AN APPROACH TO ESTIMATION OF PAH EMISSIONS

1 INTRODUCTION

One of the agreed priorities of the UNECE Task Force on Emission Inventories has been to improve the relevant Guidebook chapters with respect to emissions of heavy metals and POPs, in view of the respective UNECE Protocols.

Polycyclic aromatic hydrocarbons (PAHs) are a group of compounds composed of two or more fused aromatic rings. The UNECE POPs Protocol specified that the following 4 PAHs should be used as indicators for the purposes of emission inventories:

- benzo[b]fluoranthene
- benzo[k]fluoranthene
- benzo[a]pyrene
- indeno[123-cd]pyrene

Appendix 1 shows the molecular weight, formulae and structures of these 4 PAHs.

The importance of PAHs as persistent organic pollutants 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 re-volatilisation 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.

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. This is because:

- many of the reported emissions of PAHs only give a figure for ‘total PAHs’, without indicating which PAH compounds are included in the total;
- where emissions of individual PAHs are given, there is a lack of consistency between reports on which PAHs are included in the measurements taken;
- most of the reported emissions of individual PAHs only give data for one or two compounds (usually including benzo[a]pyrene).

In this chapter a methodology is proposed that can be used for estimating PAH emissions where limited measurement and/or emission factor data are available.

Appendix 2 indicates the well-known categories of PAHs. Emission factor profiles are given in this chapter for the 4 PAHs covered by the POPs Protocol.

Details of the processes and control technology covered by the profiles and emission factors in this chapter can be found in the relevant sector-specific chapters.

2 CONTRIBUTION TO TOTAL EMISSIONS

The main PAH sources are likely to include:

- Domestic coal combustion
- Domestic wood combustion
- Industrial coal combustion
- Industrial wood combustion
- Natural fires / open agricultural burning
- Anode baking (for pre-baked aluminium industry)
- Aluminium production
- Vehicles

The above list is not ordered in terms of size of likely emission. The contribution to total national emissions for each source will depend on the extent of the relevant activity in each country.

3 DEFINITIONS

B[b]F - benzo[b]fluoranthene

B[k]F - benzo[k]fluoranthene

B[a]P - benzo[a]pyrene

ESP - electrostatic precipitators

I[cd]P - indeno[123-cd]pyrene

PAHs - polycyclic aromatic hydrocarbons.

POPs - persistent organic pollutants.

4 SIMPLER METHODOLOGY

The simpler methodology involves the standard approach of emission factor multiplied by activity statistic.

In most sectors in most countries, emission factors are unlikely to be available for many PAHs because of the lack of measurements that have been made. It is likely that in many cases, for example, an emission factor only for benzo[a]pyrene is available.

In these cases the emission factors for other PAHs can be estimated by multiplying the known emission factors by the appropriate ratios in the default profile data in Section 7.

Where no emission factors are available for any PAHs, the emission factors for benzo[a]pyrene in Appendix 3 can be used as default, and the profile data applied to these emission factors.

The methodology is summarised by the equations and example below.

Standard equation for estimating PAH emissions

Emission estimate = emission factor x activity statistic ....[1]

Equation for estimating PAH emission factor *(example equation for B[b]F)*

Emission factor (B[b]F) = Emission factor (B[a]P) x Profile ratio B[b]F/B[a]P ....[2]

Example *(domestic wood combustion)*

Activity statistic = 2 Mt / year for Country Y

B[a]P country-specific emission factor = 1000 mg/t
(NB use default emission factor 1300 mg/t from Appendix 3 if no country-specific data available)

Profile ratio B[b]F/B[a]P = 0.05 (from Section 7)
Emission factor (B[b]F) =1000 x 0.05 = 50 mg/t

Estimated emission of B[b]F for Country Y from domestic wood combustion
= 2 Mt x 50 mg/t = 100 kg (data quality E)

A key assumption for this methodology is that for a given process the relative profiles of PAHs are similar between countries.

Emission estimations should be made for the 4 PAHs specified by the UNECE POPs Protocol:
- benzo[b]fluoranthene
- benzo[k]fluoranthene
- benzo[a]pyrene
- indeno[123-cd]pyrene

The relevant sector-specific chapters of the Guidebook contain information on processes, control technology, point source criteria etc.

5 DETAILED METHODOLOGY

The detailed methodology involves the use measurement data where available in the generation of country-specific and plant-specific emission factors.

In addition, but of secondary importance, estimations of emissions of other PAHs (for example others within the 16 US EPA priority PAHs) should be made if the data are available.

6 RELEVANT ACTIVITY STATISTICS

The required activity statistics depend on the emission source for which estimates are made (e.g. tonnes of aluminium produced, tonnes of wood burned in domestic appliances, etc). The relevant sector-specific chapters of the Guidebook indicate where activity data can be found.

7 EMISSION FACTORS, PROFILES, QUALITY CODES AND REFERENCES

Profiles for main sources, estimated in a ratio to benzo[a]pyrene, are given in the table below:

Stationary Sources

PAH	**Coal combustion (industrial and domestic)**	**Wood combustion (industrial and domestic)**	**Natural fires / agricultural biomass burning**	**Anode baking**
Benzo[b]fluoranthene	0.05	1.2	0.6	2.2 B[b]F & B[k]F
Benzo[k]fluoranthene	0.01	0.4	0.3	
Benzo[a]pyrene	1.0	1.0	1.0	1.0
Indeno[123cd]pyrene	0.8	0.1	0.4	0.5

(Profiles in the above table were estimated from emission factors in Wenborn et al. 1998, which were developed from several other references)

Vehicles

PAH	**Passenger cars – gasoline (conventional)**	**Passenger cars – gasoline (closed loop catalyst)**	**Passenger cars – diesel (direct injection)**	**Passenger cars – diesel (indirect injection)**	**Heavy Duty Vehicles (HDV)**
Benzo[b]fluoranthene	1.2	0.9	0.9	0.9	5.6
Benzo[k]fluoranthene	0.9	1.2	1.0	0.8	8.2
Benzo[a]pyrene	1.0	1.0	1.0	1.0	1.0
Indeno[123cd]pyrene	1.0	1.4	1.1	0.9	1.4

(Profiles in the above table were estimated from emission factors in BUWAL (1994), TNO (1993), VW (1989) and Koufodimos (1999))

8 CURRENT UNCERTAINTY ESTIMATES

Limited data are available on PAH emissions relative to data on many other pollutants. The emission factors that are currently available for PAHs therefore have a high uncertainty. This uncertainty is demonstrated by the wide ranges and poor data quality ratings of the default emission factors for benzo[a]pyrene in Appendix 3.

The data quality rating for any emission estimates made using the profile data in Section 7 should be assumed to be E.

9 WEAKEST ASPECTS/PRIORITY AREAS FOR IMPROVEMENT IN CURRENT METHODOLOGY

The methodology of using profiles to estimate PAH emissions is required because limited measurement data are available. Measurements of PAH emissions from the main sources are urgently required. This would enable more reliable emission factors to be developed and these could be used directly to estimate emissions, rather than having to use the less reliable method involving emission profiles.

The priority source for improvement of emission factors is Primary Aluminium Production and Anode Baking.

10 VERIFICATION PROCEDURES

Verification of this methodology and the profiles is required through measurement of PAH emissions directly from the priority sources.

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13 POINT OF ENQUIRY

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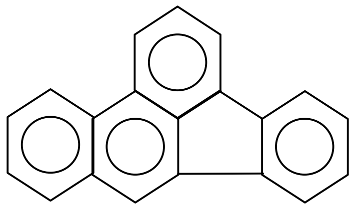
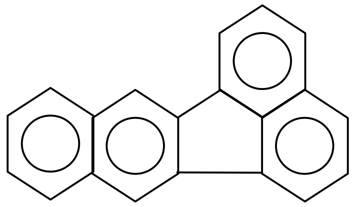
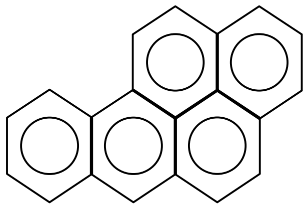
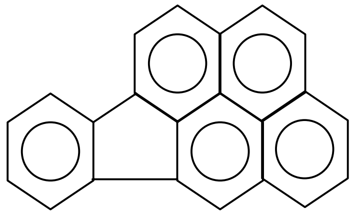
APPENDIX 1 - MOLECULAR WEIGHT, FORMULAE AND STRUCTURE OF THE FOUR PAHS IN THE POPS PROTOCOL

PAH	Molecular Weight	Formula	Structure
Benzo[b]fluoranthene	252	$C_{20}H_{12}$	
Benzo[k]fluoranthene	252	$C_{20}H_{12}$	
Benzo[a]pyrene	252	$C_{20}H_{12}$	
Indeno[1,2,3-cd]pyrene	276	$C_{22}H_{12}$	

APPENDIX 2 - CATEGORIES OF PAHS

The table below indicates the PAHs included in the following well-known categories :

- The 16 PAHs designated by the United States Environmental Protection Agency (US EPA) as compounds of interest under a suggested procedure for reporting test measurement results (US EPA 1988).
- The 6 PAHs identified by the International Agency for Research on Cancer (IARC) as probable or possible human carcinogens (IARC 1987).
- The Borneff 6 PAHs, which have been used in some emission inventory compilations.
- The 4 PAHs to be used as indicators for the purposes of emissions inventories under the UNECE POPs Protocol.

	US EPA Priority pollutants (16 PAHs)	**IARC** Probable or possible human carcinogens (6 PAHs)	**Borneff** (6 PAHs)	**UNECE POPs Protocol** Indicators for the purposes of emissions inventories (4 PAHs)
Naphthalene	✓			
Acenaphthylene	✓			
Acenapthene	✓			
Fluorene	✓			
Anthracene	✓			
Phenanthrene	✓			
Fluoranthene	✓		✓	
Pyrene	✓			
Benz[a]anthracene	✓	✓		
Chrysene	✓			
Benzo[b]fluoranthene	✓	✓	✓	✓
Benzo[k]fluoranthene	✓	✓	✓	✓
Benzo[a]pyrene	✓	✓	✓	✓
Dibenz[ah]anthracene	✓			
Indeno[123cd]pyrene	✓	✓	✓	✓
Benzo[ghi]perylene	✓		✓	

APPENDIX 3 - DEFAULT EMISSION FACTORS FOR BENZO[A]PYRENE

Source	Process type / fuel type	Emission Factor	Abatement type and efficiency	Data quality	Country or Region	Reference
Domestic coal combustion	Bituminous coal	500-2600 mg/t [best estimate 1550 mg/t]*	no control	D	W Europe / USA	TNO (1995), Radian Corporation (1995), Smith (1984), CRE (1992)
Domestic coal combustion	Manufactured smokeless coal	330 mg/t	no control	E	W Europe	Wenborn et al. (1997)
Domestic coal combustion	Anthracite	30 mg/t	no control	E	W Europe	Wenborn et al. (1997)
Domestic wood combustion	Wood	600-2000 mg/t [best estimate 1300 mg/t]*	no control	E	W Europe / USA	Radian Corporation (1995), Smith (1984)
Industrial coal combustion	Large plant	0.14 mg/t	effective end-of-pipe control	D	USA	Radian Corporation (1995)
Industrial coal combustion	Small plant	1550 mg/t	no control	E	UK	Wenborn et al. (1997)
Industrial coal combustion		[best estimate 775 mg/t]*		E		
Industrial wood combustion	Large plant	2 mg/t	effective end-of-pipe control	D	USA	Radian Corporation (1995)
Industrial wood combustion	Small plant	1300 mg/t	no control	E	UK	Wenborn et al. (1997)
Industrial wood combustion		[best estimate 650 mg/t]*		E		
Natural fires / open agricultural burning		0.2-14.3 g/t [best estimate 7.2 g/t]	no control	D	USA	Jenkins et al. (1996), Radian Corporation (1995)
Anode baking (for pre-baked aluminium industry)		5.6-135 g/t	Ranges from effective end-of-pipe technology to limited control	D	UK	Coleman (1999)

* best estimates of emission factors can be used when estimating total emission for sector for cases where no information on plant types and abatement is available

APPENDIX 3 - DEFAULT EMISSION FACTORS FOR BENZO[A]PYRENE (CONTINUED)

Source	Process type / fuel type	Emission Factor	Abatement type and efficiency	Data quality	Country or Region	Reference
Aluminium production	Pre-baked process	30-8600 mg/t [best estimate 100 mg/t]*	Ranges from effective end-of-pipe technology (e.g. dry scrubber system) to limited control	E	W Europe / USA	TNO (1995), Radian Corporation (1995), Wenborn et al. (1997)
Aluminium production	HSS process	*Emission factors to be developed*				
Aluminium production	VSS process	172 g/t	Wet scrubber and ESP	D	UK	Wenborn et al. (1997)
Vehicles	Passenger cars – gasoline	0.02 – 6.4 µg/km [best estimate 1.1 µg/km]*	conventional	D	Europe / USA	BUWAL (1994), TNO (1993), VW (1989) and Koufodimos (1999))
Vehicles	Passenger cars – gasoline	0.001 – 5.8 µg/km [best estimate 0.4 µg/km]*	closed loop catalyst	D	Europe / USA	As above
Vehicles	Passenger cars – diesel	0.3 – 1.0 µg/km [best estimate 0.7 µg/km]*	direct injection	D	Europe / USA	As above
Vehicles	Passenger cars – diesel	0.2 – 6.9 µg/km [best estimate 2.8 µg/km]*	indirect injection	D	Europe / USA	As above
Vehicles	Heavy Duty Vehicles (HDV)	0.02 – 6.2 µg/km [best estimate 1.0 µg/km]*		D	Europe / USA	As above

* best estimates of emission factors can be used when estimating total emission for sector for cases where no information on plant types and abatement is available