



# Global atmospheric emission inventory of polycyclic aromatic hydrocarbons (PAHs) for 2004

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## ABSTRACT

The global atmospheric emissions of the 16 polycyclic aromatic hydrocarbons (PAHs) listed as the US EPA priority pollutants were estimated using reported emission activity and emission factor data for the reference year 2004. A database for emission factors was compiled, and their geometric means and frequency distributions applied for emission calculation and uncertainty analysis, respectively. The results for 37 countries were compared with other PAH emission inventories. It was estimated that the total global atmospheric emission of these 16 PAHs in 2004 was 520 giga grams per year ( $\text{Gg y}^{-1}$ ) with biofuel (56.7%), wildfire (17.0%) and consumer product usage (6.9%) as the major sources, and China ( $114 \text{ Gg y}^{-1}$ ), India ( $90 \text{ Gg y}^{-1}$ ) and United States ( $32 \text{ Gg y}^{-1}$ ) were the top three countries with the highest PAH emissions. The PAH sources in the individual countries varied remarkably. For example, biofuel burning was the dominant PAH source in India, wildfire emissions were the dominant PAH source in Brazil, while consumer products were the major PAH emission source in the United States. In China, in addition to biomass combustion, coke ovens were a significant source of PAHs. Globally, benzo(a)pyrene accounted for 0.05% to 2.08% of the total PAH emission, with developing countries accounting for the higher percentages. The PAH emission density varied dramatically from  $0.0013 \text{ kg km}^{-2} \text{ y}$  in the Falkland Islands to  $360 \text{ kg km}^{-2} \text{ y}$  in Singapore with a global mean value of  $3.98 \text{ kg km}^{-2} \text{ y}$ . The atmospheric emission of PAHs was positively correlated to the country's gross domestic product and negatively correlated with average income. Finally, a linear bivariate regression model was developed to explain the global PAH emission data.

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## 1. Introduction

Although polycyclic aromatic hydrocarbons (PAHs) are not among the 'dirty dozen' of the Stockholm convention on Persistent Organic Pollutants, they were included in the Convention on Long-range Transboundary Air Pollution Protocol on Persistent Organic Pollutants (United Nations Economic Commission, [http://www.uncece.org/env/lrtap/pops\\_h1.htm](http://www.uncece.org/env/lrtap/pops_h1.htm)) and their toxic effects on both human and ecosystem health are well documented. Human exposure to PAHs has been widely associated with elevated levels of DNA adducts and mutations and also with reproductive defects (Gaspari et al., 2003; Perera et al., 2002). PAH exposure can also cause mutagenic and carcinogenic effects on marine invertebrates, fish and amphibians (Neff, 1978). A recent study suggests that PAHs can inhibit growth of diatoms and may even affect the global carbon cycle (Bopp and Lettieri, 2007). As an important component of indoor air, due to household combustion of solid fuels, PAHs have partially caused higher levels of risk for lung cancer, especially in

developing countries (Straif et al., 2006). Dispersion model results suggest that the benzo(a)pyrene equivalent concentration in ambient air in the urban area of Tianjin, China exceeded national standards (Tao et al., 2006). High levels of ambient atmospheric PAHs were also observed in India, Mexico and other developing countries and posed significant health risk there (Sharma et al., 2007; Marr et al., 2004). In addition to localized risk, PAHs can disperse regionally and intercontinentally through atmospheric long-range transport. For example, PAHs emitted from Russia influence the atmosphere PAH concentrations in the Arctic and PAHs from East Asia are transported to the west coast of the United States under certain meteorological conditions (Becker et al., 2006; Killin et al., 2003; Primbs et al., 2008).

The majority of PAHs in the environment come from incomplete combustion of carbonaceous materials during energy and industrial production processes. Natural processes, such as forest fires and volcanic eruptions, also produce PAHs (Xu et al., 2006; Baek et al., 1991). The major anthropogenic atmospheric emission sources of PAHs include biomass burning, coal and petroleum combustion, and coke and metal production (Baek et al., 1991; Zhang and Tao, 2008). As the efficiency of energy utilization has improved, emissions of PAHs in developed countries have decreased significantly in

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the past decades (Pacyna et al., 2003). However, PAH deposition on the Greenland icesheet indicates that global PAH emissions have been constant from the beginning of the industrial period up to the early 1990s (Masclat et al., 1995), suggesting that PAH emissions from developing countries have been increasing due to rapid population growth and the associated energy demand. Because of this close relationship between PAH emissions and energy consumption, a strong correlation is anticipated between PAH emissions and some social and economic parameters. Moreover, a strong correlation exists between atmospheric PAH concentrations and population (Hafner et al., 2005).

PAH emission inventories have been developed for several countries (the US and UK) and regions (the former USSR, Europe, and North America) and are listed in the Supporting information (Pacyna et al., 2003; Tsubulsky et al., 2001; US EPA, 1998; Wenborn et al., 1999; Galarneau et al., 2007; Van der Gon et al., 2007). China has the only PAH emission inventory for a developing country, with km<sup>2</sup> resolution and dynamic PAH emission changes from 1950 to 2004 (Zhang and Tao, 2008).

The aim of this study was to develop a global PAH emission inventory for 2004 and examine the relationship between PAH emissions and social-economic parameters in various countries. Such an inventory can provide necessary information for modeling PAH dispersion and atmospheric long-range transport, addressing PAH fate in the environment, and assessing the potential risk PAHs impose on humans and ecosystems.

## 2. Methodology

### 2.1. Emission inventory

The sixteen PAHs studied are listed by the US EPA as priority pollutants and include naphthalene (NAP), acenaphthylene (ACY), acenaphthene (ACE), fluorene (FLO), phenanthrene (PHE), anthracene (ANT), fluoranthene (FLA), pyrene (PYR), benz(a)anthracene (BaA), chrysene (CHR), benzo(b)fluoranthene (BbF), benzo(k)-fluoranthene (BkF), benzo(a)pyrene (BaP), dibenz(a,h)anthracene (DahA), indeno(1,2,3-cd)pyrene (IcdP) and benzo(g,h,i)perylene (BghiP). The atmospheric emission of each individual PAH from each emission source was calculated by country based on emission activities and factors, similar to the procedure used for developing the Chinese PAH emission inventory (Xu et al., 2006). The sum of the sixteen PAHs is denoted as PAH16. ARCGIS 9.0 was used for emission mapping (ESRI, Inc., CA, USA).

Monte Carlo simulation, based on the probability of distribution strengths of various emission sources and emission factors, was used to address the uncertainties in the inventory (Xu et al., 2006). The uncertainty was quantified using the semi-interquartile range ( $R_{sq}$ , half difference between the first and the third quartiles) and compared using the relative variation index (RVI, the quotient of  $R_{sq}$  divided by the median). Based on the results of the Monte Carlo simulation, the influence of the emission factors and emission activity strength were addressed separately. The uncertainty was also traced back to individual emission sources.

### 2.2. Emission activities

The consumption and transformation of coal, petroleum and biofuel in various sectors (industry, residential, transport, etc.) of 135 countries were collected from the statistical database of the International Energy Agency (2006a,b). The fossil fuels were further classified into subcategories including anthracite, bituminous, lignite and peat for coal and gasoline, diesel and kerosene for petroleum. The biofuel was reported as a single type of primary solid biomass. The percentages of straw, firewood and animal dung consumptions in residential sectors were derived based on the statistics provided by

Food and Agriculture Organization of the United Nations (UN FAO, <http://www.fao.org>). Crop production data inform 2004 was used to calculate the proportions of various kinds of straw burned indoors (UN FAO). The biomass burned in forest and savanna fires in 2004 was directly derived from the Global Fire Emission Database (Giglio et al., 2006). Other data collected from the literature included open-fire straw burning, metal production, coke production, iron production, airplane production and cigarette smoking (International Energy Agency, 2006a,b; Bond et al., 2004; Nonferrous Metals Industry Institute, 2005; Editorial Board for the Yearbook of Iron and Steel Industry in China, 2005; Editorial Board for the Yearbook of Aerospace Industry in China, 1999; NationMaster, <http://www.nationmaster.com/graph>; International Aluminium Institute, <http://www.world-aluminium.org>). The quantity of wood for non-energy use was also from the UN FAO and it was assumed that 1% and 0.1% of the wood were treated with creosote in developed and developing countries, respectively.

### 2.3. Emission factors and other data

An emission factor database for the atmospheric emissions of PAHs on a global scale was developed based on a PAH emission inventory for China (Zhang and Tao, 2008). However, new emission factors were developed for residential burning of animal dung cake, wood treatment, secondary metal production, waste incineration, iron sintering, aerospace industry and cigarette smoking based on the literature and as much data as possible was gathered to establish the statistical distributions of the emission factors. The geometric means of the distributions were used to develop the inventory and the distributions were used for uncertainty analysis. Due to the large differences in fuel sources, combustion facilities and other technical conditions, the emission factors varied dramatically among regions and countries. This is particularly true for industrial processes such as coke production and aluminum electrolysis. However, the reported data in the literature was not sufficient for compiling an emission factor database for each individual country. This data gap in the emission factors was the major limitation of this inventory. To compensate for this data gap to a certain extent, several assumptions were made for different country categories and, in some cases, proxy data were also used. For example, coke production was divided into large-scale and small-scale (indigenous) coke ovens (Bond et al., 2004). The ratio of small-scale coke ovens to the total number of coke ovens was assumed to be 0.001 for the United States, Japan and European countries and 0.01 for all other countries except China and India. China and India were assumed to be 0.15 and 0.05, respectively (Zhang and Tao, 2008; Bond et al., 2004). This resulted in a variation in the PAH emission factors for coke production of about one order of magnitude between the developed and developing countries. The atmospheric emission of PAHs from consumer product usage (including personal care products, household products, automotive after market products, adhesives and sealants, FIFRA-regulated products, and coatings) was calculated by population and per-capita emission factors for the various countries were estimated in proportion to household consumption expenditures (Zhang and Tao, 2008). Other socioeconomic data used in the study included population, gross domestic product (GDP), land area, household consumption expenditure and average income and were obtained from the World Bank website (<http://www.worldbank.org>).

## 3. Results and discussion

### 3.1. Global PAH emission inventory

The total global atmospheric emissions of PAH16 in 2004 were estimated to be 520 Gg y<sup>-1</sup> and a full list of the emissions from

individual countries in 2004 is presented in the [Supporting information](#) along with socioeconomic parameters including area, population and GDP. The annual PAH emission from Asian countries was  $290 \text{ Gg y}^{-1}$ , contributing 55% of the global total. China and India were the top two PAH emitting countries, emitting  $114 \text{ Gg y}^{-1}$  and  $90 \text{ Gg y}^{-1}$ , respectively. The PAH emissions from Africa, North America, Europe, South America and Oceania contributed 18.8%, 8.0%, 9.5%, 6.0% and 1.5% of the total global PAH emissions, respectively. The United States was the third largest emitter of PAHs at  $32 \text{ Gg y}^{-1}$ . The PAH emissions from Nigeria, Indonesia, Brazil, Pakistan, Democratic Republic of the Congo and Russia ranked 4th to 9th on a global basis and the total PAH emissions from the top nine countries accounted for over 60% of the global PAH emissions in 2004.

The calculated PAH emission rates from the United States, the United Kingdom, the former USSR countries and a number of European countries were compared with those reported in the literature in [Fig. 1](#) ([Pacyna et al., 2003](#); [Tsubulsky et al., 2001](#); [US EPA, 1998](#); [Wenborn et al., 1999](#); [Van der Gon et al., 2007](#)). For the United States and the United Kingdom, the emissions of PAH16 from various sources were compared individually. However, the emissions of 4 PAHs (BaP, BbF, BkF, and IcdP) from 36 European countries and 6 PAHs (BaP, BbF, BkF, BghiP, FLA, and IcdP) from 10 former USSR countries could only be compared because of more limited data.

In general, most data points in [Fig. 1](#) fall around the 1:1 line, suggesting that the estimated emission rates for these countries agree generally well with the previous inventories with only a few exceptions. The US EPA developed an emission inventory and estimated the total emission of PAH16 at  $26.5 \text{ Gg y}^{-1}$  in 1990 ([US EPA, 1998](#)) which is lower than the  $32.1 \text{ Gg y}^{-1}$  that we estimated in 2004. This difference could be due to the significant differences in the emission factors adopted for waste incineration and vehicle combustion of petroleum. Although country specific emission factors may be more accurate, the information available does not support this approach. In addition, the US EPA inventory often does not have emission factors for individual PAH. For instance, emission factors for the incineration of municipal, hazardous, sewage sludge and medical waste were only available for NAP; BaP, DahA, IcdP, BghiP, ANT, FLA, FLO, PHE, and PYR; all 16 PAHs except for DahA; and NAP in the US EPA inventory ([US EPA, 1998](#)). We filled this data gap with a thorough review of the most recent literature. Also, emission factors may change over time and this might account for such differences. Because of the limited data in the literature, we have no way to estimate the temporal variation in the emission factors.

In addition, our incineration, aluminum electrolysis and industrial coal combustion emission rates were significantly different from the UK inventory, primarily due to differences in emission

factors. Our emission factor for aluminum electrolysis was much lower than the one used in the UK inventory because emissions from aluminum electrolysis have dropped significantly since the mid 1990s due to strict emission control regulations ([Wenborn et al., 1999](#)). A detailed discussion of the differences in emission factors between our inventory and previously published inventories can be found in the [Supporting information](#).

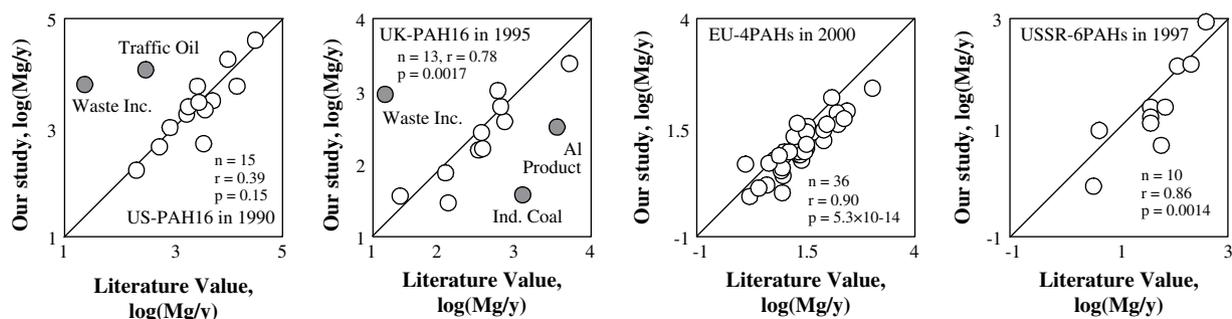
For the emission of 4 PAHs (BaP, BbF, BkF, and IcdP) from European countries, van der Gon et al. estimated a total emission of  $3.11 \text{ Gg y}^{-1}$  in 2000. Considering the significant trend in decreasing PAH emissions from European countries in recent decades ([Pacyna et al., 2003](#)), it is reasonable that the PAH emissions might have dropped to  $1.01 \text{ Gg y}^{-1}$  in 2004. On the other hand, the emission rate of 6 Borneff PAHs (BaP, BbF, BkF, BghiP, FLA, and IcdP) in 10 former USSR countries was estimated to be  $1.21 \text{ Gg y}^{-1}$  in 2004. This is slightly higher than Tsubulsky's estimate of  $1.02 \text{ Gg y}^{-1}$  ([Tsubulsky et al., 2001](#)) and may be due to recent economic recovery and increased energy consumptions in these countries (The World Bank, <http://www.worldbank.org>).

The Monte Carlo simulation results indicated that the uncertainties were relatively high. These results are provided in the [Supporting information](#). The calculated RVIs for the emission factors (16.1%) were significantly higher than the activity strength (5.41%), implying that emission factors were the main source of uncertainty in our global PAH inventory.

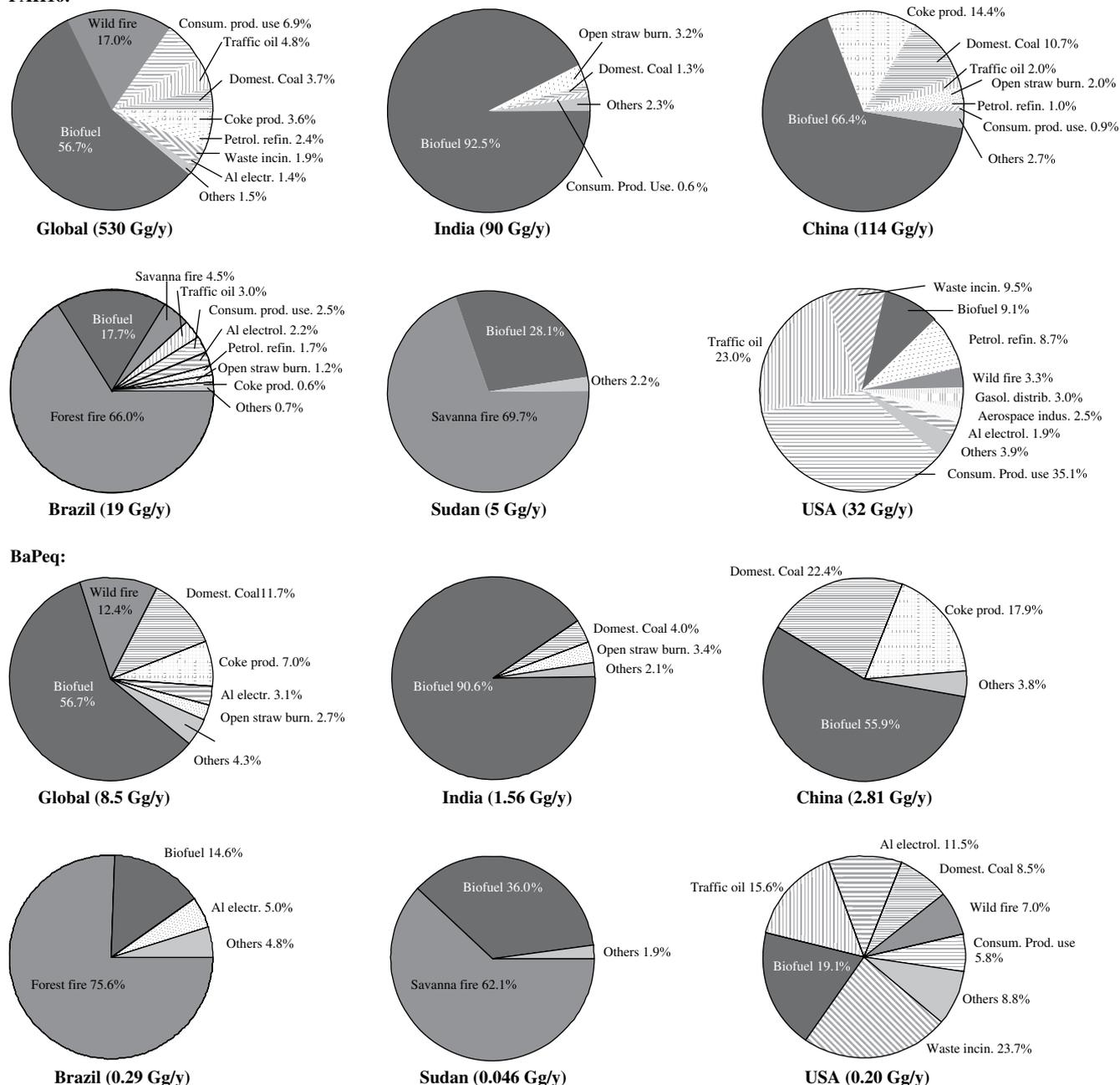
### 3.2. Major emission sources

[Fig. 2](#) shows the relative contributions of various combustion sources to the atmospheric emission of PAH16 on a global basis and for several representative countries. The emissions are also shown on a BaPeq basis. Globally, biomass burning, including both biofuel combustion and wildfires, dominated the PAH emission sources with contributions of 56.7% and 17.0% of the total global PAH emissions, respectively. Other important global PAH sources included consumer products, traffic oil combustion and domestic coal combustion which contributed 6.9%, 4.8% and 3.7%, respectively. The major industrial activities contributed less than 10% to the total global PAH emissions, with coke production contributing the most (3.6%).

The relative contribution of different PAH sources in the different countries depended on the energy structure, status of development, population density and vegetation cover of the country ([Fig. 2](#)). For example, in India, biofuel accounted for over 90% of the total PAH emissions because the country relies heavily on firewood, straw, animal dung and petroleum for domestic energy, while PAH emissions from petroleum combustion were much lower than biomass burning. In 2004, biofuel and petroleum products accounted for 82.6% and 11.5% of the total energy



**Fig. 1.** Comparison of the emission rates between our estimation and the literature reported values. From left to right: PAH16 from individual sources in the United States (US), PAH16 from individual sources in United Kingdom (UK), 4 PAHs (BaP, BbF, BkF, and IcdP) from all sources in 36 European countries (EU) and 6 PAHs (BaP, BbF, BkF, BghiP, FLA, and IcdP) from all sources in 10 former USSR countries, respectively. The 1:1 lines are also shown in these figures.

**PAH16:**

**Fig. 2.** Relative contributions of various sources to PAH16 and BaPeq emission in the world for representative countries including China, India, the United States, Brazil and Sudan, the corresponding total atmospheric emissions of PAH16 and BaPeq in 2004 are given in the parentheses.

consumption in India (International Energy Agency, 2006a), but 97.32% and 0.017% of PAH emissions in the domestic sector. Because of rich reserves, coal is extensively used in China for coke production and domestic cooking and heating (International Energy Agency, 2006a). In 2004, coal combustion accounted for 60% of the energy consumption in China (International Energy Agency, 2006a). Although biomass ranks first in PAH emission sources in China, its relative contribution was 66.4% which is significantly lower than in India. The coke industry and domestic coal combustion ranked second and third among PAH emission sources in China. According to a highly resolved emission inventory in China, the PAH emissions from the coke industry were predominately from small-scale coke ovens run by local farmers adjacent to coal mines (Zhang and Tao, 2008). Fortunately, these small-scale

coke ovens are being phased out in China under the newly issued Coal Law (Law of the People's Republic of China on the Coal Industry, 2001). In Brazil and Sudan, forest fires and savanna fires surpassed biofuel sources in PAH emissions due to the relatively high vegetation cover and low population density of these countries. With approximately one-third of the global tropical rain forest, 116,574 fire events were observed in the Amazon region and the burned biomass was as high as 550 Tg in 2004 (Giglio et al., 2006; Cristina, 2007). Savanna fires were also very serious in many Africa countries including Sudan, Angola, and Central Africa Republic where savanna coverage is high and other combustion activities were relatively low (Giglio et al., 2006). Similar to other developed countries, consumer product use and traffic oil combustion were the major PAH emission sources in the United

States, followed by waste incineration (9.5%), biofuel combustion (9.1%) and petroleum refining (8.7%). The PAH source profiles of other countries were similar to the representative countries shown in Fig. 2.

The global PAH source profile on a BaPeq (BaP toxic equivalent quality) emission basis and for the representative countries is also shown in Fig. 2. Biomass burning, including biofuel combustion (56.7%) and wildfires (12.4%), and coal related sources, including domestic coal combustion (11.7%) and coke production (7.0%), were still the most important global sources on a BaPeq basis. However, the contribution of consumer products on a BaPeq basis decreased dramatically to only 0.4%. Therefore, the PAH source profiles on a total PAH and BaPeq basis were very similar for countries where biomass and coal related sources were the dominant PAH sources, such as in China, India, Brazil and Sudan. However, developed countries, such as the United States, had much smaller contributions from consumer products on a BaPeq basis (5.8%) compared to a total PAH basis (35.1%). This is because the PAHs emitted by consumer products are primarily comprised of lower molecular weight ones which are less toxic.

The Monte Carlo simulation results for individual PAH sources are presented in Fig. 3 as median and semi-interquartile ranges of PAH16 emissions from various sources. Relatively high uncertainties were associated with emissions from aluminum electrolysis with pre-baked anode, non-transportation petroleum, industrial coal, and gasoline and kerosene consumption in transportation with calculated RVI values of 314%, 228%, 161%, 173% and 179%, respectively. This is likely due to relatively high variations in the emission factors for these sources. The uncertainty of the inventory would be reduced substantially if the emission factors for these sources were better characterized.

### 3.3. Composition of the PAH emission inventory

The individual PAH composition of the emission inventory and the various source emissions are shown in a stacked bar chart in Fig. 4. The industrial sources, which contributed a relatively small fraction of the total emission, were pooled together for simplicity. Approximately 50% of the global PAH emissions were NAP and another 38% were lower molecular weight (LMW), including 2–3 ring compounds (from ACY to FLA). In contrast, higher molecular weight (HMW) PAHs, with 5–6 rings (from BbF to BghiP), accounted for only 2.4% of the global PAH emission, although these PAHs are far more hazardous to human health (Safe, 1998). The PAH composition of the different source emissions was significantly different in the proportion of LMW and HMW PAHs produced. For

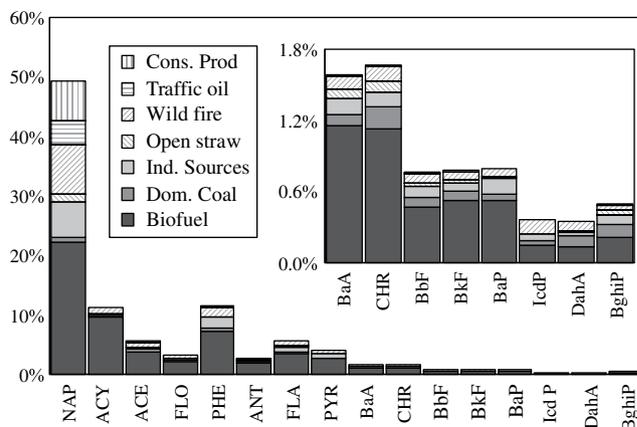


Fig. 4. Global PAH composition profiles for various emission sources.

example, biomass burning, including biofuel usage, open-fire straw burning and wildfire, produced a relatively high proportion of HMW PAHs (3.5% on average), while the PAH emission from consumer products was only NAP. Therefore, the PAH composition differences in sources and their emission volume combine to impact the human health risk due to PAH exposure in different countries.

The proportion of HMW PAH emissions from India (3.60%) and China (5.75%) was significant higher than the global average. In addition, a significant portion of the PAH emissions in these countries is from household biomass and coal combustion, resulting in high indoor exposure and increased health risk. Although Brazil has a relatively high proportion of HMW PAH emissions (3.43%) due to biomass burning, the risk to human health is likely lower than in India and China because HMW PAH emissions in Brazil were mainly due to fires in forest or savanna areas with low population densities. In order to characterize the PAH emission profile in terms of human health impact, the ratio of BaPeq to PAH16 was calculated for each country. The ratio ranged from 0.18% to 3.58%, Bosnia and Herzegovina (3.58%), North Korea (3.42%), Mauritania (3.08%), and Kiribati (3.08%) had the highest percentages and Singapore (0.18%), Trinidad and Tobago (0.21%), Kuwait (0.24%), and Netherlands Antilles (0.26%) had the lowest percentages. The PAH16 emissions from the four countries with highest BaPeq to PAH16 ratio were dominated either by domestic non-anthracite coal combustion (53.19% and 54.58% for the first two, respectively) or indoor wheat straw combustion (more than 90% for Mauritania and Kiribati). Both of these sources have

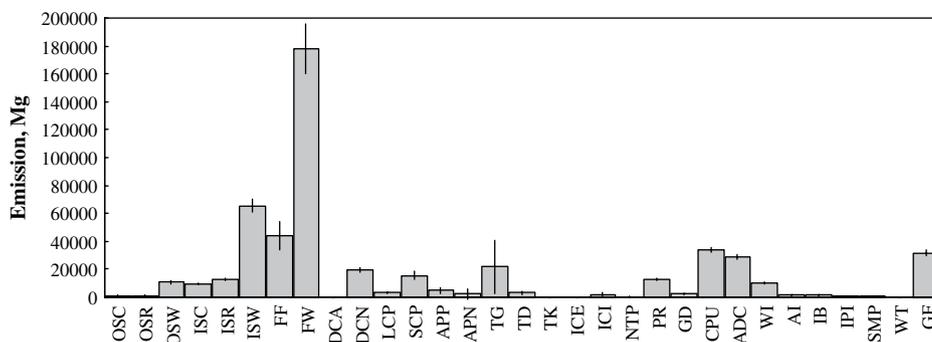


Fig. 3. Median and semi-interquartile ranges of global PAH16 emissions from various sources derived from Monte Carlo simulation. The emission sources (from left to right) are: OSC, OSR and OSW: open-fire burning of corn, rice, and wheat straws; ISC, ISR, and ISW: indoor burning of corn, rice, and wheat straws; FF, FW: forest fire and firewood burning; DCA, DCN: domestic combustion of anthracite and non-anthracite coal; LCP, SCP: large and small-scale coke production; APP, APN: primary aluminum production with pre-baked anode or not; TG, TD, and TK: traffic gasoline, diesel and kerosene; ICE, ICI: industrial coal for electricity generation utilities or others; NTP: petroleum combusted in non-transport sectors; PR: petroleum refinery; GD: gasoline distribution; CPU: consumer products usage; ADC: animal dung combustion; WI: waste incineration; AI: aerospace industry; IB: industrial biomass burning; IPI: iron production industry; SMP: secondary metal production; WT: wood treatment; GF: grassland fire.

a relatively high BaPeq proportion in their emission profiles. On the other hand, the four countries with the lowest BaPeq to PAH16 ratio were all developed countries and their PAH emissions were dominated by petroleum combustion and consumer products. Both of these sources have a relatively low BaPeq proportion in their emission profiles. The PAH emission profiles and the BaPeq/PAH16 ratios for all countries are provided in the [Supporting information](#).

#### 3.4. Geographic distribution of the PAH emission

The annual atmospheric emission densities of PAH16 were calculated for all countries based on the total PAH emissions and country area (Fig. 5). In addition, the geographic distribution of PAH16 emissions per capita and per GDP, total PAH16 emission and their PAH emissions on a BaPeq basis are also shown in this figure. The average global emission density was  $3.98 \text{ kg km}^{-2} \text{ y}$ , ranging from  $0.0013 \text{ kg km}^{-2} \text{ y}$  in the Falkland Islands to  $360 \text{ kg km}^{-2} \text{ y}$  in Singapore in 2004. In addition to having the highest PAH emissions in the world, India and China also had PAH emission densities that were significantly higher than the global average at  $30.2 \text{ kg km}^{-2} \text{ y}$  and  $12.2 \text{ kg km}^{-2} \text{ y}$ , respectively. Countries with the highest emission densities had relatively small sizes but high population densities including, Singapore ( $360 \text{ kg km}^{-2} \text{ y}$ ), Bahrain ( $320 \text{ kg km}^{-2} \text{ y}$ ) and Gibraltar ( $180 \text{ kg km}^{-2} \text{ y}$ ). In general, the PAH emission densities in East and South Asia, West Europe and central Africa were higher than other regions, while the former USSR countries, Mongolia, Australia, Canada, Greenland, North Africa countries and Argentina were among the lowest. When it comes to the per-capita PAH emission, developed countries in North America, Europe and Australia showed significant high per-capita emission for their high PAH emission from consumer product usage. In addition, some south American countries including Brazil and Bolivia, and African countries also showed high per-capita emission due to their high contributions from wildfires. Although the ratios of BaPeq to PAH16 varied dramatically among different countries, the spatial distributions of them seem very similar with each other. Actually, a significant positive correlation existed between them ( $n = 229$ ,  $p = 2.61 \times 10^{-139}$ ).

Similar to the total PAH emission density, individual PAH source emission densities can also be mapped. The maps of the PAH emission from several representative sources, including biofuel burning, consumer products, and wildfires, are provided in the [Supporting information](#). In general, high emission density from biofuel combustion occurred in Asia and Africa, particularly in China, India, Indonesia, and Nigeria, followed by west European countries with higher population densities such as France and Germany. For the PAH emission from consumer products, the emission densities were generally high in developed countries, particularly in the United States and Western Europe. Finally, the spatial distribution of wildfire emissions followed the pattern of vegetation coverage, with high emission density in South America, South and Central Africa and Southeast Asia.

These results suggest that the atmospheric emission of PAHs in a country depends largely on the socioeconomic status of the country. Fig. 6(A) shows the relationship between the total PAH emission of PAH16 and GDP for all countries in 2004. Globally, there is a positive correlation between the log-transformed annual country PAH emission rate ( $\log E$ ) and the country's Gross Domestic Product ( $\log \text{GDP}$ ), with a Pearson correlation coefficient of 0.808 ( $p < 10^{-53}$ ,  $n = 222$ ). The positive correlation is reasonable given that GDP is related to energy consumption, and energy consumption is associated with PAH emissions. However, energy consumption and the efficiency of energy utilization are different among the different countries (International Energy Agency, 2006a,b). For example, the efficiency of energy utilization in China, Japan and the

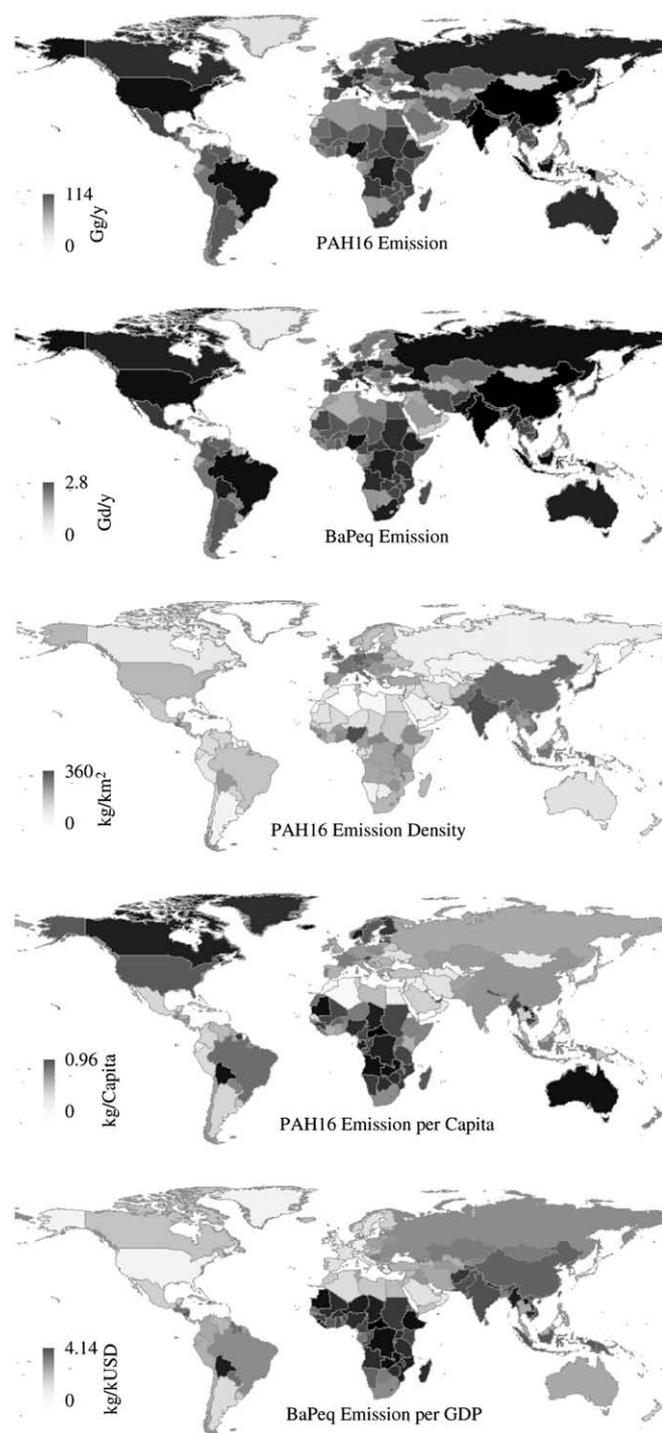


Fig. 5. Geographical distribution of PAH16 total emission, BaPeq total emission, emission density, per-capita PAH16 emission and PAH16 emission per GDP in the world in 2004.

United States is  $1.12 \times 10^{-3}$ ,  $1.06 \times 10^{-4}$  and  $2.15 \times 10^{-4}$  ton of oil equivalent per US dollar ( $\text{toe USD}^{-1}$ ), respectively, with at least an order of magnitude difference between the countries (International Energy Agency, 2006a,b). According to the International Energy Agency, the average total primary energy supplies in 2004 were  $1.5 \times 10^{-3}$ ,  $8.2 \times 10^{-4}$ ,  $6.2 \times 10^{-4}$  and  $3.5 \times 10^{-4}$   $\text{toe USD}^{-1}$  for low, lower middle, upper middle and high income countries, respectively (International Energy Agency, 2006a,b). In fact, the majority of developed countries, as defined by World Bank (grey points), are

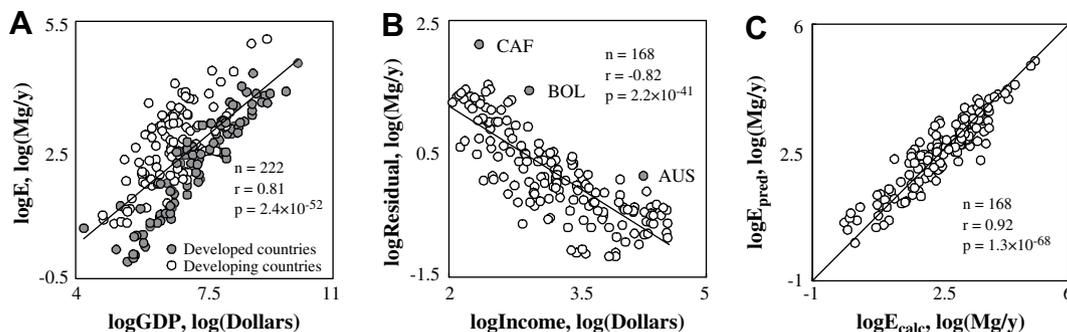


Fig. 6. Relationship between the log-transformed PAH16 emission ( $\log E$ ) and GDP ( $\log GDP$ ) of various countries in 2004 (A), plot of  $\log E$ - $\log GDP$  regression residuals against average income both log-transformed (B); and comparison between the bivariate regression model predicted ( $\log E_{pred}$ ) and inventory calculated ( $\log E_{calc}$ ) emissions (C).

below the regression line in Fig. 6(A), while emissions from developing countries (white points) are underestimated by the linear regression based on all of the global data. The residuals of the regression between  $\log GDP$  and  $\log E$  were calculated and are plotted against average income in Fig. 6(B). A negative correlation was revealed with countries with large wildfire emissions as outliers, including Central Africa Republic (CAR), Bolivia (BOL), and Australia (AUS). Accordingly, the emission of PAH16 can be predicted using a linear bivariate regression model with GDP and average income (Income) as the two independent variables:

$$\log E = 1.016 \log GDP - 0.961 \log Income - 4.582, \quad r^2 = 0.843, \quad n = 168,$$

where  $E$  and Income are total emission of 16 PAHs in  $Gg y^{-1}$  and average income in  $USD y^{-1}$ , respectively. The model predicted PAH emission is plotted against the PAH emission from the emission inventory in Fig. 6(C). The good correlation suggests that the model can predict the PAH emissions well. A number of other variables, including vegetation coverage and population were also found to be significantly correlated with total PAH emission (with  $p$  values of  $6.14 \times 10^{-8}$  and  $3.14 \times 10^{-182}$ , respectively,  $n = 229$ ). However, when these variables were tested as the third independent variable in the regression, they did not improve the prediction power of the model significantly.

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## Appendix. Supporting information

Following materials are provided in the supporting information: lists of emission inventories developed for developed countries; emission factors applied in this study; emission from individual countries in 2004; A detailed comparison of emission factors used by our study and other studies; The uncertainty of all sources originated from emission factors only, emission activities only, and from both; The BaP<sub>eq</sub> value for the emission from all the countries; The emission maps for major sources, including biofuel burning, consumer products usage and wildfires. Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.atmosenv.2008.10.050.

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