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Global Mercury Emissions from Combustion in Light of International Fuel Trading

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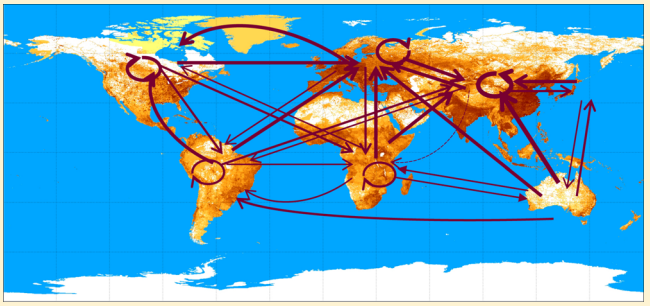
Supporting Information

ABSTRACT: The spatially resolved emission inventory is essential for understanding the fate of mercury. Previous global mercury emission inventories for fuel combustion sources overlooked the influence of fuel trading on local emission estimates of many countries, mostly developing countries, for which national emission data are not available. This study demonstrates that in many countries, the mercury content of coal and petroleum locally consumed differ significantly from those locally produced. If the mercury content in locally produced fuels were used to estimate emission, then the resulting global mercury emissions from coal and petroleum would be overestimated by 4.7 and 72%, respectively. Even higher misestimations would exist in individual countries, leading to strong spatial bias. On the basis of the available data on fuel trading and an updated global fuel consumption database, a new mercury emission inventory for 64 combustion sources has been developed. The emissions were mapped at 0.1° × 0.1° resolution for 2007 and at country resolution for a period from 1960 to 2006. The estimated global total mercury emission from all combustion sources (fossil fuel, biomass fuel, solid waste, and wildfires) in 2007 was 1454 Mg (1232−1691 Mg as interquartile range from Monte Carlo simulation), among which elementary mercury (Hg^0), divalent gaseous mercury (Hg^{2+}), and particulate mercury (Hg^p) were 725, 548, and 181 Mg, respectively. The total emission from anthropogenic sources, excluding wildfires, was 1040 Mg (886−1248 Mg), with coal combustion contributing more than half. Globally, total annual anthropogenic mercury emission from combustion sources increased from 285 Mg (263−358 Mg) in 1960 to 1040 Mg (886−1248 Mg) in 2007, owing to an increased fuel consumption in developing countries. However, mercury emissions from developed countries have decreased since 2000.



INTRODUCTION

Mercury in the environment is of major concern, given its toxicity to both humans and ecosystems,[1] and also because of its persistence in the environment and high potential for long-range transport.[2] In addition to the notorious Minamata disease,[3] mercury can lead to many other toxic effects. For example, much evidence suggests a link between methylmercury and an increased risk of cardiovascular disease,[4] immunotoxicity to the human immune system,[5] and even to IQ loss, problems with memory function, and attention deficit in children.[6]

Human activities contribute a large fraction of mercury emissions to the environment through intentional use or as a byproduct of anthropogenic activities taking place since industrialization.[7] In addition to other activities, such as gold mining and other intentional uses,[8] fossil fuel consumption is one of the main anthropogenic sources, contributing a large percentage of the total mercury emitted.[9,10]

For a better understanding of the effects of mercury on a regional or global scale, emission inventories for total mercury and different mercury species with appropriate spatial and temporal resolutions are necessary. These permit the modeling of their transport and fate in the environment, the assessment of their health and ecological impacts, and can lead to the formulation of abatement strategies. Therefore, efforts have been made to estimate mercury emissions and to develop global and regional emission inventories.[10−12] Emission factors (EFs) of mercury for the combustion of various fuels are often derived from the mercury content of the relevant fuels. In some cases, especially for developing countries, the mercury content of locally produced fuels are adopted for estimating mercury

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emissions,[11] which sometimes leads to misestimation. For example, 80.3% of coal burned in Brazil was imported in 2007, mainly from Australia and the U.S., and the mercury content of the locally produced coal is much higher.[13,14] The movement of mercury across various borders arising from coal trading has been quantified.[15] With high volumes of fossil fuels internationally traded in today's globalized world, the mercury content of fuels consumed, rather than of those produced, should be used in inventory development.

Mercury emissions to the environment involve elemental mercury (Hg^0), divalent gaseous mercury (Hg^{2+}), and particulate mercury (Hg^p), with each of these species behaving differently.[16] Therefore, a spatially resolved emission inventory with speciation information is necessary for atmospheric transport modeling and risk assessment. Spatially resolved emissions for a country are usually derived by disaggregating the total emission based on a distribution of population density.[17] This method implicitly assumes that per capita emissions are identical within a given country, an assumption that is definitely not true, especially for developing countries. Recently, a 0.1° × 0.1° fuel combustion map of 64 detailed fuel types was developed, based on subnational fuel consumption data (PKU-FUEL-2007).[18] By using these data, the uneven distribution of per capita fuel consumption has been satisfactorily demonstrated.[18]

In the current study, a global mercury emission inventory of Hg^0, Hg^{2+}, and Hg^p was developed for all combustion sources. By using the activity data in PKU-FUEL-2007, a 0.1° × 0.1° inventory was compiled for 2007 (PKU-Hg-2007). Meanwhile, annual emissions were derived for all countries from 1960 to 2007. Most importantly, the mercury content of fossil fuels consumed, rather than produced, were derived by taking the international trading of coal and petroleum into consideration. The importance of using mercury content of the consumed rather than produced fuels is evaluated in terms of total emissions and spatial distributions.

DATA SOURCES AND METHODOLOGY

Combustion Sources and Fuel Consumption. The PKU-FUEL-2007, a recently published global high-resolution (0.1° × 0.1°) fuel consumption database, provides detailed fuel consumption data, both natural and anthropogenic, for this study.[18] In brief, PKU-FUEL-2007 was developed using subnational fuel data for many large countries. In this way, spatial bias, caused by population-based disaggregation (arising from uneven per capita fuel consumptions within these countries), is substantially reduced.[18] Using the PKU-FUEL-2007, 64 detailed source types covering 222 countries/territories, five fuel categories (coal, petroleum, gas, solid waste including industrial and municipal wastes, and biomass) and six sectors (power production, industry, agriculture, transportation, residential, and wildfire) were directly applied in PKU-Hg-2007. Information on uncertainty was also derived from the PKU-FUEL-2007 for characterizing the fuel consumption uncertainty.[18] Historical fuel consumption from 1960 to 2006 was taken from the International Energy Agency (IEA) and the energy statistics of the United Nations.[19−21]

International Fossil Fuel Trading. Mercury emission levels from fuel combustion depend primarily on the mercury content of the fuels. Data on the production and international trading of hard coal (sum of coking coal and steam coal)[13] and crude oil in 2007 were taken from the IEA.[13,22] It was found that mercury content calculated from the 1978 and 2007 trading matrices were quite different (Supporting Information, SI, Table S1). However, annual trading data are not available for all years. Therefore, trading data for 1978, 1985, 1990, 1995, 2000, and 2007 were used for linear interpolation to secure trading volumes for the remaining years.[13,22]

Emission Factors. EFs of mercury for various fuel operations except coal combustion, solid waste incineration and petroleum refining, were collected from the literature and are listed in SI Table S2. EFs of mercury for coal of a given country are calculated using the following equation:

$$\mathrm{EF} = \sum_{i=1}^{5}\sum_{j=1}^{5}\left[F_{ij}C_f E_i(1 - R_j)\right] \quad (1)$$

where EF is a weighted-average EF of mercury for various combinations of five types of combustion equipment(s): household stoves (HS), pulverized coal-fired boilers (PC), stokers/cyclones (SC) in power plants, and PC and SC in industry, together with five categories of dust abatement: cyclones, scrubbers, electrostatic precipitators (ESP), ESP + flue gas desulfurization (FGD), and zero abatement. F_{ij} is the fraction of the combination of the i^{th} combustion type and the j^{th} abatement method. C_f is the average mercury content of the coal consumed in a given country. E_i is the fraction of mercury released during combustion from the i^{th} combustion facility and R_j is the fraction of mercury removed by the j^{th} abatement option. The F_{ij} values for coal were derived using the S-shaped curve developed by Grubler et al., [23] based on technology division data for developing and developed countries (SI Table S3). E_i and R_j were assumed to be constant for each specific combustion equipment and each abatement option. For coal, E_i ranges from 83% for HS and industrial SC to 99% for power plant PC.[24] R_j values are 0.1, 6.5, 29.4, and 69.0% for cyclone, scrubber, ESP, and ESP + FGD, respectively.[24−26] Time trends of the mercury release ratios of coal combustion facilities, calculated based on the S-shaped curve, are shown in SI Figure S1. The C_f values of hard coal were calculated based on the fractions of coal locally produced and imported from various countries,[22] and the mercury content of the locally produced and imported coals (SI Table S4). The total consumption of lignite and peat was 83% less than that of hard coal in 2007,[22] and the international trading volume accounted for only 2.1% of the total consumption.[22] Therefore, lignite and peat trading were ignored. Mercury content of locally produced lignite are listed in SI Table S5.[22] A geometric mean (87.8 μg/kg) and a range of mercury content (40−193 μg/kg) of peat from the literature[27] were adopted for emission calculations and uncertainty analysis.

Equation 1 was also used for calculating average EFs for the incineration of municipal and industrial wastes in power stations or by industry. F_{ij}, E_i, and R_j were taken to be identical to those used for coal. For open incineration of municipal waste, it was assumed that 50% of mercury in the wastes is released into the atmosphere.[14] The mercury content of the wastes were 1−6, 0.1−0.6, and 1−10 μg/kg for North America,[28,29] Europe,[30,31] and all other countries,[14,32] respectively.

EFs were calculated for petroleum refineries, by multiplying the mercury content of crude oil and the percentage of mercury released into the atmosphere during the refining processes. The mercury content of the crude oil consumed in a given country was calculated based on the trading volume,[22] and the mercury content of the imported petroleum (SI Table S6). It was

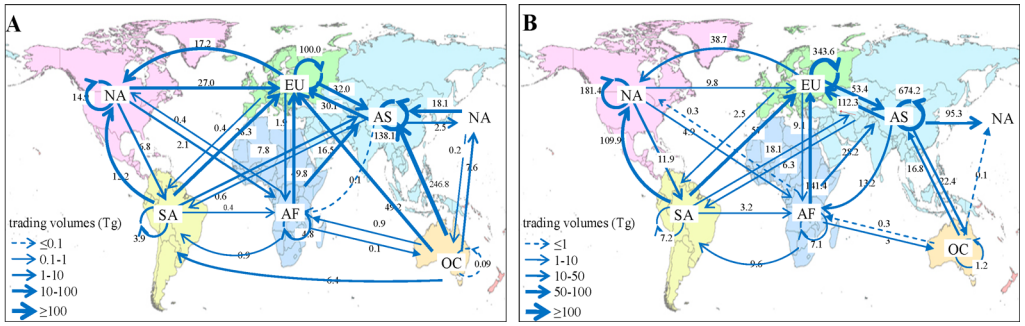

Figure 1. Major international trade of hard coal (A) and crude oil (B). Line widths are proportional to trading volumes, which are marked as numbers (Tg). The circular arrows represent the intraregional trading volumes. NA, SA, EU, AF, AS, and OC represent North America, South America, Europe, Africa, Asia, and Oceania, respectively.

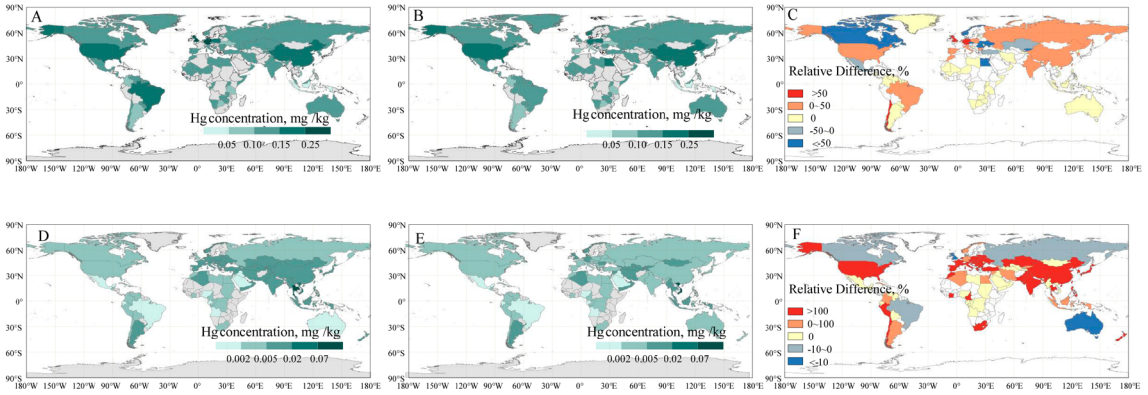

Figure 2. Map of mercury content in coal (panels A and B) and crude oil (panels D and E) produced (panels A and D) and consumed (panels B and E) in various countries. Relative differences between the two are shown in panels C and F.

assumed that 87% of mercury in petroleum was released into the atmosphere.[33,34]

*EF*s for Hg^0, Hg^{2+}, and Hg^p were obtained by multiplying mercury EFs by source-specific speciation fractions given for all 64 sources.[24]

Development of the Mercury Emission Inventory. Emissions of mercury were calculated by multiplying source strengths and EFs. The calculations were conducted for all grids to generate spatial distributions. Historical emissions were derived based on temporally varied fuel consumptions and EFs.

Uncertainty Analysis. Monte Carlo simulation was used to evaluate the overall uncertainty of the inventory. Variations in fuel consumptions, mercury content, and technology types were taken into account. The emissions were derived from iterative calculations up to 1000 times by randomly drawing all inputs from given distributions with known descriptive statistics. Log-normal distributions of fuel consumption were assumed and derived directly from the PKU-FUEL-2007.[18] For the fractions of various contributing technologies, uniform distributions with ranges listed in SI Table S3 were used. Mercury content in coal and petroleum were log-normally distributed, as further confirmed by the reported measurements in China (SI Figure S2).[24,26,35−37] The mean and standard deviations of the log-transformed mercury content were listed in SI Table S4. Mercury content in wastes were also assumed to follow a log-normal distribution. Release fraction and removal efficiency adopted for waste incineration sources and petroleum refineries were assumed to be uniformly distributed. In the absence of published data on their variations, the intervals of these parameters were assumed to be 20% of the mean. For other sources, EFs were taken from the literature and assumed to be uniformly distributed with the ranges also based on literature values. Interquartile ranges from the output of Monte Carlo simulation were derived as indicators of uncertainty.

RESULTS AND DISCUSSION

Influence of Global Fossil Fuel Trading on Mercury Content of Consumed Fuels. Content of mercury in coal and crude oil depend on the parent material.[38] The mercury contents of coal and crude oil produced in different countries differ widely (SI Figure S3). For example, the average mercury content of hard coal produced in various countries varies by a factor of 44, from 0.023 mg/kg for Indonesia to 1.005 mg/kg for Germany.[14]

Because of substantial international trade, the fossil fuels consumed in a given country are often not locally produced. For example, Australia and Indonesia produced 324 and 260 Tg coal, respectively, in 2007, and each exported 75% of this quantity.[13] In contrast, Japan consumed 187 Tg coal in 2007, and this was almost entirely imported.[13] International trade of crude oil is even more important in this respect. In 2007, the U.S. and China imported 534 and 163 Tg crude oil, respectively, accounting for over 68 and 47% of the national consumptions (782 and 345 Tg), respectively.[22] Globally, the total volumes of hard coal and crude oil traded accounted for 17.0 and 64.4% of total production, respectively.[13,22] Figure 1 shows trade volumes of hard coal and crude oil among various regions in 2007.

The mercury content of imported fossil fuels are usually very different from those produced in a given country. For example,

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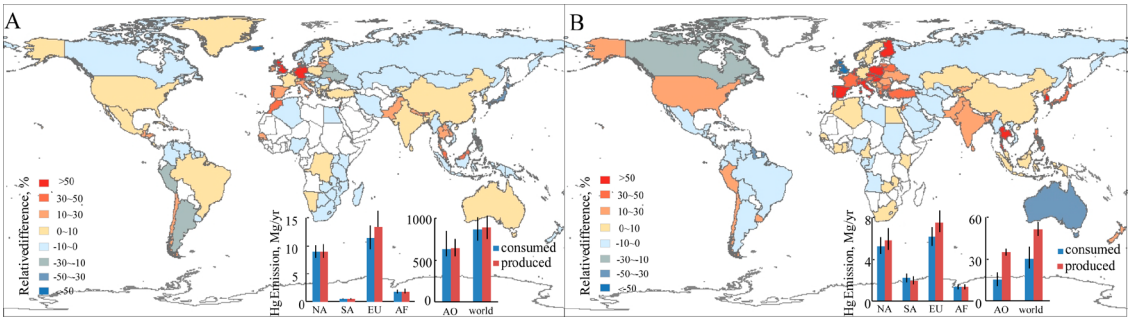

Figure 3. Differences in the calculated mercury emissions in individual countries between the two approaches based on mercury content in the locally produced or consumed coal (A) and crude oil (B). The positive values indicate the overestimation resulting from the erroneous use of mercury contents in the locally produced rather than consumed fuels.

European countries imported 55 and 50 Tg of hard coal from North/South America and Africa, respectively, in 2007.[13] The average mercury content of the imported coal were 0.20 (for America) and 0.10 (for Africa) mg/kg, compared with 0.28 mg/kg in the coal mined in Europe.[14] Consequently, the mercury content of the coal actually burned in Europe were much lower than that of locally mined coal. Similarly, the mercury content of crude oil produced in Norway (18 ng/kg)[39] is much higher than that produced in the UK (3.5 ng/kg)[39] and the export of crude oil from Norway to the UK accounts for 43% of the total UK consumption. This results in a significant increase in the mercury content of the crude oil consumed in the UK.[13] Moreover, developing countries tend to export fossil fuels to developed countries where emission abatement facilities are more efficient, thereby reducing global emissions. In fact, 57 and 56% of the imported hard coal and crude oil, respectively, used in developed countries were sourced from developing countries.[13,22] Figure 2 compares the national average mercury content in coal (panels A and B) and petroleum (panels D and E) between local production (panels A and D) and local consumption (panels B and E). Relative differences between these values, defined by the difference in mercury content between the produced and consumed fossil fuels divided by the quantities of those consumed, are depicted in panels C and F.

Accordingly, mercury content of locally consumed, rather than locally produced fossil fuels, should be used to calculate mercury emissions from various countries. Direct use of mercury content of locally produced fossil fuel will almost certainly lead to incorrect estimations and spatial biases in calculated emissions. Unfortunately, this is particularly true for mercury emission inventories estimated for many developing countries.[9,10] In fact, for other pollutants (such as sulfur dioxide), trading should also be taken into consideration if fuel compositions (such as sulfur) are used in emission calculations. In a recent study, fuel trading between provinces has been considered in an SO_2 emission inventory for China.[40]

Global Mercury Emissions from Fossil Fuel Combustion. Calculations of mercury emissions have been estimated using various factors. The calculations take into account the consumption of fossil fuels, the mercury content in the fuels consumed in individual countries, and the mercury removal efficiencies involved in combustion and other operations. Global total mercury emissions from fossil fuel consumption were calculated as 884 Mg (760−1055 Mg) in 2007, of which 854 (734−1019 Mg) and 29.9 Mg (25.7−35.7 Mg) arose from coal combustion and petroleum refineries, respectively.

Since mercury content of fossil fuels produced in major exporting countries (such as coal produced in Indonesia and Vietnam and petroleum produced in Iraq and Kuwait) are generally lower than the global averages, international trading has led to a reduction in the average mercury content of fossil fuels consumed in many countries. If the mercury content of fossil fuels produced in individual countries were used in the calculation, then the calculated emissions from coal combustion and petroleum refineries would be 894 (759−1056 Mg) and 51.7 Mg (44.8−60.1 Mg), corresponding to a 4.67 ($p > 0.05$) and 72.4% ($p < 0.05$) overestimation in emissions, respectively.

Figure 3 shows the differences in the calculated emissions using the two approaches in individual countries and positive values indicate the overestimation associated with using the mercury content in the locally produced instead of locally consumed coal (panel A) and petroleum (panel B). As can be seen, in addition to the overall overestimation of the global total emissions, the use of mercury content in locally produced fuels will also lead to a spatial bias. For six countries, including Malaysia, the overestimation of mercury emissions from coal combustion was >40%. For petroleum, there were 18 countries where the emission overestimation was >40%. The overall overestimation in Europe was 18%, largely because coal used there was mainly imported from Russia and Australia.[13] In these countries, the average mercury content of coal was 0.13 and 0.14 mg/kg, respectively, generally lower than those in coal produced in the importing countries.[14] Similarly, since mercury content of crude oil produced in major producers, including North Africa and the Middle East, are lower than those of oil produced in importing countries, overestimations would again result. These would be 12, 24, and 135% for North America, Europe, and Asia, respectively, if trading among countries were not taken into consideration. In contrast, emissions would be underestimated for South American countries (11%), since 12% of crude oil consumed originates from Europe and has relatively high mercury content.[13,14,39,41] Such spatial bias would surely have a significant influence on global transport modeling and health impact assessments.

Global Mercury Emission from All Combustion Sources. In addition to the results of anthropogenic fossil fuel consumption, atmospheric mercury can also arise from other combustion sources, including wildfires, biomass fuels, and solid wastes, for which no international trading is involved. With nonfossil fuel burning included, the estimated global total mercury emission from all combustion sources was 1454 (1232−1691) Mg in 2007, among which, the total emission from anthropogenic souces were 1040 Mg (886−1248 Mg). Hg^0, Hg^{2+}, and Hg^p emissions were 725, 548, and 181 Mg,

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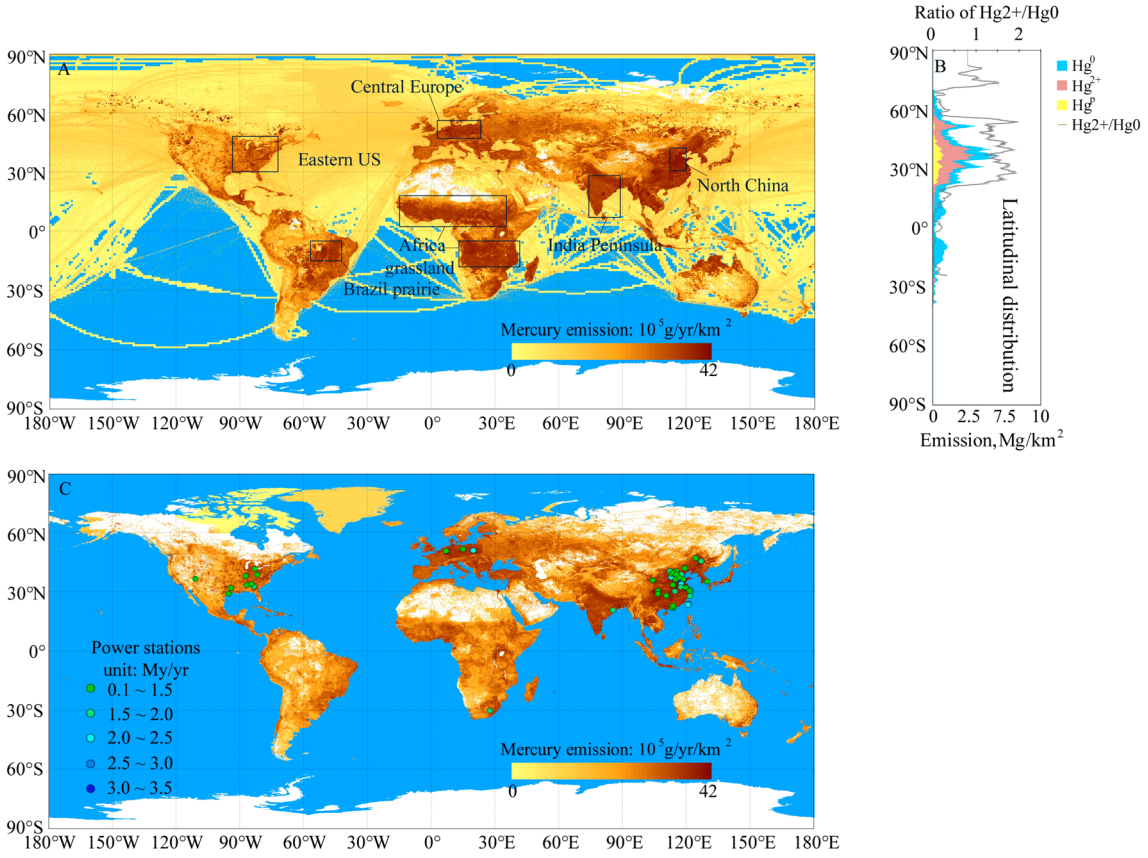

Figure 4. Geographical distributions of mercury emission densities at 0.1° × 0.1° resolution. (A) total emission from all combustion sources with six strong emission areas marked; (B) zonal average total emissions of the three species; and (C) emissions from anthropogenic combustion sources excluding shipping and aviation, with locations and emissions of top 50 mercury-emitting coal-fired power stations marked as colored circles.

respectively. SI Figure S4 shows the relative contributions of various sectors including power generation (610 Mg), industry (338 Mg), residential (97.1 Mg), transportation (3.28 Mg), agriculture (9.27 Mg), and wildfires (396 Mg). Contributions from various fuel types to various sectors differ greatly. Coal combustion dominates power generation (90%) and industry (80%) sectors, petroleum combustion dominates agriculture (84%) and transportation (99%) sectors, while biomass and coal contributes 38 and 62% of the residential and comercial sectors, respectively. Relative contributions of 64 detailed source types are provided in the SI (Table S7).

Our estimated total anthropogenic emission from stationary combustion sources in 2007 (899 Mg, 771−1071 Mg) was close to the values of 810 Mg reported by Pirrone[9] and 880 Mg presented by Pacyna[10] for the same sources in 2005. The inventories developed by these studies were based on the reported emission data from some countries, which provided reliable estimations of mercury emissions from fuels actually consumed. For countries without reported national emission data (mostly developing countries including major emitters, such as China and India), emissions were calculated based on the mercury content of the locally produced rather than the consumed fossil fuels or noncountry-specific EFs.[9,10] In the present study, however, emissions from fossil fuels for all countries were based on country-specific EFs, which were calculated based on mercury content in locally consumed fuels. Without relying on country-based emission reports, our inventory provides an independent estimate of global mercury emissions of combustion sources and can also facilitate historical emission analysis as long as fuel consumption data and trading information are available. For nonanthropogenic sources, our estimates (453 Mg, 396−516 Mg, for the 1997−2006 average) were lower than the 675 Mg reported elsewhere.[42] This was because of the use of the newly updated Global Fire Emission Database (version 3), in which wildfire burned biomass was lower than that previously estimated.[43]

The result of Monte Carlo simulation indicates that the relative uncertainty of our estimates for global emissions in 2007, defined as the interquartile range/M (median), is 32%, comparable with the uncertainty range for mercury emissions (25−30%) in other inventories.[9,10]

Geographic Distribution. With our spatially resolved fuel consumption map of detailed fuel types (PKU-FUEL-2007),[18] mercury emissions in individual countries are readily disaggregated into 0.1° × 0.1° grids globally. The improvement resulting from the use of the subnationally disaggregated fuel map on the spatial distribution of mercury emission is demonstrated in SI Figure S5. This shows significant differences in spatial distribution between the two inventories derived from nationally and subnationally disaggregated fuel databases, respectively, for 45 countries for which subnational data are available, indicating that the use of the subnational fuel data not only provides higher spatially resolved emission information, but also reduces spatial bias in population scaling.[18] Figure 4 shows the global distribution of mercury emission densities from all combustion sources (panel A), along with zonal average total emissions of the three species (panel B). Also included is a map of anthropogenic emission densities,

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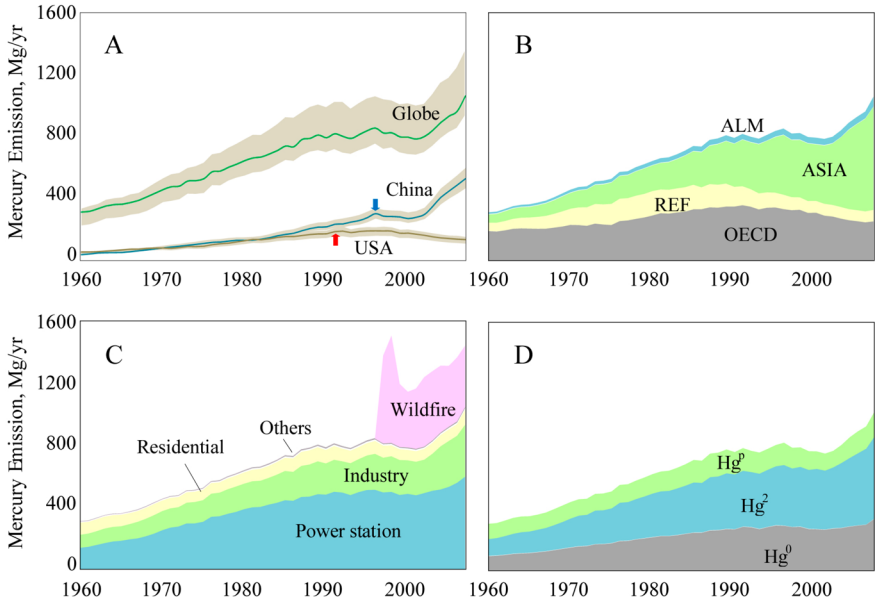

Figure 5. Temporal trends of mercury emissions from 1960 to 2007. (A) Emissions in China, the U.S., and the world total; (B) emissions from four country categories of OECD90 (all member countries of the Organization for Economic Cooperation and Development as of 1990), ASIA (all developing countries in Asia, excluding those in the Middle East), REF (countries undergoing economic reform including East and Central European countries and the Newly Independent States of the former Soviet Union), and ALM (the rest of the world, including developing countries in Africa, Latin America, and the Middle East); (C) emissions in five sectors; and (D) emissions of the three mercury species. Only anthropogenic sources are included in (A), (B), and (D). The results are presented as medians (curves) and interquartile range/M (median) (shaded areas) in (A). Two arrows in panel (A) mark the year when Flue Gas Desulfurization technology became available in developed (red) or developing (blue) countries.

excluding the emissions from the transportation sector (shipping and aviation) (panel C). The total emissions from the 50 coal-fired power plants with the highest mercury emissions contributed 7.3% of the total emission from all anthropogenic combustion sources in 2007. These significant sources are located mainly in Eastern China, Eastern and Central U.S., Germany, and Poland. Global distributions of emission densities for the three mercury species from all combustion sources are shown in SI Figure S6. Geographical distributions of the three mercury species were similar to one another with Hg^0 emission density being significantly higher than those of Hg^{2+} and Hg^P in the regions where emissions were dominated by wildfires. Spatial distributions of mercury emission densities for the six sectors and five major fuel categories are shown in SI Figure S7 and S8. Although the spatial bias caused by international trading of fossil fuels with different mercury content has been eliminated, similar biases arising from fossil fuel trading within countries, especially large countries, has not be taken into consideration, primarily because of the absence of detailed data on the mercury contents of locally consumed fuels.

Globally, there were six hot-spot regions of combustion-related mercury emission, including Eastern U.S., Western and Central Europe, the Indian Peninsula, North China, the Brazilian prairies, and the African grasslands. The latter two are strongly affected by wildfires, while the other four are areas with high population densities and concentrated anthropogenic activities, relying on coal as a major energy source.[11,44,45] In addition, the burning of municipal wastes in the U.S. and Canada made a significant contribution to the emissions in North America.[45] Although mercury migrates globally after emission, relatively high ambient concentrations are often found in high emission regions.[12] As a result of the spatial covariance between emission and population densities, 27% of the world's population lives in regions with emission densities exceeding 100 g/km^2/yr, which constitutes only 0.3% of global terrestrial land. Emissions in 2007 from Asia, Africa, North America, and Europe were 776, 225, 175, and 154 Mg, respectively. The top ten countries yielded 68.9% of the global total (SI Figure S9). All four major anthropogenic emission regions are in the Northern Hemisphere, between 20° N and 60° N, leading to the domination of emissions within this range. Hg^{2+} accounts for more than half of the total emissions within this range, because emissions are mainly from coal consumption and also, the conversion of Hg^0 to Hg^{2+} in pollution abatement.[46] The Hg^{2+} species is highly water-soluble, and its long-range transport potential is relatively weak.[16] Therefore, the global distribution of atmospheric mercury concentration can be affected by such a zonal distribution. This is consistent with the fact that global mercury deposition centers at northern- and midlatitudes.[47]

In 2007, global per capita mercury emission was 0.20 g, varying over 4 orders of magnitude per country. The extremely high or low values were those for very small countries and involve higher uncertainties. Per capita mercury emission in China (0.40 g) was much higher than that in India (0.07 g). This contrasts with many other air pollutants, such as polycyclic aromatic hydrocarbons and black carbon.[48,49] Unlike mercury, these products of incomplete combustion are mainly generated in residential stoves and per capita emissions in China and India are often similar.[48] The emission of mercury, similar to sulfur dioxide, depends largely on the quantity of coal consumed and the mercury content of the coals. The major sources are coal-fired power generation and industrial activities.[50] Regions with high per capita anthropogenic mercury emission densities were identified using gridded population densities for combustion sources (SI Figure S10).

Time Trends. Annual mercury emissions from all combustion sources in 222 countries were calculated for the period from 1960 to 2007 (data for wildfires are available only for 1997−2007) and results are shown in Figure 5. The temporal trends of the emissions in China, the U.S., and globally are shown in panel A. In panel B, temporal variations of mercury emissions are shown for four categories of countries: OECD90, ASIA, REF, and ALM[51] (for details on the countries, refer to the figure caption). Emissions from five sectors during this period are shown in panel C, and emission trends for the three mercury species are shown in panel D.

Globally, total annual anthropogenic mercury emissions increased from 242 to 1040 Mg during the 48-year period at an average annual increase of 3.0%. During this period, a peak of 836 Mg (704−981 Mg) was reached around 1995. The temporary decline after 1995 was the result of a sharp increase in energy prices[52] and the introduction of Flue Gas Desulfurization (FGD) technology in China.[53] It has been estimated that the introduction of FGD for coal boilers led to a 23.2 and 21.1% reduction in mercury emissions in developed and developing countries, respectively, within 5 years. The emissions started to increase again after 2002, owing to the rapid increase in energy demand in China. The annual emission growth rate during these years was as high as 9.8% in China, pushing the global level to a new high by 2007 (1040 Mg). Similar increasing trends and soaring coal consumption in Asia were also found to be major contributors to the increases observed.[54] Emissions in the U.S. passed peak values of 190 Mg in 1997 after a steady increase over several years. The U.S.'s first national standard, enforced in 2011, set technology-based emission limitations for mercury and other toxic air pollutants from coal- and oil-fired power plants.[55] This has certainly promoted the development of abatement technologies, and the adoption of mercury reduction facilities, a feature that will lead to a decreasing emissions trend in the future.

Temporal trends in mercury emissions for all OECD countries are similar to those of the U.S. Annual emissions have increased from 131 to 342 Mg from 1960 to 1995, pushed by a sharp increase in fuel consumption, but decreased to 248 Mg by 2007, because of a slowing of fuel consumption growth and higher mercury removal efficiency, achieved in the energy and industrial sectors. Emissions in ALM countries increased 6-fold from 1960 to 2007, and the largest emission increase of approximately 11 times occurred in Asian countries during this period. Owing to differences in the time trends among various countries, the spatial distribution of the mercury emissions from all anthropogenic sources has changed over time, as seen in SI Figure S11. In general, the emissions increased dramatically in East Asia, North America, and Africa, while they decreased in Europe where emissions dropped from 48% in 1960 to 13% in 2007. Meanwhile, contributions from Asia increased from 24 to 67%. Globally, power stations, particularly those that are coal-fired, comprise the dominant emission source. The total mercury emissions of coal-fired power plants have increased continuously from 106 Mg in 1960 to 537 Mg in 2007, contributing to 43.8 to 51.6% of the total anthropogenic sources. Emissions from industry have also increased 4-fold from 64.6 Mg in 1960 to 338 Mg in 2007. Meanwhile, emissions from residential sectors passed peak values in the late 1980s and have decreased, albeit at low rates. This is likely to be driven by the replacement of coal with natural gas and household stoves with centralized heating systems in the cities of developing countries, such as China, during the process of rapid urbanization.[52] For anthropogenic sources, emission of Hg^0 increased by 2.6 times from 95.7 to 344 Mg, emission of Hg^{2+} increased by 3.9 times from 111 to 548 Mg, and emission of Hg^p remained constant from 1960 to 2007. Relatively rapid increases in Hg^{2+} emissions during this period were primarily a result of the increase in the contribution of emissions from coal burning to the total emissions and to the further penetration of abatement facilities in coal combustion facilities, leading to the accelerated deposition of Hg near the emission sources.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Materials including determination of country- and temporal-specific EFs, emission contributions of sectors and fuel types, spatial difference of anthropogenic mercury emission using subnationally and nationally disaggregated fuel database, spatial emission distributions by mercury species, sectors, and fuel types, and other relevant information. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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