



Historical releases of mercury to air, land, and water from coal combustion[☆]



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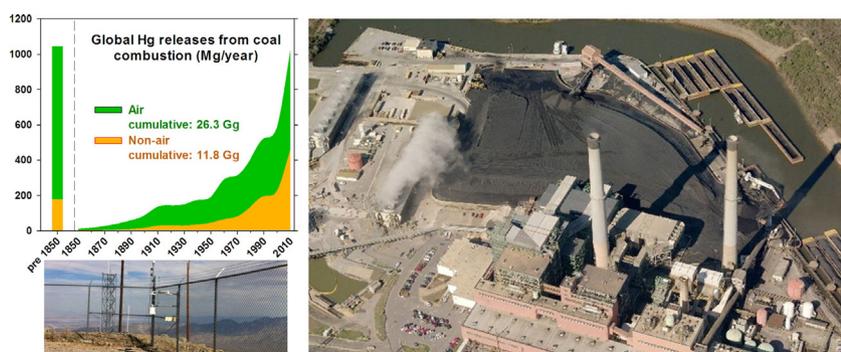
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HIGHLIGHTS

- Total Hg released to the environment from coal combustion is estimated to be 38 Gg.
- 71% of this Hg was released into the atmosphere, while 31% went to land and water.
- Most of the Hg from coal combustion was released in Asia and Europe (32% each).
- The fraction of Hg released to the air as elemental Hg has steadily increased.
- In the year 2010 about 1 Gg of Hg was released worldwide to all media.

GRAPHICAL ABSTRACT



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ABSTRACT

Coal combustion is one of the largest contemporary sources of anthropogenic mercury (Hg). It releases geologically sequestered Hg to the atmosphere, and fly ash can contaminate terrestrial and aquatic systems. We estimate that coal combustion has released a cumulative total of 38.0 (14.8–98.9, 80% C.I.) Gg (gigagrams, 10^9 g or thousand tonnes) of Hg to air, land, and water up to the year 2010, most of which (97%) has occurred since 1850. The rate of release has grown by two orders of magnitude from 0.01 Gg yr^{-1} in 1850 to 1 Gg yr^{-1} in 2010. Geographically, Asia and Europe each account for 32% of cumulative releases and an additional 18% is from North America. About 26.3 (10.2–68.3) Gg, 71% of the total, were directly emitted to the atmosphere, mostly from the industrial (45%) and power generation (36%) sectors, while the remainder was disposed of to land and water bodies. While Europe and North America were the major contributing regions until 1950, Asia has surpassed both in recent decades. By 2010, Asia was responsible for 69% of the total releases of Hg from coal combustion to the environment. Control technologies installed on major emitting sources capture mainly particulate and divalent Hg, and therefore the fraction of elemental Hg in emissions from coal combustion has increased over time from 0.46 in 1850 to 0.61 in 2010. About 11.8 (4.6–30.6) Gg of Hg, 31% of the total, have been transferred to

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land and water bodies through the disposal or utilization of Hg-containing combustion waste and collected fly ash/FGD waste; approximately 8.8 Gg of this Hg have simply been discarded to waste piles or ash ponds or rivers.

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1. Introduction

Mercury (Hg) contamination of the environment is a well-recognized global problem that poses risks to humans and wildlife (Mahaffey et al., 2011; Lavoie et al., 2013). The issue has been summarized in the Global Mercury Assessment (GMA) (UNEP, 2013) and accompanying documentation (AMAP/UNEP, 2013). Most emission estimates focus on a single year, on direct releases to the atmosphere, and on the Hg remaining at contaminated sites (e.g., UNEP, 2013). However, this is only a snapshot of the problem, because a large fraction of the water-soluble divalent Hg (Hg^{II}) deposited to terrestrial ecosystems and the ocean is reduced to gaseous elemental Hg (Hg^0) and evaded back into the atmosphere, prolonging its lifetime in the biosphere (Amos et al., 2013, 2015). This study focuses on one important component of the Hg picture, coal combustion, and its cumulative releases into the environment.

Some of the Hg liberated by coal combustion is emitted directly into the atmosphere during the combustion process, while the remainder is released to the land or nearby water bodies. The atmospheric lifetime of Hg is ~6 months (Corbitt et al., 2011; Horowitz et al., 2017), which allows for atmospheric transport on the hemispheric to global scale. Hg discarded in waste products to land and ponds can subsequently be transported into rivers and find its way into lakes and oceans (Amos et al., 2014; Fisher et al., 2012). Atmospherically deposited Hg cycles through the surface environment in oceans and soils and can be re-emitted to the atmosphere via reduction back to elemental Hg. Considerable mobilization and re-distribution of Hg therefore occurs over time. Eventually, Hg is buried in estuarine or ocean sediments or stable terrestrial reservoirs, but the time scale for this sequestration can be as long as millennia (Amos et al., 2013; Selin et al., 2008). 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 in total and what has been its fate. Single-year estimates and air-only estimates are insufficient to support biogeochemical modeling of the complete Hg cycle (Amos et al., 2013).

In this study, the cumulative amount of Hg released from coal combustion to all media (air, land, and water) is estimated. Hg is naturally enriched in any type of sulfidic ore and is thus contained as an impurity in many kinds of ores and fossil-fuel deposits. Coal is relatively enriched in Hg compared to other fossil fuels and contains 0.01–1 ppm Hg by mass (Mukherjee et al., 2008). The GMA (UNEP, 2013) reports that coal combustion released 474 Mg of Hg to air in the year 2010, 24% of total air emissions globally (1960 Mg), and was the second largest contributing source type after artisanal and small-scale gold mining (ASGM). Prior assessments for earlier years suggested that coal combustion was the largest anthropogenic source globally (Pirrone et al., 2010).

Because of its major contribution to Hg emissions in modern times, many countries have implemented emissions control technology for reducing emissions from coal combustion (Evers et al., 2016; Giang et al., 2015; Milford and Pienciak, 2009; Sunderland et al., 2016). The reduction and speciation of Hg in various combustion and control systems is an ongoing research topic (Wilcox et al., 2012). Coal combustion in power plants was the largest remaining emissions source of Hg in the U.S. by the mid-2000s (~40%), following reductions in emissions from municipal waste incinerators in the mid-1990s and the phase-out of Hg in many consumer products (Cohen et al., 2004). The U.S. Environmental Protection Agency (U.S. EPA) began developing regulations for Hg emissions from coal-fired power plants in the mid-1990s. This action

was prompted by the Agency's finding that it was "appropriate and necessary" to regulate emissions, based on plausible human health risks associated with local exposures described in the Mercury Study Report to Congress (U.S. EPA, 1997). This culminated in the 2011 Mercury and Air Toxics Standard (MATS) that used a Maximum Available Control Technology (MACT) standard to propose reductions of more than 90% of emissions from this sector. Full compliance with this regulation was set for April 2016, although legal action related to this rule is ongoing (Sunderland et al., 2016).

Globally, the Minamata Convention on Mercury, signed by 128 countries in 2013, calls for worldwide control of anthropogenic releases of Hg, in which coal-fired power plants are listed under Article 8 as point sources requiring control (Giang et al., 2015). Both in the U.S. and in other countries, the recognition in the 1980s and 1990s of coal combustion as a major pollution source led to the implementation of a range of control technologies for SO_x and NO_x emissions that have achieved co-benefits for Hg control. In some respects, the rate of implementation of these controls worldwide, especially flue-gas desulfurization (FGD), charts the future pathway for Hg emissions from coal combustion (Streets et al., 2009).

2. Data and methods

This study combines the results of previous work on Hg releases (Streets et al., 2011, 2017; Amos et al., 2013; Horowitz et al., 2014; Wu et al., 2010), extends the dataset to the year 2010, updates the implementation of emission controls, and adds the media that were not calculated previously (land and water). It thus provides a complete quantification of total Hg releases from coal combustion 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. For the period 1850–2010, decadal estimates for 17 world regions are estimated and summarized for seven larger, continental-scale regions (Streets et al., 2011). For the period prior to 1850, single estimates of coal consumption and corresponding Hg emissions are developed and assigned to Europe where the majority of coal was consumed in historical times. This analysis also incorporates updates to the Hg content of coals, coal combustion amounts, and the use of FGD systems.

Coal use around the world and in past and present times is calculated for 70 distinct combinations of fuel type, combustion technology, and emission control technology, covering four sectors: residential (11 types), industrial (32), power generation (24), and transportation (3) (Bond et al., 2004, 2007; Streets et al., 2004). It is important to include older and simpler types of combustion and pollution controls in order to correctly estimate emissions in past times and in developing countries. A complete listing of all fossil-fuel alternatives was provided in Table 3 of Streets et al. (2004), and the 70 coal options are presented here as Appendix Table A.1, with the sole change that coal combustion by power plants has recently been split into those plants with and without FGD systems, in order to reflect the growing use of FGD and its significant uptake of Hg in the flue gas.

This study assumes that FGD is applied only to coal-fired power plants that use pulverized coal units with particulate control (see Appendix Table A.1). This is by far the largest Hg-emitting sub-sector in the energy industry today. Statistics on the fractions of coal-fired capacity that use FGD around the world have been gathered (e.g., Rubin et al., 2004; Smith et al., 2011; Soud, 1994; Srivastava and Jozewicz, 2001). The energy statistics for this category are then divided into two sub-categories for each region: coal combustion without FGD, in which no additional removal of Hg occurs, and coal combustion with FGD, in

which the appropriate percentage removal of Hg is calculated. The two categories are subsequently combined to give total Hg emissions from this source category. Due to the absence of statistical information, there is no way to quantify the use of FGD in the industrial sector (which is small). Thus, industrial Hg emissions may be slightly overestimated.

National coal use for the period 1850–2010 was obtained from the World Energy Statistics published by the International Energy Agency (IEA) (IEA, 2016). Because of a re-assessment of China's coal use in recent years (see, e.g., Korsbakken et al., 2016) and the implications for the amount of Hg released from coal combustion in China, all global coal use data were updated using the latest IEA data from summer 2016. Coal use prior to 1850 is obtained primarily from the Carbon Dioxide Information Analysis Center (CDIAC) database (Andres et al., 1999). Because all major types of coal combustion technology and emission control systems are included, the temporal transitions from simple to advanced systems within countries and regions can be modeled by shifts among the 70 options (as described in Bond et al., 2004, 2007; Streets et al., 2004).

Emissions of Hg directly to the atmosphere are calculated by applying emission factors to each of the 70 fuel/technology options, according to the general formulation described in Bond et al. (2004). Global emissions for a given decadal year i of a species j are given by the sum of calculated emissions for all sector/fuel/technology combinations for all world regions, according to the following equation:

$$Em_{i,j} = \sum_k \sum_l \sum_m FC_{i,k,l,m} \left[\sum_n EF_{i,j,k,l,m,n} X_{i,k,l,m,n} \right] \quad (1)$$

where,

i,j,k,l,m,n = year, species (in this case Hg), world region, sector, fuel, technology;

Em = emissions (g yr^{-1});

FC = fuel consumption (kg yr^{-1});

EF = emission factor (g kg^{-1} of fuel burned); and

X = fraction of fuel consumed by a particular technology; note that for a particular sector/fuel combination $\sum_n X = 1$.

Emission factors take into account the Hg content of the major coal types burned in each of the 17 world regions (hard coal, brown coal, briquettes, etc., as shown in Appendix Table A.1), the amount of Hg retained in bottom ash, and the types and performance levels of combustion and pollution control devices. Wherever possible, this study uses information on the Hg content of coal as burned. It is possible that in some cases coal washing may have occurred prior to the reporting of Hg content as burned, but that information is not available. In many cases, coal washing has definitely not happened. This study does not include any Hg removed in the washing of the raw coal—nor does it include any Hg retained in mining waste. This study is limited to Hg releases during coal combustion. It is unlikely that information is available to completely account for these two other sources, and therefore it is not possible to perform a complete accounting of Hg in the entire “coal cycle”.

Data on coal parameters were obtained from a wide variety of national and international sources. Data on the Hg removal efficiencies of individual pieces of emission control equipment on coal-fired sources were gathered and summarized (AMAP/UNEP, 2013; Clack, 2009; Meij, 1991; Nolan et al., 1999; Park et al., 2008; Pavlish et al., 2003; Senior, 2001; Srivastava et al., 2006; UNEP, 2013). Regional and national information on the Hg content of coal, the installation of emission controls and their local performance levels, etc., were gathered globally (USGS/WoCQI, 2017) and for China (Feng et al., 2002; Tang et al., 2007; Tian et al., 2010; Wang et al., 2000; Wang et al., 2010; Zhang et al., 2008; Zhang Y. et al., 2016; Zhang L. et al., 2016; Zhang et al., 2002; Zheng et al., 2007), the Republic of Korea (Lee et al., 2006; Park et al., 2008), and South Africa (Dabrowski et al., 2008).

Speciated emissions from coal combustion flue gas were similarly gathered from test data around the world (Carpi, 1997; Guo et al., 2007; Laudal et al., 2000; Lee et al., 2006; Park et al., 2008; Senior, 2001; Tang et al., 2007; Wang et al., 2010; Zhang et al., 2008; Zhang Y. et al., 2016; Zhang L. et al., 2016). These included laboratory and field studies of factors affecting the chemical transformations among elemental, particulate, and divalent Hg in the flue gas (Chen et al., 2007; Galbreath and Zygarlicke, 2000; Gibb et al., 2000; Laudal et al., 2000; Presto and Granite, 2006; Senior, 2001; Wilcox et al., 2012; Zhou et al., 2007), particularly regarding the roles of chlorine and sulfur contained in the coal and unburned carbon in the flue gas. Evidence for the reduction of Hg^{II} back to Hg⁰ downwind of coal-fired power plant stacks (e.g., Edgerton et al., 2006; Landis et al., 2014; Lohman et al., 2006) is still somewhat equivocal (Horowitz et al., 2017) and was not included in the speciation profiles; this analysis focuses on the components of the flue gas at the point of release (or “top of the stack”).

The calculation of Hg emissions to air from coal combustion is much easier than emissions to land and water due to the many direct measurements of Hg concentrations in the air and in associated deposition that are aimed at minimizing the effects of airborne pollution. In-stack monitoring of Hg and aircraft observations of Hg concentrations in the vicinity of power plants have supplemented our knowledge of Hg released to the air. But if the Hg was retained in solid or liquid wastes and “disposed of” to land or water, this was generally considered to be an adequate form of control in the past, and an accounting of it was rarely deemed necessary. It is now known, however, that mobilization of such Hg can cause re-emission of elemental Hg to the air, enhancing the direct emissions. A comprehensive accounting of global Hg requires that these non-air releases be taken into account.

The total amount of Hg that can be released into the environment by the combustion of coal is constrained by the Hg content of the raw coal. The relationship between these parameters places an upper bound on the cumulative amount of Hg released due to the combustion of coal. The partitioning of emissions between air, land, and water is driven largely by the performance of the combustion technology and the degree of 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 amount of coal burned. As time went on, however, there was a transition—earlier in developed countries than in developing countries—from old, small-scale, uncontrolled processes to modern, large-scale processes with emission controls, and therefore the air emissions per unit of coal burned declined. Consequently, more of the Hg in the raw coal was released to land and water in one way or another. The use of coal has increased continuously over time, but at the same time combustion technology has improved and pollution controls have been adopted, so the resulting level of Hg released to the atmosphere at any given time and in any given place is determined by competition between production growth and technology improvement. The partitioning of the Hg between air and land/water is similarly determined by this trade-off.

The Hg that is not directly released to air is composed of Hg remaining in the waste left over from the processing of the raw coal, Hg left in discarded bottom ash during the combustion process, and Hg contained in fly ash or FGD waste that is collected at the facility. Historically, and still today to some extent, these waste products have accumulated on site in waste piles and storage ponds, which are therefore contaminated with Hg. Sometimes, waste products have been discarded into adjacent rivers (see, e.g., Amos et al., 2014). In recent years, greater efforts have been taken to secure these wastes in controlled landfills, to recycle products that may contain Hg, and to re-use the collected wastes (in products such as cement and gypsum), as discussed later. The amount of Hg released to land and water can be calculated by subtraction of the air emissions from the total Hg content of the raw coal, by direct calculation of the amount of collected fly ash or FGD waste, or by the measured ratio of air to land/water releases. Wherever possible, direct

calculation of the amounts of solid and liquid wastes is preferred, and the other two methods are used when such data are lacking.

Estimation of the production and utilization of coal combustion products is provided by a number of industry publications and research studies: the European Coal Combustion Products Association (ECOPA, 2017) database for Europe; Weir (2013) for Canada; the American Coal Ash Association (ACAA, 2017) and the U.S. EPA (U.S. EPA, 2002) for the U.S.; Kalyoncu (2000) for the U.S. and selected other countries; Yao et al. (2015), Heidrich et al. (2013), Manz (1997), and Dwivedi and Jain (2014) for comparative reviews of several countries, including China; the Ash Development Association of Australia (ADAA, 2017); the Japan Coal Energy Center (JCOAL, 2005); Haque (2013) and Ahmad et al. (2014) for India; and the Department of Environmental Affairs of the Republic of South Africa (DEA/RSA, 2012). These studies give basic information about how much solid and liquid wastes have been generated and what has happened to them in various parts of the world at various times.

3. Results and discussion

3.1. Direct Hg emissions to the atmosphere

We estimate that a cumulative total of 26.3 (10.2–68.3) Gg of Hg has been directly emitted to the atmosphere by coal combustion worldwide up to 2010. The distribution of these emissions by sector and by world region is shown in Table 1 and Fig. 1. About 868 Mg was emitted before 1850, meaning that 97% of the air emissions have occurred since 1850, which is taken to be the start of the Industrial Era. Emissions prior to 1850 were largely residential in nature, though they included some small manufacturing enterprises that could be classed as primitive “industrial,” and they occurred largely in Western Europe. Since 1850 the industrial sector has been the largest contributor to cumulative air emissions (11.8 Gg, 45%), followed by the power generation sector (9.4 Gg, 36%). The lower frame of Fig. 1 shows that Europe and North America were the largest emitting regions until 1950, but thereafter Asia grew so fast as to dominate emissions by 2010. Cumulative Hg emissions to air have seen the largest contributions from Europe (9.4 Gg, 37%) and Asia (8.4 Gg, 33%). Though this release of Hg into the atmosphere from coal combustion is large, it represents just 6% of cumulative Hg emissions from all anthropogenic sources (Streets et al., 2017). Fig. 1 shows the dramatic growth of Hg emissions to the air from 9 Mg yr⁻¹ in 1850 to 560 Mg yr⁻¹ in 2010, which can be attributed largely to the growth of the Asian power sector since 1950.

Fig. 2 shows the trends in Hg emissions to air by sector, as compared with total coal consumption, for the U.S. and Western Europe. These results for two of the most developed regions of the world are illustrative of the fact that coal combustion and Hg emissions do not have to go hand-in-hand. It is possible in the modern world to supply energy and use coal without large-scale damage to the environment from Hg. The

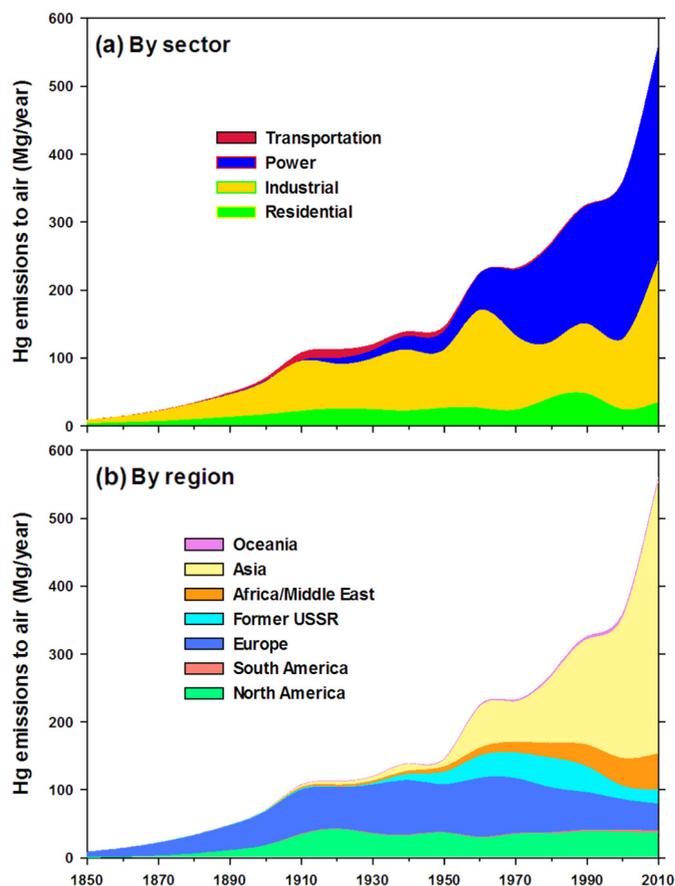


Fig. 1. Mercury emissions to the atmosphere from coal combustion, 1850–2010, by (a) sector and (b) world region.

results for these two regions show steady growth in both coal use and Hg emissions during the period 1850–1910, split between industrial and residential use. Coal-fired locomotives began to contribute toward the end of the 19th century. In both regions, we see continued growth in coal use thereafter (though rather flat in North America between 1910 and 1960), but a leveling off of Hg emissions, as coal use was rather quickly retired from the residential and transportation sectors around 1960. The installation of efficient emission controls then constrained industrial and power sector emissions, beginning in earnest at about the same time. While coal use has continued to increase in the U.S.—and Hg emissions have stabilized—additional policies to reduce coal use in Western Europe since about 1970 have led to a major decline in Hg emissions there. Thus, the lesson learned from these two regions is that Hg emissions do not have to grow in conjunction with growth in

Table 1

Cumulative emissions of Hg to the atmosphere from coal combustion up to 2010.

Component	Global emissions to air (Mg)	Regional emissions (Mg)						
		North America	South America	Europe	Former USSR	Africa/Middle East	Asia	Oceania
Pre-1850 coal use	868 ^a	0	0	868 ^a	0	0	0	0
1850–2010 coal use:								
Residential	3537	711	8.5	1512	211	107	983	3.7
Industrial	11,795	1465	95	4515	1088	542	4014	76
Power generation	9431	1725	47	2271	874	1057	3277	180
Transportation	652	288	6.0	224	4.9	24	103	2.7
Cumulative coal combustion	26,283	4189	156	9391	2179	1729	8377	262
Uncertainty range ^b	10,239–68,310	1610–10,992	83–344	3629–24,518	849–5662	674–4489	3268–21,765	101–690

¹ Mg = 10⁶ g = 1 tonne.

^a Coal use prior to 1850 was predominantly in western Europe and in the residential sector and is so assigned in this table.

^b 80% confidence intervals (P10 and P90 values).

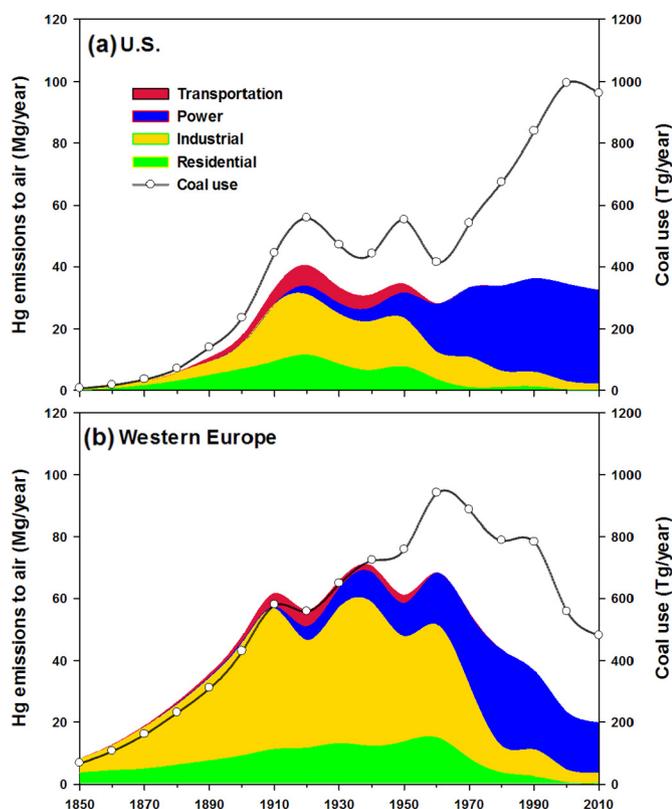


Fig. 2. Sectoral trends in Hg emissions to the atmosphere from coal combustion, 1850–2010, in (a) the U.S. and (b) Western Europe, together with the corresponding trends in total coal combustion.

coal use; if this lesson could be adopted in other parts of the world, the rapid rise in global Hg emissions from coal combustion shown in Fig. 1 would be quickly reversed.

Though there are no reliable estimates of global Hg emissions for years prior to 2000 against which these estimates can be compared, it is helpful to compare the results for air emissions against the GMA estimates for the year 2010 (AMAP/UNEP, 2013; UNEP, 2013). Global emissions to the atmosphere from coal combustion in the year 2010 are estimated at 561 (221–1473) Mg in this study, distributed among sectors and world regions as shown in Table 2. The GMA shows 474 Mg in the range of 304–678 Mg. Table 2 shows that estimates for most sectors are similar between the two studies, except for the industrial sector where the estimate in this work, 209 Mg, is about double the GMA estimate, 102 Mg. Because 87% of industrial emissions came from Asia in 2010, it is likely that the reason for the difference between this work

and the GMA lies in the treatment of Asian industrial emissions from coal combustion. This can be narrowed by focusing on results for the Asian region. In this work, 2010 industrial air emissions are estimated to be 157 Mg for East Asia (mainly China), 19 Mg for South Asia (mainly India), 5 Mg for Southeast Asia, and 1.5 Mg for Japan, for a total Asian estimate of 182 Mg. The GMA does not calculate regional emissions by sector, but there is an industry estimate for China of 55 (35–79) Mg (AMAP/UNEP, 2013). The corresponding value for India, 24 (15–34) Mg, is similar to the value in this work. It can be concluded that the difference between this study and the GMA primarily resides in the estimate of Hg emissions from industrial coal combustion in China, which is known to be a challenge (Zhao et al., 2017). This work uses detailed information on industrial coal use by 32 combinations of fuel, combustion technology, and emission control technology—including those that perform relatively poorly, like stoker-fired boilers and wet particulate controls—so it is likely that studies using less-detailed characterization of this sector may underestimate Hg emissions in a country like China.

The speciation profiles for Hg emissions from coal combustion have also been calculated at the same level of detail as total Hg emissions. In the period 1850–1950, the fraction of total, cumulative global emissions to air from coal combustion that was in the form of elemental mercury (Hg^0) rose slowly from about 0.46 to 0.52, as industrial and power emissions gradually supplemented and then replaced residential and transportation emissions, thereby eliminating most of the particulate Hg that had been released in historical times. Fig. 3 shows recent speciation trends (since 1950) for power generation and industry in four key world regions. Fig. 3 also shows that the global average Hg^0 fraction over all coal sectors continued to rise, from 0.52 in 1950 to 0.61 in 2010.

For the power sector, the results are striking. The speciation factor for Hg^0 in the developed world (U.S. and Western Europe) continued to increase over time, reaching values of 0.73 in the U.S. and 0.69 in Western Europe by 2010. This is indicative of the widespread use of emission controls (including FGD) in the power sector that have captured a portion of the particulate and divalent Hg, leaving (lower) levels of Hg in flue-gas streams that are enriched in Hg^0 . In contrast, the trends in the power sectors in East Asia (mainly China) and South Asia (mainly India) show sharp declines in the Hg^0 fractions after 1990. This can be attributed to rapid growth in the power sectors using poorly controlled plants, followed by something of a recovery by 2010. This is particularly true in China, where the installation of FGD systems became widespread by 2010 and the Hg^0 fraction rose to 0.72—about the same value as in Western Europe and the U.S.

For the industrial sector, the speciation results are different and less dramatic. Until about 1980, the Hg^0 fraction declined in all four regions, which can be attributed to economic growth outstripping environmental protection. These trends were reversed in 1980–1990, due to greater control of emissions from industrial facilities, and trends after 1990 have been varied. Somewhat surprisingly, the Hg^0 fraction in Western

Table 2
Emissions of Hg to the atmosphere from coal combustion in the year 2010.

Component	Global emissions to air (Mg)	Regional emissions (Mg)						
		North America	South America	Europe	Former USSR	Africa/Middle East	Asia	Oceania
This work:								
Residential	34.3	0.32	0.05	1.8	1.4	3.7	27.0	0.01
Industrial	209	3.0	1.9	4.9	5.8	10.9	182	0.4
Power generation	317	33.4	1.7	32.2	13.3	38.9	192	5.1
Transportation	0.49	0.0	0.0	0.0	0.0	0.0	0.48	0.0
Total coal combustion	561	36.7	3.6	39.0	20.5	53.5	402	5.4
Uncertainty range ^a	221–1473	13.8–99.7	2.1–7.6	15.0–104.9	8.0–53.8	21.1–140.9	158–1055	2.1–14.6
GMA (2013):								
Industrial	102	N/A	N/A	N/A	N/A	N/A	N/A	N/A
Power generation	316	N/A	N/A	N/A	N/A	N/A	N/A	N/A
Other	56	N/A	N/A	N/A	N/A	N/A	N/A	N/A
Total coal combustion	474 ^b	43.4	5.7	44.1	26.9	53.6	297.1	3.6

^a 80% confidence intervals (P10 and P90 values).

^b The GMA range is given as 304–678 Mg (UNEP, 2013).

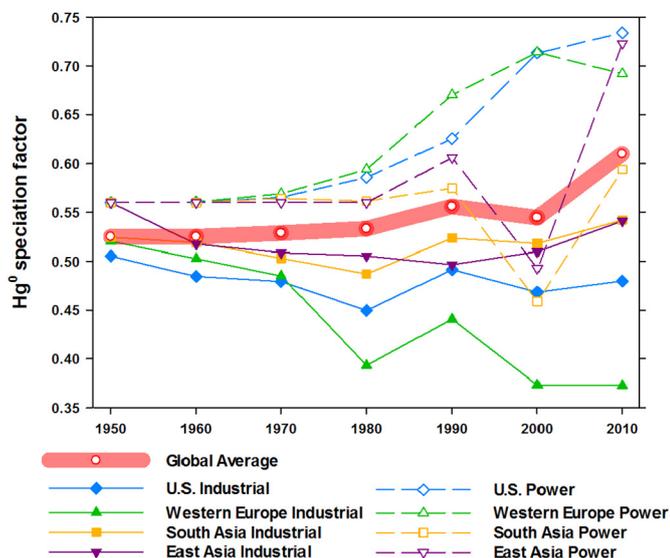


Fig. 3. Trends in the fraction of Hg that is emitted to the atmosphere in elemental form (Hg^0), 1950–2010, in the industrial and power sectors for four selected world regions. The solid red line represents the global average across all sectors.

Europe has tended to decrease throughout the period 1950–2010. Because industrial coal use in Western Europe declined dramatically over this period (as shown in Fig. 2), reaching very low levels by 2010, only a few coal-fired industrial facilities remain. These remaining facilities may, because of their special characteristics or poor levels of emission control, yield Hg emissions relatively depleted in Hg^0 .

The implications of these speciation shifts are very important for Hg cycling, air concentrations, and deposition. For example, the directionality of the shift implies greater importance of local sources when the fractions of particulate and divalent Hg are high and greater importance of global sources when the fraction of Hg^0 is high. It is conceivable, for example, that unexpected trends in measurements of Hg concentrations or deposition might be the result of changes in the speciation of Hg emissions from sources that strongly influence the measurement site. For example, Zhang Y. et al. (2016) and Zhang L. et al. (2016) suggested that declines in atmospheric concentrations of Hg in Europe and North America were driven in large part by declines in Hg^{II} releases from domestic coal combustion.

3.2. Releases of Hg to land and water

Averaged over all coal combustion source types and all time periods, 71% of the Hg in the raw coal has been directly emitted into the air during the combustion process. The balance, 11.8 (4.6–30.6) Gg, has been released onto land or into water bodies surrounding the emissions sources. It is important to take this Hg into consideration because: (a)

human and wildlife health risks are driven by Hg levels in ecosystems, particularly water bodies; and (b) some of the deposited Hg will be remobilized back to the air. The Hg released to land and water may redistribute between the two on variable time scales, though it takes millennia for all of it to reach long-term sinks in the deep ocean or land repositories. Table 3 shows the cumulative releases of Hg to land and water by region. Asia has experienced the greatest input (33%), most of it in the last few decades, followed by Europe (25%) and North America (23%).

The Hg that is not directly released into the air during combustion is in the form of bottom ash or fly ash that is collected in particulate control systems. Fly ash typically contains 0.2–0.6 ppm Hg by mass (Mukherjee et al., 2008), more concentrated than the raw coal. Table 3 shows that 68% of the Hg released to land and water is in this form. In historical times everywhere and still today in many parts of the world, coal fly ash was simply dumped onto land or into waste ponds near to the source, often making its way into adjacent rivers and streams over time. In recent years, storage in more secure disposal sites has occurred, though it is not possible to calculate how much Hg is presently stored there. Coal ash has its uses, particularly as fill material and in the manufacture of cement, and we estimate that, globally, 10% has gone into fill and 14% into cement. The ultimate fate of the Hg that was contained in the ash used in these and other processes is not easy to determine. If high temperatures are involved in the manufacturing process, then it is conceivable that a portion of the Hg is rather quickly re-emitted to the atmosphere; some other portion may be released at a slower rate if the Hg-containing material is exposed to water and sunlight.

Some Hg has been captured in FGD systems used on power plants (mainly) for the capture of SO_x (mainly). Typically, 50–70% of the Hg in the flue gas is captured, consisting of the Hg that is in particulate and divalent forms. Hg^0 is non-reactive and passes through the collection system. Though FGD is relatively common today, it is a comparatively recent technology that has contributed little to all-time, non-air Hg releases globally: 5% of the cumulative Hg going to FGD waste that is discarded and 1.7% to FGD waste that is used in manufacturing, for example, wallboard. Once again, what ultimately happens to the Hg in these processes is not well known. Gustin and Ladwig (2010) showed from laboratory tests that discarded FGD waste products containing captured Hg will release Hg back into the atmosphere over time, particularly upon the addition of water. Release of Hg contained in fly ash landfills was found to be not significant in similar tests (Gustin and Ladwig, 2004). Nevertheless, Yang et al. (2012) warned that ignoring emissions of Hg from coal ash and desulfurized gypsum and their subsequent re-use in China would lead to ineffective Hg control.

Fig. 4 shows the extremely rapid growth in global releases of Hg from coal to land and water, particularly in the period 1950–2010. Much of it is still disposed of, but increasingly uses are found for the products. Fig. 4 also shows that in the U.S. (and in other developed countries) the disposal of wastes to land and water is no longer increasing; direct disposal is now declining and the uses of coal ash and FGD

Table 3
Cumulative releases of Hg to land and water from coal combustion up to 2010.

Component	Global releases to land and water (Mg)	Regional releases (Mg)						
		North America	South America	Europe	Former USSR	Africa/Middle East	Asia	Oceania
Pre-1850 coal use	178 ^a	0	0	178 ^a	0	0	0	0
1850–2010 coal use:								
Ash disposed	8021	2030	55	1775	1348	341	2228	244
Ash used as fill	1169	169	16	505	97	26	338	19
Ash used in cement	1626	243	9	322	36	11	977	28
FGD waste disposed	567	176	1	43	5	13	319	10
FGD waste used	198	51	0	75	0	0	71	1
Cumulative coal combustion	11,759	2667	80	2899	1486	390	3932	303
Uncertainty range ^b	4581–30,561	1025–6999	43–176	1120–7570	579–3862	152–1013	1534–10,217	116–798

^a Coal use prior to 1850 was predominantly in western Europe and is so assigned in this table; these pre-1850 releases all consisted of direct ash disposal.

^b 80% confidence intervals (P10 and P90 values).

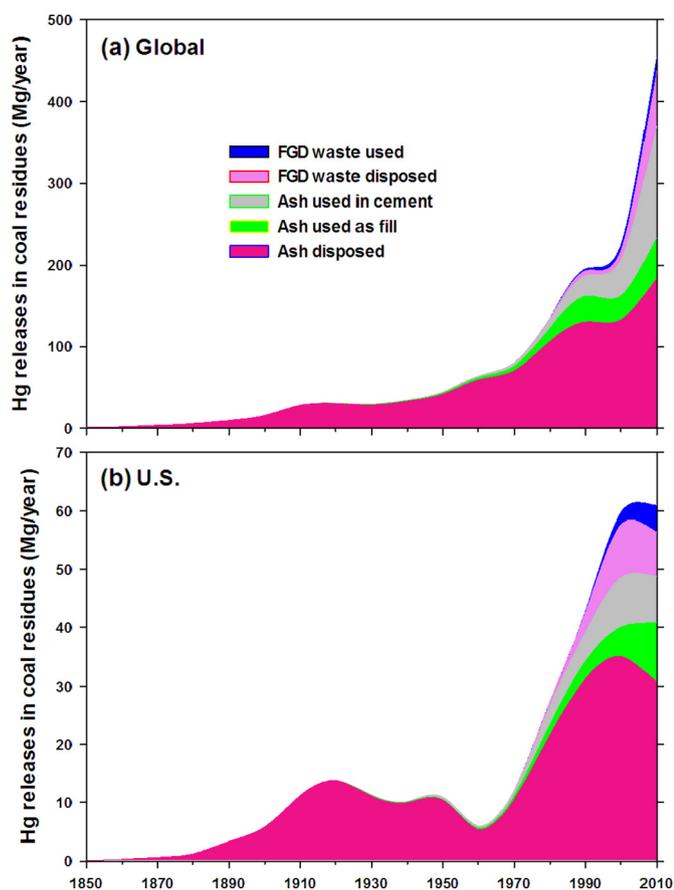


Fig. 4. Trends in the releases of Hg in solid/liquid wastes and in products associated with coal combustion, 1850–2010, (a) globally and (b) in the U.S. Note that the axes are on very different scales.

products are growing. The irony of greater control of air emissions is that the partitioning of Hg among air and non-air releases shifts toward the latter, meaning that increased attention needs to be paid to the disposal and/or usage of captured Hg-containing solids and liquids. Note that this work presents combined releases to land and water. It is not possible to separate the releases between land and water a priori, because in the past industrial facilities, power plants, and waste disposers were guarded about how they disposed of their waste products, and therefore statistics are lacking.

3.3. Total Hg releases into the environment

Table 4 and Fig. 5 summarize the total environmental releases of Hg arising from coal combustion. We estimate that coal combustion has released a cumulative total of 38.0 (14.8–98.9) Gg of Hg to air, land, and

water up to the year 2010, accounting for 2.5% of cumulative Hg releases from all anthropogenic sources (Streets et al., 2017). Almost equal amounts of Hg have been released in Asia and Europe (32% each). About 18% has been released in North America. While the releases in Europe and North America occurred mostly in earlier times, the Asian component is large today and steadily increasing. For the year 2010, total releases to all media were 1020 (400–2670) Mg. Asia was responsible for 69% of total global Hg releases from coal combustion in 2010. Huang et al. (2017) estimated that about 860 Mg of Hg were released to all media from coal combustion in China in 2012. They also showed that Hg from coal combustion in China has continuously increased each year.

An uncertainty analysis was carried out for the releases of Hg from coal combustion, following the method initially developed for power plants in China (Wu et al., 2010) and subsequently expanded for global emissions (Streets et al., 2011). This method uses a Monte Carlo framework of 10,000 simulations and uncertainty estimates for all emission factors and activity levels. The greatest source of uncertainty in the estimation of Hg releases from coal combustion is the variability of the Hg content of coals, but the performance of emission control technology also contributes. Fig. 6 summarizes the global air and non-air releases of Hg from coal combustion for all time up to 2010. A sobering observation from this figure is that annual Hg releases from coal combustion in 2010 are approximately the same as total historical releases prior to the year 1850: about 1 Gg or one thousand tonnes. Fig. 6 also shows the uncertainty range for each decadal estimate, 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, –61% to +163% in 2010, consistent with the known uncertainty in the Hg content of coals (see, e.g., Mukherjee et al., 2008; Wu et al., 2010). The uncertainty range does not vary much over time.

4. Conclusions

Now that many of the largest historical sources of Hg pollution—such as Hg mining, metals smelting, and amalgamation processes—have either been retired or greatly controlled (ASGM excepted), the role of coal combustion has grown. This study suggests that 38 Gg of Hg have been released from coal combustion over all time. This represents 2.5% of the cumulative Hg releases to the environment from all sources, yet by 2010 coal combustion contributed 11% of the total Hg to all media (Streets et al., 2017). This can be attributed to the remarkable growth in coal combustion for power generation in Asia in recent decades. With respect to emissions just to the atmosphere, coal combustion was the second largest source after ASGM in 2010, contributing 25% of the total. Annual releases of Hg from coal combustion continue to increase today.

Because of its important role in present-day Hg releases, coal combustion has become a target for Hg emission control in developed regions and globally. This study shows that control measures have

Table 4

Cumulative releases of Hg to air, land, and water from coal combustion up to 2010.

Component	Global releases (Mg)	Regional releases (Mg)						
		North America	South America	Europe	Former USSR	Africa/Middle East	Asia	Oceania
Pre-1850 to air	868 ^a	0	0	868 ^a	0	0	0	0
Pre-1850 to land/water	178 ^a	0	0	178 ^a	0	0	0	0
1850–2010 coal use:								
Emissions to air	25,415	4189	157	8522	2178	1730	8377	262
Waste disposal	8588	2206	56	1818	1353	354	2547	254
Utilization of waste	2993	463	25	902	133	37	1386	48
Cumulative releases	38,042	6857	236	12,290	3665	2120	12,309	565
Uncertainty range ^b	14,820–98,871	2635–17,990	126–520	4749–32,088	1428–9523	826–5502	4802–31,982	217–1488

^a Coal use prior to 1850 was predominantly in western Europe and is so assigned in this table.

^b 80% confidence intervals (P10 and P90 values).

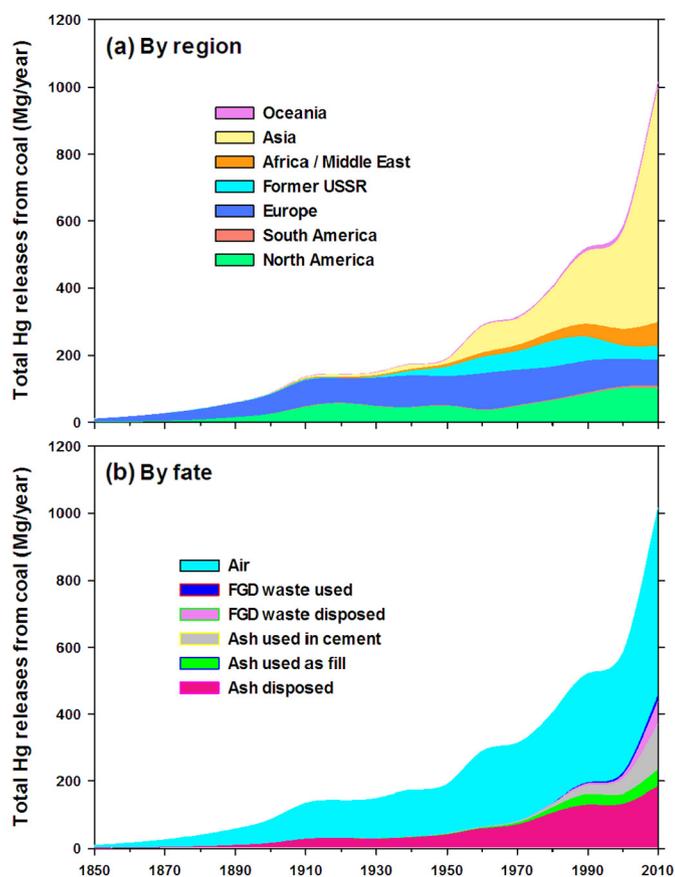


Fig. 5. Total mercury releases to air, land, and water from coal combustion, 1850–2010, by (a) world region and (b) fate.

already been successful in the developed world, halting growth or reducing emission levels. For example, in the U.S., the rate of Hg released per ton of coal consumed has dropped from 0.063 g Mg^{-1} in 1950 to 0.034 g Mg^{-1} in 2010, while in Western Europe it has dropped from 0.080 to 0.041 g Mg^{-1} . Further declines are likely as emission controls become even more efficient and more widely used, and as older plants are retired from service. If these kinds of improvements could be achieved in Asia, then great strides would be made toward reducing worldwide Hg pollution attributed to coal combustion.

In China, the implementation of SO_x controls on coal-fired power plants has increased rapidly, such that today there are few uncontrolled

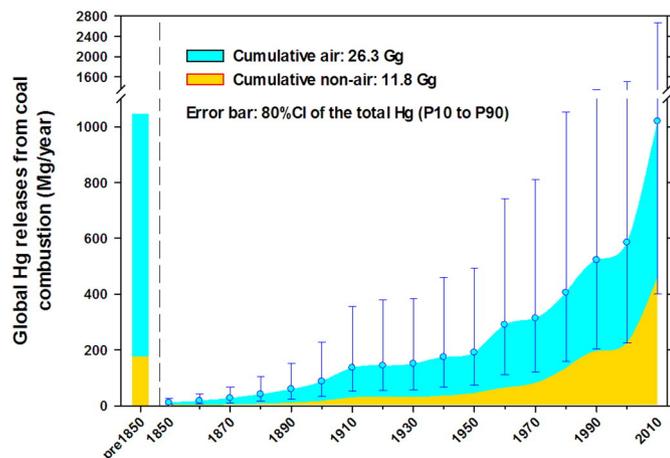


Fig. 6. Cumulative global air, non-air, and total mercury releases from coal combustion, with uncertainty estimates for total releases.

plants. This has had the co-benefit of applying a brake on Hg emissions growth from this large source. In the future, further improvements can be expected, especially if coal use for electricity generation is replaced by renewable energy. The use of coal in the industrial, residential, and transportation sectors in China will also need to be curtailed. The situation in India is less hopeful, because of the rapid increase in coal use in recent years with very few instances of emission control. But the lessons from the developed world, as depicted in Fig. 2, are clear. Streets et al. (2009) showed that global Hg emissions in 2050 could be returned back to mid-1990s levels simply by the implementation of 70% reduction in Hg emissions from coal-fired power plants worldwide. Further reductions could be achieved by the addition of NO_x controls like Selective Catalytic Reduction (SCR). In future work, we intend to include Hg removal by installed NO_x emission controls in estimations of Hg emissions.

As time goes on, the partitioning of primary Hg releases among media is changing: In 1950, 77% of the Hg released from coal combustion went directly into the air; by 2010 this fraction had dropped to 55%. With more Hg now finding its way onto land and into water bodies, it is critical to ensure that discarded coal combustion wastes containing Hg are transferred to secure landfills or other repositories, so that the Hg is not re-emitted to the air or washed into rivers and streams and thus re-enter the ecosystem. There is also an urgent need to know more about what happens to trace Hg contaminants when coal wastes are used in commercial applications.

The Hg that is emitted directly into the atmosphere from coal combustion is increasingly enriched in Hg^0 . The ratio of Hg^0 to total Hg increased from 0.52 in 1950 to 0.61 in 2010. This is because Hg^0 is less reactive and less susceptible to capture than are particulate and divalent Hg. As a result, local Hg pollution is slowly being replaced by global pollution, because of the long atmospheric lifetime of Hg^0 . Such redistribution of Hg can affect the interpretation of measurement trends and the attribution and quantification of damage to the health of humans and wildlife. This study provides not only an estimate of the total budget of released Hg from coal combustion, but also how those releases have been distributed across time, space, and environmental media. This will support biogeochemical modeling of the fate of anthropogenic Hg and contribute to the design of efficient and effective mitigation measures (Gustin et al., 2016).

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