A EUROPEAN SPATIALLY DISTRIBUTED EMISSION INVENTORY OF THE INDICATOR PAHs BENZO(A)PYRENE, BENZO(B)FLUORANTHENE, BENZO(K)FLUORANTHENE, AND INDENO(1,2,3-CD)PYRENE FOR 2005

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Introduction

Polycyclic aromatic hydrocarbons (PAHs) are a group of compounds composed of two or more fused aromatic rings. The importance of PAHs as persistent organic pollutants (POPs) is increasing due to concerns regarding health effects, particularly their carcinogenic properties. The semi-volatile property of PAHs makes them highly mobile throughout the environment via deposition and revolatilisation between air, soil and water bodies. It is possible that a proportion of PAHs released are subject to long range transport making them a global environmental problem. Therefore the UNECE Convention on Long-range Transboundary Air Pollution (CLRTAP) 1998 POP includes PAHs with the objective to control, reduce or eliminate discharges, emissions and losses of these POPs. Furthermore, there is interest in the particulate matter (PM) bound PAHs which may provide a better indicator of the health relevance of PM emissions than the mass-based PM10 approach. Limited data are available on emission factors for PAHs, and the data that are available are often reported in different manners which means comparison of data for verification purposes is difficult. The UNECE POPs Protocol (ECE/EB.AIR/60) specified in its Annex III that the following 4 PAHs should be used as indicators for the purposes of emission inventories: benzo[a]pyrene (BaP) , benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF) and indeno[1,2,3-cd]pyrene (Indeno). The objective of this study is to provide a bottom-up emission inventory for these four indicator PAHs for the year 2005 which is suitable for air quality and transport modelling as well as analyzing source contributions and potential mitigation measures.

Methodology and approach for a new bottom-up PAHs inventory

An inventory for the four indictor PAHs for the year 2000 was previously published by Denier van der Gon et al. (2007). This inventory identified the key sources for the indicator PAHs; the most important sources (accounting for almost 99% of the BaP emission) were residential combustion of wood and coal, followed by industry, and transport. Denier van der Gon et al. took account of all existing European national emission inventories which makes it unlikely that major PAHs sources were missed. Compared to the inventory of Denier van der Gon et al. (2007) we also included the open burning of agricultural waste and household waste although this is often not reported and cover a more recent base year (2005). More important, Denier van der Gon et al. (2007) did not review emission factors in detail and merged official reported data and expert estimates into one inventory which made the final result policy relevant, but scientifically less consistent. The four indicator PAH compounds have in common that their molecular weight is relatively high and their volatility is low. This means that emission sources are restricted to combustion and other thermal sources, rather than fugitive emissions. Virtually all of the emission will be particle-bound and not gaseous. In the next section we will discuss the methodology for the major source category residential combustion in detail and provide a more general description of our approach for the other source categories. Next we will briefly discuss the approach to spatially distribute the emissions.

Residential combustion of wood and coal causes PAHs emission by incomplete combustion due to a combination of solid organic fuel with the typical low temperatures and limited oxygen supply of household heating appliances. An extensive literature review was performed on coal, wood and oil emission factors for combustion in household appliances. Emission factors varied widely, more than two orders of magnitude, depending on air supply and combustion temperature, and fuel characteristics such as moisture and in case of coal, tar content. We derived average emission factors for a typical operation cycle involving hot and cold start-up, steady burning and smoldering conditions, representative for four coal types, fuel wood and fuel oils and six appliance types currently in used in Europe (Table 1).

Table 1 Best estimate of PAH emission factors for residential combustion (mg/kg)

Fuel	Appliance[a)]	BaP	BbF	BkF	Indeno
(Sub-) Bituminous coals	Conventional heating stove	15	30	15	15
	Single house boiler, manual feed	15	30	15	15
	Single house boiler, automatic feed	3.8	4.5	2.5	2.0
	Medium boiler, manual feed	1.4	1.8	0.74	0.58
	Medium boiler, automatic feed	0.38	0.44	0.21	0.16
Lignites	Conventional heating stove	5.0	8.0	3.0	2.4
	Single house boiler, manual feed	5.4	5.0	2.0	1.8
	Single house boiler, automatic feed	3.8	4.5	2.5	2.0
	Medium boiler, manual feed	1.4	1.8	0.74	0.58
	Medium boiler, automatic feed	0.38	0.44	0.21	0.16
(Semi-) Cokes	Conventional heating stove	1.3	2.3	1.0	1.0
	Single house boiler, manual feed	1.3	1.3	0.75	0.50
	Single house boiler, automatic feed	0.31	0.19	0.13	0.067
	Medium boiler, manual feed	0.12	0.077	0.037	0.019
	Medium boiler, automatic feed	0.031	0.018	0.011	0.0054
Anthracites	Conventional heating stove	0.22	0.70	0.62	0.21
	Single house boiler, manual feed	0.22	0.70	0.62	0.21
	Single house boiler, automatic feed	0.054	0.11	0.10	0.029
	Medium boiler, manual feed	0.020	0.043	0.030	0.0082
	Medium boiler, automatic feed	0.0054	0.010	0.0088	0.0023
Fuel wood	Fireplace	2.7	2.7	1.5	2.1
	Traditional wood stove	3.8	3.6	2.3	2.7
	Single house log boiler	0.80	0.61	0.38	0.52
	Single house pellet boiler	0.23	0.24	0.15	0.14
	Medium boiler, manual feed	0.40	0.31	0.19	0.26
	Medium boiler, automatic feed	0.11	0.12	0.075	0.068
Distillate oil	All appliances	0.0043	0.0023	0.0035	0.0086
Heavy fuel oil	All appliances	0.086	0.045	0.071	0.17

[a)] Definition of appliance types according to the IIASA GAINS model (http://gains.iiasa.ac.at/gains/.)

Wood and coal combustion in other sectors than residential combustion and/or small scale commercial combustion, e.g., power generation and industry was not deemed relevant for PAHs emission, because PAH emission factors are consistently at least a factor 100 lower mostly due to the much higher combustion temperatures .

The emission factors in Table 1 were combined with activity data by country including an allocation of the amount of fuel to various appliance types. The distribution over appliance type is based on the GAINS model (http://gains.iiasa.ac.at/gains/.) with an update of fireplace occurrence for Central and Eastern European countries. Activity data for commercial fuels were obtained from the International energy statistics (www.iea.org). Activity data for (non-commercial) fuel wood were updated and improved by compiling various statistics and information sources and the construction country clusters that were expected to have similar fuel wood use per capita based on climatic similarities, the local availability of fuel wood resources and considering the energy balances in the domestic sector. This resulted in a significant increase of 20-30% in the estimated wood consumption in many parts of Central and Eastern Europe.

Industry is the second major source of PAH, especially in Central and Eastern Europe. The following processes are relevant for high molecular particle-bound PAH: Soederberg aluminium production, coke ovens, and to a lesser extent primary aluminium using prebaked anodes, anode baking, and iron ore sinter production.

In 2005 there were 23 Soederberg plants in operation in UNECE Europe (European part of Russia only), of which 17 used vertical stud soederberg (VSS) and 6 horizontal stud soederberg (HSS) technology. Our emission factor review showed a considerable range of the emission factors for Soederberg aluminium production, depending on plant age and emission abatement measures taken. In our final emission factor compilation we distinguised three levels of emission control (low, medium, high).

We identified 84 operational coke ovens (including a few that had an idle or moth balled status in 2010) in UNECE Europe. It should be noted that our domain included only the European part of Russia and did not include Kazakhstan. A very high range in measured emissions of BaP was reported, therefore we defined four

standards of emission abatement for coke ovens; low, medium-low, medium-high, and high. Each standard represents a certain emission factor range typical for the particular level of emission control.
Sinter plants make a modest contribution to PAH emission and there are about 77 plants in the domain of study. Reported BaP emission factors vary again widely, necessitating again four levels of emission abatement similar to coke ovens. An equally modest contribution is made by primary aluminium production using prebaked anodes and separate anode baking. Again reported emission factors vary widely, which we translated to four levels of emission abatement. All abatement levels are based on actual observations.
However, as emission factors for industrial processes range in excess of two orders of magnitude it is crucial to characterize each plant correctly with respect to the degree of emission control. We followed a novel manifold approach to this. For each individual primary aluminium plant as well as each coke oven we analysed plant facts such as the year the plant was first commissioned and the year in which the latest modernisation took place (Plant Fact database) in order to get an idea of the technical standard. We collected recent photographs of each plant taken on site as well as satellite images of the sites provided by Google Maps (http://maps.google.com). The visibility and colouring of chimney plumes were used as additional information to estimate the level of emission control, yielding a fairly accurate assessment of industrial BaP emissions. Emissions of BbF, BkF and Indeno were estimated based on their emission ratio relative to BaP based on PAHs emission profiles derived from literature.

Open burning of waste causes PAHs emission due to similar incomplete burning as in smaller residential stoves,. Although emission factors are uncertain the main uncertainty are the activity data as uncontrolled waste burning is often prohibited but may occur illegally. Available emission factors and activity data were complied to provide a first order estimate of the source strength.

Transport emission is traditionally regarded as an important source of PAHs but the progress in emission reduction technology in the last two decades diminished its relevance as a source of PAH considerably. However, the number of emission factor measurements by technology levels (e.g. the EURO emissions standards) is sometimes limited making the representativeness questionable. Emission factors per fuel type, vehicle type and age and subsequent technological standard were compiled based on e.g. Boulter et al. (2009). Road vehicle fleet were obtained from the TREMOVE model supplemented by a reassessment of vehicle fleets in Central and Eastern Europe (including Russia) to account for the higher share of older vehicles in these countries. A similar approach was followed for non-road transport.

Spatial distribution of PAHs emissions

The estimated PAHs emissions were spatially distributed over a 1/8 º x 1/16º longitude – latitude grid. The area domain is Europe from -10° to +60° Lon and +35° to +70° Lat (excl. Kazakhstan and the African continent, but incl. Turkey). The distribution methodology was developed by TNO in a sequence of projects and consist of a linking of each individual emission source to a proxy map or point source database and is described in Denier van der Gon et al. (2010). Additional improvement specifically for the PAHs emission distribution was placed on distributing residential combustion emissions and industrial point sources. The residential combustion emissions by country were spatially distributed assuming the following emission source - proxy map linkage: 1) Coal used in stoves and single house boilers: rural population density, 2) Coal used in medium boilers (for block heating etc.): urban population density, 3) Wood used in any domestic appliance: special household wood consumption distribution map, 4) Liquid fuels: total population density. Aluminium production sites were identified Aluminium industry database (http://www.genisim.com/aluminum/smelter.htm) and verified using Google maps and google earth. Location and capacity of cokes ovens were re-assessed based on recent EC funded TNO project assessing the energy efficiency in the Iron and Steel industry.

Results and discussion

Total European emissions of BaP, BbF, BkF and Indeno in 2005 were estimated as 1020, 1186, 1164 and 669 tonnes/yr respectively. The emissions are strongly dominated by residential combustion and industrial emissions (Figure 1). Industrial emissions dominate in the Non-EU countries whereas residential combustion is dominating in the EU25. Although various types of appliances are used in Europe, the bulk of the appliances in use were still of traditional conventional design. Since the emission factors vary orders of magnitude (Table 1) a switch to improved appliances with better emission control is an obvious mitigation measure. Within the group of EU(25) countries there are large differences in PAHs emissions per capita because the importance of solid fuels in residential combustion varies widely between the memberstates.

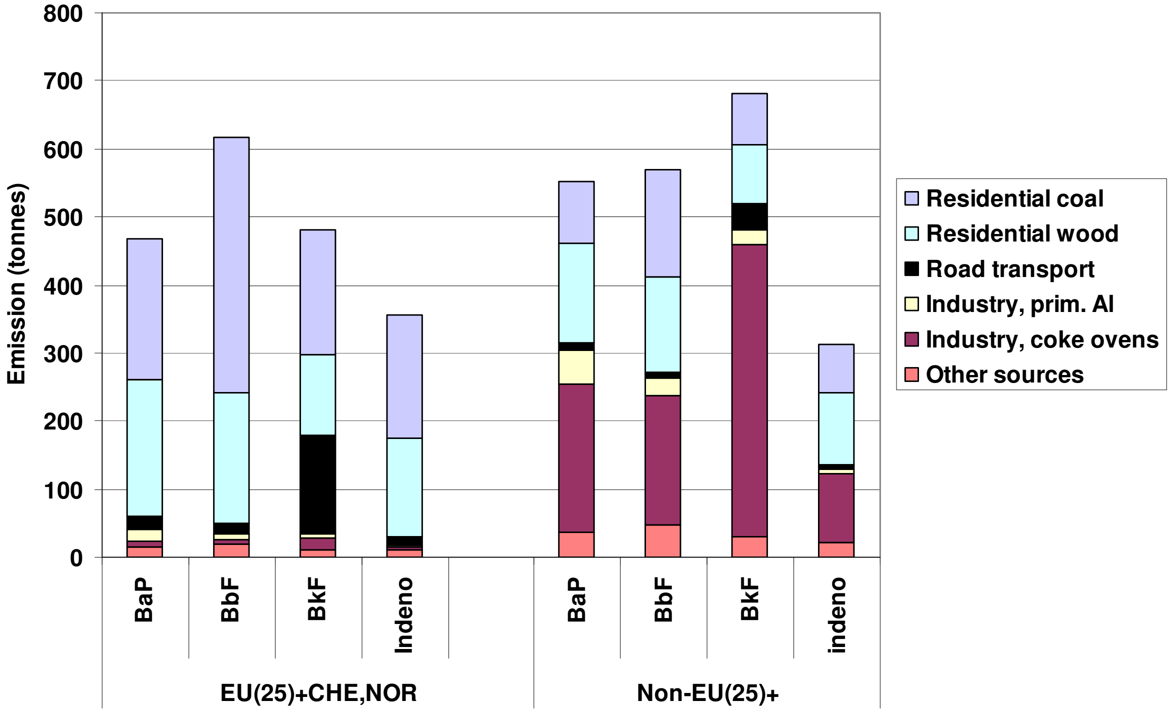

Figure 1 Emissions of benzo(a)pyrene, benzo(b)fluoranthene, benzo(k)fluoranthene, and indeno(1,2,3-cd)pyrene in the EU25+CHE and NOR and non-EU25 countries by source sector in 2005

Industrial PAHs emissions in non-EU25 countries could be significantly reduced by implementation of better emission control technologies in combination of closing and/or replacing out-dated installations. Especially coke ovens appear to have a large mitigation potential in the Non-EU(25) countries.

Road transport was found to be a relatively unimportant source of PAHs (Figure 1) with the exception of BkF. This is due to particularly high BkF emission factors for petrol-fuelled EURO 3 and 4 vehicles. This warrants further investigation especially since in combustion processes, BkF and BbF are usually emitted in at least the same order magnitude.

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