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Five hundred years of anthropogenic mercury: spatial and temporal release profiles^{*}

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Five hundred years of anthropogenic mercury: spatial and temporal release profiles*

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Supplementary material for this article is available [online](#)

Abstract

When released to the biosphere, mercury (Hg) is very mobile and can take millennia to be returned to a secure, long-term repository. Understanding where and when Hg was released as a result of human activities allows better quantification of present-day reemissions and future trajectories of environmental concentrations. In this work, we estimate the time-varying releases of Hg in seven world regions over the 500 year period, 1510–2010. By our estimation, this comprises 95% of all-time anthropogenic releases. Globally, 1.47 Tg of Hg were released in this period, 23% directly to the atmosphere and 77% to land and water bodies. Cumulative releases have been largest in Europe (427 Gg) and North America (413 Gg). In some world regions (Africa/Middle East and Oceania), almost all (>99%) of the Hg is relatively recent (emitted since 1850), whereas in South America it is mostly of older vintage (63% emitted before 1850). Asia was the greatest-emitting region in 2010, while releases in Europe and North America have declined since the 1970s, as recognition of the risks posed by Hg have led to its phase-out in commercial usage. The continued use of Hg in artisanal and small-scale gold mining means that the Africa/Middle East region is now a major contributor. We estimate that 72% of cumulative Hg emissions to air has been in the form of elemental mercury (Hg⁰), which has a long lifetime in the atmosphere and can therefore be transported long distances. Our results show that 83% of the total Hg has been released to local water bodies, onto land, or quickly deposited from the air in divalent (Hg^{II}) form. Regionally, this value ranges from 77% in Africa/Middle East and Oceania to 89% in South America. Results from global biogeochemical modeling indicate improved agreement of the refined emission estimates in this study with archival records of Hg accumulation in estuarine and deep ocean sediment.

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1. Introduction

Mercury (Hg) can be converted to an organic species, mono-methylmercury, in aquatic environments that bioaccumulates in fish and wildlife and has been associated with long-term neurocognitive deficits in exposed children and increased cardiovascular risks in

adults [1, 2]. Hg is a naturally occurring element found everywhere in the Earth's crust that is released by weathering of rocks, geothermal activity, and volcanism. About 4000 years ago, humans began extracting gold, silver, copper, zinc, lead, coal, and other materials—all of which contained Hg as an impurity. In addition, Hg was found to be useful in extracting gold and silver, and hence Hg itself became a target of extraction and refinement. In modern times, direct emissions of anthropogenic Hg have been an order of magnitude greater than natural emissions [3, 4].

Mercury in the atmosphere, which consists mostly of elemental Hg (Hg^0), has a long lifetime (3–6 months) against removal by deposition, allowing it to be transported on a hemispheric- to global-scale [5]. Compounds of Hg that are emitted into the atmosphere in divalent (Hg^{II}) form have a much shorter atmospheric lifetime (approximately 26 d against deposition) and are thus deposited much closer to emission sources [5]. In addition, much of the Hg resulting from human activities is released onto land or into water bodies close to the point of extraction or use [6]. This locally-deposited Hg can then be transported into rivers and find its way into lakes and oceans [5, 6], and a substantial fraction is reduced back to Hg^0 and reemitted to the atmosphere. For example, evasion of Hg^0 from terrestrial ecosystems and the ocean is more than double present-day anthropogenic emissions [5, 7]. The magnitude of this re-emission source and how it will change in the future depend on the historical trajectory of anthropogenic emissions. It can take from decades to millennia for the Hg to be permanently sequestered in estuarine or deep ocean sediment or stable terrestrial reservoirs [7–10].

It is clear, therefore, that there is considerable mobilization and redistribution of Hg over time. Hg accumulates in the global environment, redistributing itself spatially and among different media, with continuous augmentation from human activities and natural sources. Because of this persistence in the environment, it is important to know how much anthropogenic Hg has been liberated in the past and what has been its fate. Knowing the profiles of primary releases and the reaction and deposition/re-emission rates of the different forms of Hg, it is possible through biogeochemical modeling to reproduce observed modern-day concentrations of Hg in the environment and to project future concentrations [3, 4, 11–15]. This is an important component of the design of efficient and effective mitigation measures, such as the Minamata Convention, and assessment of the benefits of such measures [16–19].

Many forms of anthropogenic pollution of the environment can be traced back to the start of the Industrial Revolution, ca. 1760, but not so Hg pollution. Releases in antiquity and after the opening up of Spanish America contribute to the present-day Hg burden. Most archives of atmospheric deposition recorded in remote peat and lake sediments only

extend back to the 1800s. These records consistently indicate a three-to-five-fold enrichment in atmospheric deposition of Hg relative to pre-industrial levels [20, 21]. Both global biogeochemical models and selected records of long-term deposition suggest that this pre-industrial baseline was in turn enhanced by more ancient anthropogenic emissions, so that the actual enrichment above natural levels may be significantly larger [7, 12, 22–24]. These results emphasize the need to quantify and characterize all-time anthropogenic releases of Hg.

In previous work, we focused initially on Hg emissions from China, one of the most important and difficult regions to characterize [25–27]. This was followed by an assessment of global atmospheric emissions of Hg from human activities, with emphasis on the period 1850 to 2008 [28]. Projections to 2050 were also reported [29]. This previous body of work culminated in a complete analysis of global Hg releases to air, land, and water up to 2010 [30–32]. Though this work quantified total global Hg releases back to antiquity, it did not attempt to assign pre-1850 emissions to world regions nor to characterize the temporal evolution of pre-1850 regional emissions. This presented difficulties for the modeling of biogeochemical Hg cycling, because it was known that pre-1850 anthropogenic emissions were significant, but it was not known how large they were nor where they were located. Presumptive distributions were forced to be made for pre-1850 releases [7, 12]. The present work should facilitate a more accurate representation of global Hg distributions: past, present, and future.

2. Methods

In this work, we present estimates of the global and regional amounts of Hg that have been released into the environment (to air, land, and water) by human activities over the 500 year period, 1510–2010; as we will show later, this comprises roughly 95% of all-time Hg releases. We calculate Hg releases every decade (i.e. 50 time slices) for 18 source types in each of 17 world regions, following the same methodologies as described in our previous work [25–32]. Releases to air are sub-divided into Hg^0 and Hg^{II} . We incorporate some updates to emission factors and some new estimation methods, as described below.

For the period 1850–2010, the methods and data are essentially the same as was used in our previous estimate of total Hg releases [30]. Further details on the calculation of emission factors are provided in the supplementary information section 1.0 (available online at stacks.iop.org/ERL/14/084004/mmedia). The only changes made for 1850–2010 from previous work were for consistency with the new approach to calculating emissions from silver extraction in Spanish America described below. In this respect, we assume that the use of the *patio* process persisted in South

America until 1900 and in Central America until 1880, transitioning to modern extraction techniques beginning in 1850. This had a very small effect on total global Hg releases since 1850, lowering our previous value by 1% from 1120 Gg [30] to 1110 Gg.

Releases of Hg for the period 1510–1850 are calculated here for the first time. Though 18 source types were evaluated previously for the post-1850 period [28], only seven of them are relevant for this earlier period: coal combustion; and the extraction and refinement of copper, zinc, lead, gold, silver, and mercury itself. Releases are dominated by mercury and silver [28]. Prior to 1800, Europe was essentially the only regional source of coal combustion, with North America and the Former USSR slowly emerging between 1800 and 1850. Our main source of information on early coal combustion amounts is the work of the Carbon Dioxide Information Analysis Center [33].

The main new contribution to our estimates of early Hg releases was the discovery of an old series of reports by the US Department of Commerce, Bureau of Mines (BOM), published in the period 1928–1930, which had been scanned and preserved by the University of North Texas Digital Library. Among these reports are volumes on copper [34], zinc [35], lead [36], gold [37], and silver [38]. They are especially valuable because (a) they go back to the beginnings of recorded production (ca. 1500 in the cases of gold and silver); (b) they present production data by country; and (c) they are based on an extensive review of extant data sources by mining experts at the BOM. We use these data to compile production data from 1510–1850 at the country level, subsequently aggregated to each of our 17 world regions. For the seventh and final source category, the extraction and refinement of Hg itself, we rely on the global production data of Hylander and Meili [39, 40], supplemented by other sources of regional data [41–44].

For emission factors in the period 1510–1850, we use the same emission factors that were used for the year 1850 [28, 30, 32], with the exception of releases from silver mining in Spanish America. The technique used then was called the *patio* process, in which the silver ore was crushed and mixed with Hg in an open enclosure called a *patio* to a depth of 1–2 feet; after several weeks of mixing in the hot sun an amalgam was formed, from which the silver was subsequently recovered. In early analyses of the releases of Hg from the *patio* process in South and Central America in the 16th–19th centuries, it was thought that a significant fraction (60%–75%) of the Hg escaped to the atmosphere [41–44]. Guerrero, however, cast doubt on these high values [45–47], asserting that much of the lost Hg was in fact captured in solid form as mercurous chloride (Hg_2Cl_2), also known as calomel, and only 3%–5% was lost to air. If that is true, then the bulk of the Hg lost during the *patio* process initially found its way to land and water, not directly to air. In combination, the releases from Hg and silver mining are consistent with

the high levels of Hg measured today in South and Central America [48–51].

In this work, we use the values of Hg released to air recommended by Guerrero for silver mining [47]. We assume that all the remaining lost Hg found its way into local land/water bodies. Guerrero asserts that the calomel (Hg_2Cl_2) produced during the *patio* process is somewhat akin to a permanent sink. He says that it is ‘an insoluble solid, and would have been buried within millions of tons of fine mineral silt ... (and) would have functioned as a chemical sink for anthropogenic mercury emissions from silver refining’ [47]. We feel that it is not yet confirmed that Hg could never be reemitted from calomel under the variety of soil and water conditions it may subsequently encounter. Though the literature is sparse on the subject, it is known that Hg_2Cl_2 is relatively stable, but susceptible to chemical reactions with ammonia and sulfur; Boer [52] claimed that Hg_2Cl_2 slowly decomposes in soil, producing volatile Hg^0 and HgCl_2 . Clearly, additional research is needed on this topic.

Based on the absence of a clear 1880s Hg peak in sedimentary and ice-core archives, several studies [20, 53, 54] have questioned the magnitude of atmospheric emissions during the gold rush days in North America that we estimated in our previous work [28, 30]. However, other archives do show a peak in this time period [55, 56]. The archival evidence seems to be inconclusive at present, though perhaps suggesting that the effects of early gold mining are regional rather than global [57]. Though the total amount of Hg lost during the amalgamation process is relatively well known from Hg production and consumption statistics, the distribution of those losses among air, land, and water is far from certain. In past work [28, 30] we used the foundational research by Nriagu and others [41, 42, 44, 58] to estimate the releases to air from 19th century gold mining in North America—which were large. We have since further reviewed accessible engineering literature e.g. [59, 60] and find a complete absence of quantitative data on air releases and the collection efficiency of, for example, the retorting of the amalgam to yield elemental gold and to recover Hg. In the absence of such data, we continue to use the emission factors recommended by the Nriagu group, but plan to do additional work in the future to test alternative hypotheses on the amount of Hg that was released to the air from 19th century gold mining in North America.

In addition to identifying separately the releases to air and to land/water, we also separate the air emissions into speciated emissions of Hg^0 and Hg^{II} , as in previous work [30, 32]. For this we acknowledge our use of the valuable work of Zhang *et al* [61]. As described below, we use these partitioned release values to give an idea of how much of the Hg was likely to have traveled ‘far’ or been retained ‘locally’ following its initial release.

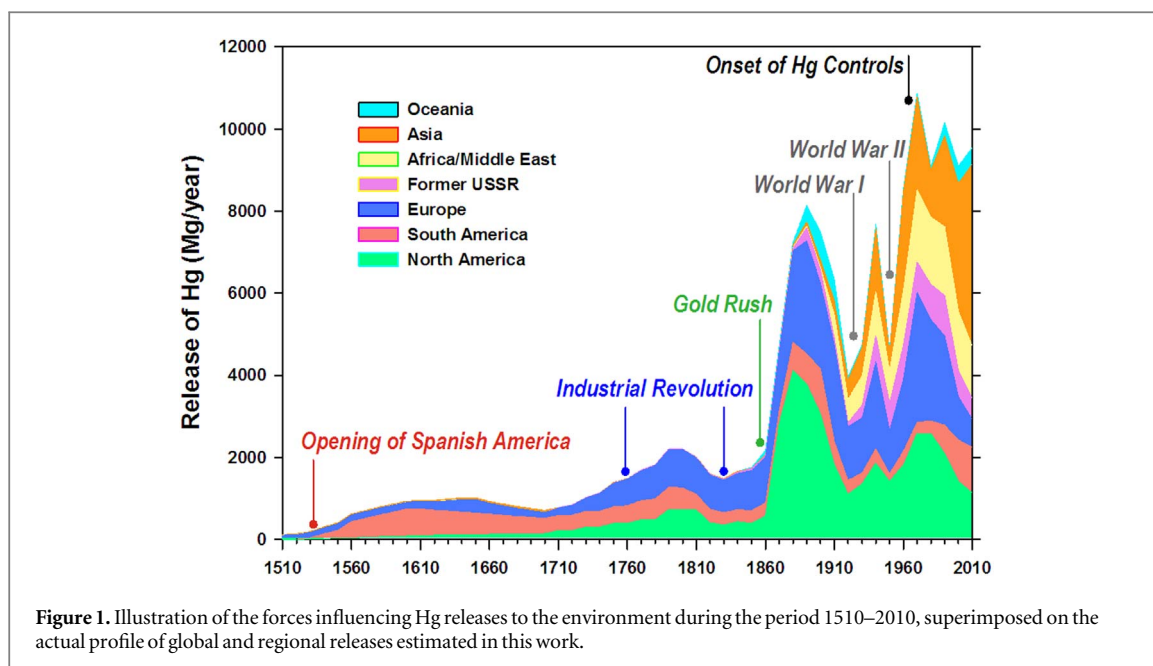


Figure 1. Illustration of the forces influencing Hg releases to the environment during the period 1510–2010, superimposed on the actual profile of global and regional releases estimated in this work.

3. Results

Figure 1 shows that the release of Hg from human activities over this 500 year period was greatly influenced by events that triggered impacts on industrial production and consumption, both worldwide and in specific regions of the world. Though Hg was involved in many activities prior to 1510 (see later discussion), releases did not seriously commence until the opening up of Spanish America. Large-scale processing of silver ore began in the 1530s in Mexico and the 1540s in Bolivia and Peru [45]. Releases of Hg in Spanish America peaked ca. 1600. By 1810, production began to decline but persisted into the late 1800s [41].

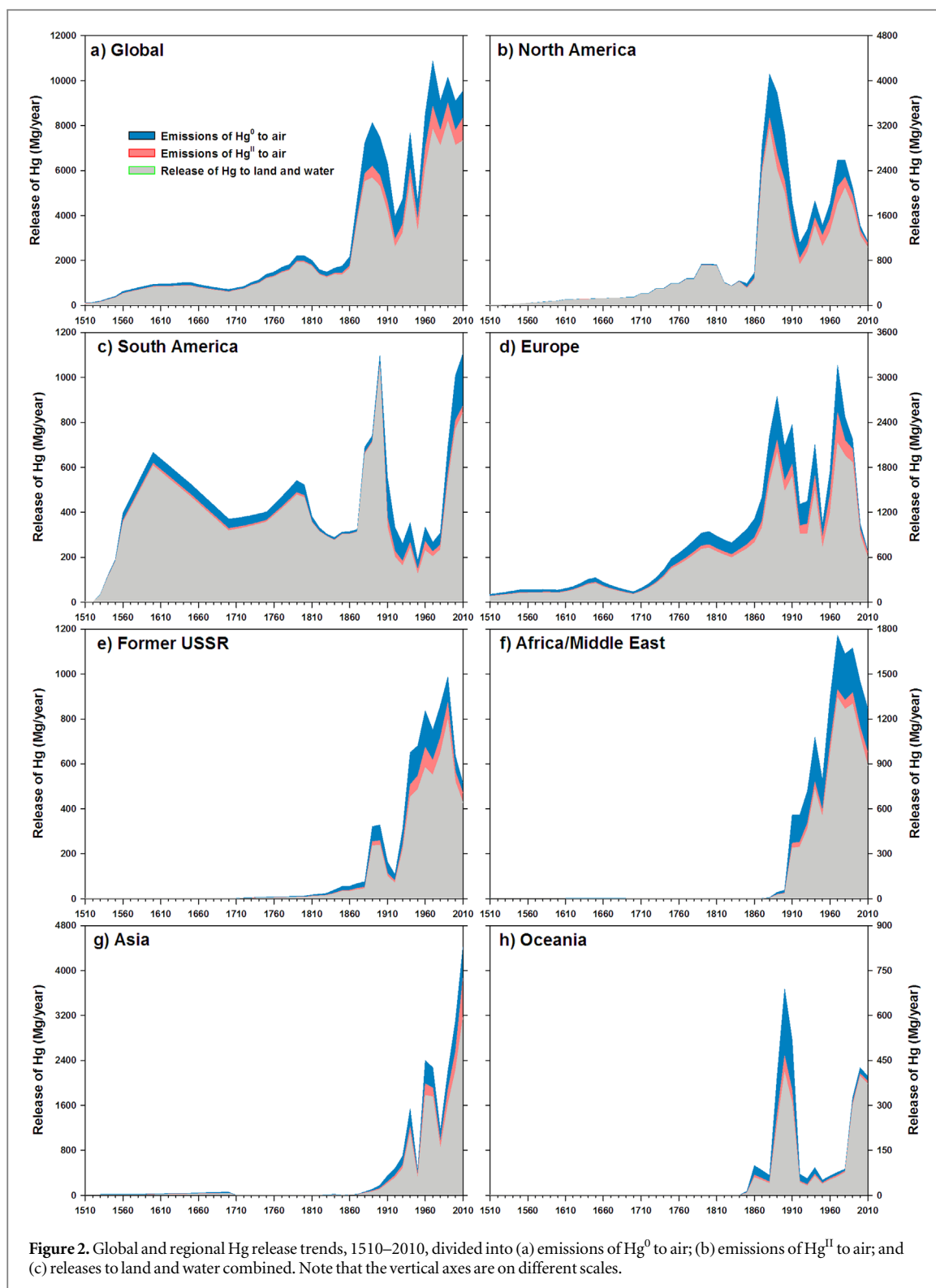
Coal had been used in Europe since well before 1600, but took off at the beginning of the Industrial Revolution, commonly dated to ca. 1760. The increase in Hg releases from coal combustion partially offset the decline in Hg use in silver extraction. Global emissions increased sharply in 1850 as a result of the gold rush in North America and, to a lesser extent, Australia. Production of Hg to facilitate the extraction of gold and silver through amalgamation combined with general industrial expansion in the production and use of chemicals and metals to yield a peak in Hg releases ca. 1890. As amalgamation fell out of favor, releases declined and reached a trough in 1920 driven by the devastations of World War I and the Russian Revolution. Emissions grew again until a similar trough resulted from World War II.

After 1950 there was a dramatic increase in Hg releases due to the post-war economic boom. This continued until 1970, when preventative measures began to be introduced, both for Hg itself and for other pollutant species (like SO_2) that also mitigated Hg emissions. The most effective of such measures were the installation of flue-gas desulfurization systems on

coal-fired power plants, the phase-out of artisanal metal smelters (particularly zinc), and the collection of mercury-containing gases by sulfuric acid plants in modern metal smelters [17]. However, the banning of Hg use in many components of the world economy was the most effective advancement [31]; this led to a sharp drop in Hg production, as shown later. The decline in global Hg releases continued after 1970, but may have ended shortly before 2010, as gains from the removal of Hg from commercial products lessened and the expansion of Asian economies continued and gained dominance [62].

These socioeconomic driving forces are reflected in the production and consumption statistics that we use to calculate emissions. Global Hg releases would have grown at a much higher rate than shown in figure 1, if they had been simply proportional to industrial production, population, or economic growth [28, 62]. The lower rate of Hg growth is the result of technological progress that has replaced old-fashioned, high-polluting systems with more modern processes incorporating emission controls.

Figure 2 presents the anthropogenic Hg release trends over the period 1510–2010 for seven aggregated world regions and the world as a whole (note that the vertical scales vary among regions); tabular data for this figure are presented in the supplementary information section 2.0. In each figure, we divide the releases into three categories: emissions of Hg^0 to air, emissions of Hg^{II} to air, and the combined releases of Hg 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 [30, 32]. The modeling of biogeochemical Hg cycling, constrained by archival records and



measurements from different regions, may be the best, if not the only, way to disentangle the fate of non-air releases [31]. Table 1 summarizes the cumulative regional contributions by species and media, and table 2 estimates some key component contributions and their differences pre- and post-1850.

Figure 2 shows that Europe and North America dominate historical releases, each having released ~ 420 Gg over the 500 year period (table 1). Europe

had the largest contributions in the early centuries, consisting primarily of coal combustion and the production of Hg for use in Spanish America. Note also that the reduction of Hg in Europe since 1970 is the most pronounced, returning Hg releases in 2010 to levels that had not been seen since 1770 (~ 680 Mg yr^{-1}). North American releases consisted of silver extraction in Mexico until the North American gold rush that generated a large peak in emissions in

Table 1. Cumulative anthropogenic Hg releases by world region over the period 1510–2010 (Gg)^a.

World region	Total air emissions	Hg ⁰ air emissions	Hg ^{II} air emissions	Releases to land/water	Total releases
North America	89.0	62.6	26.4	323.6	412.6
South America	29.6	23.6	5.9	192.1	221.6
Europe	111.6	79.8	31.8	315.0	426.6
Former USSR	19.4	13.4	6.0	53.9	73.3
Africa/Middle East	34.6	28.9	5.7	89.8	124.4
Asia	51.2	32.6	18.6	129.3	180.4
Oceania	9.6	7.5	2.1	23.8	33.3
Global Total	344.9	248.4	96.5	1127.3	1472.2

^a 1 Gg = 10⁹ grams = 1000 tonnes.

Table 2. Contributions to regional anthropogenic Hg releases over the period 1510–2010 (%).

World region	Releases since 1850 to total releases	Hg ⁰ to total air emissions	L/W to total releases	Local ^a to total releases	Local ^a to total releases since 1850
North America	80.7	70.3	78.4	84.8	82.9
South America	37.2	79.9	86.7	89.3	88.1
Europe	68.6	71.5	73.8	81.3	82.9
Former USSR	97.4	69.1	73.5	81.7	83.0
Africa/Middle East	99.4	83.6	72.2	76.8	77.2
Asia	96.5	63.6	71.6	82.0	84.3
Oceania	99.8	78.2	71.3	77.6	77.6
Global total	75.4	72.0	76.6	83.1	82.7

^a Defined as the sum of Hg^{II} emissions to air and all releases to land and water.

1880 (~4100 Mg yr⁻¹). Reductions in releases since 1970 have returned levels in 2010 (~1100 Mg yr⁻¹) back to the levels of the early days of the gold rush. In the Former USSR, emissions are much lower (cumulatively 73 Gg), and the general growth in industrial emissions that began in 1870–1880 was severely disrupted by the Russian Revolution. The trend for South America is very different. Cumulative emissions are 220 Gg and reflect a slowing down of emissions associated with silver extraction, coupled with a surge in releases since 1970 due to industrial expansion, reaching ~1100 Mg yr⁻¹ by 2010.

Serious industrial development in the remaining three regions can be considered to start ca. 1850. The gold rush in Australia [63, 64] yielded a peak in the late 1800s of ~690 Mg yr⁻¹, similar in structure to that of North America, falling away by 1910–1920. Emissions in Africa/Middle East have been boosted by contributions from artisanal and small-scale gold mining (ASGM), which has only recently slowed [62]. Finally, the booming industrial economies of Asia show a rapid increase since 1880, interrupted briefly by the two world wars, rising to 4400 Mg yr⁻¹ by 2010, and with a cumulative release of 180 Gg.

The global trend is also shown in figure 2. The cumulative release of anthropogenic Hg over the period 1510–2010 is estimated to be 1470 Gg (table 1). Compared with our earlier all-time release estimate of 1540 Gg [30], this suggests that 95% of the Hg has been released since 1510, with the remainder spread out over the years prior to 1510, dating back to antiquity. Table 1 also shows the partitioning of the 1470 Gg

among direct releases to air and land/water. We estimate that 345 Gg of this Hg (23%) was released directly to air over the 500 year period, with the remainder, 1130 Gg (77%), going to land/water. The regional releases to air range from a low of 13% (South America) to a high of 29% (Oceania), driven by the time-varying mix of source types in each region. Table 1 also shows that the global total of 345 Gg emitted directly to the air was comprised of 248 Gg of Hg⁰ (72%) and 97 Gg of Hg^{II} (28%).

Table 2 summarizes some of the component contributions to this total amount of released Hg. The first column quantifies how much of the cumulative 500 year total was released since 1850. Globally, 75% was released after 1850, ranging from a low of 37% in South America to highs of 99% in Africa/Middle East and Oceania. Such information is valuable in determining the varying fates of Hg around the world subsequent to the time of release and hence in refining both the modeling of reemissions and the cycling of Hg. Table 2 also shows the regional variation in percentage of Hg⁰ in total air emissions, which ranges from 64% in Asia to 84% in Africa/Middle East. In the final two columns we give an estimate by region of how much of the Hg was likely to have been initially retained ‘locally,’ i.e. close to the primary emitting source, and how much could have been transported ‘far’ from the source and potentially made its way into the global background. For the 500 year period, we estimate that 83% (77%–89% across regions) has been deposited locally. This percentage has not changed greatly over time.

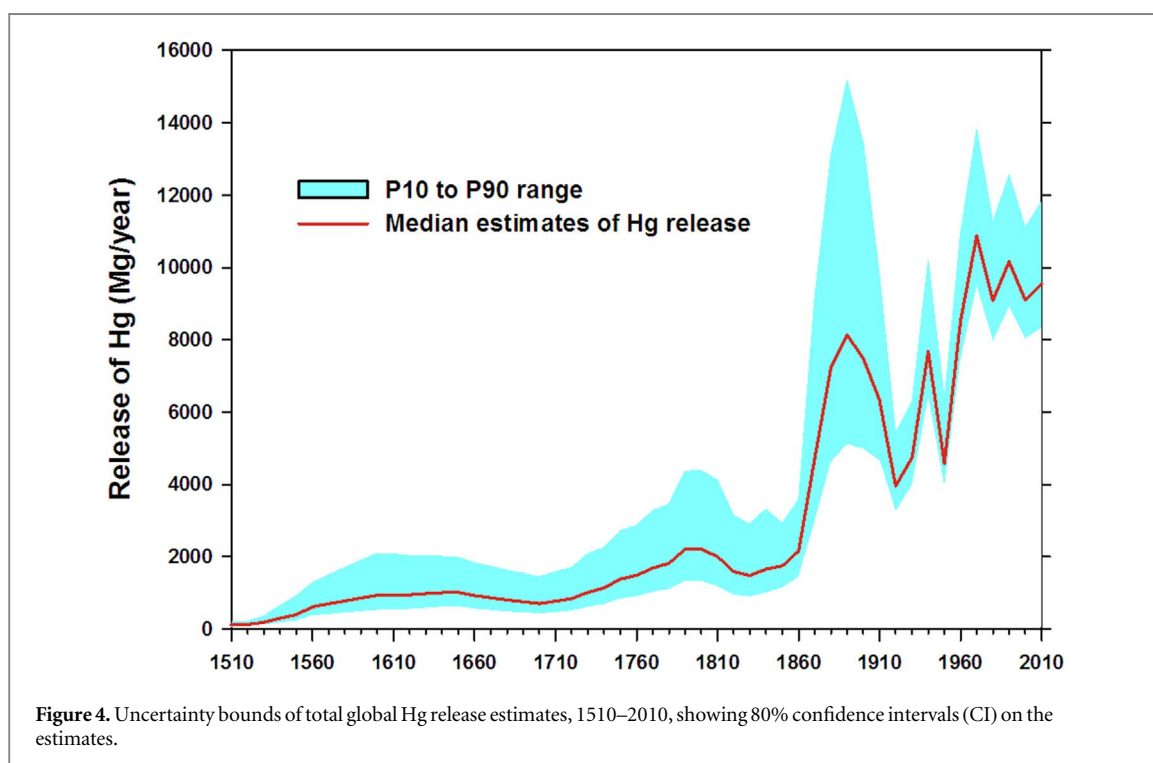
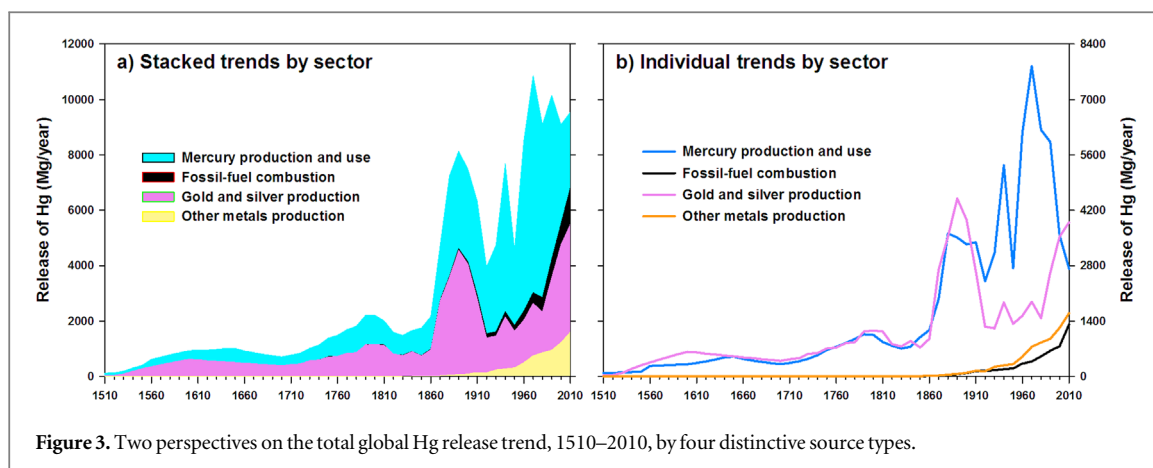
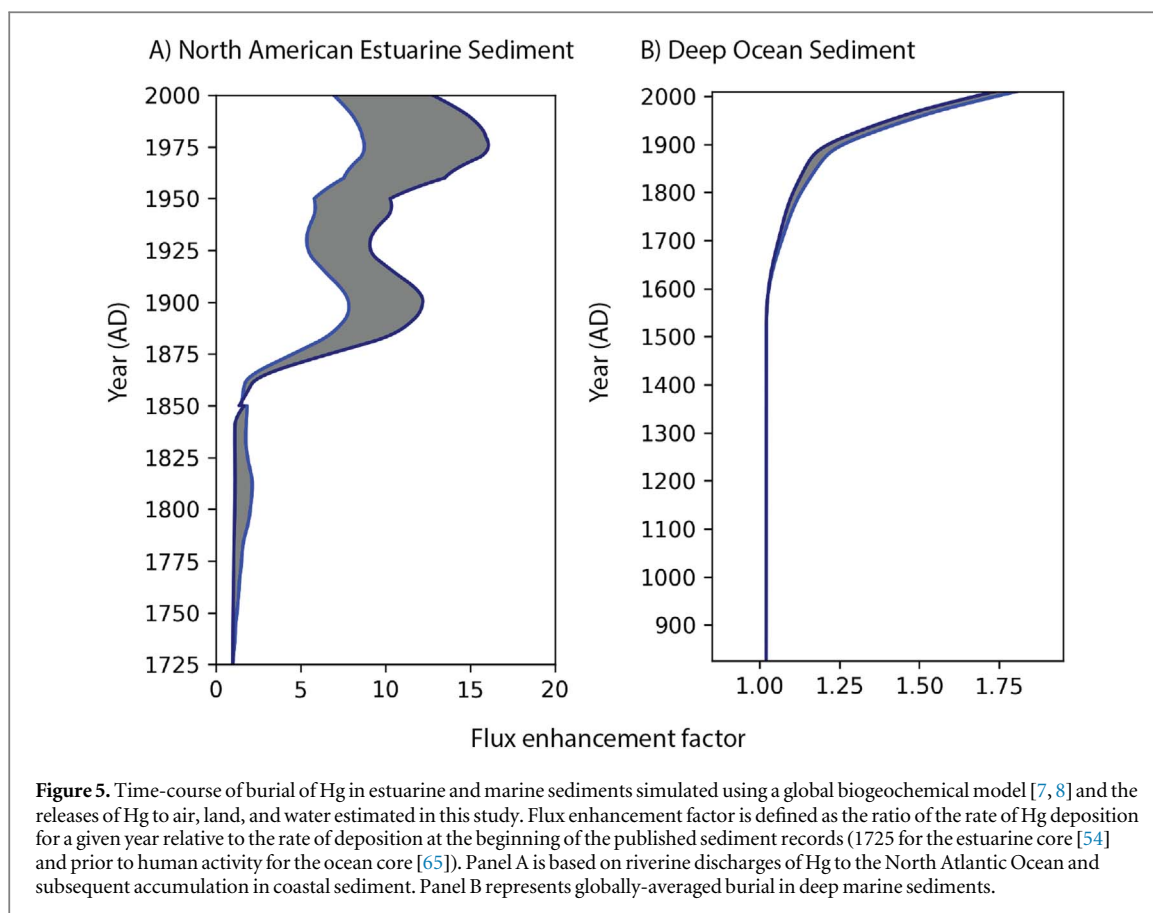


Figure 3 presents the same global Hg results as figure 2 but disaggregated into four major groupings of source type: mercury production and use, fossil-fuel combustion, gold and silver production, and other metals production. Figure 3 shows that over this 500 year period, Hg releases to the environment have been dominated by: (a) the production of gold and silver; and (b) the production of Hg to extract that gold and silver through amalgamation techniques and to be used in a variety of other commercial applications. It is only in the last century of the period that Hg from fossil-fuel combustion and the extraction of non-precious metals has grown rapidly. This figure also illustrates the recent decline in Hg production and use that was mentioned earlier—and this would also be reflected in releases during the production of gold and silver, but for the contribution from ASGM.

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

China [27] and subsequently expanded for global emissions [28, 30], which uses a Monte Carlo framework of 10 000 simulations and uncertainty estimates for all emission factors and activity levels. Figure 4 shows the uncertainty bounds for total Hg releases in this work, expressed as 80% confidence intervals 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 and 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 and other processing. It can be seen that the upper bound for the year 1890, 15.9 Gg, is the highest in the entire time period.

We investigated the consistency of historical releases from this work with a high-resolution sediment accumulation record from an estuary on the east coast of North America [54]. To do this, we forced the 7-box



biogeochemical model developed by Amos *et al* [7, 8] with the historical amount of anthropogenic Hg released in North America in this work. We estimated pre-1510 inputs to the terrestrial environment for North America based on its fraction of global land surface (i.e. 1/6th of the global geogenic and antiquity emission-driven reservoirs). Riverine fluxes from North America reflect the accumulated reservoir in the terrestrial environment, as described elsewhere [8].

Figure 5(A) shows two historical deposition scenarios for coastal sediment in North America that constrain the potential mobility of historical releases to land and water: (a) lower envelope of releases: all sequestered Hg in land/water by North American mining is permanently removed from environmental cycling; and (b) upper envelope of releases: a fraction of the Hg released to land/water is reemitted to the atmosphere and released to rivers [30]. Similar to Fitzgerald *et al* [54], the results show an initial increase in Hg deposition fluxes between 1850 and 1925 followed by a larger increase and subsequent decline in 1925–2000. Large aquatic Hg releases to coastal systems during this period dominate the global background releases to the atmosphere, as supported by the archival record [54].

Figure 5(B) shows the simulated average global burial of Hg in deep ocean sediment [7], based on the global emissions described in this work. The shaded

region in the figure is bounded by two emission scenarios in which either all or none of the Hg released to land and water in New World silver mining is available for environmental cycling. It can take hundreds of years for anthropogenic Hg emitted to the atmosphere to reach the deep ocean [7]. This varies across marine regions based on local productivity, ocean circulation, and the characteristics of settling marine snow [10], but the model provides a spatially-averaged first approximation of the global average scenario. There is little evidence of Hg accumulation until approximately 1600 and a relatively steeper increase in accumulation that begins around 1900. The long time-scales required for Hg to reach the deep ocean mean that anthropogenic releases lag atmospheric emissions by hundreds of years and are temporally integrated. These results are consistent with a deep marine sediment record from the Southern Ocean [65] and show an approximately two-fold overall enrichment from human activity in deep marine sediment. This contrasts with the assertion of Zaferani *et al* [65] that globally significant anthropogenic Hg releases were confined to the last 150 years. Instead, we conclude that the new emissions inventory produced in this study provides better agreement with historical archive data than earlier inventories and reinforces the significance of the last 500 years of anthropogenic Hg pollution.

4. Discussion and conclusions

In this work, we quantify the time-varying characteristics of anthropogenic Hg releases to the environment by world region over the period 1510–2010. This represents 95% of total all-time releases by our estimation. The majority of these releases have been in Europe and North America, consistent with flourishing economies and the extraction and use of Hg in the production of gold and silver. Today, however, Hg releases are declining in these two regions, while releases in Asia are growing fast. ASGM remains a problem, especially in Africa, but global actions achieved in coordination with the Minamata Convention may facilitate a decline in the coming years.

The regional estimates prior to 1850 presented in this work have not been previously reported, and biogeochemical cycling models have been forced to use rather primitive characterizations of pre-1850 releases, based largely on early estimates of Hg used in silver mining in Spanish America [41–44]. Amos *et al* [12] used a pre-1850 value of emissions to air of ~43 Gg, based on our earlier global inventory [28]. There was no information at that time to develop temporal or regional variation. In this work, we estimate 1510–1850 emissions to air at 53 Gg, which is well within the uncertainty range of these historical estimates.

In conclusion, this work stresses the importance of early historical releases of Hg to the environment by humans in pursuit of gold and silver and Hg for amalgamation. Much of this Hg persists on land and in water bodies close to where the gold, silver, and Hg were originally extracted: mainly in Bolivia, Peru, and Mexico; in western North America; and in western and central Europe. The remainder of those early Hg releases have been either temporarily or permanently fixed in sediments, peat, ice, and oceans or remain in the global biogeochemical system and contribute to the global background and re-emission. Today, Hg releases are more widespread and diversified, and it will require a global response like the Minamata Convention to cap future increases and enable continued emission reductions to improve environmental conditions. We recommend emphasis on: (a) reducing ASGM releases; (b) reduction in the use of Hg in products and the associated production of Hg; (c) careful treatment and disposal of Hg-containing wastes, especially when combusted; (d) effective control of air emissions from coal combustion and disposal of ash and captured particulate matter; and (e) continued modernization of industrial processes (metal smelters, caustic soda production, cement plants, etc).

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References

- [1] Karagas M R, Choi A L, Oken E, Horvat M, Schoeny R, Kamai E, Cowell W, Grandjean P and Korrick S 2012 Evidence on the human health effects of low-level methylmercury exposure *Environ. Health Perspect.* **120** 799–806
- [2] Roman H A *et al* 2011 Evaluation of the cardiovascular effects of methylmercury exposures: current evidence supports development of a dose-response function for regulatory benefits analysis *Environ. Health Perspect.* **119** 607–14
- [3] United Nations Environment Programme (UNEP) 2013 *Global Mercury Assessment 2013: Sources, Emissions, Releases and Environmental Transport* (Geneva: UNEP Chemicals Branch)
- [4] Arctic Monitoring and Assessment Programme (AMAP)/United Nations Environment Programme (UNEP) 2013 *Technical Background Report for the Global Mercury Assessment 2013* (Geneva: Oslo, Norway/UNEP Chemicals Branch)
- [5] 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 and Sunderland E M 2017 A new mechanism for atmospheric mercury redox chemistry: implications for the global mercury budget *Atmos. Chem. Phys.* **17** 6353–71
- [6] Kocman D, Wilson S J, Amos H M, Telmer K H, Steenhuisen F, Sunderland E M, Mason R P, Outridge P and Horvat M 2017 Towards an assessment of the global inventory of present-day mercury releases to freshwater environments *Int. J. Environ. Res. Public Health* **14** 138–54
- [7] Amos H M, Jacob D J, Streets D G and Sunderland E M 2013 Legacy impacts of all-time anthropogenic emissions on the global mercury cycle *Glob. Biogeochem. Cycles* **27** 410–21
- [8] Amos H M, Jacob D J, Kocman D, Horowitz H M, Zhang Y, Dutkiewicz S, Horvat M, Corbitt E S, Krabbenhoft D P and Sunderland E M 2014 Global biogeochemical implications of mercury discharges from rivers and sediment burial *Environ. Sci. Technol.* **48** 9514–22
- [9] Fisher J A, Jacob D J, Soerensen A L, Amos H M, Steffen A and Sunderland E M 2012 Riverine source of Arctic Ocean mercury inferred from atmospheric observations *Nat. Geosci.* **5** 499–504
- [10] Sunderland E M and Mason R 2007 Human impacts on open ocean mercury concentrations *Glob. Biogeochem. Cycles* **21** GB4022
- [11] Selin N E, Jacob D J, Yantosca R M, Strode S, Jaeglé L and Sunderland E M 2008 Global 3D land-ocean-atmosphere model for mercury: present-day versus preindustrial cycles and anthropogenic enrichment factors for deposition *Glob. Biogeochem. Cycles* **22** GB2011
- [12] Amos H M *et al* 2015 Observational and modeling constraints on global anthropogenic enrichment of mercury *Environ. Sci. Technol.* **49** 4036–47

- [13] Soerensen A L, Sunderland E M, Holmes C D, Jacob D J, Yantosca R M, Skov H, Christensen J H, Strode S A and Mason R P 2010 An improved global model for air-sea exchange of mercury: high concentrations over the North Atlantic *Environ. Sci. Technol.* **44** 8574–80
- [14] Soerensen A L, Jacob D J, Streets D G, Witt M L I, Ebinghaus R, Mason R P, Andersson M and Sunderland E M 2012 Multi-decadal decline of mercury in the North Atlantic atmosphere explained by changing subsurface seawater concentrations *Geophys. Res. Lett.* **39** L21810
- [15] Smith-Downey N V, Sunderland E M and Jacob D J 2010 Anthropogenic impacts on global storage and emissions of mercury from terrestrial soils: insights from a new global model *J. Geophys. Res.* **115** G03008
- [16] Evers D C, Egan Keane S, Basu N and Buck D 2016 Evaluating the effectiveness of the Minamata Convention on mercury: principles and recommendations for next steps *Sci. Total Environ.* **569** 888–903
- [17] Giang A, Stokes L C, Streets D G, Corbitt E S and Selin N E 2015 Impacts of the Minamata Convention on mercury emissions and global deposition from coal-fired power generation in Asia *Environ. Sci. Technol.* **49** 5326–35
- [18] Gustin M S *et al* 2016 Importance of integration and implementation of emerging and future mercury research into the Minamata Convention *Environ. Sci. Technol.* **50** 2767–70
- [19] Selin N E 2018 A proposed global metric to aid mercury pollution policy *Science* **360** 607–9
- [20] Engstrom D R, Fitzgerald W F, Cooke C A, Lamborg C H, Drevnick P E, Swain E B, Balogh S J and Balcom P H 2014 Atmospheric Hg emissions from preindustrial gold and silver extraction in the Americas: a reevaluation from lake-sediment archives *Environ. Sci. Technol.* **48** 6533–43
- [21] Fitzgerald W F, Engstrom D R, Mason R P and Nater E A 1998 The case for atmospheric mercury contamination in remote areas *Environ. Sci. Technol.* **32** 1–7
- [22] Enrico M, Le Roux G, Heimbürger L-E, Van Beek P, Souhaut M, Chmieleff J and Sonke J E 2017 Holocene atmospheric mercury levels reconstructed from peat bog mercury stable isotopes *Environ. Sci. Technol.* **52** 5899–906
- [23] Clackett S P, Porter T J and Lehnher I 2018 400 year record of atmospheric mercury from tree-rings in Northwestern Canada *Environ. Sci. Technol.* **52** 9625–33
- [24] Martínez-Cortizas A, Pontevedra-Pombal X, García-Rodeja E, Nóvoa-Muñoz J C and Shotyk W 1999 Mercury in a Spanish peat bog: archive of climate change and atmospheric metal deposition *Science* **284** 939–42
- [25] Streets D G, Hao J, Wu Y, Jiang J, Chan M, Tian H and Feng X 2005 Anthropogenic mercury emissions in China *Atmos. Environ.* **39** 7789–806
- [26] Wu Y, Wang S, Streets D G, Hao J, Chan M and Jiang J 2006 Trends in anthropogenic mercury emissions in China from 1995–2003 *Environ. Sci. Technol.* **40** 5312–8
- [27] Wu Y, Streets D G, Wang S X and Hao J M 2010 Uncertainties in estimating mercury emissions from coal-fired power plants in China *Atmos. Chem. Phys.* **10** 2937–47
- [28] Streets D G, Devane M K, Lu Z, Bond T C, Sunderland E M and Jacob D J 2011 All-time releases of mercury to the atmosphere from human activities *Environ. Sci. Technol.* **45** 10485–91
- [29] Streets D G, Zhang Q and Wu Y 2009 Projections of global mercury emissions in 2050 *Environ. Sci. Technol.* **43** 2983–8
- [30] Streets D G, Horowitz H M, Jacob D J, Lu Z, Levin L, ter Schure A F H and Sunderland E M 2017 Total mercury released to the environment by human activities *Environ. Sci. Technol.* **51** 5969–77
- [31] Horowitz H M, Jacob D J, Amos H M, Streets D G and Sunderland E M 2014 Historical mercury releases from commercial products: global environmental implications *Environ. Sci. Technol.* **48** 10242–50
- [32] Streets D G, Lu Z, Levin L, ter Schure A F H and Sunderland E M 2018 Historical releases of mercury to air, land, and water from coal combustion *Sci. Total Environ.* **615** 131–40
- [33] Andres R J, Fielding D J, Marland G, Boden T A, Kumar N and Kearney A T 1999 Carbon dioxide emissions from fossil-fuel use, 1751–1950 *Tellus* **51B** 759–65
- [34] Julihn C E 1928 *Summarized Data of Copper Production. Economic Paper 1* (Washington, D.C.: Department of Commerce, Bureau of Mines) p 33
- [35] Pehrson E W 1929 *Summarized Data of Zinc Production. Economic Paper 2* (Washington, D.C.: Department of Commerce, Bureau of Mines) p 48
- [36] Smith L A 1929 *Summarized Data of Lead Production. Economic Paper 5* (Washington, D.C.: Department of Commerce, Bureau of Mines) p 45
- [37] Ridgway R H 1929 *Summarized Data of Gold Production. Economic Paper 6* (Washington, D.C.: Department of Commerce, Bureau of Mines) p 64
- [38] Merrill C W 1930 *Summarized Data of Silver Production. Economic Paper 8* (Washington, D.C.: Department of Commerce, Bureau of Mines) p 59
- [39] Hylander L D and Meili M 2003 500 years of mercury production: global annual inventory by region until 2000 and associated emissions *Sci. Total Environ.* **304** 13–27
- [40] Hylander L D and Meili M 2005 The rise and fall of mercury: converting a resource to refuse after 500 years of mining and pollution *Crit. Rev. Environ. Sci. Technol.* **35** 1–36
- [41] Nriagu J O 1993 Legacy of mercury pollution *Nature* **363** 589
- [42] Nriagu J O 1994 Mercury pollution from the past mining of gold and silver in the Americas *Sci. Total Environ.* **149** 167–81
- [43] Camargo J A 2002 Contribution of Spanish-American silver mines (1570–1820) to the present high mercury concentrations in the global environment: a review *Chemosphere* **48** 51–7
- [44] Lacerda L D 1997 Global mercury emissions from gold and silver mining *Water Air Soil Pollut.* **97** 209–21
- [45] Guerrero S 2012 Chemistry as a tool for historical research: identifying paths of historical mercury pollution in the Hispanic new world *Bull. Hist. Chem.* **37** 61–70
- [46] Guerrero S 2012 Chemistry as a tool for historical research: estimating the contraband of silver from Potosí and Oruro, 1576–1650 *Bull. Hist. Chem.* **37** 72–80
- [47] Guerrero S 2018 The environmental history of silver production, and its impact on the United Nations Minamata Convention on mercury *Presented at the World Economic History Congress (Boston, 29 July–3 August)*
- [48] Cooke C A, Balcom P H, Biester H and Wolfe A P 2009 Over three millennia of mercury pollution in the Peruvian Andes *Proc. Natl Acad. Sci.* **106** 8830–4
- [49] Cooke C A, Balcom P H, Kerfoot C, Abbott M B and Wolfe A P 2011 Pre-colombian mercury pollution associated with the smelting of argentiferous ores in the Bolivian Andes *Ambio* **40** 18–25
- [50] Hagan N, Robins N, Hsu-Kim H, Halabi S, Morris M, Woodall G, Zhang T, Bacon A, Richter D and Vandenburg J 2011 Estimating historical mercury concentrations from silver mining and their legacies in present-day surface soil in Potosí, Bolivia *Atmos. Environ.* **45** 7619–26
- [51] Cooke C A, Hintelmann H, Ague J J, Burger R, Biester H, Sachs J P and Engstrom D R 2013 Use and legacy of mercury in the Andes *Environ. Sci. Technol.* **47** 4181–8
- [52] Booer J R 1944 The behaviour of mercury compounds in soil *Ann. Appl. Biol.* **31** 340–59
- [53] Beal S A, Osterberg E C, Zdanowicz C M and Fisher D A 2015 Ice core perspective on mercury pollution during the past 600 years *Environ. Sci. Technol.* **49** 7641–7
- [54] Fitzgerald W F, Engstrom D R, Hammerschmidt C R, Lamborg C H, Balcom P H, Lima-Braun A L, Bothner M H and Reddy C M 2018 Global and local sources of mercury deposition in coastal New England reconstructed from a multiproxy, high-resolution, estuarine sediment record *Environ. Sci. Technol.* **52** 7614–1620
- [55] Swain E B, Engstrom D R, Brigham M E, Henning T A and Brezonik P L 1992 Increasing rates of atmospheric mercury deposition in midcontinental North America *Science* **257** 784–7
- [56] Eyrikh S, Eichler A, Tobler L, Malygina N, Papina T and Schwikowski M 2017 A 320 year ice-core record of

- atmospheric Hg pollution in the Altai, Central Asia *Environ. Sci. Technol.* **51** 11597–606
- [57] Navrátil T, Nováková T, Shanley J B, Rohovec J, Matoušková S, Vaňková M and Norton S A 2018 Larch tree rings as a tool for reconstructing 20th century Central European atmospheric mercury trends *Environ. Sci. Technol.* **52** 11060–8
- [58] Pirrone N, Allegrini I, Keeler G J, Nriagu J O, Rossmann R and Robbins J A 1998 Historical atmospheric mercury emissions and depositions in North America compared to mercury accumulations in sedimentary records *Atmos. Environ.* **32** 929–40
- [59] Bowie A J 1905 *A Treatise on Hydraulic Mining in California* (New York: D. van Nostrand Co.) p 313
- [60] US Environmental Protection Agency 2005 *Proceedings and Summary Report of a Workshop on Assessing and Managing Mercury from Historic and Current Mining Activities* EPA/625/R-04/102 San Francisco, CA p 205 28–30 November
- [61] Zhang L, Wang S, Wu Q, Wang F, Lin C-J, Zhang L, Hui M, Yang M, Su H and Hao J 2016 Mercury transformation and speciation in flue gases from anthropogenic emission sources: a critical review *Atmos. Chem. Phys.* **16** 2417–33
- [62] Streets D G, Horowitz H M, Lu Z, Levin L, Thackray C P and Sunderland E M 2019 Global and regional trends in mercury emissions and concentrations, 2010–2015 *Atmos. Environ.* **201** 417–27
- [63] Bycroft B M, Collier B A W, Deacon G B, Coleman D J and Lake P S 1982 Mercury contamination of the Lerderberg River, Victoria, Australia, from an abandoned gold field *Environ. Pollut. A* **28** 135–47
- [64] Davies P, Lawrence S and Turnbull J 2015 Mercury use and loss from gold mining in nineteenth-century Victoria *Proc. R. Soc. Vic.* **127** 44–54
- [65] Zaferani S, Pérez-Rodríguez M and Biester H 2018 Diatom ooze—a large marine mercury sink *Science* **361** 797–800