



Published in final edited form as:

*Environ Sci Technol.* 2013 June 18; 47(12): 6415–6424. doi:10.1021/es400857z.

## Global atmospheric emissions of polycyclic aromatic hydrocarbons from 1960 to 2008 and future predictions

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### Abstract

Global atmospheric emissions of 16 polycyclic aromatic hydrocarbons (PAHs) from 69 major sources were estimated for a period from 1960 to 2030. Regression models and a technology split method were used to estimate country and time specific emission factors, resulting in a new estimate of PAH emission factor variation among different countries and over time. PAH emissions in 2007 were spatially resolved to  $0.1^\circ \times 0.1^\circ$  grids based on a newly developed global high-resolution fuel combustion inventory (PKU-FUEL-2007). The global total annual atmospheric emission of 16 PAHs in 2007 was 504 Gg (331–818 Gg, as interquartile range), with residential/commercial biomass burning (60.5%), open-field biomass burning (agricultural waste burning, deforestation, and wildfire, 13.6%), and petroleum consumption by on-road motor vehicles (12.8%) as the major sources. South (87 Gg), East (111 Gg), and Southeast Asia (52 Gg) were the regions with the highest PAH emission densities, contributing half of the global total PAH emissions. Among the global total PAH emissions, 6.19% of the emissions were in the form of high molecular weight carcinogenic compounds and the percentage of the carcinogenic PAHs was higher in developing countries (6.22%) than in developed countries (5.73%), due to the differences in energy structures and the disparities of technology. The potential health impact of the PAH emissions was greatest in the parts of the world with high anthropogenic PAH emissions, because of the overlap of the high emissions and high population densities. Global total PAH emissions peaked at 592 Gg in 1995 and declined gradually to 499 Gg in 2008. Total PAH emissions from developed countries peaked at 122 Gg in the early 1970s and decreased to 38 Gg in 2008. Simulation of PAH emissions from 2009 to 2030 revealed that PAH emissions in developed and developing countries would decrease by 46–71% and 48–64%, respectively, based on the six IPCC SRES scenarios.

### Keywords

Polycyclic aromatic hydrocarbons; global emission; source profile; time trend

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Supporting information. The following materials are provided in the supporting information: summary of 69 PKU-PAH sources; adopted PAHs emission factors; parameterization for regression models and technology splits; comparison with previous inventories; source profiles of BaP<sub>eq</sub> emissions; geographical distributions of urban and rural emissions and total relative contribution of all sources; world PAH emissions by country in 2007; total and per capita PAH emissions from six sectors for nine regions in 2007. These materials are available free of charge via the Internet at <http://pubs.acs.org>.

## Introduction

Polycyclic aromatic hydrocarbons (PAHs) are an important class of organic pollutants and their primary source in the environment is from the incomplete combustion of carbonaceous materials.<sup>1</sup> PAHs are of great concern because of their widespread occurrence and toxic effects on ecosystem and human health.<sup>2,3</sup> It was estimated that the overall population attributable fraction for lung cancer in China, caused by inhalation exposure to ambient air PAHs, was 1.6%.<sup>4</sup>

Efforts have been made to estimate PAH emissions in the United States, United Kingdom, the former USSR, Europe, North America, China, as well as globally.<sup>5–11</sup> Some of these emission estimates have been used for atmospheric transport modeling and exposure risk evaluating.<sup>12–15</sup> However, fuel consumption data is an important source of uncertainty in PAH emission inventories.<sup>11</sup> In addition, spatially-resolved PAH emission inventories, which are required for atmospheric transport modeling, are commonly disaggregated based on population,<sup>16,17</sup> leading to significant spatial bias because per capita fuel consumption varies significantly within a country.<sup>18,19</sup> Recently, a global fuel consumption database (PKU-FUEL-2007,<sup>18</sup> where PKU stands for Peking University), with 64 fuel types,  $0.1^\circ \times 0.1^\circ$  resolution, and uncertainty information, was created based on a newly developed sub-national disaggregation method. By using this sub-national disaggregation method, the spatial bias in fuel consumption was significantly reduced.<sup>18</sup>

In top-down emission inventories, even larger uncertainty can be induced from the variation in PAH emission factors ( $EF_{PAHs}$ , the mass of PAHs emitted per unit mass of fuel burned).<sup>11</sup> For a given PAH,  $EFs$  from a particular combustion source often vary over several orders of magnitude, depending on the country, facility, operation method, emission control device, environmental setting, measuring time and procedure, and other factors.<sup>1</sup> For example,  $EFs$  of benzo(a)pyrene for light-duty gasoline vehicles vary over four orders of magnitude from 0.204 to 1910 ng/kg.<sup>20</sup> These sources of uncertainty should be taken into consideration in the development of a global PAH emission inventory.

In our previous study, the effect of technical progress on  $EF_{PAHs}$  for on-road motor vehicles was quantified using a regression model which projected  $EF_{PAHs}$  for vehicles produced in a given country and a particular year, based on per-capita gross domestic production (GDPc).<sup>20</sup> Although all of the factors affecting  $EF_{PAHs}$  cannot be eliminated with a simplified model, the overall uncertainty in PAH emission estimation was reduced by approximately one order of magnitude.<sup>20</sup> In the development of a black carbon emission inventory, Bond *et al.* proposed a technology split method to classify an individual source into sectoral divisions and differentiate  $EFs$  for various regions, taking fuel type, combustion type, and control measures into account.<sup>21</sup> A Gauss curve was applied to simulate the technology shift among sectors,<sup>22</sup> assuming that  $EFs$  for individual technology divisions remained unchanged.<sup>21</sup> By using this approach, region and time specific  $EFs$  were derived in order to reduce the overall uncertainty of the black carbon and organic carbon emission inventories on global scale.<sup>21</sup>

In this study, a  $0.1^\circ \times 0.1^\circ$  gridded global PAH emission inventory was developed for 2007 (PKU-PAH-2007). The newly developed fuel consumption database (PKU-FUEL-2007) was used. A previously compiled  $EF_{PAHs}$  database<sup>11</sup> was fully updated, and, whenever possible, the regression modeling<sup>20</sup> and modified technology splitting<sup>21</sup> was also used. The uncertainty in the PAH emission inventory was characterized and the spatial distributions of the total and per-capita PAH emissions, as well as their potential health effects, were investigated. Historical time trends in PAH emissions from 1960 to 2008 were estimated at country level, and future trends to 2030, were simulated based on the six IPCC

(Intergovernmental Panel on Climate Change) scenarios (A1/A1B, A2, B1, B2, A1FI/A1G, and A1T) on future energy consumptions, defined and described in the Special Report on Emissions Scenarios (SRES).<sup>24</sup>

## Methodology

### Inventory Development

The inventory was developed using a top-down approach based on the PKU-FUEL-2007<sup>18</sup> and an updated  $EF_{PAHs}$  database. Among the 64 fuel sub-types defined in the PKU-FUEL-2007,<sup>18</sup> the category of crude oil (used in petroleum refinery) was replaced with catalytic cracking. In addition, five process emission sources in the iron-steel industry (iron sintering, open hearth furnace, convertor, arc furnace, and hot rolling) were added,<sup>23</sup> increasing the total fuel sub-types to 69 (Table S1). They were divided into six categories (coal, petroleum, natural gas, solid wastes, biomass, and an industrial process category) or six sectors (energy production, industry, transportation, commercial/residential sources, agriculture, and deforestation/wildfire). PKU-PAH-2007 covered 222 countries/territories and was gridded to  $0.1^\circ \times 0.1^\circ$  resolution for the year 2007. In addition, annual PAH emissions from individual countries were derived from 1960 to 2008 and simulated from 2009 to 2030 based on the six IPCC SRES scenarios.<sup>24</sup>

The 16 PAHs included in the inventory were: 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). In this study, the term “total PAHs” means the sum of the 16 PAHs.

### Fuel Consumption Data

The detailed fuel consumption data are listed in Table S1. For the  $0.1^\circ \times 0.1^\circ$ - resolution inventory of 2007, PKU-FUEL-2007 was directly used for 63 sources. Details about the strengths and weaknesses of PKU-FUEL-2007 were previously discussed.<sup>18</sup> In brief, PKU-FUEL-2007 was established based on sub-national data so that the spatial disaggregation bias caused by unequal per-capita fuel consumptions, within individual countries, could be substantially reduced. The main constraints of PKU-FUEL-2007 include the lack of sub-national data for some large countries such as Indonesia and Argentina, inaccuracy of geo-locations of power plants from the Carbon Monitoring for Action (CARMA) database version 2.0,<sup>25</sup> and relatively high disaggregation uncertainty for aviation, dung cake, and cement production.<sup>18</sup> Nonetheless, considering that the sub-national fuel consumption data of PKU-FUEL-2007 covered approximately 70% of global fuel consumption, the spatial accuracy for these 63 sources can be improved using PKU-FUEL-2007. For catalytic cracking<sup>26</sup> and the five processes in iron-steel industry,<sup>27</sup> which are not included in PKU-FUEL-2007, activity strengths for all countries were derived from the literature and disaggregated to  $0.1^\circ \times 0.1^\circ$  grids using gas flaring and industrial coal consumptions as proxies, respectively.

Annual country fuel consumptions from 1960 to 2006 and for 2008 were taken from International Energy Agency (IEA),<sup>28</sup> except primary aluminum production,<sup>29</sup> deforestation/wildfire,<sup>30</sup> brick kiln,<sup>31</sup> gas flaring,<sup>32</sup> petroleum cracking,<sup>26</sup> agriculture waste burning,<sup>33</sup> firewood/crop residue ratios,<sup>33</sup> non-organized waste burning,<sup>34</sup> shipping (global total),<sup>35</sup> and 5 processes in iron-steel industry,<sup>27</sup> which were taken from other studies. For the future PAH emission trend simulations, the fuels were classified into coal, oil, gas, biomass, other renewable fuels, crop residue, and biomass burned in deforestation/wildfire.

The utilization rates of these fuels in the future was derived from the six IPCC SRES scenarios.<sup>24</sup>

### Emission Factor Data

The  $EF_{PAHs}$  database, previously developed for a country-resolution inventory,<sup>11</sup> was fully updated by including data published during the past 3 years. A total of 5,822 reported  $EF_{PAHs}$ , which were all based on actual measurements, were compiled. The database were used in three ways: 1) regression modeling for transportation (13 sources), 2) technology splitting for industrial sources and anthropogenic biomass burning (28 sources), and 3) medians and frequency distributions for all other sources (28 sources). Time and country specific  $EF_{PAHs}$  were derived with the first two approaches.

For transportation sources, a previously developed regression model was used.<sup>20</sup> The model is generally presented as  $\log EF_{icy} = k_i GDP_{cy} + C_i$ , where  $EF_{icy}$  (mg/t) is the  $EF_{PAHs}$  of the  $i^{\text{th}}$  compound for  $y$  model year vehicles (or ships) in country  $c$ , and  $GDP_{cy}$  is the per capita gross domestic production (purchasing power parity) of a given country  $c$  in year  $y$  in 1000 USD (Table S2), which was found to be the best index representing the variation of  $EF_{PAHs}$  associated with improvement of technology and implementation of legislation.<sup>20</sup> The slope ( $k_i$ ) and intercept ( $C_i$ ) for compound  $i$  represent the decreasing rate of  $\log EF$  as  $GDP_{cap}$  increases and the  $EF_{PAHs}$  without any control, respectively. The difference of  $k_i$  among different PAHs is primarily due to difference in partitioning between the gaseous and particulate phases in the atmosphere. The robustness of the model was further confirmed in this study using a jackknife test (details in Figure S1 and S2).

For the technology splitting approach, each source was divided into 2 or 3 divisions with or without different emission mitigation measures. The 222 countries/territories were classified into 5 categories: 1) the United States and Canada, 2) other developed countries (39 countries), 3) former USSR federals (14 countries), 4) China, and 5) all other developing countries (166 countries). For each country category, the time-dependent fractions of the technology divisions were either derived from the literature or calculated using an S-shaped regression model.<sup>21</sup> The details are provided in Tables S3 and S4.

For the remaining 28 sources, fixed  $EF_{PAHs}$ , which are not time and country dependent, were used.  $EF_{PAHs}$  for all sources are listed in Table S5.

### Uncertainty Analysis

Monte Carlo simulation was used to characterize the overall uncertainty of the PKU-PAH-2007. The emissions were repeatedly calculated 10,000 times by randomly drawing all inputs from given distributions with known coefficients of variation. The activity rates were assumed to be uniformly distributed. Based on previous studies, variation intervals of historical consumptions were set to be 20% of the means for indoor biomass burning and open fires, 15% for ships and aviation, 5% for energy production and industrial sectors, 30% for non-organized waste burning, and 10% for all other sources.<sup>10,21,35</sup> Variation intervals of future consumptions were assumed to increase from original intervals of historical consumptions to double of those for the period from 2009 to 2030. The measured  $EF_{PAHs}$  collected for this study were found to be log-normally distributed and distribution statistics of them were calculated based on these data and applied in the Monte Carlo simulation.

## Results and Discussion

### Global Total Emission and Source Profile

The annual global atmospheric emission of the 16 PAHs in 2007 was 504 Gg (331-818 Gg, as interquartile range from the Monte Carlo simulation), which is equivalent to 76 g per capita per year. Emissions of individual PAH compounds, from various sources in various countries, are listed in Table S6. The updated total PAH emission for 2004 in this study (527 Gg) was slightly higher than previously estimated for 2004 (520 Gg) by Zhang et al.<sup>11</sup> because of the updated  $EF_{\text{PAHs}}$  databases.

Figure 1 shows the relative contributions of various sources to the total PAH emissions for the world and for several countries in 2007. Globally, biomass fuels, including mainly firewood and crop residues, consumed in residential/commercial sectors were the major PAH sources, contributing 60.5% of the global total PAH emissions. The consumption of petroleum products in transportation (12.8%) and deforestation/wildfire (11.2%) were also important PAH emission sources. Considerable difference in PAH source profiles among individual countries was primarily due to energy structure, development status, and vegetation cover. In many developing countries, such as India, China, and Indonesia, indoor biomass burning was the most important PAH emission source, contributing more than half of the total PAH emissions. Indoor firewood combustion was also a major PAH emission source in some developed countries, such as the United States, where certified woodstoves were popular in many rural households.<sup>23</sup> Significant deforestation/wildfire emissions occurred primarily in a dozen of countries, including Brazil, Democratic Republic of the Congo, and Angola, where widespread forest or prairie fires occurred every year. Motor vehicle exhaust was also an important source of PAH emissions, accounting for one eighth of the global total PAH emissions. This source was particularly important in many developed countries. The relative contribution of PAH emissions from motor vehicles is increasing in China and other countries under economic transition. Coke production was also an important source in some countries, including China and Russia. However, because of the rapid decline in the use of beehive coke ovens, PAH emissions from coke production is rapidly declining.

A detailed comparison of this study with Zhang et. al's study<sup>11</sup> is discussed in the supporting material (see Figure S4 and S5). In general, compared with Zhang et. al's 2004 PAH emission inventory,<sup>11</sup> this 2004 PAH emission inventory showed a reduction in PAH emissions associated with developed countries and an increase in PAH emissions with developing countries within technology-based sources due to the use of country/region-specific  $EF_{\text{PAHs}}$ .

### Composition Profile

Figure 2 shows the PAH emission composition profiles of seven important source categories for global total, developing, and developed countries in 2007. Globally, NAP contributed 45.0% of the total, followed by ACY (17.1%), PHE (10.6%). The total of eight high molecular weight carcinogenic compounds<sup>37</sup> (from BaA to BghiP) accounted for 6.19% of the global total, and this percentage was higher for developing countries (6.22%) compared to developed countries (5.73%). Transportation contributed approximately 14.8% of the global total PAH emission, with 82.5% of the transportation emissions in the form of NAP. On the other hand, residential fuel consumption, industrial emission, and non-organized waste burning contributed more high molecular weight carcinogenic PAHs, accounting for more of the adverse health effect potential. This is of particular concern in the case of residential biomass fuel combustion because the emission of PAHs from this source can lead to direct human exposure.<sup>38</sup> In developing countries, the domination of emissions from



residential biomass burning led to relatively high percentages of high molecular weight PAHs. In contrast, emission mitigation measures are more strictly implemented in developed countries and are more effective in controlling high molecular weight PAH emissions on fine particulate matter. The PAH composition profile derived in this study was similar to that of Zhang et al.'s, with the exceptions of CHR and BkF.<sup>11</sup> The relative contributions of CHR and BkF in Zhang's study (1.7 and 0.8%) were higher than ours (1.2 and 0.6%, respectively), which resulted from the use of the new  $EF_{PAHs}$  for indoor crop residue burning in this study.

To describe and compare the combined toxicities of the emissions of the 16 PAHs from various sources and areas, BaP toxic equivalent quantity (g) per unit mass emission (kg) from individual sources (BaP<sub>eq</sub>/u) were defined and calculated based on the toxicity equivalent factors<sup>37</sup> of individual PAHs and emission profiles. On a global scale, the average BaP<sub>eq</sub>/u from all PAH emission sources was 15.0 g/kg in 2007. The most toxic sources in terms of PAH composition were aluminum production (80.0 g/kg), residential/commercial coal burning (excluding anthracite) (52.4 g/kg), non-organized waste burning (50.6 g/kg), and coke production (23.7 g/kg). Sources with relatively low BaP<sub>eq</sub>/u included motor vehicles (3.28 g/kg), industrial boilers (6.26 g/kg), and the iron industry (9.86 g/kg). The average BaP<sub>eq</sub>/u in developed countries (13.0 g/kg) was lower than that in developing countries (15.1 g/kg), not only due to the differences in energy structures but also the disparities of technology. For example, BaP<sub>eq</sub>/u for primary aluminum production in developed countries (57.8 g/kg) was much lower than that in developing countries (83.2 g/kg). The reasons for this difference include: 1) emission control devices in aluminum production, as well as in many other processes, are more widely used in developed countries than in developing countries; and 2) these emission control devices are more effective in removing high molecular weight carcinogenic PAHs sorbed to fine particulate matter.

Based on the calculated BaP<sub>eq</sub>/u and total PAH emission mass, BaP toxic equivalent quantities were calculated as indicators to relative health effect potential of all individual sources. The results are shown in Figure S6. Due to significant difference in BaP<sub>eq</sub>/u, sources with high BaP<sub>eq</sub>/u, such as primary aluminum production and domestic coal combustion, contributed much more to health effect potential than those to the total PAH emission. Still, solid fuels burned in residential sectors dominated toxic effects on a global scale.

### Geographic Distribution

With the  $0.1^\circ \times 0.1^\circ$  resolution fuel combustion inventory (PKU-FUEL-2007)<sup>18</sup> and the country-specific  $EF_{PAHs}$  available, individual PAH emissions in 2007 were mapped on  $0.1^\circ \times 0.1^\circ$  grids. Figure 3A shows the global distribution of total PAH emission density in 2007. The annual total PAH emissions from 12 geographic regions are listed in Table S7. The relative contributions of the five source sectors (energy/industry, residential/commercial, transportation, agriculture, and deforestation/wildfire) for the main geographic regions are shown as pie charts in the inset of Figure 3A. The areas of the pie charts are proportional to the total PAH emissions in the different geographic regions.

Globally, almost two-thirds (63.4%) of the total PAH emissions occurred in the residential/commercial sector, and this was particularly true for west-central Africa (79.9%), south-southeast Asia (79.8%), and south-east Africa (67.1%), mainly because of the extensive use of biomass fuels in developing countries for cooking and heating.<sup>28</sup> All Asian countries contributed 53.5% of the global total PAH emission, with the highest emissions from China (106 Gg) and India (67 Gg) during 2007. The other top PAH emitting countries included Brazil, Indonesia, Nigeria, Ethiopia, Pakistan, Congo Democratic Republic, Vietnam, and Russia. The total PAH emission from the above mentioned top ten emission countries was

297 Gg in 2007, accounting for 59.0% of the global total PAH emissions. In South America, 50.8% of the PAH emissions were from deforestation/wildfire, mainly deforestation fires. Other regions with relatively high PAH emission from this sector were Oceania (30.6%) and East and South Africa (26.2%). PAH emissions from transportation only contributed 12.8% of the global total, but they were relatively important in western and central Asia (50.3%), North America (24.6%), and Europe (23.8%). Although industrial sources contributed only 6.7% of the global total PAH emissions, they were significant in East Asia (20.4%) and Europe (15.1%). The main contributors to the industrial sources were coke production (13.3%), iron and steel production (2.6%), and industrial boilers (2.3%) in East Asia and coke production (6.2%), primary aluminum production (4.5%), and iron and steel industry (2.9%) in Europe, respectively. Compared to developed countries, the relatively large contribution of heavy industries and relatively low level of the application of emission mitigation measures were the main reasons for the higher industrial PAH emissions in China and Eastern European countries.

Figure 3B shows the global distribution of per-capita PAH emissions derived from the gridded PAH emission densities and population densities.<sup>39</sup> The average per-capita PAH emissions from 12 regions are listed in Table S7. The per-capita PAH emissions for the various regions are not proportional to the per-capita energy consumptions, but they appear to be highly dependent on the region's energy structure and status of development. For example, although per-capita energy consumptions in North America (5.6 toe/cap, where toe is short for ton oil equivalent) and Europe (3.4 toe/cap) were relatively high, per-capita PAH emissions in these regions (43 and 48 g/cap) were among the lowest. In contrast, per-capita PAH emissions were much higher in Africa (145 g/cap), Asia (70 g/cap), and South America (123 g/cap), although the per-capita energy consumptions were relatively low (0.8, 1.3, and 1.3 toe/cap, respectively). In general, the proportion of residential/commercial solid biomass burning in the region's energy structure was the key factor affecting per-capita PAH emissions. It is interesting to note that the spatial pattern of per-capita CO<sub>2</sub> emissions<sup>18</sup> is very different from that of per capita PAH emission, because CO<sub>2</sub> was mainly from power generation and industry, while PAHs were largely from residential sectors.

We assumed that the uneven development of urban and rural areas in developing countries, especially those under economic transition, would lead to differences in energy consumption and structure and, subsequently, to PAH emission density between urban and rural areas.<sup>18</sup> We investigated these differences using the high spatially resolved inventory derived from the sub-nationally spatialized data. The previously developed method for distinguishing between rural and urban grids was used<sup>18</sup> and each 0.1° × 0.1° grid-point was defined as either 'urban' or 'rural'. Using this urban-rural mask, the geographic distributions of anthropogenic PAH emissions from urban and rural areas (see Figure S7) were extracted separately. Globally, the annual total PAH emission from rural areas (297 Gg) was twice as much as that from urban areas (141 Gg). For developing countries, the difference in PAH emissions between rural and urban areas was even larger (281 vs. 120 Gg). With the similarity in global total rural and urban populations, per-capita PAH emission was also significantly higher in global rural areas (90 g/(cap·yr)) than that of urban areas (45 g/(cap·yr)), mainly due to the wide use of biomass fuels in rural areas. The calculated global BaPeq emissions were 0.46 and 0.20 Gg in rural and urban areas, respectively. This trend was opposite to that of CO<sub>2</sub> and per-capita CO<sub>2</sub> emission, the emission of which in rural areas was only one third of that in urban areas.<sup>18</sup>

It should be noted that, due to fast urbanization in countries under economic transition (such as China and India),<sup>40</sup> the spatial distribution patterns of fuel consumption and energy structure have been changing rapidly.<sup>41</sup> This trend is expected to continue for years to come.<sup>42</sup> In China alone, 140 million rural residents have resettled in cities and towns during

the last two decades.<sup>43</sup> Unlike rural residents, who rely largely on biomass fuels for cooking and heating, those migrating to urban areas shift their way of energy use as other city dwellers who rely more on electricity and fossil fuels.<sup>44</sup> The potential influence of such large scale urbanization, occurring in countries like China, on the emissions of PAHs and other incomplete combustion by-products could be considerable. Thus its effect on the total and spatial distribution pattern of PAH emissions (as well as other combustion by-products, such as CO<sub>2</sub>, black carbon, and primary aerosol) should be addressed quantitatively in the future so as to understand the overall impact of urbanization on the environment and health, as well as on climate change.

Using the high spatially resolved inventory, we developed a simple method to roughly assess the potential health impact of PAH emissions based on both emission densities and distances between source and receptor grids. To do this, we assumed that the effects of PAH emissions from a grid were dominated within a 5 × 5 grid or 50 km × 50 km area, beyond which the influence could be ignored. Therefore, the overall health effect potential of PAH emissions (as BaP toxic equivalence) on a receiving grid (0.1° × 0.1°) was quantified as the total potential of effects of the PAH emissions from the receiving grid itself, as well as the PAH emissions from the 24 surrounding grids. The individual health effect potential from a source grid was proportional to the total PAH emission of the source grid and the total population of the receiving grid but inversely proportional to the distance between the source and receiving grids. The distance weight factor was 1 when the source grid was the receiving grid itself, 1/4 for the 8 source grids immediately adjacent to the receiving grid, and 1/9 for the other 16 grids. The result was a dimensionless indicator, defined as Relative Potential Health Effect (RPHE) in this study. Because the absolute value of RPHE was meaningless, the global RPHE for all emission sources were normalized to global total emission for comparative purpose. It should be indicated that this approach is only a rough estimation on the potential of health effect, since the transport processes of PAHs from source to receptors, which depend on meteorological conditions, are not taken into consideration. Atmospheric transport modeling is required for a full assessment on the exposure and risk.

The global distribution of RPHE is shown in Figure S8 and the relative contributions of various emission sources are shown in Figure S9. Compared with the global PAH emission map (Figure 3), the potential health effects in the high PAH emission areas such as East, South, and Southeast Asia were generally intensified, because the higher population density often leads to both higher PAH emissions and higher health effects. The few exceptions were the regions (e.g. South America) with high PAH emissions from aviation, shipping, and deforestation/wildfire which were generally further away from highly populated areas. Although the total PAH emissions from industrial sources and motor vehicles were relatively low, their potential health effects were relatively high because these sources occurred primarily in cities with high population densities. Residential emission sources showed strong potential health effects due to both high PAH emissions and close proximity to people, which in fact could be underestimated, because the PAH emissions from household solid fuel combustion are often very close to receptors in rural settlements. A combined consequence of the relatively high per-capita PAH emissions and biomass source domination in rural areas was that the potential of health effect of the PAH emissions in rural areas was more than double that of urban areas. Unfortunately, this sub-kilometer proximity could not be well characterized in this study using 10 km resolution.

### Historical Time Trends

With the historical fuel consumption data available and time-dependent  $EF_{PAH}$  characterized, annual PAH emissions from all countries/territories were calculated from 1960 to 2008. Our results were compared with those previously reported in the



literature.<sup>5,6,7</sup> The emissions of individual PAHs from all sources in the United States in 2002 and 2005 estimated in this study were plotted against those reported by USEPA (Figure S10-A).<sup>5</sup> Similarly, the emissions of individual PAHs from all sources in the UK were compared with those reported by NAEI (National Atmospheric Emissions Inventory) from 1990 to 2009 (Figure S10-B).<sup>6</sup> The majority of the data points fell around the 1:1 line, indicating no systematic difference between them. The correspondence between PKU-PAH and that reported by USEPA was further confirmed when individual sources were compared separately (Figure S11).<sup>5</sup> A comparison was also conducted for the total of the four PAHs (BaP, BbF, BkF, and IcdP) with those reported to EMEP (European Monitoring and Evaluation Programme), by each of the 27 European countries from 1990 to 2008 (Figure S12).<sup>7</sup> Although similar trends between PKU-PAH and EMEP were found for many countries, there were striking differences for the Czech Republic, Bulgaria, Belgium, Lithuania, and Romania. The variation in  $EF_{PAHs}$  is likely to be one of the reasons for these differences. In PKU-PAH, regression and technology split methods were used to simulate time trends in  $EF_{PAHs}$ . The application of the country-specific  $EF_{PAHs}$  also caused differences between PKU-PAH and EMEP in Sweden, Germany, and Slovakia, where downward trends in PAH emissions were identified by PKU-PAH, while estimates reported to EMEP show an increasing trend in PAH emissions over the last several years.<sup>7</sup> The PKU-PAH prediction was partially verified by the fact that the ambient air PAH concentrations in all European countries have decreased in recent years.<sup>45,46</sup>

Figure 4 shows the time trend of global PAH emissions from 1960 to 2008. The results are presented as the global total (A) and the totals of developed (B) and developing countries (C). The PAH emissions of developed countries peaked in the early 1970s and decreased gradually since, primarily due to the introduction of emission mitigation technologies and the subsequent decline in the PAH emissions from on-road motor vehicles.<sup>20</sup> Although the total number of motor vehicles increased more than five times from  $1.2 \times 10^8$  to  $6.5 \times 10^8$  in developed countries during this time period, the total PAH emissions from motor vehicles decreased dramatically. Because the average gas mileage decreased from 0.2 to 0.08 L/km, and the mean  $EF_{PAH16}$  for on-road motor vehicles decreased from 130 to 7 mg/kg in these countries during the same time period.<sup>47</sup> Significant PAH emission decreases in the industrial sectors occurred for similar reasons. While only relatively slow decreases in PAH emissions occurred in the residential/commercial sources. In contrast, the total PAH emissions in developing countries from the transportation sector had increased continuously during the modeled time period. Although both the gas mileage and  $EF_{PAH}$  for motor vehicles in developing countries had also decreased during the past three decades,<sup>20,48</sup> an even faster increase in the number of motor vehicles in these countries, especially in China, Brazil, and India, had negated the decreasing trend.<sup>47</sup> For example, the number of motor vehicles in China increased from  $3.7 \times 10^6$  to  $4.4 \times 10^7$  from the early 1970s to 2007, while the gas mileage and  $EF_{PAH}$  only decreased 27% from 0.132 to 0.098 L/km and 26% from 178 to 131 mg/kg, respectively. Fortunately, PAH emissions from motor vehicles in developing countries was predicted to peak around 2010, till then the expansion of vehicle fleet and reductions in both gas mileage and  $EF_{PAH}$  would finally reach a balance,<sup>20</sup> followed by a declining trend in PAH emissions.

After continuous increases in PAH emissions for decades, the PAH emissions from residential, commercial, and industrial sources in developing countries started to slowly decrease around 1995. As a result, the total PAH emission from developing countries reached its peak around 1995. The main reasons for this decrease include the promotion of centralized heating systems,<sup>49</sup> replacement of residential coal cooking stoves with natural gas stoves in large and median cities,<sup>41</sup> dissemination of improved biomass cook stoves in rural households,<sup>50</sup> and the phasing out of beehive coke ovens in China.<sup>51</sup> Because the

global PAH emission was dominated by those from developing countries (90% in the year 2000) in recent years, it also reached its peak of 592 Gg in 1995 and decreased afterwards.

### Future Time Trends

The annual PAH emissions of individual countries/territories from 2009 to 2030 were simulated using the six IPCC SRES scenarios.<sup>24</sup> These results are shown in Figure 4 for the global, developed and developing countries. The uncertainty in these predictions is relatively large because the fuel consumption predictions are not accurate and the changes in  $EF_{PAHs}$  and technology splitting fractions can be affected by the changes in socioeconomic development. Even with this significant uncertainty, decreasing trends in PAH emissions are expected in both developed (46-71% decrease by 2030 compared with 2008) and developing countries (48-64% decrease by 2030 compared with 2008). A slower decrease in global PAH emissions was associated with the A2 scenario, which described a heterogeneous world with slower technology diffusion.<sup>24</sup>

In 2007, PAH emissions from residential sources contributed 65% of the global total and a significant reduction in PAH emission in the future will be achieved by taking effective mitigation measures in this sector. Based on the A1 scenario, 34% of the reduction in PAH emission can be achieved by 2030 due to the optimization of the energy structure in residential consumption (108 Gg) and improvement of residential devices (70 Gg). Moreover, the relatively high percentage of carcinogenic PAH emissions and the close proximity to residents will make the effort in the residential sector more effective in terms of health implications. Unlike industrial and transportation sources, PAH emissions from the residential sector are primarily from millions of residential stoves. Because of this, socioeconomic development is critical in PAH emission mitigation instead of technology development. In China, the percentage of urban population has increased from 36.2 to 51.3% during the past decade.<sup>52</sup> This rapid urbanization has been leading to an extensive change in the ways of energy use in China. Millions of former rural residents have gotten rid of biomass fuel stoves, and the younger generations in rural eastern China also have started to use electricity and liquid natural gas.<sup>41</sup> This is one of the major driving forces causing the decrease in PAH emissions in the future projections across all of the IPCC SRES scenarios.<sup>24</sup> In addition, environmental policy also plays a key role in PAH emission reduction. Rapid decreases in PAH emissions from on-road motor vehicles and industrial processes in developed countries since the early 1970s were due to the promulgation and implementation of a series of legislations which drove the development of energy saving and emission abatement technologies.<sup>53</sup> Similar legislation occurred in developing countries years later. An example was the implementation of the Coal Law in China in 1996, which banned the use of beehive coke ovens.<sup>51,54</sup> Almost all beehive coke ovens have been phased out over the past decade, resulting in a total PAH emission reduction of 18.2 Gg. In the future, legislation on emission abatement in the transportation sector will benefit the developing world. A total reduction of 74 Gg PAH emission in this sector was estimated by 2030, based on the A1 scenario. Also, the promotion of cleaner burning fuels, such as liquid petroleum gas, biogas, and pellet biomass fuel<sup>23</sup> in rural areas in developing countries will help to reduce PAH emissions significantly. Both regulations and economic incentives can play important roles in reducing future PAH emissions.

In developing countries, education and risk communication are also important in terms of reducing the PAH emissions from solid fuel burning. Most rural residents are unaware of the potential adverse health effects of PAHs, preventing them from taking the initiative to reduce emissions. For example, open burning of garbage in the household yard is still a common practice in rural China<sup>55</sup> and solid fuel stoves without chimneys can still be seen in poor countries.<sup>56</sup> Educating rural primary school students on the health impacts of

residential solid fuel combustion can be an inexpensive and effective way to reduce PAH emissions in these countries.

## Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

## Acknowledgments

Funding for this study was provided by the National Natural Science Foundation of China (41130754), Ministry of Environmental Protection (201209018), Beijing Municipal Government (YB20101000101), and NIEHS (P42 ES016465). We thank Dr. Staci L. Massey Simonich of Oregon State University for providing valuable comments on the manuscript.

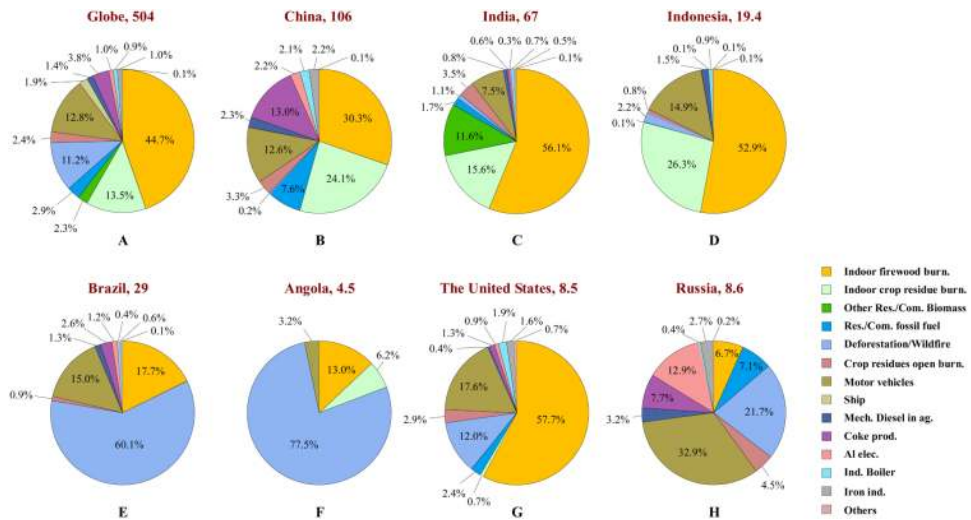
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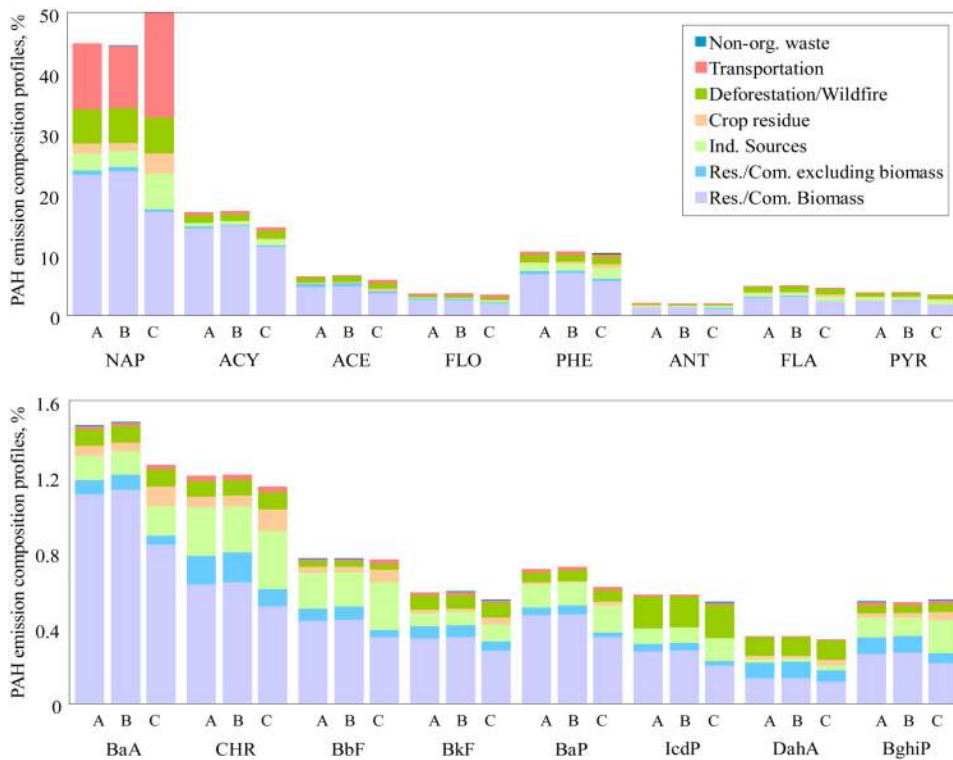
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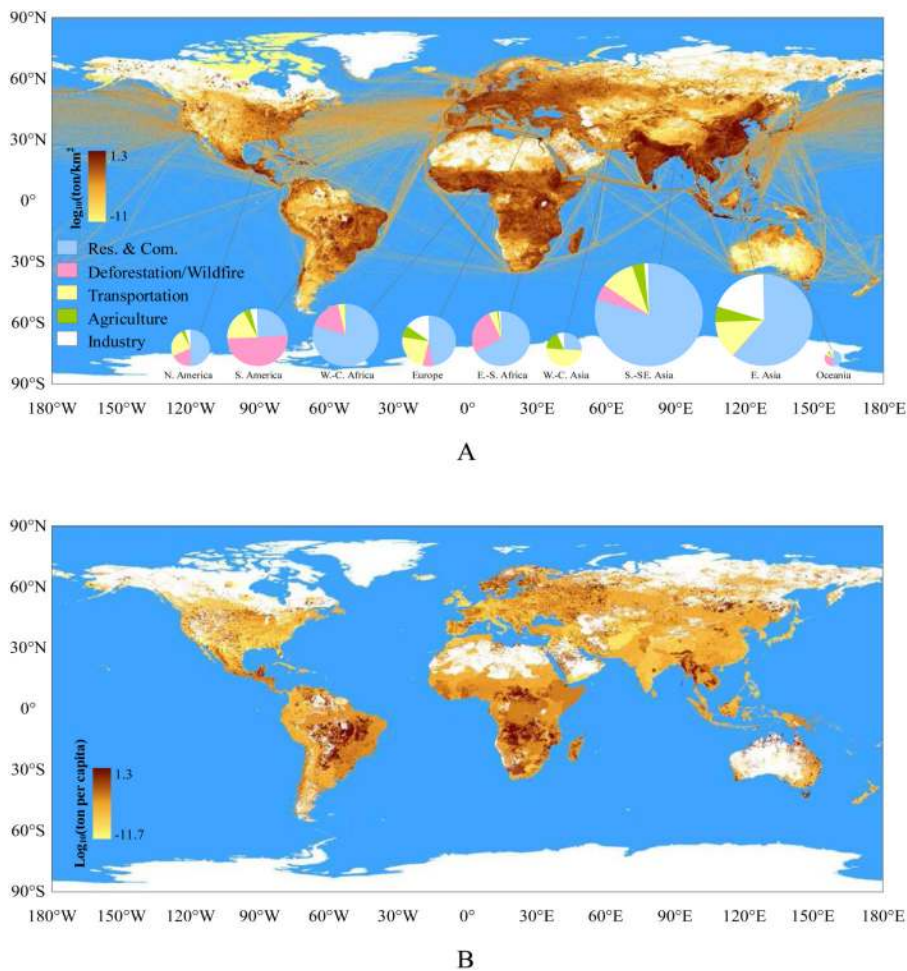




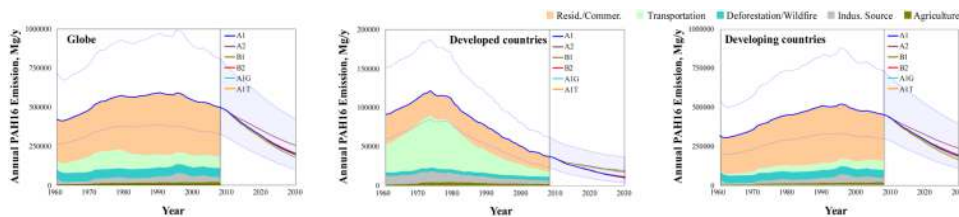
**Figure 1.** Source profiles of PAH emissions (Gg) in the world (A) and several representative countries including China (B), India (C), Indonesia (D), Brazil (E), Angola (F), the United States (G), and Russia (H) in 2007.



**Figure 2.** PAH emission composition profiles of seven important source categories for A) global total, B) developing countries, and C) developed countries. The lower molecular weight PAHs are shown in the top panel, while the higher molecular weight PAHs are shown in the bottom panel. Note the difference in scale between the two panels.



**Figure 3.** Spatial distributions of total (A) and per-capita (B) PAH emissions globally in 2007 at  $0.1^\circ \times 0.1^\circ$  resolution. For each region, the relative contribution of major sources is shown as pie charts, with the areas of the pie charts proportional to the total PAH emissions, in (A). Northern Africa, Central America, and Caribbean are not shown as pie charts.



**Figure 4.** Time trends of PAH emissions during a period from 1960 to 2030 for the world (A), developed countries (B), and developing countries (C). Emissions from the five sectors are marked with different colors (see upper-right) and the uncertainties of total emissions, derived from Monte Carlo simulations, are shown as interquartile ranges using light blue curves. Future time trend simulations were conducted based on the six IPCC SRES scenarios and are presented as medians and interquartile ranges derived from Monte Carlo simulations.