less. The uncertainty range is large prior to 1920 with the largest range occurring in 1870 (−37% to +94%). This is associated with the great uncertainty in knowing how much gold and silver was produced historically and how much Hg was used in associated amalgamation processing. It can be seen that the upper bound for the year 1890, 15.9 Gg, surpasses any other value. The smallest uncertainty range is for the year 2000 (−12% to +22%). In previous work,⁶ we found that the upper bound on emissions is inconsistent with constraints on the global biogeochemical budget, suggesting that the central estimate is most plausible. The uncertainty range for total releases is −32% to +82% at 80% C.I., implying a range of 1060–2800 Gg around the central estimate of 1540 Gg.

We compare our estimated atmospheric emissions with those of the GMA emission inventory for the year 2010 (Table 2).¹ Because methods to estimate emissions for years prior to 2010 are inconsistent with the GMA,¹ we do not make comparisons for earlier years. Our estimates are well within the GMA ranges for all but one source type, the production of Hg, in which our estimate is about double the GMA value and outside the upper bound (Table 2). Our source types do not exactly match the GMA sources, as can be seen from Table 2, though there is overlap for some of the unmatched types, particularly waste burning. In sum, our estimate for 2010, 2270 Mg, is 15% higher than the GMA value of 1960 Mg. We believe this is mainly due to an underestimate of emissions from global burning of uncontrolled Hg-containing waste in the GMA, which has recently been estimated to be much higher than previously thought.³¹

There are a few observational estimates about releases to land/water against which we can compare, mainly for Hg mining and production, which had specific release locations. For example, regarding historical Hg releases in the U.S., we estimate a total of 42 Gg of Hg was released to land/water and

Table 2. Comparison of Hg Emissions to Air (Mg)^a in This Work with Estimated Emissions in Global Mercury Assessment for Year 2010

process	this work	GMA	GMA range
copper, zinc, and lead smelting	241 ^b	194 ^b	82.0–660
ironmaking	37.9	45.5	20.5–241
steelmaking	9.9	X ^h	X
mercury production	22.4	11.7	6.9–17.8
gold, large-scale production	85.8	97.3	0.7–247
gold, artisanal production	727 ^c	727 ^c	410–1040
silver production	0.0	X	X
cement production	153	173	65.5–646
caustic soda production	14.8	28.4	10.2–54.7
coal combustion	561	474	304–678 ^d
oil combustion	14.5	9.3	4.3–15.3 ^d
municipal waste incineration	124	X	X
other waste burning	149	X	X
electrical and measuring equipment	81.1	X	X
chemicals manufacturing	26.4	X	X
dental	21.5 ^e	X	X
oil refining	X	16.0	7.3–26.4
natural gas combustion	X	0.6	0.2–1.0 ^d
waste disposal	X	95.6 ^f	23.7–330 ^d
cremation	— ^g	3.6	0.9–11.9
contaminated sites	X	82.5	70.0–95.0
total	2270	1960	1010–4070

^a1 Mg = 10⁶ grams = 1 tonne. ^bThis work does not include aluminum production, whereas GMA does. ^cThis work and GMA use the same data source for ASGM in 2010. ^dGMA range obtained by adding the ranges of subcomponents. ^eIncludes cremation. ^fConsisting of landfill of consumer products and controlled incineration of consumer products. ^gIncluded in dental. ^hX = not included. There is considerable overlap between categories such as waste burning, but the categories are not identical in the two studies. Therefore, they are listed separately in this table.

12 Gg to air, for a total release of 53 Gg over all time. Much of this Hg was released in mining activities in the Sierra Nevada mountains of California, with lesser amounts in Nevada and a few other states. Churchill³⁷ estimated that approximately 35 Gg of Hg was released by historical Hg mining in California,

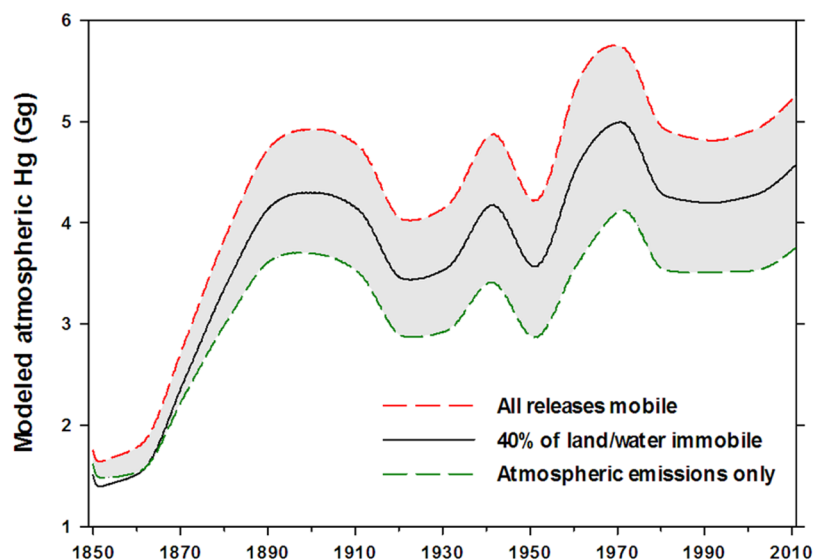


Figure 6. Trend in simulated atmospheric Hg from 1850 to 2010. Final model results most consistent with observational constraints are shown as a solid black line. Simulations including only atmospheric emissions (green dashed line) and all releases with all land/water releases assumed mobile (red dashed line) are shown for comparison.

which is in good agreement with our estimate. This Hg was subsequently washed into lakes, rivers, and streams, with a large quantity ending up in the sediments of San Francisco Bay.³⁸ Our time- and media-resolved release estimates should be valuable in interpreting Hg concentrations in sediments, peat, ice, and snow around the world. Regarding Hg production in Europe, this predominantly occurred in two locations: Idrija in Slovenia and Almadén in Spain. We estimate all-time releases from Hg mining in Europe of 164 Gg to land/water and 47 Gg to air for a total of 211 Gg. Studies concerning total releases from Hg production at Idrija^{21,28} suggest that they are in the range of 37–45 Gg, while studies at Almadén^{21,39} suggest 10 Gg were released to air alone. Assuming additional releases to land/water from Almadén and from the Amiata mine in Italy, for which all-time releases have not been estimated but the surrounding area remains heavily contaminated,⁴⁰ our estimates for European releases are still somewhat higher. Globally, we estimate all-time releases from Hg production at 410 Gg, which is higher than the value of Kocman et al.²¹ of 250 Gg.

We use the global biogeochemical model for Hg developed by Amos et al.^{5,6,10} (<http://bgc.seas.harvard.edu/models.html>) to examine the impacts of these historical emissions on the global Hg budget and consistency with observational constraints. We updated the atmospheric lifetime of total Hg in the model to 6 months to be consistent with best understanding of Hg oxidation chemistry.⁹ The model is forced from 2000 BC to 2010 AD with the time-dependent anthropogenic releases described here. The division of total nonair releases among the soil, water, and landfill reservoirs follows Horowitz et al.¹⁶

We evaluate model performance against best available observational constraints reviewed in Amos et al.^{5,6} These include a 3-to-5-fold increase in global atmospheric deposition from 1850 to the present recorded in archival sediment core records and an atmospheric Hg burden based on observations in the range of 4.4–6.0 Gg.^{5,6,9} Figure 6 shows that including atmospheric emissions alone (neglecting land and water releases) results in a present-day atmospheric reservoir that is too low (<4.0 Gg). Model simulations that include releases to all media under a variety of scenarios for land and water

releases produce anthropogenic enrichment factors for the atmosphere since 1850 that all fall within the observed 3-to-5-fold range (Figure 6).

The biogeochemical model results for recent years (say, 1970 to 2010) mirror the air emissions, e.g., Figures 2(b) and (e), showing a rapid decline after 1970, a mostly flat period from 1980 to 2000, and a small increase between 2000 and 2010. This latter feature seems to be inconsistent with observations at mid-latitude surface sites in North America and Europe, which, in general, show declining trends in atmospheric Hg concentrations between 1995 and 2010.^{41–43} We suspect, however, that there might have been a short-term increase in emissions and observations in the period 2008–2011 associated with a resurgence of industrial manufacturing and power generation following the 2007–2008 economic recession. There are indications of this in some recent measurement studies. For example, Martin et al.⁴⁴ reported a downward trend in GEM concentrations at Cape Point, South Africa, between 1995 and 2005, followed by an upward trend between 2007 and 2015. Weigelt et al.⁴⁵ found a slowly decreasing trend in Hg concentrations at Mace Head in Ireland during 1996–2013, but with a significantly smaller trend for subtropical air masses, which seems consistent with our calculations of a generalized southward shift in emissions shown in Figure 3. Finally, Weiss-Penzias et al.⁴⁶ examined trends in Hg deposition and concentrations in the U.S. and Canada during 1997–2013, finding a generally decreasing trend during the early part of the period, but with increasing trends starting to appear at a number of monitoring sites after 2007. We believe this short-term trend may have reversed after 2011 as coal use began to decline due to climate concerns, SO₂ controls in China became widespread, and there were renewed efforts to eliminate or capture Hg in industry and commerce. We should stress that it may not be justified to draw too many inferences about recent trends from our work because our data are decadal, not annual, and the shapes of the trend lines are obtained from smoothing algorithms between decadal points.

In Figure 6, the dashed red line shows the modeled global atmospheric reservoir from 1850–2010 with land/water releases assumed to be entirely mobile in the environment.

Although this is consistent with the enrichment factor and present-day atmospheric reservoir constraints, the atmospheric Hg reservoir increases sharply after 1990, which seems to overstate any short-term increases in emissions after 2008. Also, some portion of the releases to land/water are undoubtedly immobilized close to the point of release, consistent with archival records³ and the large reservoirs of Hg observed to be stored at contaminated sites.²¹ Our best estimate is that approximately 40% of land/water releases are sequestered (solid black line in Figure 6), which leads to a flat global trend between 1990 and 2000 that is more consistent with observations of relatively flat global background atmospheric concentrations between 1995 and the mid-2000s.⁴⁷ This estimate yields a global atmospheric burden of 4.57 Gg in 2010 (3.2-fold increase relative to 1850), which is well within the range of observations.

In the inventory presented in this work, atmospheric emissions of Hg in North America and Europe are shown to have declined sharply over the period 1970 to 2010 and releases to land/water have also declined, though less rapidly (Figure 2). These reductions, combined with changing fractions of globally transported Hg⁰ versus locally deposited Hg^{II} and changing splits of hemispheric emissions, are consistent with trends in observed regional deposition and concentrations.^{41–47} However, further work on a regional basis is needed to fully assess the implications of this emission inventory in the context of observed regional trends and to reduce uncertainty in the present global Hg budget.

Inventories of all-time Hg releases to all media are essential for understanding cumulative human impacts on biogeochemical Hg reservoirs and likely future exposure levels. The time scales for removal of Hg from land and water have been shown to range from decades to millennia.^{5,6,10} Thus, the substrate of Hg in these systems available for conversion to methylmercury and subsequent bioaccumulation in food webs reflects both present and past Hg releases to the environment. The inventory presented in this work is essential for quantifying the global-scale impacts of Hg pollution on land, water, and air.

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REFERENCES

(1) *Global Mercury Assessment 2013: Sources, Emissions, Releases and Environmental Transport*; United Nations Environment Programme (UNEP), Geneva, Switzerland, 2013.

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

(3) 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.

(4) 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.

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

(6) 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.

(7) Goldwater, L. J. *A History of Quicksilver*; York Press: Baltimore, MD, 1972.

(8) Corbitt, E. S.; Jacob, D. J.; Holmes, C. D.; Streets, D. G.; Sunderland, E. M. Global source-receptor relationships for mercury deposition under present-day and 2050 emissions scenarios. *Environ. Sci. Technol.* **2011**, *45*, 10477–10484.

(9) Horowitz, H. M.; Jacob, D. J.; Zhang, Y.; Dibble, T. S.; Slemr, F.; Amos, H. M.; Schmidt, J. A.; Corbitt, E. S.; Marais, E. A.; Sunderland, E. M. A new mechanism for atmospheric mercury redox chemistry: Implications for the global mercury budget. *Atmos. Chem. Phys. Discuss.* **2017**, *1*.

(10) 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.

(11) Fisher, J. A.; Jacob, D. J.; Soerensen, A. L.; Amos, H. M.; Steffen, A.; Sunderland, E. M. Riverine source of Arctic Ocean mercury inferred from atmospheric observations. *Nat. Geosci.* **2012**, *5*, 499–504.

(12) Sunderland, E. M.; Mason, R. Human impacts on open ocean mercury concentrations. *Global Biogeochem. Cycles* **2007**, *21*, GB4022.

(13) Selin, N.; Jacob, D.; Yantosca, R.; Strode, S.; Jaegle, L.; Sunderland, E. 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.

(14) Evers, D. C.; Egan Keane, S.; Basu, N.; Buck, D. Evaluating the effectiveness of the Minamata Convention on Mercury: Principles and recommendations for next steps. *Sci. Total Environ.* **2016**, *569*–570, 888–903.

(15) 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.

(16) 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.

(17) Grübler, A.; Nakicenovic, N.; Victor, D. G. Dynamics of energy technologies and global change. *Energy Policy* **1999**, *27*, 247–280.

(18) Riahi, K.; Rubin, E. S.; Taylor, M. R.; Schrattenholzer, L.; Hounshell, D. Technological learning for carbon capture and sequestration technologies. *Energy Econ.* **2004**, *26*, 539–564.

(19) Nakicenovic, N. The automotive road to technological change: diffusion of the automobiles as a process of technological substitution. *Technol. Forecast Soc.* **1986**, *29*, 309–340.

(20) Streets, D. G.; Zhang, Q.; Wu, Y. Projections of global mercury emissions in 2050. *Environ. Sci. Technol.* **2009**, *43*, 2983–2988.

- (21) Kocman, D.; Horvat, M.; Pirrone, N.; Cinnirella, S. Contribution of contaminated sites to the global mercury budget. *Environ. Res.* **2013**, *125*, 160–170.
- (22) Jasinski, S. M. *The Materials Flow of Mercury in the United States*; Bureau of Mines Information Circular IC 9412; U.S. Bureau of Mines: Washington, DC, 1994.
- (23) 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: Reston, VA, 2005; p 21.
- (24) Lam, C. H. K.; Ip, A. W. M.; Barford, J. P.; McKay, G. Use of Incineration MSW Ash: A Review. *Sustainability* **2010**, *2*, 1943–1968.
- (25) Mukherjee, A. B.; Zeevenhoven, R.; Bhattacharya, P.; Sajwan, K. S.; Kikuchi, R. Mercury flow via coal and coal utilization by-products: A global perspective. *Resour. Conserv. Recy.* **2008**, *52*, 571–591.
- (26) Zhang, L.; Wang, S.; Wu, Q.; Meng, Y.; Yang, H.; Wang, F.; Hao, J. M. Were mercury emission factors for Chinese non-ferrous metal smelters overestimated? Evidence from onsite measurements in six smelters. *Environ. Pollut.* **2012**, *171*, 109–117.
- (27) Wu, Q. R.; Wang, S. X.; Zhang, L.; Song, J. X.; Yang, H.; Meng, Y. Update of mercury emissions from China's primary zinc, lead and copper smelters, 2000–2010. *Atmos. Chem. Phys.* **2012**, *12*, 11153–11163.
- (28) Žagar, D.; Knap, A.; Warwick, J. J.; Rajar, R.; Horvat, M.; Četina, M. Modelling of mercury transport and transformation processes in the Idrijca and Soča river system. *Sci. Total Environ.* **2006**, *368*, 149–163.
- (29) Li, P.; Feng, X.; Qiu, G.; Shang, L.; Wang, S.; Meng, B. Atmospheric mercury emission from artisanal mercury mining in Guizhou Province, Southwestern China. *Atmos. Environ.* **2009**, *43*, 2247–2251.
- (30) Eckley, C. S.; Gustin, M.; Miller, M. B.; Marsik, F. Scaling non-point-source mercury emissions from two active industrial gold mines: influential variables and annual emission estimates. *Environ. Sci. Technol.* **2011**, *45*, 392–399.
- (31) Wiedinmyer, C.; Yokelson, R. J.; Gullett, B. K. Global emissions of trace gases, particulate matter, and hazardous air pollutants from open burning of domestic waste. *Environ. Sci. Technol.* **2014**, *48*, 9523–9530.
- (32) Muntean, M.; Janssens-Maenhout, G.; Song, S.; Selin, N. E.; Olivier, J. G. J.; Guizzardi, D.; Maas, R.; Dentener, F. Trend analysis from 1970 to 2008 and model evaluation of EDGARv4 global gridded anthropogenic mercury emissions. *Sci. Total Environ.* **2014**, *494–495*, 337–350.
- (33) Zhang, L.; Wang, S.; Wu, Q.; Wang, F.; Lin, C.-J.; Zhang, L.; Hui, M.; Yang, M.; Su, H.; Hao, J. Mercury transformation and speciation in flue gases from anthropogenic emission sources: a critical review. *Atmos. Chem. Phys.* **2016**, *16*, 2417–2433.
- (34) Korsbakken, J. I.; Peters, G. P.; Andrew, R. M. Uncertainties around reductions in China's coal use and CO₂ emissions. *Nat. Clim. Change* **2016**, *6*, 687–691.
- (35) Key World Energy Statistics, 2016 ed.; International Energy Agency. <https://www.iea.org/publications/freepublications/publication/KeyWorld2016.pdf> (accessed August 2016).
- (36) Wu, Y.; Streets, D. G.; Wang, S. X.; Hao, J. M. Uncertainties in estimating mercury emissions from coal-fired power plants in China. *Atmos. Chem. Phys.* **2010**, *10*, 2937–2947.
- (37) Churchill, R. K. Contributions of Mercury to California's Environment from Mercury and Gold Mining Activities — Insights from the Historical Record. In *Proceedings and Summary Report of the Workshop on Assessing and Managing Mercury from Historic and Current Mining Activities*; EPA/625/R-04/102; U.S. Environmental Protection Agency, 2005; pp 36–40.
- (38) Conaway, C. H.; Ross, J. R. M.; Looker, R.; Mason, R. P.; Flegal, A. R. Decadal mercury trends in San Francisco Estuary sediments. *Environ. Res.* **2007**, *105*, 53–66.
- (39) Ferrara, R.; Maserti, B. E.; Andersson, M.; Edner, H.; Ragnarson, P.; Svanberg, S.; Hernandez, A. Atmospheric mercury concentrations and fluxes in the Almadén District (Spain). *Atmos. Environ.* **1998**, *32*, 3897–3904.
- (40) Ferrara, R.; Mazzolai, B.; Edner, H.; Svanberg, S.; Wallinder, E. Atmospheric mercury sources in the Mt. Amiata area, Italy. *Sci. Total Environ.* **1998**, *213*, 13–23.
- (41) Slemr, F.; Brunke, E. G.; Ebinghaus, R.; Kuss, J. Worldwide trend of atmospheric mercury since 1995. *Atmos. Chem. Phys.* **2011**, *11*, 4779–4787.
- (42) Soerensen, A. L.; Jacob, D. J.; Streets, D. G.; Witt, M. L. I.; Ebinghaus, R.; Mason, R. P.; Andersson, M.; Sunderland, E. M. Multi-decadal decline of mercury in the North Atlantic atmosphere explained by changing subsurface seawater concentrations. *Geophys. Res. Lett.* **2012**, *39*, L21810.
- (43) 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 anthropogenic emissions. *Proc. Natl. Acad. Sci. U. S. A.* **2016**, *113*, 526–531.
- (44) Martin, L. G.; Labuschagne, C.; Brunke, E.-G.; Weigelt, A.; Ebinghaus, R.; Slemr, F. Trend of atmospheric mercury concentrations at Cape Point for 1995–2004 and since 2007. *Atmos. Chem. Phys.* **2017**, *17*, 2393–2399.
- (45) Weigelt, A.; Ebinghaus, R.; Manning, A. J.; Derwent, R. G.; Simmonds, P. G.; Spain, T. G.; Jennings, S. G.; Slemr, F. Analysis and interpretation of 18 years of mercury observations since 1996 at Mace Head, Ireland. *Atmos. Environ.* **2015**, *100*, 85–93.
- (46) Weiss-Penzias, P. S.; Gay, D. A.; Brigham, M. E.; Parsons, M. T.; Gustin, M. S.; ter Schure, A. Trends in mercury wet deposition and mercury air concentrations across the US and Canada. *Sci. Total Environ.* **2016**, *568*, 546–556.
- (47) Prestbo, E. M.; Gay, D. M. Wet deposition of mercury in the U.S. and Canada, 1996–2005: Results and analysis of the NADP mercury deposition network (MDN). *Atmos. Environ.* **2009**, *43*, 4223–4233.