

Ambient Air Pollution by Polycyclic Aromatic Hydrocarbons (PAH)

Position Paper Annexes

July 27th 2001

**Prepared by the Working Group
On Polycyclic Aromatic Hydrocarbons**

PAH Position Paper Annexes
July 27th 2001

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Annex 1

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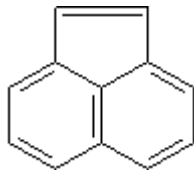
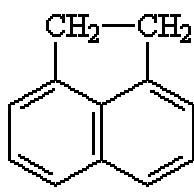
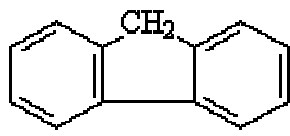
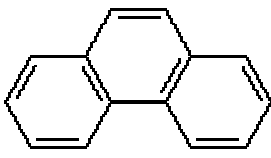
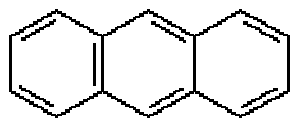
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Annex 2

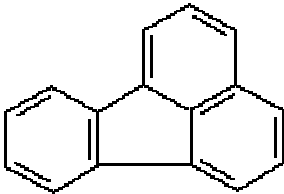
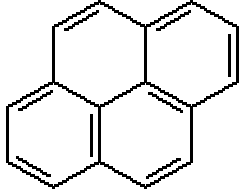
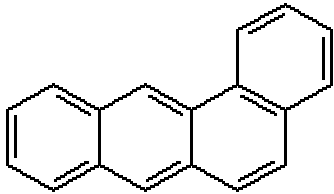
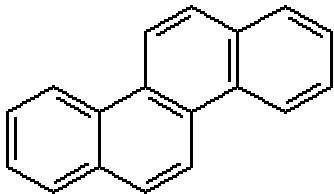
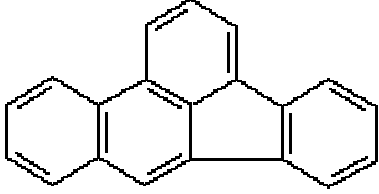
Tables and Figures

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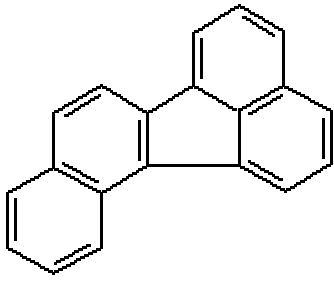
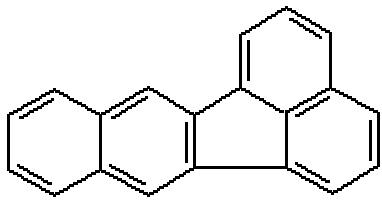
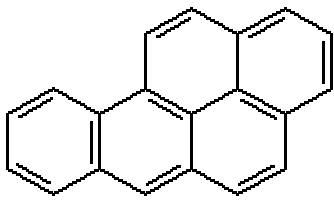
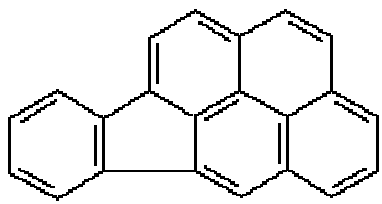
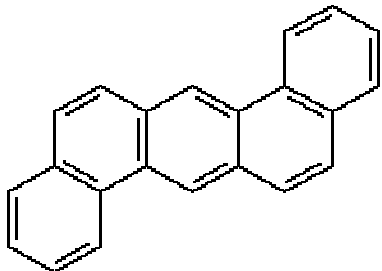
Table 1: Physical Properties and Structures of Selected PAH

<p>Acenaphthylene ACL Acenaphthalene Cyclopenta[de]naphthalene</p> <p>Molecular formula: $C_{12}H_8$ CAS Registry No.: 208-96-8 Boiling point °C: 280 Melting point °C: 92 - 93 Vapour Pressure (Pa at 25 °C) 9×10^{-1} [1]</p>	
<p>Acenaphthene AC 1,2-Dihydroacenaphthylene 1,8-Ethylenenaphthalene</p> <p>Molecular formula: $C_{12}H_{10}$ CAS Registry No.: 83-32-9 Boiling point °C: 279 Melting point °C: 95 Vapour Pressure (Pa at 25 °C) 3×10^{-1} [1]</p>	
<p>Fluorene FL o-Biphenylenemethane Diphenylenemethane 9H-Fluorene 2,2'-Methylenebiphenyl 2,3-Benzidene o-Biphenylmethane</p> <p>Molecular formula: $C_{13}H_{10}$ CAS Registry No.: 86-73-7 Boiling point °C: 295 Melting point °C: 115 - 116 Vapour Pressure (Pa at 25 °C) 9×10^{-2} [1]</p>	
<p>Phenanthrene PHE Phenanthrin</p> <p>Molecular formula: $C_{14}H_{10}$ CAS Registry No.: 85-01-8 Boiling point °C: 340 Melting point °C: 100.5 Vapour Pressure (Pa at 25 °C) 2×10^{-2} [1]</p>	
<p>Anthracene AN Anthracin Paranaphthalene</p> <p>Molecular formula: $C_{14}H_{10}$ CAS Registry No.: 120-12-7 Boiling point °C: 342 Melting point °C: 216.4 Vapour Pressure (Pa at 25 °C) 1×10^{-3} [1]</p>	

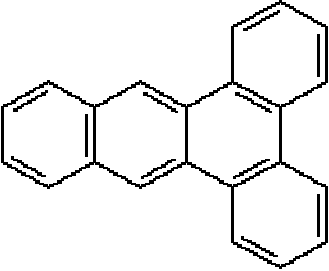
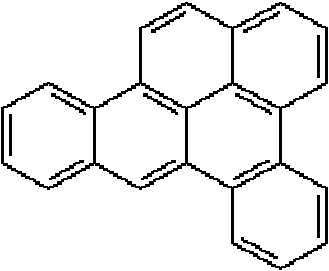
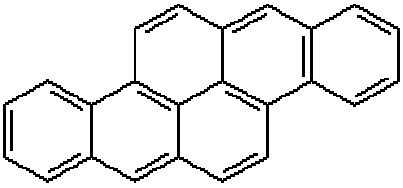
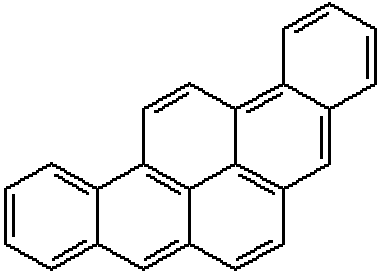
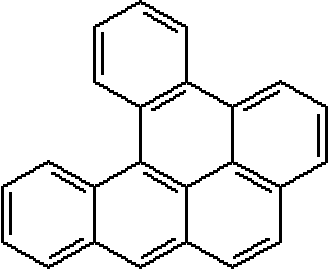
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<p>Fluoranthene FA Benzo[jk]fluorene Idryl 1,2-(1,8-Naphthalenediyl)benzene Benz[a]acenaphthylene 1,2-Benzoacenaphthylene Molecular formula: C₁₆H₁₀ CAS Registry No.: 206-44-0 Boiling point °C: 375 Melting point °C: 108.8 Vapour Pressure (Pa at 25 °C) 1.2 x 10⁻³ [1]</p>	
<p>Pyrene PY Benzo[def]phenanthrene Pyren Molecular formula: C₁₆H₁₀ CAS Registry No.: 129-00-0 Boiling point °C: 150.4 Melting point °C: 393 Vapour Pressure (Pa at 25 °C) 6.0 x 10⁻⁴ [1]</p>	
<p>Benz[a]anthracene BaA 1,2-Benzanthracene 1,2-Benzanthrene Benzo[b]phenanthrene 2,3-Benzophenanthrene Tetraphene Naphthanthracene Molecular formula: C₁₈H₁₂ CAS Registry No.: 56-55-3 Boiling point °C: 400 Melting point °C: 160.7 Vapour Pressure (Pa at 25 °C) 2.8 x 10⁻⁵</p>	
<p>Chrysene CHR Benzo[a]phenanthrene 1,2-Benzophenanthrene Molecular formula: C₁₈H₁₂ CAS Registry No.: 218-01-9 Boiling point °C: 448 Melting point °C: 253.8 Vapour Pressure (Pa at 25 °C) 5.7 x 10⁻⁷ [1]</p>	
<p>Benzo[b]fluoranthene BbFA 3,4-Benz[e]acephenanthrylene Benzo[b]fluoranthene Benzo[e]fluoranthene 2,3-Benzofluoranthene 3,4-Benzofluoranthene Molecular formula: C₂₀H₁₂ CAS Registry No.: 205-99-2 Boiling point °C: 481 Melting point °C: 168.3 Vapour Pressure (Pa at 20 °C) 6.7 x 10⁻⁵</p>	

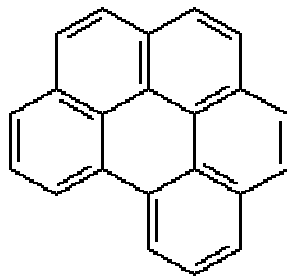
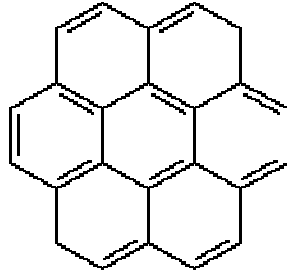
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<p>Benzo[j]fluoranthene BjFA 7,8-Benzfluoranthene Benzo[l]fluoranthene 10,11-Benzofluoranthene Dibenzo[a,jk]fluorene Molecular formula: C₂₀H₁₂ CAS Registry No.: 205-82-3 Boiling point °C: 480 Melting point °C: 165.4 Vapour Pressure (Pa at 25 °C) 2.0 x 10⁻⁶</p>	
<p>Benzo[k]fluoranthene BkFA 11,12-Benzofluoranthene 8,9-Benzofluoranthene 2,3:1',8'-Binaphthylene Dibenzo[b,jk]fluorene Molecular formula: C₂₀H₁₂ CAS Registry No.: 207-08-9 Boiling point °C: 480 Melting point °C: 215.7 Vapour Pressure (Pa at 20 °C) 5.2 x 10⁻⁸ [1]</p>	
<p>Benzo[a]pyrene BaP Benzo[def]chrysene 3,4-Benzopyrene 6,7-Benzopyrene 1,2-Benzpyrene 4,5-Benzpyrene Molecular formula: C₂₀H₁₂ CAS Registry No.: 50-32-8 Boiling point °C: 496 Melting point °C: 178.1 Vapour Pressure (Pa at 25 °C) 7.0 x 10⁻⁷ [1]</p>	
<p>Indeno[1,2,3-cd]pyrene IP 1,10-(1,2-Phenylene)pyrene 1,10-(o-Phenylene)pyrene o-Phenylenepyrene 2,3-(o-Phenylene)pyrene 2,3-Phenylenepyrene Molecular formula: C₂₂H₁₂ CAS Registry No.: 193-39-5 Boiling point °C: 536 Melting point °C: 163.6 Vapour Pressure (Pa at 20 °C) 1.3 x 10⁻⁸</p>	
<p>Dibenz[a,h]anthracene DBA_hA 1,2:5,6-Benz[a]anthracene 1,2:5,6-Benzanthracene 1,2:5,6-Dibenzoanthracene Molecular formula: C₂₄H₁₄ CAS Registry No.: 53-70-3 Boiling point °C: 524 Melting point °C: 266.6 Vapour Pressure (Pa at 25 °C) 3.7 x 10⁻⁸ [1]</p>	

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<p>Dibenz[a,c]anthracene DBaCA Benzo[b]triphenylene 1,2:3,4-Dibenzanthracene 2,3-Benztriphenylene</p> <p>Molecular formula: $C_{24}H_{14}$ CAS Registry No.: 215-58-7 Boiling point °C: 518[†] Melting point °C: 205 - 207[†] Vapour Pressure (Pa at 25 °C) 1.3×10^{-9} [1]</p>	
<p>Dibenzo[a,e]pyrene DBaEP Naphtho[1,2,3,4-def]chrysene 1,2:4,5-Dibenzopyrene</p> <p>Molecular formula: $C_{24}H_{14}$ CAS Registry No.: 192-65-4 Boiling point °C: 592 Melting point °C: 244.4 Vapour Pressure (Pa at 25 °C)</p>	
<p>Dibenzo[a,h]pyrene DBaHP Dibenzo[b,def]chrysene 3,4:8,9-Dibenzpyrene</p> <p>Molecular formula: $C_{24}H_{14}$ CAS Registry No.: 189-64-0 Boiling point °C: 596 Melting point °C: 317 Vapour Pressure (Pa at 25 °C)</p>	
<p>Dibenzo[a,i]pyrene DBaIP Benzo[rst]pentaphene Dibenzo[b,h]pyrene 3,4:9,10-Dibenzopyrene 1,2:7,8-Dibenzpyrene 4,5,8,9-Dibenzopyrene</p> <p>Molecular formula: $C_{24}H_{14}$ CAS Registry No.: 189-55-9 Boiling point °C: 594 Melting point °C: 282 Vapour Pressure (Pa at 25 °C) 3.2×10^{-10}</p>	
<p>Dibenzo[a,l]pyrene DBaLP Dibenzo[def,p]chrysene 2,3:4,5-Dibenzopyrene 3,4:8,9-Dibenzopyrene 4,5:6,7-Dibenzopyrene 1,2:9,10-Dibenzopyrene 1,2:3,4-Dibenzpyrene</p> <p>Molecular formula: $C_{24}H_{14}$ CAS Registry No.: 191-30-0 Boiling point °C: 595 Melting point °C: 162.4 Vapour Pressure (Pa at 25 °C)</p>	

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<p>Benzo[ghi]perylene BghiP 1,12-Benzoperylene Molecular formula: C₂₂H₁₂ CAS Registry No.: 191-24-2 Boiling point °C: Melting point °C: 277 Vapour Pressure (Pa at 25 °C)</p>	
<p>Coronene COR Dibenzo[ghi,pqr]perylene Hexabenzobenzene Molecular formula: C₂₄H₁₂ CAS Registry No.: 191-07-1 Boiling point °C: 525 Melting point °C: >350 Vapour Pressure (Pa at 25 °C) 2 x 10⁻¹⁰ [1]</p>	

N.B Vapour pressures vary according to reference

References:

[1] Mackay D, Shiu W Y, Ma K C. Illustrated handbook of physical-chemical properties and environmental fate for organic chemicals. Volume II. Lewis Publishers, Michigan 1992, ISBN 0-87371-583-7.

Other data:- WHO IPCS, Environmental Health Criteria 202, Selected Non-heterocyclic Aromatic Hydrocarbons, 1998 and NIST Special Publication 922, Polycyclic Aromatic Hydrocarbon Structure Index, Lane C. Sander and Stephen A. Wise

Aldrich Catalogue 1999-2000.

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Table 2: Details of carcinogenic groups and measurement lists of PAH

PAH	IARC Group (note 1)	US EPA 16	UNECE POPs Protocol (note 2)	FRANCE (note 3)	GERMANY (note 4)	ITALY (note 5)	SWEDEN (note 6)
Acenaphthylene	n.e.	✓					
Acenaphthene	n.e.	✓					
Fluorene	3	✓					
Phenanthrene	3	✓					✓
Anthracene	3	✓					
Fluoranthene	3	✓					✓
Pyrene	3	✓					✓
Benz[a]anthracene	2A	✓		✓	✓	✓	
Benzo[c]phenanthrene	3				✓		
Cyclopenta[cd]pyrene	3				✓		
Chrysene	3	✓			✓		
Triphenylene	3				✓		
Benzo[b]fluoranthene	2B	✓	✓	✓	✓	✓	✓
Benzo[j]fluoranthene	2B				✓	✓	
Benzo[k]fluoranthene	2B	✓	✓	✓	✓	✓	✓
Benzo[ghi]fluoranthene	3				✓		
Benzo[e]pyrene	3				✓		
Benzo[a]pyrene	2A	✓	✓	✓	✓	✓	✓
Indeno[1,2,3-cd]pyrene	2B	✓	✓	✓	✓	✓	✓
Dibenz[a,h]anthracene	2A	✓		✓	✓	✓	✓
Dibenzo[a,l]pyrene	2B						✓
Methylanthracenes/ phenanthrenes	n.e. (note 7)						✓
Retene (1-methyl-7- isopropylphenanthrene)	n.e.						✓
Benzo[ghi]perylene	3	✓		✓	✓		✓
Anthanthrene	3				✓		
Coronene	3				✓		
Naphthalene	n.e.	✓					

Notes

1. Overall evaluation of carcinogenicity to humans. 2A: probably carcinogenic; 2B: possibly carcinogenic; 3: not classifiable (IARC, Suppl. 7, 1987). n.e.: not evaluated.
2. PAH to be used as indicators for the purposes of emissions inventories under the United Nations Economic Commission for Europe (UNECE) 1998 Protocol to the 1979 convention on long-range transboundary air pollution on Persistent Organic Pollutants (UNECE POPs) Protocol.
3. Considered in the French standard method as representatives of PAH, on the basis of their carcinogenicity or occurrence (See Figure 4)
4. Proposed as relevant substances for measurement, based on their carcinogenicity or occurrence (see Figure 4: VDI Guideline 3875).
5. Recommended by the Italian National Advisory Toxicological Committee for health-related studies.
6. Recommended by the Swedish Environmental Protection Agency for monitoring programs (Swedish Environmental Protection Agency 1999).
7. Out of this sub-class, only 1-methylphenanthrene was evaluated (Group 3).

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Table 3: Review of Legislation or Guidance intended to limit ambient air concentrations of PAH.

Country	Ambient Air Standards		Comments concerning Emissions
	Significance of the standard(s) and reference	Standard(s)	
Austria	X	X	
Belgium-Brussels		No legislation [5]	Legislation on emissions exists (VLAREM II = TA Luft)
Belgium-Flemish area	Proposed values [5]	BaP (annual average): 1 ng/m ³ as a limit value 0.5 ng/m ³ as a guide value 0.017 ng/m ³ as a target value	All facilities with licence class 1 or 2 are obliged to produce emission reports yearly if they are above the threshold of 4 kg/year ¹ .
Croatia	Guidelines [4]	BaP (annual average): 2 ng/m ³ as a limit guide value 0.1 ng/m ³ as a recommended guide value	
Denmark	X	X	Recommended emission limit for the total amount of PAH ³ compounds is 0.1 – 0.5 mg/normal m ³ (10% O ₂ , dry air, 0 C, 101.3Pa).
Finland			No reply Received.
France	Recommended values [3]	BaP (annual average): 0.7 ng/m ³ as a limit value 0.1 ng/m ³ as a quality objective	Limits for BaP and DB[ah]A, if emission rates >0.5g/h, to be decided on a case by case basis depending upon the region and plant
Germany	Target value [8]	BaP: 1.3 ng/m ³	TA-Luft (1986) No. 2.3 Carcinogenic Substances Maximum permitted emission concentrations (for licenced installations) for BaP 0.1 mg/m ³ and DBahA 0.1 mg/m ³ for an exhaust gas mass flow of 0.5g/h or more. [9].
Greece			No reply received
Ireland	X	X	
Italy	Legal quality objective [7]	BaP (running annual average): 1 ng/m ³	Incinerators: legal limit for the sum of 11 carcinogenic PAHs. Industrial plants: legal limit for a group of carcinogenic/ mutagenic/teratogenic compounds, including 10 PAH
Iceland	X	X	
Luxembourg	X	X	
Netherlands	Non-legal air quality objectives [2]	BaP (annual average) ² 1 ng/m ³ as a 'limit' value 0.5 ng/m ³ as a 'guidance' value	
Portugal	X	X	
Spain	X	X	
Sweden	Recommended guidelines [1]	BaP: 0.1 ng/m ³ ; Fluoranthene: 2 ng/m ³	
Norway	X	X	
Switzerland	X	X	Have emission standard for some PAH: Napthalene 100mg/m ³ , 0.1mg/m ³ BaP and 0.1mg/m ³

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			Dibenzo(a,h) anthracene
United Kingdom	Recommended [6]	BaP (annual average): 0.25ng/m ³	
WHO	Unit risk	BaP: 8.7 x 10 ⁻² [µg/m ³]	

Table 3: Notes:

- ¹ Sum of the following PAH: naphthalene, phenanthrene, anthracene, fluoranthene, chrysene, benzo(a)anthracene, benzo(a)pyrene, benzo(k)fluoranthene, indene(1, 2, 3 cd)pyrene, benzo(g, h, i)perylene, benzo(e)pyrene, benzo(j)fluoranthene, benzo(b)fluoranthene, dibenzo(a, b)anthracene.
- ² The Netherlands: Limit value may not be exceeded and exceeding Guidance value should be avoided whenever possible.
- ³ Main group 1 compounds: Acenaphthene, benzo(a)anthracene, benzo(b)fluoranthene, benzo(j)fluoranthene, benzo(k)fluoranthene, benzo(b)fluorene, benzo(a)pyrene, chrysene, dibenzo(ah)anthracene, indeno(1,2,3-c,d)pyrene.

Table 3: References:

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Table 4: Emissions estimates from European countries - Anthropogenic emissions of PAH (tonnes/year) in the ECE region

	PAHs (1) [1995] (5) (EMEP)	PAHs (2) [1990] (UBA Berlin 1997)	BaP (3) [1995] (4) (Pacyna et al. 1999)
Albania		35.8	0.22
Austria	520.8	243	6.11
Belarus		191	5.25
Belgium	274.5	818	3.35
Bulgaria	521.4	54.9	6.71
Cyprus		0.18	
Czech Republic	1357.2	259	14.3
Denmark	10.36	76.7	1.44
Estonia	0.19	28.4	0.37
Finland		104	6.88
France	1889 (7)	3479	26.4
Germany		420	26.4
Greece		153	2.89
Hungary	67.6	192	10.3
Iceland		6.35	
Ireland		73.7	1.24
Italy		694	13.9
Latvia		38.4	3.00
Lithuania	71.2 (6)	52.3	2.20
Luxembourg	638 (8)	6.24	0.24
Moldova	0.17	58.0	1.01
Netherlands	128	184	2.29
Norway	172 (9)	140	2.24
Poland	242.3	372	65.2
Portugal		138	1.64
Romania		723	19.0
Russian federation	15.28 (10)	3146	262
Slovak Republic	30.1	310	6.71
Spain	232.5	521	9.61
Sweden	153	282	6.78
Switzerland		96.1	1.65
Ukraine	2.95 (6)	1137	51.8
United Kingdom	113.6	1437	12.0
Yugoslavia (former) Boznia and Herzegovovina Croatia Macedonia Slovenia Serbia and Montenegro	9.3	47.8 54.0 21.7 50.5 172	24.7

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Notes

1. The components that comprise total PAHs in the data from EMEP are unknown, unless otherwise stated.
2. PAH refers to the “Borneff six” (benzo[*a*]pyrene, benzo[*b*]fluoranthene, benzo[*ghi*]perylene, benzo[*k*]fluoranthene, fluoranthene and indeno[1,2,3-*c,d*]perylene).
3. benzo[*a*]pyrene
4. The reference year is 1995, or for some countries, 1993 or 1994.
5. The reference year is 1995, except Lithuania, Ukraine (1997) and Croatia (1996). Data contents supplied by EMEP by correspondence with V. Vestreng.
6. 1997
7. Emissions within the EMEP area.
8. Including source categories, SNAP 1,2,3,4.
9. Provisional figures
10. Figures are calculated by TNO.

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Table 5: Summary of recent (not older than 1990) typical European PAH- and BaP concentrations in ng/m³ as annual mean value.

Compound	Remote site	Rural site	Urban	Traffic	Industrial
Acenaphthene	0.01	0.3 – 2.6			98
Acenaphthylene	0.01				
Anthracene	n.d. ¹	0.04 – 15		0.2 – 0.6	1.1
Benz(a)anthracene	0.00 – 0.02	0.01 – 0.9	0.2 – 1.3	0.6 – 4.2	0.37 – 42
Benzo(a)pyrene	0.02	0.02 – 1.6	0.4 – 2	0.7 – 3.1	0.5 – 39
Benzo(e)pyrene	0.01 – 0.02	0.18 – 1.1	0.2 – 2.1	0.9 – 3.7	0.65 – 80
Benzo(b)fluoranthene	0.00 – 0.01	0.04 – 0.6			0.3 – 34
Benzo(ghi)perylene	0.01	0.15 – 1.0	0.5 – 2.8	1 – 4.7	0.7 – 52
Benzo(j)fluoranthene					
Benzo(k)fluoranthene		0.04 – 0.32	0.2 – 1		0.3 – 17
Chrysene		0.02 – 4.4	0.3 – 2.2		0.3 – 37
Coronene	0.00 – 0.01	0.02 – 0.5	0.1 – 0.6	0.4 – 2.5	0.26 – 5.2
Dibenz(a,h)anthracene	n.d.	0.02 – 1.1	0.06 – 0.3	0.1 – 0.4	0.05 – 7.5
Fluoranthene	0.14	0.04 – 7.4			42
Fluorene	0.2 – 0.4	0.3 – 46		9.9 – 16.7	
Indeno(123-cd)pyrene	0.02 – 0.04	0.04 – 0.21	0.3 – 2.1	1.3 – 2.6	0.4 – 37
Phenanthrene	0.1 – 0.3	0.42 – 150			16
Pyrene	0.08	0.1 – 6.1	0.24 – 1.2	9.2 – 15	75

¹ Not detected

N.B. Table 5 summarises recent (not older than 1990) typical European PAH- and BaP concentrations in ng/m³ as annual mean value. It has to be emphasised that the data reported within the response to the questionnaire and in the literature are derived from different measurement techniques and are often of unknown quality. In addition, the ranges for different compounds are not always directly comparable, since different data sets were combined. These original data sets partly comprise different single compounds.

SOURCES OF DATA INCLUDE FOR TABLE 5 INCLUDE:

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and

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Table 6: Summary of benzo[a]pyrene Emissions in the UK 1990-2010

BaP Emissions	1990		1995		2010 Estimated	
	Emission (tonnes)	% Contribution to total BaP Emissions from sources in this table	Emission (tonnes)	% Contribution to total BaP Emissions from sources in this table	Emission (tonnes)	% Contribution to total BaP Emissions from sources in this table
Vehicles – diesel	1.4	1.7	2.0	5.4	3.3	20.0
Vehicles – gasoline	8.5	10.6	5.7	15.5	0.7	4.0
Natural fires / open agric. Burning	31	38.7	2.9	7.8	2.9	17.5
Creosote use	0.06	0.07	0.06	0.16	0.06	0.4
Aluminium production	1.9	2.4	1.4	3.9	0.03	0.2
Anode baking	22.7	28.3	14.8	40.3	1.0	5.9
coke production	1.3	1.6	1.1	2.9	1.1	6.7
Domestic wood combustion	1.2	1.5	1.2	3.2	1.2	7.1
Industrial wood combustion	0.1	0.2	0.1	0.4	0.2	1.0
Domestic coal combustion	5.3	6.6	2.2	6.1	1.9	11.3
Industrial coal combustion	6.3	7.8	4.9	13.3	3.8	23.3
other sources	0.4	0.5	0.4	1.0	0.4	2.4
Total BaP Emission	80.2	100	36.8	100	16.4	100

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Table 7: Current network designs at national level (end-1999)

Country	Number of agglomerations/ Zones	Number of sampling sites per agglomeration/ zone	Characteristics of sampling sites	Sampling duration and frequency	Collected phase
Germany	6 federal states (out of 16)	Variable (from 1 to 35-67)	Variable. At least one 'urban street' in each state; other possible sites: 'urban area', 'rural area', 'industrial area'. Height: ca. 3 m.	Two 24-h samples per week	PM10 or TSP ^a
Italy	7 towns with > 150 000 inhabitants (foreseen: 23 towns, totally)	1-3 (foreseen: 3 in all 23 towns)	1 st site: high traffic and low ventilation; 2 nd site: densely populated area; 3 rd site: 'background' area (public park or pedestrian-reserved area). At street level.	One 24-h sample every 3 to 6 days	TSP or PM10 ^b
United Kingdom	5 towns 7 industrial areas 3 rural areas	1	Urban sites: background (on building roofs in, or near, the centre).	One continuous 2-week sample every 2-week period	TSP + vapour phase

^a General until 2000 PM10 was not distinguished from TSP

^b Not specified.

Additional information

Urban networks are operative in two French towns (E. Leoz, INERIS, personal communication; Thomas & Voisin 1993). In Paris, one 24-h sample per week is collected at three sites (TSP + vapour phase), including a traffic-oriented site and an industrial one. In Lille, weekly particulate samples are collected at four sites.

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Table 8: PAH sampling and analysis methods used in several European countries.

	Sampling	Extraction	Clean Up	Analysis	PAH	Calibration Methods	Standard Methods
UK	HVS (particle + gas), TSP Filter; PUF	Soxhlet; DCM, hexane or toluene	Silica gel or alumina chromatography columns Solid phase extraction cartridges	HPLC – UV HPLC – FLUO GC-MS	EPA list PAH + COR + BNT	Standard reference material (SRM) 1647 (priority pollutant polynuclear hydrocarbons in acetonitrile) 16 PAH NIST SRM Urban particulate matter SRM 1648 and SRM 1649	US-EPA method TO-13A (1997), for quantitative analysis and method calibration
FINLAND	HVS (particle), PM 10 66 m ³ /h (24 hours); Teflon filters; 6 samples pooled to monthly	Soxhlet	Liquide - liquide Extraction, DMSO Silica gel or alumina chromatography columns	GC-MS, SIM Internal Standard, deuterated PAH	PAH, methyl-PAH, BNT, 31 PAH and derivatives	CRM – 088 Certified standard materials (sewage sludge) SRM – 1650 Certified standard materials (diesel particulate matter)	
AUSTRIA	HVS (particle + gas), 15 m ³ / h (24 hours) GFF; 5 samples per month in one week	Soxhlet, hexane : diethylether; (20 hours)	Solid phase extraction cartridges	GC-MS, SIM Internal Standard, deuterated PAH	EPA list PAH + 4 specific tracers of traffic and heating combustion	Deuterated PAH solution	ISO 12884
ITALY	HVS (particle), TSP or PM 10 (24 hours); GFF; every 3 to 6 days	Ultrasonic extraction, cyclohexane	Thin layer chromatography on silica gel	GC-FID GC-MS External standard	IARC classification 2A or 2B PAH, (7 PAH) (only the BAP is legally regulated)	Standard solution	DM (Ministerial decree) (1994)
SPAIN	HVS (particle), TSP cascade impactor (particle); GFF	Soxhlet, cyclohexane or DCM or DCM : acetone	Silica gel or alumina chromatography columns	GC-MS	17 PAH		
GREECE	HVS (particle), TSP 60 m ³ /h (24 hours); GFF cascade impactor (particle), 60 m ³ /h HVS (particle + gas),	Soxhlet, cyclohexane or benzene Ultrasonic extraction, DCM or Hexane :cyclohexane or CAN	Liquide - liquide Extraction, dimethylformamide : water Silica gel or alumina chromatography	GC-FID GC-MS Internal Standard HPLC – FLUO Internal Standard	EPA list PAH		

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	Sampling	Extraction	Clean Up	Analysis	PAH	Calibration Methods	Standard Methods
	50 m ³ /h filter + PUF LVS (particle + gas), 30 l/min.		columns				
GERMANY	HVS (particle + gas), filter PUF			HPLC – FLUO GC-FID Internal Standard	32 PAH		VDI Guideline 3875 part 1 (1996)
SWEDEN	HVS (particle + gas), filter PUF; 1 week per month			GC-MS	16 PAH	Deuterated PAH solution	
BELGIUM (Brussels)	Particulate phase only Fluoroporo filters 1 sampling each week			HPLC – FLUO	8 PAH		
BELGIUM (Flandres)	LVS (particle), TSP (40 l/min); GFF; 1 sampling every day	Ultrasonic extraction, DCM		HPLC – FLUO	10 PAH (from fluoranthène to IP)	Standard reference material (SRM) 1647 (priority pollutant polynuclear hydrocarbons in acetonitrile) 16 PAH	
FRANCE (Paris)	HVS (particle + gas), 15 m ³ /h; QFF; PUF LVS (particle + gas), XAD – 2; filter	Soxhlet, DCM ASE (accelerated solvent extraction), DCM		HPLC –UV HPLC – FLUO External standard	EPA list PAH		
DENMARK	LVS (particle), 40 l/min; cellulosa nitrate/acetate filters	Soxhlet, toluene (24 h)	Silica gel or alumina chromatography columns	GC-FID GC-MS	6 PAH	Deuterated PAH solution	
LUXEMBOURG	Particulate phase only				EPA list PAH		
NORWAY				GC-MS	38 PAH		

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Table 9: BaP collected as vapour phase in European investigations: percent relative to total (vapour + particles) BaP

	Location type	Period	T (°C)	BaP in vapour phase	Reference
Oslo, N	street level	Jan, Feb	n.g.	n.d.	Thrane & Mikalsen, 1981
Rotterdam, NL	roof, 25 m	Jan, Feb	n.g.	ca. 10%	De Raat et al., 1987
	seaport, roof	n.g.	n.g.	n.d.	
Jülich, D	non urban	Jan	-5 - 10	n.d.	Niehaus et al., 1990
	“	Jul, Aug	10 - 30	n.d. or n.q.	
Birmingham, UK	roof, 15 m	Feb	n.g.	10%	Smith & Harrison, 1996
	“	Aug	n.g.	8%	
	road tunnel	n.g.	n.g.	n.d. (<7%)	
Augsburg, D	urban	Whole year	0 - 20 ^a	n.d.	Kaupp & McLacian, 1999
Rome, I	street level	Whole year	11 - 31 ^a	n.d.	Menichini, unpublished

n.d.: not detected; n.q.: not quantified; n.g.: not given.

^a Range of average temperatures during sampling periods.

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Table 10: Sources of uncertainties for the PAH analysis

Source	Uncertainty value, %	
	A	B
a) Standards - Pure solid compound - Certified standard solution - Gas standard	_____	1-2 ^(1,2)
b) Reference Material: Air Sample	2 ⁽³⁾	_____
c) Sampling: (Flow regulation + Sampling Efficiency)	10 ⁽⁴⁾	10 ⁽⁴⁾
d) Extraction, concentration and clean-up	_____	10 ⁽⁵⁾
e) Gas/particle equilibrium	4 ⁽⁶⁾	
f) Calibration, quantification, (analytical error)	5 ^(5,7)	
g) Storage	< 5	
Combined uncertainty	13	16.5
Expanded Uncertainty, %	26-33 %	

- Note: A and B represent different alternatives to the combination of uncertainties' budget, according to the source of information.
- The combined uncertainty is calculated by the following expression:

$$\text{Combined Uncertainty} = \sqrt{a^2 + b^2 + c^2 + d^2 + e^2 + f^2 + g^2}$$

- In those cases, where the uncertainty changes significantly between PAH, benzo-a-pyrene (BaP) was taken as a representative
- The uncertainty for sampling was established in basis of the admitted PM10 sampling variability
- The uncertainty assigned to the gas particle-equilibrium does not include the uncertainty, which would range between extreme sampling temperature conditions, for instance, seasonal variations. Correction factors could be used to reduce such an uncertainty for the semi-volatile PAHs, if only one of the phases is analysed.
- When certified air sample reference material was used for calibration, the uncertainty associated with the extraction, concentration and clean-up steps were considered negligible.

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Table 11: The degree of evidence for carcinogenicity of PAH in experimental animals and, and overall evaluations of carcinogenicity to humans according to IARC 1983; 1987^a

PAH Compound	Number of Rings	IARC	
		Animals	Humans
Anthracene	3	I	3
Phenanthrene	3	I	3
Benzo[c]phenanthrene	4	I	3
Chrysene	4	L	3
Benz[a]anthracene	4	S	2A
Pyrene	4	I	3
Triphenylene	4	I	3
Benzo[b]fluoranthene	5	S	2B
Benzo[j]fluoranthene	5	S	2B
Benzo[k]fluoranthene	5	S	2B
Benzo[a]pyrene	5	S	2A
Benzo[e]pyrene	5	I	3
Dibenz[a,c]anthracene	5	L	3
Dibenz[a,h]anthracene	5	S	2A
Dibenz[a,j]anthracene	5	L	3
Perylene	5	I	3
Anthanthrene	6	L	3
Benzo[ghi]perylene	6	I	3
Indeno[1,2,3-cd]pyrene	6	S	2B
Coronene	6	I	3
Dibenzo[a,e]pyrene	6	S	2B
Dibenzo[a,h]pyrene	6	S	2B
Dibenzo[a,i]pyrene	6	S	2B
Dibenzo[a,l]pyrene	6	S	2B

(I: inadequate evidence; L: limited evidence; S: sufficient evidence; 2A: probably carcinogenic to humans; 2B: possibly carcinogenic to humans; 3: not classifiable)

^a: From: Bostrom CE, Gerde P, Hanberg A, Jernstrom B, Johansson C, Kyrklund T, Rannug A, Tornqvist M, Westerholm R, Victorin K. Cancer risk assessment, indicators and guidelines for polycyclic aromatic hydrocarbons (PAH) in the ambient air. [Swedish Environmental Protection Agency 1999].

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Table 12: IARC evaluations of certain complex mixtures and occupational exposures involving exposure to PAH compounds^a

Mixture/Exposure	IARC Classification			
	Group 1: Carcinogenic to humans	Group 2A: Probably Carcinogenic to humans	Group 2B: Possibly Carcinogenic to humans	Group 3: Not Classifiable
Bitumen				X
Bitumen extracts			X	
Carbon black				X
Carbon black extracts			X	
Coal dust				X
Coal tar pitches	X			
Coal tars	X			
Creosotes		X		
Crude oil				X
Diesel fuels				
Diesel fuels; light				X
Diesel fuels; marine diesel			X	
Fuel oils				
Fuel oils; heavy			X	
Fuel oils; light				X
Gasoline			X	
Jet fuel				
Mineral oils				
Mineral oils, untreated	X			
Mineral oils, mildly-treated	X			
Mineral oils, highly refined				X
Petroleum solvents				X
Shale oils	X			
Soots	X			
Diesel exhausts		X		
Gasoline exhausts			X	
Tobacco smoke	X			
Aluminium production	X			
Coal gasification	X			
Coke production	X			
Petroleum refining		X		

^a: From: Bostrom CE, Gerde P, Hanberg A, Jernstrom B, Johansson C, Kyrklund T, Rannug A, Tornqvist M, Westerholm R, Victorin K. Cancer risk assessment, indicators and guidelines for polycyclic aromatic hydrocarbons (PAH) in the ambient air. [Swedish Environmental Protection Agency 1999].

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Table 13: Historic levels of polynuclear aromatic compounds ($\mu\text{g}/\text{m}^3$) in the atmosphere of areas of an aluminium production plant^a

Polynuclear aromatic compound	Vertical-stud Söderberg plant (range of 10 samples)		Prebake plant (range of 6 samples)	
	Particulate	Gaseous	Particulate	
Naphthalene	ND-40	0.72-311.3	--	ND-12.04
Methylnaphthalene	ND-0.12	1.22-123.5	--	ND-22.3
Biphenyl	ND-0.42	5.38-381.0	--	ND-14.48
Dibenzofuran	ND-0.46	2.09-61.0	--	ND-3.57
Fluorene [*]	ND-0.53	6.31-135.2	--	ND-8.85
9-Methylfluorene	ND-0.1	0.12-11.0	--	ND-0.28
2-Methylfluorene	ND-0.34	0.85-13.0	--	ND-0.86
1-Methylfluorene	ND-0.23	0.27-13.0	--	ND-1.1
Dibenzothiophene	0.2-1.2	3.46-58.0	--	ND-5.2
Phenanthrene [*]	ND-12.0	39.9-446	ND-0.16	1.91-49.0
Anthracene [*]	ND-1.8	2.98-32.6	--	ND-5.27
Carbazole [*]	ND-2.8	ND-1.4	--	ND-0.20
Methylphenanthrene [*] and methylantracene	ND-3.2	0.17-15.3	--	ND-1.5
Fluoranthene [*]	5.5-30.0	14.1-162	0.14-0.66	0.88-13.4
Dihydrobenzo[a]- and dihydrobenzo[b]fluorene	ND-0.91	ND-1.8	--	ND-0.20
Pyrene [*]	3.7-24.8	8.03-91.1	0.08-0.37	0.40-7.84
Benzo[a]fluorene [*]	1.4-9.1	ND-7.5	--	ND-0.70
Benzo[b]fluorene [*]	0.9-5.7	ND-2.3	--	ND-0.15
1-Methylpyrene	0.3-3.0	ND-0.16	--	--
Benzo[c]phenanthrene [*]	0.4-7.9	ND-0.36	--	--
Benz[a]anthracene	1.0-15.0	ND-0.21	0.05-0.26	--
Chrysene/triphenylene [*]	2.1-30.1	ND-0.44	0.07-0.36	--
Benzo[b]- and benzo[k]fluoranthene [*]	1.1-26.9	--	ND-0.28	--
Benzo[e]pyrene [*]	0.8-12.2	--	ND-0.09	--
Benzo[a]pyrene [*]	0.7-9.0	--	ND-0.05	--
Perylene [*]	ND-2.4	--	--	--
o-Phenylene-pyrene	0.4-5.3	--	ND-0.16	--
Benzo[ghi]perylene [*]	0.4-5.8	--	ND-0.32	--
Anthanthrene [*]	ND-0.32	--	--	--
Coronene [*]	ND-1.2	--	--	--
Dibenzopyrene [*]	ND-1.2	--	--	--
Total polynuclear aromatic compounds	19.7-202	86.0-1564.1	0.56-1.7	4.56-123.95

^a: From: Bjørseth A, Bjørseth O, Fjeldstad PE. Polycyclic aromatic hydrocarbons in the work atmosphere. 1. Determination in an aluminum reduction plant. *Scand J Work Environ Health* 1978; 4:212-223.

Compounds marked with an asterisk (*) were considered Volume 32 of the IARC Monographs (1983). ND = not detected.

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Table 14: Concentrations of polycyclic aromatic compounds (PAH) ($\mu\text{g}/\text{m}^3$) in the atmosphere of a coke plant; stationary sampling at the battery top, 1976^a

PAC	Range	
	Particulates	Gaseous
Naphthalene	0-4.4	278-1151
2-Methylnaphthalene	0-3.0	43-186
1-Methylnaphthalene	0-0.08	0-86
Biphenyl	0-0.39	0-34
Acenaphthalene	0-30	0-251
Acenaphthene	0-17	6.0-104
Dibenzofuran	0-60	19-81
Fluorene	0-58	23-125
9-Methylfluorene	0-70	0.7-1231
2-Methylfluorene	4.6-20	2.0-10
1-Methylfluorene	0.7-2.0	0-10
Dibenzothiophene	0-76	1.2-49
Phenanthrene	27-891	6.7-276
Anthracene	9.6-314	6.0-91
Carbazole	3.0-19	0-11
2-Methylanthracene	2.8-23	<0.7-16
1-Methylphenanthrene	2.7-21	0-7.0
9-Methylanthracene	3.2-17	0.8-16
Fluoranthene	45-427	0-24
Dihydrobenzo[a]- and dihydrobenzo[b]fluorene	9.2-115	0-2.8
Pyrene	35-319	0-14
Benzo[a]fluorene	9.7-90	0-6.8
Benzo[b]fluorene	3.1-61	0-0.3
4-Methylpyrene	0-3	-
1-Methylpyrene	2.5-24	0-0.2
Benzo[c]phenanthrene	2.6-49	-
Benz[a]anthracene	5.4-156	<0.4-1.6
Chrysene triphenylene	26-189	0-1.8
Benzo[b]fluoranthene	5.5-67	0-0.7
Benzo[j]- and benzo[k]fluoranthene	0-35	0-0.7
Benzo[e]pyrene	8-73	0-0.2
Benzo[a]pyrene	14-135	0-1.5
Perylene	3.3-19	0-0.1
o-Phenylene-pyrene	6.3-74	0-1.2
Benzo[ghi]perylene	8.7-45	-
Anthanthrene	2.6-62	-
Dibenzo[a,l]pyrene	3.6-24	-
Coronene	1.0-19	-

^a: From Bjorseth A, Bjorseth O, Fjeldsted PE. Polycyclic aromatic hydrocarbons in the work atmosphere. II. Determination in a coke plant. Scand J Work Environ Health 1978; 224-236.

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Table 15: Summary of Unit Risk Estimates for BaP and for PAH with BaP as indicator substance (life-time risk per ng/m³ of BaP)^a

Basis for calculation	Unit Risk	Reference
1) Animal experiments	0.28 x 10 ⁻⁶ *	RIVM, 1989
Inhalation of BaP in hamsters (Thyssen <i>et al</i> , 1981)		
(Thyssen <i>et al</i> , 1981)	0.37 – 1.7 x 10 ⁻⁶ **	Collins <i>et al</i> , 1991; CARB 1994; Muller <i>et al</i> , 1997
Inhalation of BaP + SO ₂ in rats (Laskin <i>et al</i> , 1970)	0.59 x 10 ⁻⁶ *	RIVM, 1989
Inhalation of BaP in mice (Knizhikow <i>et al</i> , 1982)	400 x 10 ⁻⁶ *	RIVM, 1989
Intratracheal instillation of hamsters Saffiotti <i>et al</i> , 1972 Feron <i>et al</i> , 1973	4.4 x 10 ⁻⁶ ** 4.8 x 10 ⁻⁶ **	Collins <i>et al</i> , 1991; CARB 1994 -"
Inhalation of coal tar/pitch aerosol with BaP as indicator substance	20 x 10 ⁻⁶ **	Heinrich <i>et al</i> , 1994
2) Epidemiology (PAH with BaP as indicator)		
US coke oven workers	87 x 10 ⁻⁶	WHO, 1987; 1988
US coke oven workers	23 x 10 ⁻⁶	Muller <i>et al</i> , 1998
US coke oven workers	50 x 10 ⁻⁶	Pott, 1985
UK gas workers	430 x 10 ⁻⁶	Pike, 1983
Smoky coal indoors in China	67 x 10 ⁻⁶	RIVM, 1989
"Most appropriate" estimate	100 x 10 ⁻⁶	RIVM, 1989
Aluminium smelters	90 x 10 ⁻⁶	Armstrong <i>et al</i> , 1994, converted from workplace exposure to continuous life-time exposure

*: Linear extrapolation

**: Linearized multistage model

^a: From: Bostrom CE, Gerde P, Hanberg A, Jernstrom B, Johansson C, Kyrklund T, Rannug A, Tornqvist M, Westerholm R, Victorin K. Cancer risk assessment, indicators and guidelines for polycyclic aromatic hydrocarbons (PAH) in the ambient air. Swedish Environmental Protection Agency, 1999.

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Table 16: Relative potency of individual PAH compared to BaP (TEF-values), according to different authors^a

Compound	Chu and Chen, 1984 (cited by Nisbet and LaGoy, 1992)	Clement, 1986 (cited by Nisbet and LaGoy 1992); Krewski <i>et al</i> , 1989	Nisbet and LaGoy, 1992	The Netherlands (RIVM, 1989)	California EPA (CARB 1994); Collins <i>et al</i> , 1998	Canada (Meek <i>et al</i> , 1994)	Ontario (Muller 1997)	Larsen and Larsen, 1998
Anthracene			0.01	0				0.0005
Phenanthrene			0.001	0.01			0.00064	0.0005
Benzo[a]-anthracene	0.013	0.145	0.1	0-0.04	0.1		0.014	0.005
Benzo[c]-phenanthrene							0.014	0.005
Chrysene	0.001	0.0044	0.01	0.05-0.89	0.01		0.026	0.03
Fluoranthene			0.001	0-0.06				0.05
Pyrene		0.081	0.001				0	0.001
Benzo[a]pyrene	1	1	1	1	1	1	1	1
Benzo[e]pyrene		0.004					0	0.002
Benzo[b]-fluoranthene	0.08	0.14	0.1		0.1	0.06	0.11	0.1
Benzo[j]-fluoranthene		0.061			0.1	0.05	0.045	0.05
Benzo[k]-fluoranthene	0.04	0.066	0.1	0.03-0.09	0.1	0.04	0.037	0.05
Cyclopenta[cd]-pyrene		0.023					0.012	0.02
Dibenzo[ah]-anthracene	0.69	1.11	5				0.89	1.1
Anthranthrene		0.32					0.28	0.3
Benzo[ghi]-perylene		0.022	0.01	0.01-0.03			0.012	0.02
Dibenzo[ae]-pyrene					1		1.0*	0.2
Dibenzo[ah]-pyrene					10		1.2	1
Dibenzo[ai]-pyrene					10		1.2	1
Dibenzo[al]-					10		100*	1

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Compound	Chu and Chen, 1984 (cited by Nisbet and LaGoy, 1992)	Clement, 1986 (cited by Nisbet and LaGoy 1992); Krewski <i>et al</i> , 1989	Nisbet and LaGoy, 1992	The Netherlands (RIVM, 1989)	California EPA (CARB 1994); Collins <i>et al</i> , 1998	Canada (Meek <i>et al</i> , 1994)	Ontario (Muller 1997)	Larsen and Larsen, 1998
pyrene								
Indeno[1,2,3-cd]-pyrene	0.017	0.232	0.1	0-0.08	0.1	0.12	0.067	0.1

*: Muller P, Leece B, Raha D. Estimated risk of cancer from exposure to PAH fractions of complex mixtures: In: Fifteenth international symposium on polycyclic aromatic compounds: Chemistry, biology and environmental impact, Belgirate, Italy, 19-22 September. ISPRA, Joint Research Centre European Commission, pp159-160. 1995

^a: From: Bostrom CE, Gerde P, Hanberg A, Jernstrom B, Johansson C, Kyrklund T, Rannug A, Tornqvist M, Westerholm R, Victorin K. Cancer risk assessment, indicators and guidelines for polycyclic aromatic hydrocarbons (PAH) in the ambient air. [Swedish Environmental Protection Agency 1999].

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Table 17: The estimated contribution of selected PAHs (particulate and gaseous) to total carcinogenic activity of PAH mixtures from different sites of exposure

Site Type	London: average 1991-95			Middlesbrough: average 1993-95			Aluminium Smelter			Coke Oven fumes			
Source	DETR, 1999 ¹			DETR, 1999 ¹				Farant and Gariépy 1998		Menichini 1998			
PAH ^a	RC	RP	RC x RP	RC	RP	RCxRP	RC	RP	RC x RP	RC Range	Med	RP	RC x RP ^d
Benzo[a]pyrene	1	1	1	1	1	1	1	1	1	1	1	1	1
Benzo[a]anthracene	1.2	0.1 ^b	0.1	1.3	0.1	0.1	1.8	0.1	0.2	0.9-2.8	1.7	0.1	0.2
Dibenzo[ah]anthracene	0.3 ^c	1.91	0.6	0.5 ^c	1.91	1.0	0.1	1.91	0.2	0.04-0.2	<0.2	1.91	0.2
Benzo[b]fluoranthene	2.4	0.11	0.3	2.4	0.11	0.3	3.8	0.11	0.4	-	-	-	-
Benzo[k]fluoranthene	2.1	0.03	0.1	1.9	0.03	0.1	1.2	0.03	0.1	-	-	-	-
Benzo[b+k+j]fluoranthene	-	-	-	-	-	-	-	-	-	0.6->2.3	2.2	0.11 ^f	0.2
Indeno[1,2,3-cd]pyrene	1.8	0.08	0.1	1.5	0.08	0.1	0.7	0.08	0.1	0.4-0.7	0.6	0.08	0.05
Chrysene	2.0	0.03	0.1	2.3	0.03	0.1	3.5	0.03	.01	<1.2-<2.2	<1.5	0.03	0.05
% Contribution of BaP to total carcinogenic activity	44.6			37.5			49.3			53.0			

¹: Department of the Environment, Transport and the Regions. Expert Panel on Air Quality Standards. Polycyclic Aromatic Hydrocarbons. London: The Stationery Office, 1999; 21.

^a: Contributions from other PAHs are expected to be small although some PAHs with similar levels of carcinogenic activity have not been measured at all sites (eg, anthanthrene) and the carcinogenic activity of some PAHs has not been tested.

^b: The figure for benzo[a]anthracene is based on studies of its carcinogenic effect on the skin.

^c: Also includes dibenz[ac]anthracene.

^d: From RC median value, without considering the "<"

^f: the RP of BbFA was attributed to the sum of the three isomers.

RC = Relative Concentrations RP = Relative Potency; in both cases, relative to benzo[a]pyrene

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Table 18: Summary of PAH and related substances recommended in Sweden to be included in ambient air monitoring^a

Substance	Physical State	Reason for Selection
1. Abundance		
Phenanthrene	Volatile	High concentration
Methylated anthracenes/Phenanthrenes	Volatile	High concentration
Pyrene	Semi volatile	High concentration
2. Carcinogenicity		
Fluoranthene	Volatile	High concentration, carcinogenic
Benzo[a]pyrene	Particulate-bound	Carcinogenic, well studied
Dibenz[a,h]anthracene	Particulate-bound	Carcinogenic
Dibenzo[a,l]pyrene	Particulate-bound	Strongly carcinogenic
Benzo[b and k]fluoranthene	Particulate-bound	Carcinogenic; indicator of gasoline exhaust
Indeno[1,2,3-cd]pyrene	Particulate-bound	Carcinogenic; indicator of gasoline exhaust
3. Source-specificity		
Retene	Semi volatile	Indicators of wood combustion emissions
Dibenzothiophene	Semi volatile	Indicators of sulphur-containing fuel (diesel exhaust)
Benzonaphthothiophene	Semi volatile	Indicator of sulphur-containing fuel (diesel exhaust)
Benzo[ghi]perylene	Particulate-bound	Indicator of gasoline exhaust

^a: From: Bostrom CE, Gerde P, Hanberg A, Jernstrom B, Johansson C, Kyrklund T, Rannug A, Tornqvist M, Westerholm R, Victorin K. Cancer risk assessment, indicators and guidelines for polycyclic aromatic hydrocarbons (PAH) in the ambient air. [Swedish Environmental Protection Agency 1999].

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Table A4.1: Summary of reported saturation vapour concentrations of PAHs, and some typical observed concentrations and gas-particle phase partitioning

PAH (number of rings)	Molecular weight	Vapour pressure	Saturation vapour concentration	Observed mean concentration	Observed % in particulate phase			
		Pa (a)	ng m ⁻³ (b)	Ng m ⁻³ (c)	(d)	(e)	(f)	(g)
Napthalene (2)	152	1.1 x 10 ⁻¹	6.7 x 10 ⁸		0 %			0.0 %
Acenaphthylene (3)	164	1.3 x 10 ⁻¹	8.6 x 10 ⁶	2.1				
Acenaphthene (3)	166	4.0 x 10 ⁻¹	2.7 x 10 ⁷	1.1				
Fluorene (3)	166	1.1 x 10 ⁻¹	7.4 x 10 ⁶	5.1	0 %			
Anthracene (3)	178	8.7 x 10 ⁻⁴	6.2 x 10 ⁴	1.4	3 %			0.5 %
Phenanthrene (3)	178	2.0 x 10 ⁻²	1.4 x 10 ⁶	2.0 x 10 ¹	3 %	12.4 %	1.9 %	0.4 %
Fluoranthene (4)	202	1.6 x 10 ⁻³	1.3 x 10 ⁵	4.8	54 %	49.7 %	19.1 %	5.9 %
Pyrene (4)	202	4.4 x 10 ⁻⁴	3.6 x 10 ⁴	4.0	57 %	61.4 %	29.6 %	7.5 %
Benz[a]anthracene (4)	228	2.1 x 10 ⁻⁶	1.9 x 10 ²	4.9 x 10 ⁻¹	97 %	89.4%	62.7 %	
Chrysene (4)	228	1.4 x 10 ⁻⁶	1.3 x 10 ²	1.0	99 %			
Benzo[b]fluoranthene(5)	252	1.0 x 10 ⁻⁶	1.0 x 10 ²	6.3 x 10 ⁻¹	100 %	92.2 %	92.3 %	
Benzo[a]pyrene (5)	252	5.3 x 10 ⁻⁸	5.4	2.9 x 10 ⁻¹	100 %	100%	100%	98.3 %
Perylene (5)	252	1.8 x 10 ⁻⁸	1.9		100 %			90.0 %
Dibenz[ac]anthracene (5)	278	5.7 x 10 ⁻⁹	6.4 x 10 ⁻¹	8.0 x 10 ⁻²	100 %			
Dibenz[ah]anthracene (5)	278	4.9 x 10 ⁻⁹	5.5 x 10 ⁻¹	8.0 x 10 ⁻²	100 %	100%	100%	
Benzo[ghi]perylene (6)	276	1.0 x 10 ⁻⁸	1.1	9.3 x 10 ⁻¹	100 %	100%	100%	
Coronene (7)	300	2.9 x 10 ⁻¹⁰	3.5 x 10 ⁻²		100 %	100%	100%	
N.B Vapour pressures vary according to reference hence any differences with Table 1 above								
Notes								
(a) Vapour pressures taken from Neiderfellner et al. (1997) and Oja and Suuberg (1998).								
(b) Saturation vapour concentrations calculated for 298K and 1 atmosphere pressure.								
(c) 1997 annual mean concentrations in London (Coleman et al., 1998).								
(d) Measurements made in Oslo, January/February 1979 (Thrane and Mikalsen, 1981).								
(e) Annual mean measurements made in Bayreuth, Germany, May 1995-April 1996 (Horstmann and McLachlan, 1998).								
(f) Summer mean measurements made in Bayreuth, Germany, May-October 1995 (Horstmann and McLachlan, 1998).								
(g) Measurements made in Torrance, California, February 1986 (Arey et al., 1987)								

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Table A4.2: Representative lifetimes of some 4- and 5-ring PAHs with respect to thermal reaction with nitrogen dioxide (NO₂), ozone (O₃) and dinitrogen pentoxide (N₂O₅) on “wood soot” particles

PAH (number of rings)	Representative lifetime with respect to reaction with		
	O ₃ (a)	NO ₂ (b)	N ₂ O ₅ (c)
Pyrene (4)	1.8 days (d)		4 years (d)
Benz[a]anthracene (4)	1.2 days (d)		
Chrysene (4)	2.2 days (d)		
Benzo[b]fluoranthrene (5)			19 years (e)
Benzo[k]fluoranthrene (5)	1.2 days (d)		14 years (e)
Benzo[a]pyrene (5)	1.6 days (d)	19 days (e)	5.1 years (e)
	1.8 days (e)		
Benzo[ghi]perylene (6)			10 years (e)
Notes (a) Typical UK background O ₃ concentration of 30 ppbv assumed (PORG 1997). (b) Average UK urban NO ₂ concentration taken to be 50 ppbv, on the basis of data presented by PORG (1997). (c) A typical 24-hour averaged N ₂ O ₅ concentration estimated to be 50 pptv, on the basis of observed concentrations of NO ₃ (Carslaw et al., 1997) and NO ₂ (PORG, 1997), and the equilibrium constant for the reaction NO ₂ +NO ₃ ↔ N ₂ O ₅ (Wayne et al., 1991). (d) Based on environmental chamber data of Kamens et al. (1985b). (e) Based on environmental chamber data of Kamens et al. (1990).			

Table A4.3: Representative lifetimes of some surface-adsorbed PAHs with respect to photolysis under conditions representative of a cloudless sky over the southern UK. The group classifications refer to fly ash of different compositions, as defined by Behymer and Hites (1988)

PAH (number of rings)	Classification of ash (a)							
	“White group”		“Red group”		“Grey group”		“Black group”	
	Summer	Winter	Summer	Winter	Summer	Winter	Summer	Winter
Fluoranthene (4)	7.7 hr	23 hr	1.5 day	4.5 day	1.9 day	5.7 day	1.2 day	3.6 day
Pyrene (4)	3.7 hr	11 hr	17 hr	2.1 day	1.6 day	4.8 day	1.1 day	3.3 day
Benz[a]anthracene (4)	15 min	45 min	6.6 hr	20 hr	17 hr	2.1 day	1.1 day	3.3 day
Chrysene (4)	10 hr	1.3 day	2.6 day	7.8 day	2.3 day	6.9 day	1.0 day	3.0 day
Benzo[e]pyrene (5)	9.1 hr	1.1 day	2.4 day	7.2 day	2.5 day	7.5 day	1.1 day	3.3 day
Benzo[a]pyrene (5)	15 min	45 min	8.0 hr	1.0 day	18 hr	2.3 day	20 hr	2.5 day
Perylene (5)	24 min	1.2 hr	7.0 hr	21 hr	18 hr	2.3 day	21 hr	2.6 day
Indeno[123,cd]pyrene (6)	6.5 hr	20 hr	2.5 day	7.5 day	1.1 day	3.3 day	1.0 day	3.0 day
Benzo[ghi]perylene (6)	1.9 hr	5.7 hr	2.0 day	6.0 day	2.5 day	7.5 day	23 hr	2.9 day
Anthranthrene (6)	3.0 min	9.0 min	2.9 hr	8.7 hr	9.0 hr	1.1 day	23 hr	2.9 day
Coronene (7)	12.7 hr	38 hr	2.5 day	7.5 day	2.2 day	6.6 day	21 hr	2.6 day
Notes (a) The classification of the ash into four groups depends on the relative contents of 10 elements, which influences the colour of the substrate (Behymer and Hites, 1988). The photolysis lifetimes measured in that study have been scaled to provide values representative of 24-hour averaged conditions in the boundary layer over the southern UK.								

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Table A4.4: Representative lifetimes of some 2- to 4-ring PAHs with respect to gas-phase reaction with hydroxyl (OH) radicals, nitrate (NO₃) radicals and ozone (O₃)

PAH (number of rings)	Representative lifetime with respect to reaction with			
	OH (a,b)		NO ₃ (a,c)	O ₃ (a,d)
	Summer	Winter		
Napthalene (2)	12 hours	2.7 days	6.0 years	>80 days
1-methyl napthalene (2)	5.3 hours	1.1 days	2.7 years	>125 days
2-methyl napthalene (2)	5.3 hours	1.1 days	2.0 years	>40 days
2,3-dimethyl napthalene (2)	3.7 hours	18 hours	1.4 years	>40 days
Acenapthene (3)	3.5 hours	18 hours	4.8 hours	>30 days
Acenapthylene (3)	2.6 hours	13 hours	24 minutes	43 minutes
Fluorene (3)	1.8 days	9 days		
Phenanthrene (3)	9.0 hours	1.9 days		
Anthracene (3)	2.1 hours	10 hours		
Fluoranthene (4)	5.6 hours	1.2 days	340 days	
Pyrene (4)	5.6 hours	1.2 days	120 days	

Notes

(a) Lifetimes calculated using rate coefficients summarised by Atkinson and Arey (1994) and Brubaker and Hites (1998).

(b) 24 hour-average summer and winter OH concentrations of 1×10^6 molecule cm^{-3} (0.04 pptv) and 2×10^5 molecule cm^{-3} (0.008 pptv) assumed for boundary layer UK (Collins et al., 1995).

(c) 24 hour-average NO₃ concentration of 1.2×10^8 molecule cm^{-3} (5 pptv) assumed for boundary layer UK based on typical night-time values (Carslaw et al., 1997). Note that the NO₃ concentration is very variable and may be significantly suppressed under polluted conditions (see discussion in text). The reaction also requires the presence of NO₂, which is assumed to be present at a concentration of 2.5×10^{11} molecule cm^{-3} (10 ppbv), based on the average southern UK level (PORG, 1997).

(d) Typical UK background O₃ concentration of 7.5×10^{11} molecule cm^{-3} (30 ppbv) assumed (PORG 1997).

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Table A4.5: The identities and yields of nitroarenes generated from the OH-initiated oxidation of a series of gas-phase PAHs

PAH (number of rings)	Nitroarene product	Yield (%)	Reference
Napthalene (2)	1-nitronapthalene 2-nitronapthalene	1.2 1.3	Sasaki <i>et al.</i> (1997)
Acenapthene (3)	3-nitroacenapthene 4-nitroacenapthene 5-nitroacenapthene	total = 0.2	Arey <i>et al.</i> (1989)
Acenapthylene (3)	4-nitroacenapthylene	2.0	Arey <i>et al.</i> (1989)
Fluorene (3)	1-nitrofluorene 2-nitrofluorene 3-nitrofluorene 4-nitrofluorene	0.6 0.1 1.4 0.3	Helmig <i>et al.</i> (1992)
Phenanthrene (3)	two nitroisomers	Detected	Arey <i>et al.</i> (1989)
Anthracene (3)	1-nitroanthracene 2-nitroanthracene	Detected detected	Arey <i>et al.</i> (1989)
Fluoranthene (4)	2-nitrofluoranthene 7-nitrofluoranthene 8-nitrofluoranthene	3.0 1.0 0.3	Arey <i>et al.</i> (1986), Atkinson <i>et al.</i> (1990)
Pyrene (4)	2-nitropyrene 4-nitropyrene	0.5 0.06	Arey <i>et al.</i> (1986), Atkinson <i>et al.</i> (1990)

Table A4.6: Representative lifetimes of the nitronapthalene isomers with respect to gas-phase reaction with hydroxyl (OH) radicals, nitrate (NO₃) radicals, ozone (O₃) and direct photolysis

Nitroarene (number of rings)	Representative lifetime with respect to reaction with					
	OH (a,b)		NO ₃ (a,c)	O ₃ (a,d)	Photolysis (e)	
	Summer	Winter			Summer	Winter
1-nitronapthalene (2)	4.1 days	20 days	72 years	> 28 days	3.5 hr ^f 1.6 hr ^g	11 hr ^f 4.8 hr ^g
2-nitronapthalene (2)	3.9 days	20 days	80 years	> 28 days	4.6 hr ^f 22 hr ^f	14 hr ^f 2.8 days ^g

Notes

- (a) Lifetimes calculated using rate coefficients summarised by Atkinson and Arey (1994).
 (b) 24 hour-average summer and winter OH concentrations of 1×10^6 molecule cm⁻³ (0.04 pptv) and 2×10^5 molecule cm⁻³ (0.008 pptv) assumed for boundary layer UK (Collins et al., 1995).
 (c) 24 hour-average NO₃ concentration of 1.2×10^8 molecule cm⁻³ (5 pptv) assumed for boundary layer UK based on typical night-time values (Carslaw et al., 1997). Note that the NO₃ concentration is very variable and may be significantly suppressed under polluted conditions (see discussion in text). The reaction also requires the presence of NO₂, which is assumed to be present at a concentration of 2.5×10^{11} molecule cm⁻³ (10 ppbv), based on the average southern UK level (PORG, 1997).
 (d) Typical UK background O₃ concentration of 7.5×10^{11} molecule cm⁻³ (30 ppbv) assumed (PORG 1997).
 (e) Representative 24-hour average for conditions in the boundary layer over the southern UK.
 (f) Based on parameters presented by Atkinson and Arey (1994)
 (g) Based on parameters presented by Feilberg et al. (1999).

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Table A4.7: Reported deposition velocities of a series of gas-phase and particle-bound PAHs to vegetation surfaces, and corresponding representative lifetimes with respect to removal by deposition

PAH (number of rings)	Deciduous forest (a)		Coniferous forest (a)	
	Deposition velocity(b)	Lifetime (c)	Deposition velocity(b)	Lifetime (c)
<i>gas-phase</i>				
Phenanthrene (3)	0.37	1.6 day	0.035	17 day
Fluoranthene (4)	1.9	7.3 hr	0.15	3.9 day
Pyrene (4)	2.4	5.8 hr	0.16	3.6 day
<i>particle-phase</i>				
Benzo[e]pyrene (5)	0.78	18 hr	0.051	11 day
Benzo[a]pyrene (5)	0.88	16 hr	0.061	9.5 day
Dibenz[ah]anthracene (5)	0.73	19 hr	0.055	11 day
Indeno[123,cd]pyrene (6)	0.60	23 hr	0.038	15 day
Benzo[ghi]perylene (6)	0.74	19 hr	0.047	12 day
Coronene (7)	0.65	21 hr	0.048	12 day
Notes				
(a) Data from Horstmann and McLachlan, 1998. (b) Units of deposition velocities are cm s ⁻¹ . (c) Lifetimes calculated for removal from a mean boundary layer height of 500 m.				

Table A5.1: Annual mean BaP data from a selection of German monitoring sites

BaP Annual Means in ng/m³

SITE	1985 :	1986 :	1987 :	1988 :	1989 :	1990 :	1991 :	1992 :	1993 :	1994 :	1995 :	1996 :	1997 :	1998 :	1999 :
BOTT	9.69	10.69	6.78	6.22	6.70	4.19	3.35	3.51	4.49	2.48	3.28	3.73	2.68	3.93	2.15
MEID	4.79	4.59	4.40	2.92	4.24	2.09	2.71	2.40	2.58	1.80	2.87	3.80	2.29	2.34	0.77
EVOG		5.65	5.96	2.38	4.07	2.32	2.84	2.84	2.96	1.59	1.87	2.16	1.76	1.77	0.91
GELS	6.79	8.00	7.13	3.72	5.35	3.82	3.55	2.82	3.43	1.88	2.44	2.55	2.29	1.67	0.92
ICKE	13.06	8.07	6.20	4.35	6.33	5.03	2.84	1.94	1.97	1.30	1.39	1.49	0.96	1.09	0.58
LISE		1.78	1.91	1.13	1.82	1.05	1.07	1.04	0.93	0.63	0.65	1.30	0.62	0.53	0.34
LOER	2.68	1.71	1.86	0.89	1.39	0.66	1.00	1.10	0.68	0.45	0.52	0.88	0.60	0.48	0.30
REIS	2.53	2.26	2.31	1.54	2.38	1.30	1.49	1.50	0.93	0.74	0.80	1.08	0.76	0.73	0.43
RODE	2.41	1.76	1.99	1.25	1.57	0.93	1.21	1.14	0.90	0.49	0.58	0.90	0.64	0.56	0.35
STYR	4.41	4.52	3.58	1.97	3.06	1.78	2.01	2.51	1.76	1.48	2.42	2.60	1.93	1.51	0.51
WALS	4.05	4.95	4.32	2.87	4.37	1.98	2.06	2.03	2.10	1.71	2.07	1.50	1.81	1.69	0.52
WESS	2.43	2.33	2.42	1.48	2.44	1.56	1.67	1.58	1.07	0.65	0.65	0.91	0.68	0.66	0.38
CHOR	2.58	1.98	1.95	1.14	1.70	0.82	1.22	1.24	1.06	0.59	0.57	0.70	0.52	0.59	0.34
VDDF						3.15	2.82	2.42	1.79	1.27	1.44	1.73	1.17	1.24	0.73
VESN						2.88	2.97	2.18	2.26	1.55	2.15	2.71	1.81	1.36	0.85

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Table A5.2: Site characteristics

Site	Inter-annual average value (1985-1999) (I-AAV)	Inter-annual Standard Deviation (1985-1999)	Normalised Inter-annual Standard deviation (N I-ASD)	Upper Assessment Thresholds, (X)	Lower Assessment thresholds, (Y)	Site Characteristic
BOTT	4.9	2.6	0.52	0.49	0.39	Cokery (Industrial influence)
MEID	3.0	1.2	0.39	0.56	0.46	mixed (Industrial influence)
EVOG	2.8	1.5	0.53	0.48	0.39	mixed (Industrial influence)
GELS	3.8	2.1	0.57	0.47	0.37	mixed (Industrial influence)
ICKE	3.8	3.5	0.92	0.35	0.27	urban background
LISE	1.1	0.5	0.47	0.51	0.41	urban background
LOER	1.0	0.7	0.64	0.44	0.34	urban background
REIS	1.4	0.7	0.50	0.50	0.40	urban background
RODE	1.1	0.6	0.54	0.48	0.38	urban background
STYR	2.4	1.1	0.46	0.52	0.42	urban background
WALS	2.5	1.3	0.51	0.50	0.40	urban background
WESS	1.4	0.7	0.53	0.48	0.38	urban background
CHOR	1.1	0.7	0.58	0.46	0.37	urban background
VDDF	1.8	0.8	0.44	0.53	0.43	Traffic influence
VESN	2.1	0.7	0.33	0.60	0.50	Traffic influence
Average value			(N I-ASD)	X	Y	
Cokery & Industrial			0.50	0.50	0.40	
Urban background			0.57	0.47	0.37	
Traffic Influence			0.39	0.57	0.47	
All Sites			0.53	0.49	0.39	

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Figure 1: Current and projected emission of BaP for the EU15 + 6 accession countries (from Holland et al 2001)

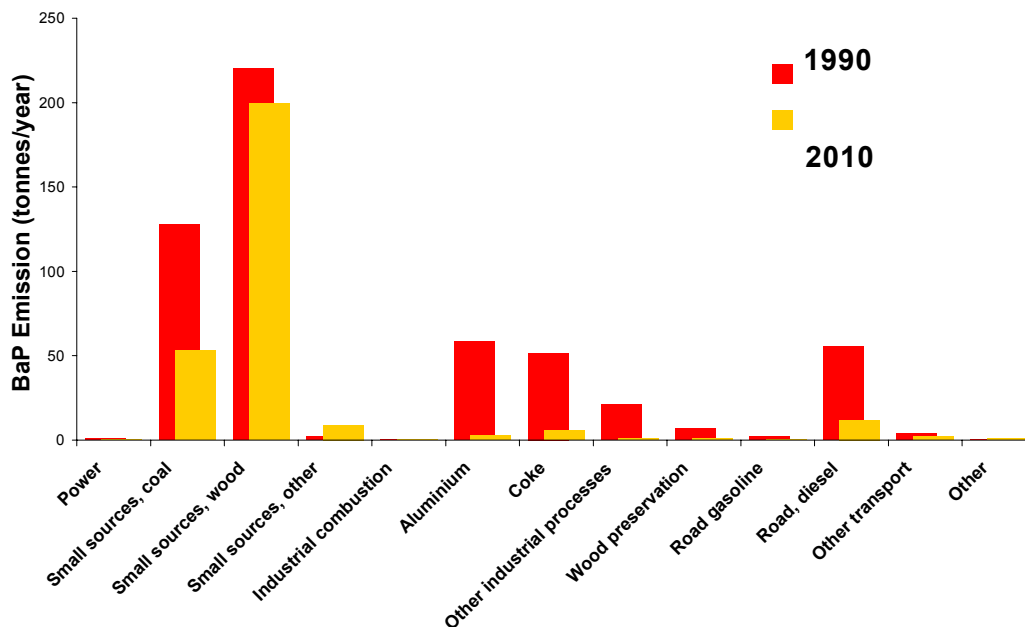
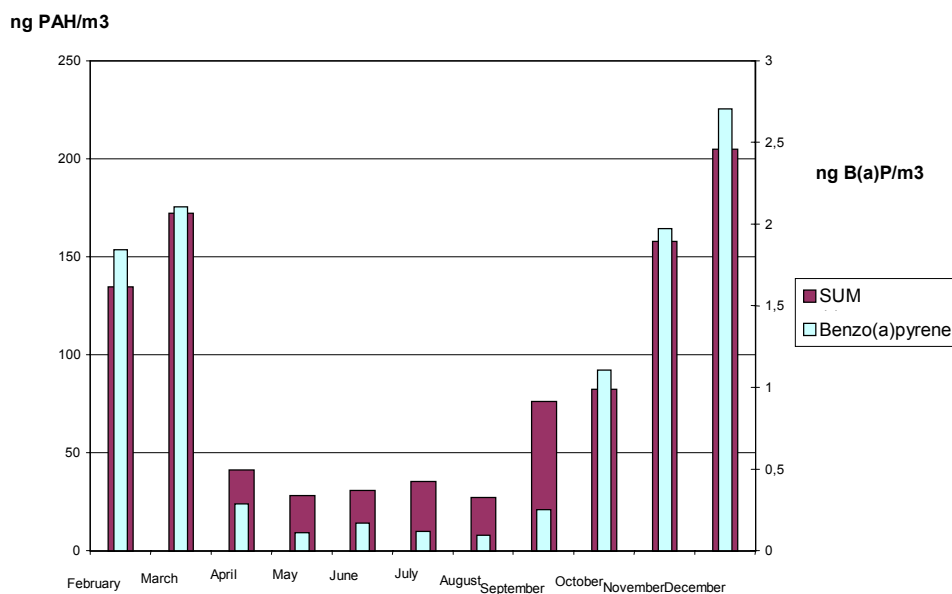


Figure 2: Inter-seasonal variation of PAH in Vienna, Austria

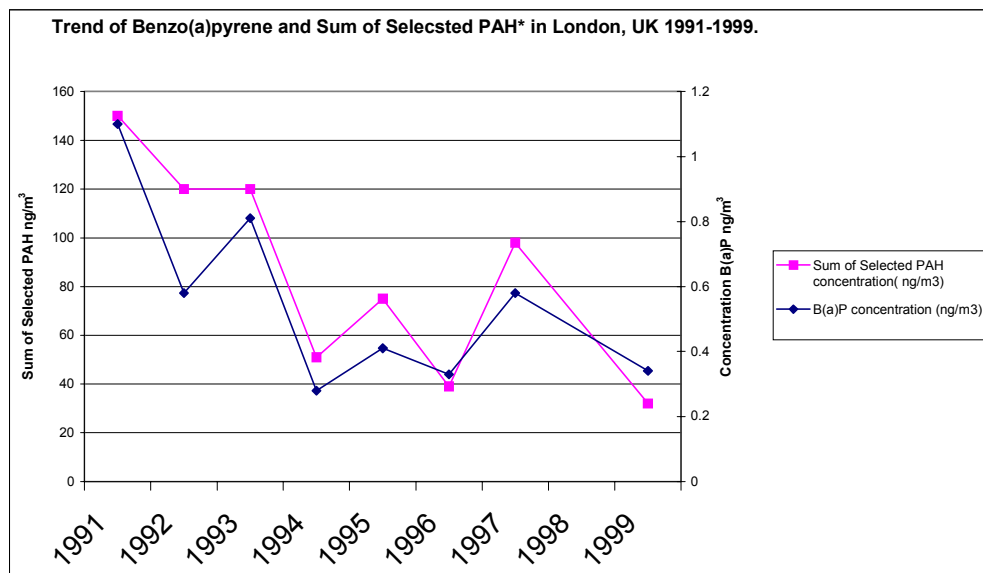


Reference UBA Wien 2000

N.B Sum consists of: 16 EPA PAH + Benzo[e]pyrene (BEP), Coronene (COR), Cyclo[cd]pentapyrene (CCP) and Benzo[b]naphthothiophen (BNT). The sampling included gaseous and particulate phase.

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Figure 3: Trend of sum of selected PAHs and Benzo[a]pyrene in London, UK



* Sum of selected PAH = acenaphthene, fluorene, phenanthrene, anthracene, pyrene, benz[a]anthracene, chrysene, benzo[b]fluoranthene, benzo[a]pyrene and benzo[ghi]perylene

Reference: <http://www.aeat.co.uk/netcen/airqual/>

Figure 4: National and International Standard Methods

EPA – Method TO-13A:

“Determination of Polycyclic Aromatic Hydrocarbons (PAH) in ambient air using gas chromatography/mass spectrometry (GC/MS)” [US EPA 1999]. This American standard method was originally published in March of 1989 (TO-13): “The determination of benzo(a)pyrene and other polynuclear aromatic hydrocarbons (PAH) in ambient air using gas chromatographic (GC) and high performance liquid chromatographic (HPLC) analysis”. In January of 1997 a revised version of this method was published. In the two different versions sampling is carried out with a HVS and both phases of PAH are collected. The filters and PUF are soxhlet extracted. In the first version GC/FID, GC/MS and HPLC are described as analytical methods, in the second version only GC/MS method is described. This method covers 19 PAH.

ISO 12884:

“Air Quality – Determination of Gas and Particle-phase Polycyclic Aromatic Hydrocarbons in Ambient Air – Collection on Sorbent-backed Filters with Gas Chromatographic/mass Spectrometric Analysis” [ISO Ambient Air 1999]. The method has been evaluated for 22 PAH, including the 19 compounds covered by the EPA method TO-13A. Both phases of PAH are collected with a HVS. Extraction is done with a soxhlet, concentration with a Kuderna-Danish apparatus, and analysis is carried out by GC/MS.

ISO/TC 146/SC 3/WG 17:

“Air quality – Determination of particle-phase polycyclic aromatic hydrocarbons by high performance liquid chromatographic analysis” [ISO (1999) Air quality]. It is still a working draft standard. The method covers the determination of PAH in particulate phase only. Air samples are collected on GFF by medium- or high-volume sampling devices (16 and ca. 2.7 m³/min, respectively), solvent extracted (by a reflux condenser or by Soxhlet or in an ultrasonic bath), cleaned-up by column chromatography and analysed by HPLC/UV-DAD.

AFNOR NF X43-025:

“Qualité de l’air – Air ambiant – Détermination des hydrocarbures aromatiques polycycliques. Dosage par chromatographie liquide haute performance et par chromatographie gazeuse” (Air Quality – Ambient air- Determination of Polycyclic Aromatic Hydrocarbons. Analysed by High Performance Liquid Chromatography and Gas Chromatography) [AFNOR 1998]. In this French standard method, the sampling procedure is not described and two analytical methods are proposed: HPLC and GC – FID. 7 PAH are analysed: benzo(a)anthracene, benzo(k)fluoranthene, benzo(b)fluoranthene, benzo(a)pyrene, dibenzo(ah)anthracene, benzo(ghi)perylene and indeno(1,2,3-cd)pyrene. They are all the heavy PAH therefore mostly adsorbed in the particulate phase.

VDI Guideline 3875 part 1:

“Outdoor-air Pollution Measurement, Indoor-air Pollution Measurement, Measurement of Polycyclic Aromatic Hydrocarbons (PAH) Gas-Chromatographic Determination” [VDI Guideline 3875 Part 1 1996]. This German standard method was published in December of 1996. Only the particle phase is sampled, and GC-FID is the analytical method used.

DM (Ministerial decree):

Italian reference method (for the determination of PAH in ambient air) [DM (Ministerial decree) 1994]. Only particulate phase is collected. Filter samples are ultrasonically extracted, cleaned-up by TLC and analysed by GC/FID and GC/MS.

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Figure A4.1: Relative distribution of 3- to 5-ring PAHs at urban (black) and rural (white) sites

The data have been normalised to a value of 1.0 for the 5-ring PAH, benzo[a]pyrene (see text). The selected PAHs are those for which data are available at all the three urban and two rural sites in the network, with the exception of phenanthrene which has exceptionally high concentrations at one rural site, Hazelrigg.

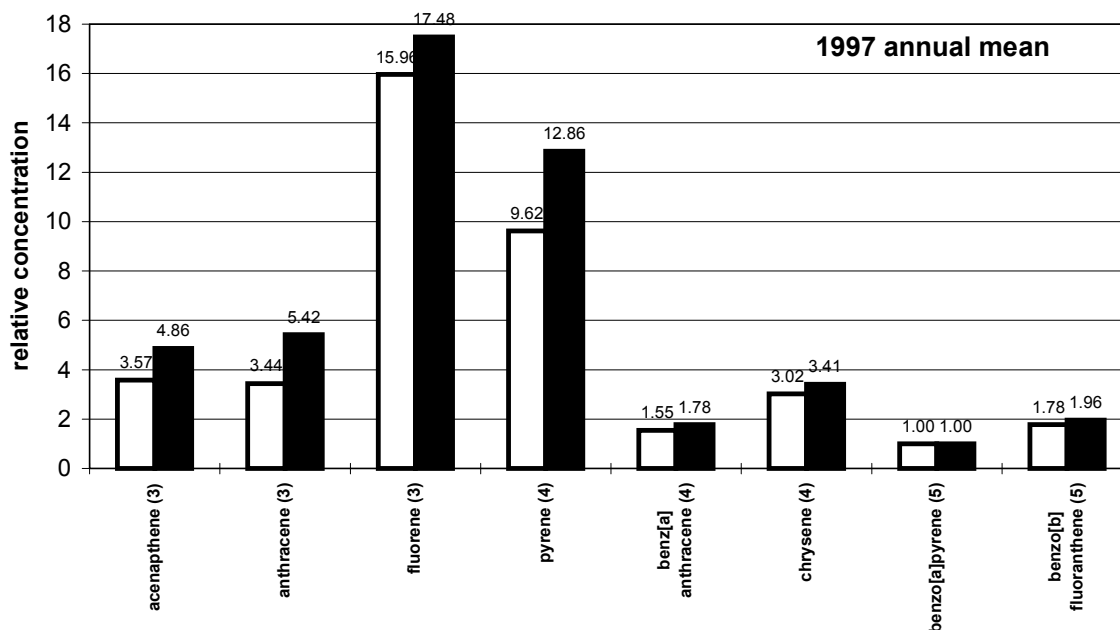


Figure A5.1: Inter-annual variation for 1985 -1999

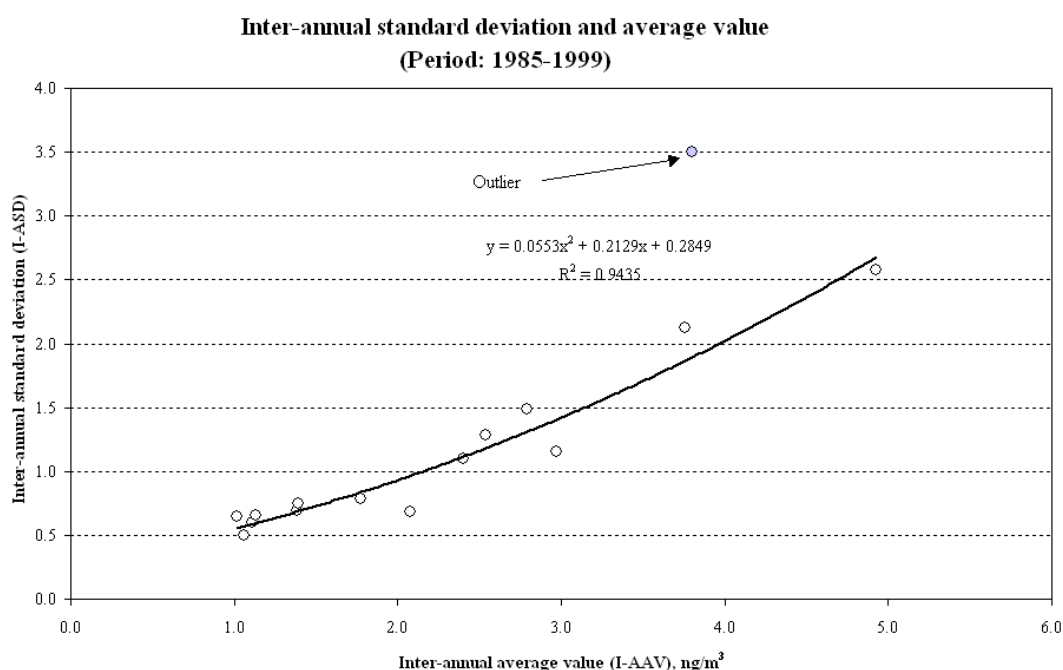


Figure A5.2: Upper and lower assessment threshold

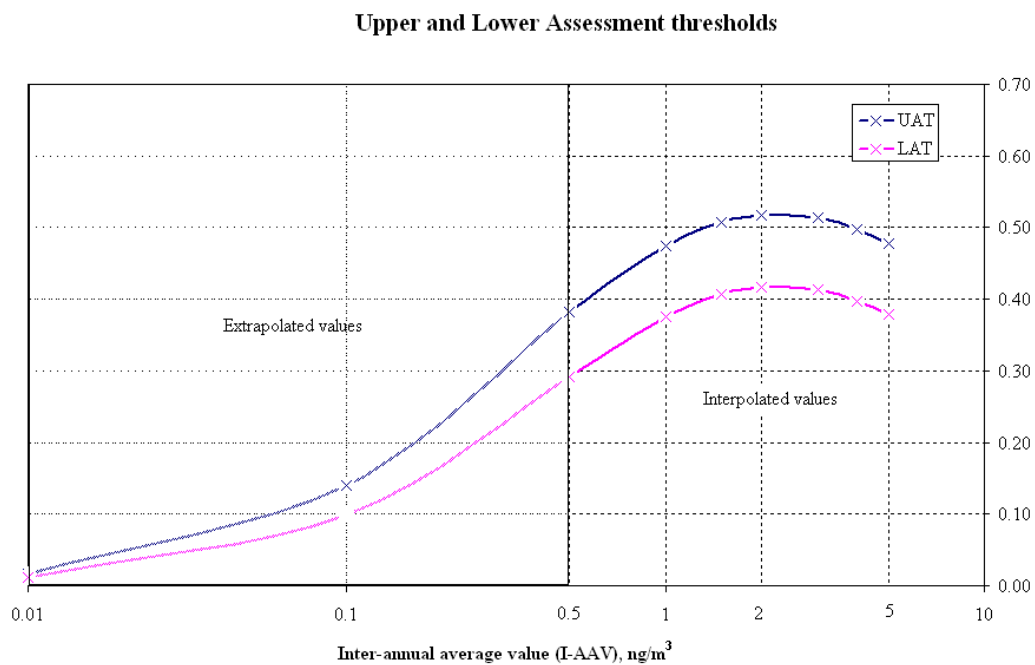


Figure A5.3: Frequency distribution by year

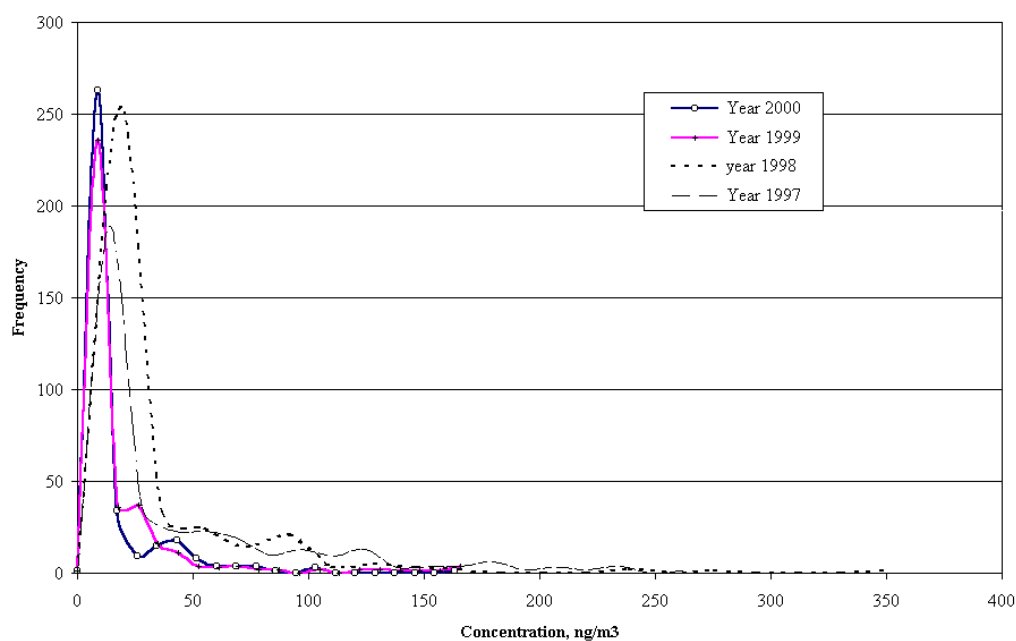


Figure A5.4a: Expanded uncertainty as a result of incomplete time coverage – analytical uncertainty 35%

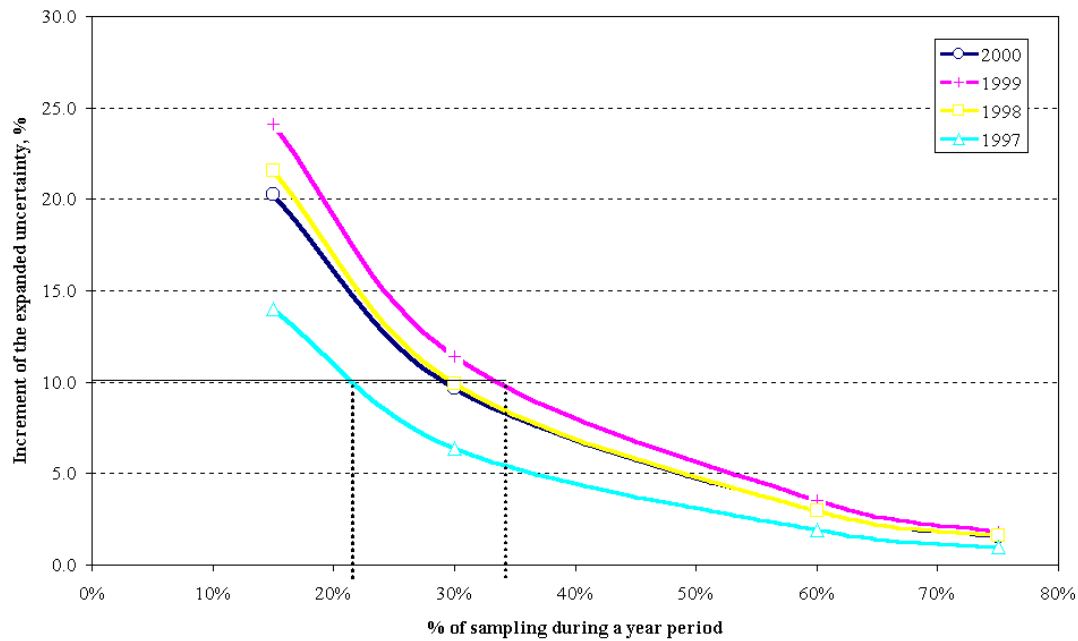
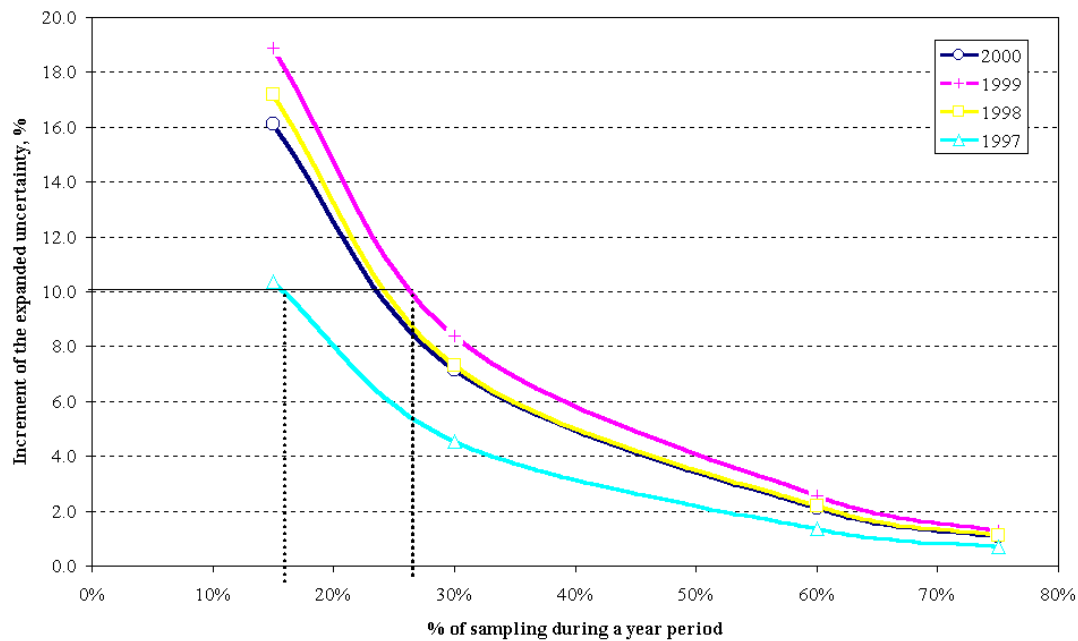


Figure A5.4b: Expanded uncertainty as a result of incomplete time coverage – analytical uncertainty 50%



Annex 3

Industrial Sources of PAH Emissions

The most important industrial sources of PAH include the following. It should be noted that most of these will be regulated by the IPPC Directive (Council Directive 96/61/EC).

- A3.1 Commercial heat and power generation: Combustion of fossil fuels leads to the production of PAH. Solid fuels lead to higher PAH concentrations in the raw flue gas. Liquid and gas fuel tend to produce lower levels of PAH in the raw gas. The levels of PAH emission are very much dependent on the fuel, the technology implemented, and the abatement measures adopted. Operation at higher temperatures will generally lead to lower organic emissions. Conditions favouring higher combustion efficiency also favour lower emissions. The total mass of PAH emitted per installation is relatively high, however this needs to be seen in relation to the high tonnage of fossil fuel burnt.
- A3.2 Reduction in the PAH emissions due to heat and power generation can be expected as installations are modernised or withdrawn from service. The reduction in the use of brown coal and an increase in the use of gas and oil fired power stations also has a positive effect on the total PAH emissions.
- A3.3 Waste incineration: The inhomogeneous nature of the "fuel" means that greater technological controls are necessary than for heat and power generation to achieve the same emission limits. However the European Directives on waste incineration (89/369/EEC, 89/429/EC, 94/67/EC, 2000/76/EC) and the improvements in incineration technology, particularly in relation to the building of dioxins, which are required most probably have a positive effect on the emission of PAH.
- A3.4 Coke production: Coking plant has been recognised as a major PAH emission source for a long time. Coking installations can be seen as single sources with localised, often high impact due to diffuse emissions which are difficult to reduce through abatement measures. Some of the installation are very old and have extremely high emissions leading to local high ambient air concentrations. Modern technology can improve the levels markedly in comparison with old installations. One of the most modern coking plants in the world has achieved BaP emission levels of 0.0036 mg BaP/m³ [UBA Berlin 1998]. Older plant has been estimated to emit 7.5 times this amount and recent measurements show that in the immediate vicinity (250 m) concentrations of up to 14 ng/m³ BaP can be found. [Bruckmann P 2001]. Coking plant emissions of BaP in Germany for 1994 are estimated at 1090 kg/a [UBA Berlin 1998].
- A3.5 Iron and steel production: Electric steel production is the process in which the raw materials for the steel production are melted in an electric arc between graphite electrodes. The emission data discussed in a recent German publication [UBA Berlin 1998] varies widely but conventional dust extraction techniques applied to the waste gases appears sufficient to reduce the emission level to 0.1 mg BaP /m³.
- A3.6 Graphite electrode production for arc furnaces are produced from coal tar and coke or petroleum coke. The BaP emissions are related to the mass of electrode produced.

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Conventional emission abatement measures are geared towards dust and hydrocarbon reduction. Filters of various types are used throughout the process and waste gas incineration and waste gas recycling are practised. For the graphite electrode production an emission factor of 10.2 g BaP / t electrode is given, this results in an annual contribution of 227 kg to the total BaP load for Germany in 1994 [UBA Berlin 1998] for example.

- A3.7 Sintering plants are also potential sources of PAH. As the sintering process involves the use of coke, it can be argued that the emissions of PAH are at the most equivalent to those from the coking process. Indications are that in practice the emissions are low, around 0.001 mg BaP/m³, giving an emission factor of around 0.002 g BaP/t sinter. The use of various filter types, including electrostatic filters for dust reduction purposes enable low emission rates to be attained.
- A3.8 One of the largest sources are the cast iron and steel processes due to emissions from the oils and binding materials in the moulding. There is however a lack of information regarding the size of the emissions.
- A3.9 Aluminium production: PAH emissions in the aluminium industry are due to the use of carbon anodes produced from pitch and petroleum coke. To what extent these emissions are as relevant today as they were in the 1980s is unclear. The emissions are dependent on the type of process used. Emission factors per tonne Aluminium of 4.4 kg total PAH (0.11 kg BaP) for the horizontal Söderberg aluminium process, and 0.7 kg total PAH (0.01 kg BaP) for the vertical Söderberg aluminium process have been recorded. However the Aluminium industry reports only three Söderberg plants remaining in Europe.
- A3.10 The baked anodes have higher emissions in the anode production process than the Söderberg-anodes. Conversely for the electrolysis the baked anodes have lower emissions. In the anode baking process the abatement measures adopted are directed towards dust and hydrocarbon emissions. Thus filters and waste gas incineration are implemented.

In Europe, average PAH emissions from pre-bake anode plants lie in the region of 0.05 kg / tonne aluminium. In newer installations this value is less than 0.01 kg / tonne. For Söderberg installations the PAH emissions are of the order of 0.25 kg / Tonne aluminium. The newest primary aluminium production facilities use a variant on pre-bake technology called Centre Worked Pre-bake Technology (CWPB). This technology provides for computer controlled precise alumina feeding through the use of multiple "point feeders" and other automated controls. A key feature of CWPB plants is the enclosed nature of the process. Fugitive emissions from these cells are very low, less than 2% of the generated emissions. The balance of the emissions is collected inside the cell itself and carried away to very efficient scrubbing systems (removing particulates and gases) that return the collected material to the cells. Computer technology controls the process down to the finest detail, which means that occurrence of the anode effect - the condition which causes small quantities of PFC's to be produced - can be minimised. All new plant and most expansion of existing plant are based on pre-bake technology. [www.world-aluminium.org]

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- A3.11 In the electrolysis process PAH is released as the anodes are consumed. The waste gas treatment is designed to deal with dust and fluorides. This means that a number of wet and dry systems are implemented which have a positive effect on the PAH emissions. [UBA Berlin1998]
- A3.12 Cement production: Cement, lime and similar production processes are thermal processes involving the combustion of fossil fuels and the parallel dehydration of the magnesium and calcium hydroxides. Emission data for these processes is not readily available. Although the emissions are not expected to be major, due to the high temperatures involved in the process the variation in the emissions dependent on the raw materials and on the fuels used is of particular interest especially with regard to co-incineration (eg waste tyres, waste solvents, etc.)
- A3.13 Petrochemical and related industries: Refineries: PAH compounds occur in crude oil and may be released to the atmosphere or hydrosphere through stack gases or in the waste water. Abatement measures over the last ten years have reduced the emissions substantially. The actual emissions are dependent on the process involved and the abatement technology implemented.
- A3.14 Bitumen and Asphalt industries: Bitumen is a heavy, fraction obtained in the crude oil distillation process. Eighty percent of bitumen goes into road surfacing as asphalt. Fresh asphalt contains less than 0.1 mg/kg BaP. In its lifetime as road surfacing this can increase due to traffic deposition. This becomes an important factor in the recycling of road asphalt. It is also important to avoid the addition of coal-tar or old asphalt containing high quantities of coal tar to the recycling process as coal-tar has a very high proportion of PAH. PAH emissions from modern asphalt installations can be classed as relatively low. Emissions of PAH from road asphalt do occur in the road construction process.
- A3.15 Rubber tyre manufacturing: Highly aromatic oils and carbon black are added to the rubbers used to manufacture tyres. These compounds contain PAH. The PAH concentration in the oils has been given as between 700 ppm and 30% [Ahlbom and Duus 1994], depending on the measurement method. The polyaromatic content is dependent on the manufacturer and the designated use of the final tyre, that is high-speed tyres have a higher content than other tyres. Some manufacturers have decided to reduce the PAH content of their tyres. The size of PAH emissions during the tyre production process is unknown.
- A3.16 Creosote and wood preservatives: Creosote is a product of the fractional distillation of coal tar, a by-product of bituminous coal coking. The majority of all creosoted wood is impregnated under pressure. Emissions of PAH occur when the treatment vessel is opened at the end of the cycle. The duration is short as the vessels are opened only once or twice during a working shift. Other emissions may occur in the transfer process at the loading and unloading of road or rail tankers. Modern equipment is able to keep these emissions to a minimum. Freshly treated wood has higher emissions than aged products. This means that not only facilities in which wood is treated may have PAH emissions due to creosote, but also those facilities in which the wood is stored afterwards and used further. Most of the end products are used in the open e.g. telegraph poles, fencing posts, railway sleepers and the use of freshly treated products may lead to localised PAH emissions.[EPA 1998]. Within

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the EU there are regulations limiting the use of products impregnated with creosotes and tar-oils (Council Directive 76/769/EEC as amended by Council Directive 94/60/EC). In Germany the restrictions, set out in the Hazardous Substance Ordinance (Gefahrstoffverordnung), are more stringent.

- A3.17 Other industrial sources: Motor test rigs – Testing rigs for engines in the automobile industry emit large amounts of PAH in comparison to other industrial installations. The installations can be considered as localised sources, they have a similar emission profile to mobile sources, in particular road transport. There is great reluctance by industry to fit emission control equipment to what are basically experimental systems. Annual emissions of between 8 and 9.5 kilograms BaP per location have been reported [LfU 1999].

Annex 4

Post Emission Transformation ¹

- A4.1 The rates and mechanisms of the chemical removal of PAH from air are influenced by whether the PAH is in the gas-phase, or associated with airborne ambient particulate. The higher molecular weight PAH are more likely to be associated with the particle phase. This is not simply as a result of condensation; in practice, the majority of PAH are generally found to be present in the particulate phase, some almost exclusively, despite the saturation vapour concentrations rarely being exceeded. (See **Table A4.1: Summary of reported saturation vapour concentrations of PAH, and some typical observed concentrations and gas-particle phase partitioning.**) This results from the either the adsorption of the PAH on to particle surfaces, or the absorption (i.e. dissolution) of the PAH into the bulk aerosol. The importance of these processes depends on temperature, humidity and the composition and abundance of the atmospheric aerosol consequently some variability in the gas-particle partitioning is observed on a temporal and geographical basis.
- A4.2 In general, PAH containing 5 or more rings, including BaP, are found predominantly in the particulate phase; those containing 2 or 3 rings are almost entirely present in the vapour. The observed variability therefore relates mainly to 4-ring PAH, such as fluoranthene, pyrene, benz[a]anthracene and chrysene.

Particle Phase PAH

- A4.3 The reactions of particle-phase PAH under atmospheric conditions are not well characterised - despite particulates being one of the more important vectors for PAH carcinogenicity in humans. Much of the uncertainty arises from the large variation in the composition of the airborne particulate potentially containing the PAH, and the possible influence the nature of the substrate has on the chemical reaction rates. Thermal (i.e. non-photolytic) reactions of PAH toward O₃ appear to have 1/e lifetimes* of about 1 - 2 days. The reactivity with NO₂ seems to be much lower and the reactivity with N₂O₅ under typical atmospheric conditions is negligible (see **Table A4.2: Representative lifetimes of some 4- and 5-ring PAH with respect to thermal reaction with nitrogen dioxide (NO₂), ozone (O₃) and dinitrogen pentoxide (N₂O₅) on "wood soot" particles.** Sulphur dioxide (SO₂), at ppmv levels, does not appear to have any significant influence. The atmospheric chemical lifetimes of particle-bound PAH with respect to thermal reactions tend to be longer than those of gas-phase PAH.

* (N.B. 1/e lifetime are used because they are derived directly from the first order decay equation and are simply the inverse of the decay 'rate constant' half life = 0.693 x 1/e lifetime)

- A4.4 Surface-adsorbed and solution-phase PAH absorb UV and visible solar radiation and the photolysis of particle-bound PAH is a significant removal process (see **Table A4.3: Representative lifetimes of some surface-adsorbed PAH with**

¹ This summary is based on the work of Coleman et al., [1999] which reviewed available information on the lifetimes of PAH with respect to physical and chemical breakdown in both gaseous and particulate phases.

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respect to photolysis under conditions representative of a cloudless sky over the southern UK. The group classifications refer to fly ash of different compositions, as defined by Behymer and Hites 1988). PAH adsorbed on “white” fly ashes have a lifetime of about 6 hours for summer conditions and 17 hours for winter conditions. The lifetimes increase as the colour of the fly ash gets darker because darker substrates are more efficient at absorbing light thereby inhibiting PAH photolysis. But atmosphere aerosol, particularly during summertime, will have a large “secondary” component of photochemically generated sulphate and involatile organic oxygenates which has condensed on, and partition into, the existing primary aerosol (PORG 1997, APEG 1999). Under such conditions it is possible that particle-phase PAH are not purely surface adsorbed species, but incorporated into the bulk aerosol, where they may be fully or partially protected from photolysis, and from removal by the thermal reactions.

Vapour Phase PAH

A4.5 PAH in the gas-phase primarily react with OH although other radicals are important. OH is predominantly generated in the atmosphere by photochemical processes, most notably the photolysis of ozone in the presence of water vapour. OH radicals are more abundant during the summer than the winter and can be present at significant concentrations during daylight hours. The typical resistance of 2- to 4-ring PAH to reaction with OH, indicated by their lifetimes are between 2 and 12 hours under averaged summertime conditions, and between 10 hours and 2.7 days under averaged wintertime conditions. During daylight, NO₃ is photolysed extremely efficiently and is unable to accumulate to a significant concentration, at night-time, however, NO₃ may be present at significant concentrations. The lifetimes for the majority of PAH are calculated to be greater than a year, and removal by reaction with NO₃ is, in most cases, not significant. Reaction with O₃ can potentially occur throughout the diurnal cycle. The majority of gas-phase PAH are resistant to O₃. The estimated lower limit lifetimes with respect to reaction with O₃ at typical ambient levels are greater than 30 days in most cases. (See **Table A4.4: Representative lifetimes of some 2- to 4-ring PAH with respect to gas-phase reaction with hydroxyl (OH) radicals, nitrate (NO₃) radicals and ozone (O₃)**)

Secondary Product Formation

A4.6 The more important degradation processes, for gas-phase PAH, are expected to generate a large variety of nitro-, hydroxy- and carbonyl-substituted products which will be mainly (but not exclusively) associated with airborne particulate. Of these products, the nitro-substituted PAH (or nitroarenes) have received particular attention because certain isomers are implicated as direct-acting mutagens and carcinogens. Monitoring data for 3- to 7-ring PAH indicates that the total gas-phase PAH concentration is typically more than an order of magnitude greater than the total particle bound PAH concentration (and two orders of magnitude greater than that of benzo[a]pyrene alone). Although degradation product yields are low in all cases (ranging from $\leq 0.2\%$ to *ca.* 4 %), nitroarenes are frequently observed in ambient samples at levels comparable to that of benzo[a]pyrene. (See **Table A4.5: The identities and yields of nitroarenes generated from the OH-initiated oxidation of a series of gas-phase PAH.**) A small proportion of the observed nitroarenes may be attributed to direct emissions, such as diesel exhaust,

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but these species are formed mainly from the atmospheric degradation of the parent 2- to 4-rings.

- A4.7 There is very limited published information relating to the degradation mechanisms of nitro PAH in the particle phase, these reactions are of only minor importance under typical atmospheric conditions, by virtue of their slow rates. See **Table A4.6: Representative lifetimes of the nitronaphthalene isomers with respect to gas-phase reaction with hydroxyl (OH) radicals, nitrate (NO₃) radicals, ozone (O₃) and direct photolysis.**
- A4.8 Most of the nitroarenes are likely to be particle-bound species with atmospheric lifetimes not too dissimilar from those of the particle-bound PAH.

Deposition of PAH

- A4.9 Dry deposition of gas-phase species is usually more rapid than that of particulate deposition but dry scavenging of the aerosol phase removes the greater mass of material on a European scale. Over land dry deposition is greater than wet deposition, over sea both wet and dry deposition are comparable [EMEP MSC-E Report 2/99]. Gas-phase deposition velocity strongly depends on the surface-type, dry deposition to deciduous forests being particularly efficient. See **Table A4.7: Reported deposition velocities of a series of gas-phase and particle-bound PAH to vegetation surfaces, and corresponding representative lifetimes with respect to removal by deposition.**
- A4.10 PAH lifetimes, with respect to removal by deposition, are usually significantly longer than the chemical lifetimes discussed above, at least for the gas-phase species. But the relative importance of chemistry and deposition for vapour phase species will be strongly dependent on conditions and it could be that over forested European regions deposition dominates. Re-suspension and PAH re-emission from soil/sea surfaces is generally held to be relatively unimportant EMEP Report 4/2000.
- A4.11 As discussed above, some preferential depletion of gas-phase PAH is expected (and observed) under 'normal' atmospheric conditions. More significant depletion of gas-phase PAH might be expected under extreme conditions, such as a summertime photochemical pollution episode, characterised by elevated concentrations of OH radicals and a stable boundary layer air mass (i.e. longer processing times). Under such circumstances, gas-phase PAH lifetimes as short as *ca.* 30 minutes are possible, and these are therefore expected to decay away much more rapidly than benzo[a]pyrene and other particle phase PAH, even though some removal of particle-bound PAH by photolysis might also be expected under these conditions. Although the predominantly gas-phase PAH are generally not considered to contribute to the overall carcinogenic activity, some depletion might also be expected for the (normally predominantly particle-bound) 4-ring PAH benz[a]anthracene and chrysene under such conditions, since a greater proportion is likely to be partitioned into the gas-phase at the associated elevated temperatures. However, it is difficult to identify circumstances when benzo[a]pyrene is likely to be removed preferentially, and its concentration relative to those of the other predominantly particle-bound PAH is likely either to

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remain about the same, or to increase under conditions when significant chemical processing occurs.

Monitoring based evidence for changes in PAH composition

A4.13 **Figure A4.1: Relative distribution of 3- to 5-ring PAH at urban (black) and rural (white) sites** shows a comparison of the 1997 annual average distribution of measured 3- to 5-ring PAH at three UK urban sites and two rural sites. The measured concentrations have been normalised with respect to benzo[a]pyrene at each site, and shows an average of the ratios at the three urban sites and at the two rural sites, respectively. The predominantly gas-phase 3- and 4-ring PAH (acenaphthene, anthracene, fluorene and pyrene) are noticeably depleted at the rural sites. The air masses reaching rural sites will have had time to chemically age relative to those at the urban locations (which are closer to major PAH sources), allowing differential depletion of the gas-phase species relative to the particle-phase ones in general, and to benzo[a]pyrene in particular. Deposition rates are relatively slow by contrast and are less likely to be responsible for the shifts in speciation pattern in this case.

Annex 5

Data Quality Objectives

Upper And Lower Assessment Thresholds

A5.1 The Air Quality Framework Directive (96/62/EC) contains provisions for setting limit values and alert thresholds for ambient air; when such limits and thresholds are set guidance is to be given regarding the air quality assessment to be undertaken by member states. Consequently in the daughter directives to 96/62/EC limit values, upper assessment thresholds (UAT) and lower assessment thresholds (LAT) have been specified; these levels define three assessment regimes. Measurement is mandatory in zones: with a population exceeding 250.000 inhabitants, with high population concentrations (agglomerations), and where the ambient concentrations exceed the UAT. Between the UAT and the LAT measurement can be combined with modelling. Below the LAT model calculations or objective estimations are sufficient. Various criteria have been used for setting the UAT and LAT levels depending on the nature of the pollutant of concern and the variability of the determinand over the averaging period of the limit value. In all cases however the values chosen are based on the inter-annual variability of time series data obtained from representative measurement sites.

A5.2 Self consistent long time series data are not available for most member states. Table A5.1 is a suitable data set obtained from a variety of monitoring stations in Germany for the period (1985-1999), Table A5.2 shows the inter-annual standard deviation calculated for these locations. The following equations calculate upper and lower assessment thresholds such that probability that the limit value would be exceeded in successive years due to inter-annual variations are less than 5 % and 1% respectively:

$$Y \Rightarrow \frac{1}{1 + 3 \cdot NSD}; \text{ Lower assessment threshold}$$

$$X \Rightarrow \frac{1}{1 + 2 \cdot NSD}; \text{ Upper assessment threshold}$$

(where LV is the limit value and NSD is the normalised inter-annual standard deviation) This approach was also adopted in other position papers (e.g. by the NO_2 Working Group). The X and Y values of 0.5 and 0.4 respectively calculated from the German data are, to some extent verified by results obtained with a more limited UK data set². Consequently the estimated upper and lower assessment thresholds would fall at 50 % and 40 % of the limit value, respectively.

² Equivalent results are also obtained by de-trending the time series data and normalising with respect to the current annual average value of each series.

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A5.3 The X and Y values from sites apparently influenced by industrial and traffic sources are indistinguishable from those of urban background sites on the limited data available. However there is a clear relationship between inter-annual average concentration and inter-annual standard deviation see Figure A5.1. If this correlation is real it is possible to estimate an upper and a lower assessment threshold for a range of site conditions, see Figure A5.2. This relationship suggests that any limits value chosen between 0.5 and 1 ng/m³ would have associated with it an upper and lower assessment threshold ranging between (0.4–0.5) and (0.3–0.4), respectively. This is in agreement with the upper and lower assessment thresholds already determined: 0.5 and 0.4, i.e. 50 and 40 % of the limit value.

A5.4 Setting the UAT at 50% of the limit value will ensure a low probability of the limit value being exceeded. Setting the LAT at 40% of the limit value would add little additional confidence and information while creating practical difficulties. Setting the LAT at a threshold, below which measurement has little value and objective estimations and modelling are the most cost effective course of action, consistent with the overall aims of the Framework Directive, would have practical benefits. Such a level, at 25% of a limit value, provided the limit value was set in the range 0.5 – 1.0 ng/m³, would ensure a very low probability of the limit value being exceeded, collect valuable data and also provide member states with a cut off point for costly monitoring work. The analytical approach used by the other FWD pollutant working groups leads to the setting of UAT and LAT at similar levels.

Sampling Frequency

A5.5 According to ISO 11222 (Section 5.2, Eq. 7), it is possible to calculate the additional standard uncertainty of the mean value due to incomplete time coverage by the following expression:

$$u^2_{RS}(C_M) = s(C_S)^2 [1 - N/N_{max}] / N$$

The corresponding variance $s(C_S)^2$ (as a function of N) is estimated by taking the averaged of a limited number of random samplings (for the purposes of this work a minimum number of N-random daily point samplings was fixed as 50).

$$s(C_S)^2 = \frac{\sum_{i=1}^N [C_S(i) - C_M]^2}{N-1}$$

Again suitable data was limited but 24 hourly measurements, taken daily, over the whole year ($N_{max} = 365$) were available from the proximity of an industrial plant in the German network. Data from 1997 to 2000 were selected for the exercise. Figure A5.3 shows the frequency distribution of the concentration of BaP for over this period. The combined standard uncertainty $u(C_M)$, describing the uncertainty of the annual mean value C_M , is determined from the variance equation (Eq. 4 Section 5.1 of ISO 11222):

$$u^2(C_M) = u^2_{MS}(C_M) + u^2_{RS}(C_M)$$

where $u^2_{RS}(C_M)$ is estimated as described above and $u^2_{MS}(C_M)$ is the variance uncertainty of the analytical method. The expanded uncertainty of the analytical method has been

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estimated to be $\pm 35\%$ (see Chapter 3 above). The increment in the expanded uncertainty due to incomplete time coverage is:

$$\text{Increment in the Expanded uncertainty (\%)} = (u(C_M) - u_{MS}(C_M)) / C_M * 200$$

(where C_M corresponds to the annual average value).

A5.6 Figure A5.4a shows the estimated increments in the expanded uncertainty due to incomplete time coverage for the corresponding sampling population of the German data (from 1997 to 2000), assuming an analytical expanded uncertainty of $\pm 35\%$; it would be necessary to cover 30 % of the year by random daily sampling in order to approximate the increment in the expanded uncertainty to a level of 10 %. Given the variability in the data set a similar data collection frequency would be required even were the uncertainty of the analytical method to be $\pm 50\%$ (see Table A5.4b). Similar calculations based on a less complete UK data set were consistent with these findings. For practical purposes a 24 hourly sample every 3 days would generate the frequency and 'randomness' required provided that a sampling regime was adopted that ensured, over a year, all days of the week were sampled with equal frequency.

Annex 6

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