Review

Atmospheric polycyclic aromatic hydrocarbons: Source attribution, emission factors and regulation

Khaiwal Ravindraa,b,*, Ranjeet Sokhić, René Van Griekenb

aCentre for Atmospheric and Instrumentation Research (CAIR), University of Hertfordshire, Hatfield AL10 9AB, UK
bEnvironmental Analysis Group, Micro and Trace Analysis Center, Department of Chemistry, University of Antwerp, Universiteitsplein 1, B-2610 Antwerp, Belgium

Received 29 January 2007; received in revised form 21 November 2007; accepted 3 December 2007

Abstract

There is an increasing concern about the occurrence of polycyclic aromatic hydrocarbons (PAHs) in the environment as they are ubiquitous in ambient air and some of them are among the strongest known carcinogens. PAHs and their derivatives are produced by the incomplete combustion of organic material arising, partly, from natural combustion such as forest and volcanic eruption, but with the majority due to anthropogenic emissions. The PAH concentration varies significantly in various rural and urban environments and is mainly influenced by vehicular and domestic emissions. The review serves as a database to identify and characterize the emission sources of PAHs and hence various approaches including diagnostic ratio (DR) and principal component analysis (PCA) are discussed in detail. These approaches allow individual PAHs to be associated with their origin sources. The factors that effect PAH emission and estimated emission rate are also discussed in this paper. Although the levels of low molecular weight PAHs are high in vapor phase, most of the probable human carcinogenic PAHs are found to be associated with particulate matter, especially in fine mode particles in ambient air. Many countries have proposed a non-mandatory concentration limit for PAHs, whereas the health risk studies conducted in relation to PAH exposure, urge that these pollutants should be given a high priority when considering air quality management and reduction of impacts.

© 2007 Elsevier Ltd. All rights reserved.

Keywords: PAH formation; Emission factors; Source apportionment; Air quality standards and regulation

Contents

1. Introduction ................................................................. 2
2. Formation of PAHs .......................................................... 2
3. Priority PAHs ................................................................. 4
4. Sampling artefact ............................................................. 4
5. Sources of PAHs ............................................................... 5
5.1. Domestic emissions ......................................................... 7

*Corresponding author at: Centre for Atmospheric and Instrumentation Research (CAIR), University of Hertfordshire, Hatfield, AL10 9AB, UK. Tel.: +44 1707 285232; fax: +44 1707 284208.
E-mail addresses: Khaiwal@yahoo.com, r.khaiwal@herts.ac.uk (K. Ravindra).

Please cite this article as: Ravindra, K., et al., Atmospheric polycyclic aromatic hydrocarbons: Source attribution, emission factors and regulation. Atmospheric Environment (2008), doi:10.1016/j.atmosenv.2007.12.010
1. Introduction

Polycyclic (Polynuclear) aromatic hydrocarbon (PAHs) compounds are a class of complex organic chemicals, which include carbon and hydrogen with a fused ring structure containing at least 2 benzene rings. PAHs may contain additional fused rings that are not six-sided and some representative structures of various PAHs are shown in Fig. 1. PAHs of 3 rings or more have low solubility in water and a low vapor pressure. The best known PAH is benzo[a]pyrene (B[a]P), which contains 5 rings. Because of their low vapor pressure, some PAHs are present at ambient temperature in air, both as gas and associated with particles. The lighter PAHs, such as phenanthrene, are found almost exclusively in gas phase whereas the heavier PAHs, such as B[a]P, are almost totally adsorbed on to particles.

These compounds are widely distributed in the atmosphere and are one of the first atmospheric pollutants to have been identified as suspected carcinogen. As molecular weight increases, the carcinogenicity of PAHs also increases, and acute toxicity decreases. B[a]P, is notable for being the first chemical carcinogen to be discovered. PAHs known for their carcinogenic and teratogenic properties are benzaanthracene and chrysene \([C_{18}H_{12}]\); benzo[b]fluoranthene, benzo[j]fluoranthene, benzo[k]fluoranthene and B[a]P \([C_{20}H_{12}]\); indeno[1,2,3-cd]pyrene \([C_{22}H_{12}]\); and dibenz[a,h]anthracene \([C_{20}H_{14}]\) (Ravindra et al., 2001 and reference therein).

Considering the increasing evidence of the ubiquitous presence of PAHs and health risk associated with their exposure, the present study examines the literature for the source profile of PAHs and their abatement and control policies to serve as a knowledge base for managing urban, regional as well as global air pollution. The review is organized in sections to provide a logical structure to the information. Section 2 discusses the various mechanisms of PAH formation; Section 3 discusses priority PAHs, while Section 4 covers possible artifact bias during PAHs sampling. PAHs are formed primarily during the incomplete combustion of fossil fuel (petroleum, natural gas and coal) and burning vegetation. These sources are discussed extensively in Section 5. Section 6 covers various approaches to identify the PAHs sources, while Section 7 discusses emission inventories. Atmospheric transport, residence and reaction of PAHs are briefly considered in Section 8. Regulation and control of PAHs emission plus air quality standards for PAHs are reviewed in Sections 9 and 10, respectively.

2. Formation of PAHs

PAHs may be synthesized from saturated hydrocarbons under oxygen-deficient conditions. Pyro-synthesis and pyrolysis are two main mechanisms...
that can explain the formation of PAHs. Low hydrocarbons form PAHs by pyrosynthesis. When the temperature exceeds 500°C, carbon–hydrogen and carbon–carbon bond are broken to form free radicals. These radicals combine to acetylene which further condenses with aromatic ring structures, which are resistant to thermal degradation. Fig. 2 illustrates the formation of such rings starting with ethane. The tendency of hydrocarbons to form PAH structure by pyrosynthesis varies in the order—aromatics > cycloolefins > olefins > parafins (Manahan, 1994).

Haynes (1991) suggested three possible mechanisms of PAH formation during combustion, i.e. slow Diels–Alder condensations, rapid radical reactions, and ionic reaction mechanism. However, the radical formation mechanism is favored as the combustion process within the internal combustion engine has
to occur very rapidly. It seems that gaseous hydrocarbon radicals rearrange quickly, providing the mechanism of PAHs formation and growth. The addition of hydrocarbon radicals to lower molecular weight PAHs then leads, via alkyl PAHs, to the formation of higher PAHs (Wiersum, 1996). Recently, Lima et al. (2005) reviewed and discussed some of the factors (type of fuel, amount of oxygen, and temperature) that affect the production and environmental fate of combustion-derived PAHs. The survivability and pyrosynthesis of PAHs during combustion of pulverized coal and tire crumb was studied by Atal et al. (1997). Significant amounts of PAHs were detected in the effluent of the combustion of both fuels under sufficiently fuel-rich conditions [bulk equivalent ratio \((\phi) > 1.6\)] and especially, under pyrolytic conditions in nitrogen. These PAHs were mostly attributed to pyrosynthesis as Atal et al. (1997) observed that deuterated PAHs, adsorbed on the fuels, survived the combustion process. Furthermore, small amounts of some PAHs survived in high-temperature pyrolytic conditions, but not in oxidative environments. These observations suggest that pyrosynthesis is the major contributing mechanism to the PAH emissions from the combustion of pulverized coal and tire crumbs. However, survivability of parent PAHs may be a minor mechanism at very high equivalent ratios.

The existing ring structure of cyclic compounds is conducive to PAH formation. Unsaturated compounds are especially susceptible to the reactions involved in PAH formation. The higher alkanes present in fuels and plant material form PAHs by the process of pyrolysis, i.e. the cracking of organic compounds.

3. Priority PAHs

The United States Agency for Toxic Substances and Disease Registry has considered 17 priority PAHs (Table 1) based on their toxicological profile (ATSDR, 1995), although the health effects of individual PAHs are not exactly alike. These 17 PAHs were chosen to be included in the priority list because (1) more information is available on them than on others; (2) they are suspected to be more harmful than others, and they exhibit harmful effects that are representative of PAHs in general; (3) there is a greater chance for exposure to these PAHs than to the others; and (4) of all the PAHs analyzed, these exhibited the highest concentrations.

Table 1 lists the priority PAHs, emission sources and phase distribution (ATSDR, 1995). Except for benzo[j]fluoranthene in Table 1, the other compounds are also known as 16 priority United States Environmental Protection Agency (US EPA) PAHs.

4. Sampling artefact

Representative PAHs sample should depict their true levels in ambient air. PAH monitoring is usually performed using high- or low-volume samplers (HVS, LVS) and is complex because of the reactive breakdown of PAHs between the gas and particulate phases. In HVS or LVS the particulate phase is first trapped on a filter and the gaseous phase is trapped on a solid adsorbent (e.g. polyurethane foam) located downstream from the filter. However, these sampling procedure have also been shown to be affected by several sampling artefacts (Kavouras et al., 1999; McMurry, 2000). In the particulate phase, positive artefacts (overestimation of the particle phase concentrations) are mainly due to sorption of gaseous compounds on the filter, while negative artefacts (underestimation of the particle phase concentrations) result from the volatilization of particulate PAH from the filter (McMurry, 2000; Goriaux et al., 2006). Moreover, chemical degradations of PAHs by oxidizing compounds such as nitrogen oxides \((NO_x = NO + NO_2)\),

<table>
<thead>
<tr>
<th>PAHs</th>
<th>Particle/gas phase distribution</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acenaphthene</td>
<td>Gas phase</td>
</tr>
<tr>
<td>Acenaphthylene</td>
<td>Gas phase</td>
</tr>
<tr>
<td>Anthracene</td>
<td>Particle gas phase</td>
</tr>
<tr>
<td>Phenantherene</td>
<td>Particle gas phase</td>
</tr>
<tr>
<td>Pyrene</td>
<td>Particle gas phase</td>
</tr>
<tr>
<td>Benzo[a]anthracene</td>
<td>Particle phase</td>
</tr>
<tr>
<td>Chrysene</td>
<td>Particle phase</td>
</tr>
<tr>
<td>Benzo[b]fluoranthene</td>
<td>Particle phase</td>
</tr>
<tr>
<td>Benzo[j]fluoranthene</td>
<td>Particle phase</td>
</tr>
<tr>
<td>Benzo[k]fluoranthene</td>
<td>Particle phase</td>
</tr>
<tr>
<td>Benzo[a]pyrene</td>
<td>Particle phase</td>
</tr>
<tr>
<td>Benzo[e]pyrene</td>
<td>Particle phase</td>
</tr>
<tr>
<td>Fluoranthene</td>
<td>Particle gas phase</td>
</tr>
<tr>
<td>Fluorine</td>
<td>Gas phase</td>
</tr>
<tr>
<td>Dibenzo[a,h]anthracene</td>
<td>Particle phase</td>
</tr>
<tr>
<td>Benzo[ghi]perylene</td>
<td>Particle phase</td>
</tr>
<tr>
<td>Indeno[1,2,3-c,d]pyrene</td>
<td>Particle phase</td>
</tr>
</tbody>
</table>

*aPredominant sources are motor vehicles and wood smoke.  
*bNot included in 16 US EPA priority list.
hydroxyl radical (OH), halogens, nitric acid (HNO₃), hydrogen peroxide (H₂O₂), and ozone (O₃) may occur during sampling (Pitts et al., 1986; Tsapakis and Stephanou, 2003; Schauer et al., 2003). Very recently Goriaux et al. (2006) reported that the atmospheric PAH concentrations measured using conventional samplers not equipped with an ozone trap can underestimate the PAH concentration by more than 200%. This was especially found when the samples were collected in the vicinity of a point source of particulate PAHs and for highly reactive compounds such as B[a]P.

The importance of the sampling artefacts depends mainly on sampling conditions such as temperature or atmospheric concentrations of PAH and oxidants (Mcdow and Huntzicker, 1990; Mader and Pankow, 2001; Goriaux et al., 2006). To reduce artifacts induced by conventional samplers, denuder sampling devices were developed (Coutant et al., 1989, 1992; Lane and Gundel, 1996). The denuder sampler systems were designed to trap the gas phase on a solid sorbent coated on the surface of the trap prior to collecting the particulate phase on a filter. This methodology avoids the phenomenon of adsorption of the gas phase on the filter and reduces the desorption artefact by collecting the volatilized fraction on a sorbent cartridge placed downstream from the filter. Finally, the chemical degradation of particulate PAHs may be reduced as the sorbent coated on the denuder tubes can remove the oxidizing species included in the gas phase (Coutant et al., 1988; Tsapakis and Stephanou, 2003). It is interesting to notice, however, that most of the studies on ambient levels of PAHs were carried out (or are still being carried out) using a HVS or LVS and hence it is important to modify these samplers to avoid artefacts bias.

5. Sources of PAHs

PAHs are the most stable form of hydrocarbons having low hydrogen-to-carbon ratio and usually occur in complex mixtures rather than single compounds. These pollutants are mostly formed during the incomplete combustion and pyrolysis of fossil fuels or wood, and from the release of petroleum products (Manahan, 1994). Other sources of PAHs include petroleum spills, oil seepage, and diagenesis of organic matter in anoxic sediments.

PAHs are also found in coal tar, crude oil, creosote, and roofing tar, and a few are used in medicine or to make dyes, plastics, and pesticides. PAHs produced for commercial use, include naphthalene, fluorene, anthracene, phenanthrene, fluoranthene, and pyrene (Franck and Stadelhofer, 1987). These pure PAHs usually exit as colorless, white or pale yellow–green solids. In general, there are five major emission sources of PAHs, i.e. domestic, mobile, industrial, agricultural, and natural. Furthermore, some cosmic sources of PAHs have also been proposed (Wing and Bada, 1992; Beegle et al., 2001).

The emission of PAHs by various anthropogenic combustion sources have been briefly discussed by Marchand et al. (2004) and hence in the present study the approach is further elaborated. The emission rates of PAHs from various sources are listed in Table 2 and the details are discussed below according to the main categories (domestic, mobile, industrial, agricultural, and natural). Emission factors are useful for the estimation of the amount of air pollutants (e.g. PAHs) released and therefore for setting national and international environmental policies for protection strategies and regulations.

<table>
<thead>
<tr>
<th>PAHs sources</th>
<th>Emission rate</th>
<th>Remarks</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Domestic</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Natural gas home appliances</td>
<td>1–2000 pg kg⁻¹</td>
<td>pg/kg of natural gas burned</td>
<td>Rogge et al. (1993c)</td>
</tr>
<tr>
<td>Pine</td>
<td>6.9 mg kg⁻¹</td>
<td>Wood combustion in residential fireplaces</td>
<td>Rogge et al. (1998)</td>
</tr>
<tr>
<td>Oak</td>
<td>4.9 v</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Wood/root-fuel</td>
<td>5.3–13.2 mg kg⁻¹</td>
<td>B[a]P</td>
<td>Gupta et al. (1998)</td>
</tr>
<tr>
<td>Wood/coal briquettes/charcoal</td>
<td>25–100 mg kg⁻¹</td>
<td>18 PAHs highest from wood</td>
<td>Oanh et al. (1999)</td>
</tr>
<tr>
<td>Coal</td>
<td>0.95 mg kg⁻¹</td>
<td>Average of 4 coal ranks</td>
<td>Oros and Simoneit (2000)</td>
</tr>
<tr>
<td>Pine</td>
<td>13.7 mg kg⁻¹</td>
<td>Wood combustion in residential fireplaces</td>
<td>Schauer et al. (2001)</td>
</tr>
</tbody>
</table>

Table 2
Estimated PAHs emission rate from various sources

Please cite this article as: Ravindra, K., et al., Atmospheric polycyclic aromatic hydrocarbons: Source attribution, emission factors and regulation. Atmospheric Environment (2008), doi:10.1016/j.atmosenv.2007.12.010
Table 2 (continued)

<table>
<thead>
<tr>
<th>PAHs sources</th>
<th>Emission rate</th>
<th>Remarks</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oak</td>
<td>5 mg kg⁻¹</td>
<td></td>
<td>Venkataraman et al. (2002)</td>
</tr>
<tr>
<td>Eucalyptus</td>
<td>3.7 mg kg⁻¹</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Wood</td>
<td>2.0–3.2 mg kg⁻¹</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Briquette</td>
<td>2.8–3.0 mg kg⁻¹</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dung cake</td>
<td>3.1–5.5 mg kg⁻¹</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Wood fuel</td>
<td>24–114 mg kg⁻¹</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Rice husk briquettes</td>
<td>140 mg kg⁻¹</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Anthracite coal</td>
<td>2 mg kg⁻¹</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Domestic burning</td>
<td>~100 mg kg⁻¹</td>
<td></td>
<td>Lee et al. (2005)</td>
</tr>
<tr>
<td>Fire wood</td>
<td>1.6–8.2</td>
<td>B[a]P</td>
<td>Kakareka et al. (2005)</td>
</tr>
<tr>
<td>Peat Briquette</td>
<td>0.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mobile</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Gasoline engine</td>
<td>350 or 26 μg km⁻¹</td>
<td>Catalytic convertor equipped light vehicles (average of 7)</td>
<td>Rogge et al. (1993a)</td>
</tr>
<tr>
<td>Gasoline engine</td>
<td>72.5 μg kg⁻¹</td>
<td>Light vehicles</td>
<td>Miguel et al. (1998)</td>
</tr>
<tr>
<td>Gasoline engine</td>
<td>8.1 or 0.7 μg kg⁻¹</td>
<td>Catalytic convertor equipped light vehicles (average of 9)</td>
<td>Schauer et al. (2002)</td>
</tr>
<tr>
<td>Light-duty gasoline</td>
<td>21 μg kg⁻¹</td>
<td>For benzo[ghi]perylene</td>
<td>Marr et al. (1999)</td>
</tr>
<tr>
<td>Heavy-duty diesel</td>
<td>~1000 μg kg⁻¹</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Diesel engine</td>
<td>240 or 60.2 μg km⁻¹</td>
<td>Heavy-duty trucks</td>
<td>Rogge et al. (1993a)</td>
</tr>
<tr>
<td>Diesel engine</td>
<td>14.3 μg kg⁻¹</td>
<td>Heavy-duty trucks</td>
<td>Miguel et al. (1998)</td>
</tr>
<tr>
<td>Two-stroke engines (with out</td>
<td>1.6 mg km⁻¹</td>
<td>ECE R40 simulation</td>
<td>Gambino et al. (2000)</td>
</tr>
<tr>
<td>catalytic converter) (with</td>
<td>21 μg kg⁻¹</td>
<td>For pyrene (particle phase)</td>
<td></td>
</tr>
<tr>
<td>catalytic converter)</td>
<td>0.9 mg km⁻¹</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Aircrafts</td>
<td>1.24 mg l⁻¹ Fuel</td>
<td>Per landing-take off cycle for B[a]P</td>
<td>EPAQS (1998)</td>
</tr>
<tr>
<td>Helicopter</td>
<td>63.4 mg l⁻¹ Fuel</td>
<td>22 PAHs</td>
<td>Chen et al. (2006)</td>
</tr>
<tr>
<td>Ships</td>
<td>500 μg kg⁻¹</td>
<td>Marine diesel engine, sum of 25 PAHs</td>
<td>Westerholm and Li (1994)</td>
</tr>
<tr>
<td>Ships</td>
<td>410–2300 μg kWh⁻¹</td>
<td>23 PAHs</td>
<td>Cooper (2001)</td>
</tr>
<tr>
<td>Ships</td>
<td>0.2–2 mg kWh⁻¹</td>
<td>29 PAHs (normal real word operation)</td>
<td>Cooper (2003)</td>
</tr>
<tr>
<td>Break dust</td>
<td>16 mg kg⁻¹</td>
<td>Emitted from the hydraulic break system</td>
<td>Rogge et al. (1993d)</td>
</tr>
<tr>
<td>Industrial</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Industrial stacks</td>
<td>77–3970 μg kg⁻¹</td>
<td>9 different stacks</td>
<td>Yang et al. (1998)</td>
</tr>
<tr>
<td></td>
<td>2–16 μg kg⁻¹</td>
<td>For B[a]P</td>
<td></td>
</tr>
<tr>
<td>Industrial boiler</td>
<td>13,300 μg kg⁻¹</td>
<td>Lower molecular weight PAHs</td>
<td>Li et al. (1999)</td>
</tr>
<tr>
<td>Heavy oil</td>
<td>2900 μg kg⁻¹</td>
<td>Lower molecular weight PAHs</td>
<td></td>
</tr>
<tr>
<td>Diesel</td>
<td>2880 μg kg⁻¹</td>
<td>Only 3 PAHs were detected</td>
<td>Pisupati et al. (2000)</td>
</tr>
<tr>
<td>Heavy oil + natural gas coke</td>
<td>208 μg kg⁻¹</td>
<td>Total emissions gaseous, particulate, and residual PAHs</td>
<td>Chen et al. (2007)</td>
</tr>
<tr>
<td>Oven gas + blast furnace gas</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>boiler</td>
<td>85–320 μg kg⁻¹</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Water tube boiler</td>
<td>4000 μg kg⁻¹</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Waste-tire pyrolysis</td>
<td>3.400 μg kg⁻¹</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>200 μg kg⁻¹</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>400 μg kg⁻¹</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Joss paper furnaces</td>
<td>71 mg kg⁻¹</td>
<td>21 PAHs</td>
<td>Yang et al. (2005)</td>
</tr>
<tr>
<td>Agricultural</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Open burning</td>
<td>5–683 mg kg⁻¹</td>
<td>Wind tunnel simulations of agricultural and forest biomass fuels burning</td>
<td>Jenkins et al. (1996)</td>
</tr>
<tr>
<td>Open burning</td>
<td>240–571 mg kg⁻¹</td>
<td>Simulation of agricultural debris</td>
<td>Kakareka and Kukharchyk (2003)</td>
</tr>
</tbody>
</table>
Emission factors should be based on the most recent and accurate data from various sources. Furthermore, they should be revised after a certain period as there might be changes/improvements in production processes, air pollution control devices and/or in policies.

5.1. Domestic emissions

Domestic emissions are predominantly associated with the burning of coal, oil, gas, garbage, or other organic substances like tobacco or char broiled meat (Smith, 1987). Furthermore, wood, dried animal-dung-cake and crop waste (agricultural residue) are also used extensively for cooking in developing nations as noted by WHO (2002). The WHO report also estimates that over 75% people in China, India, and South East Asia, and 50–75% people in parts of South America and Africa use these solid fuels for daily cooking.

The levels of B[a]P were measured during wood and dung-cake combustion and ranged from 1.3 to 9.3 μg m⁻³ over an average sampling periods of 15–30 min (Aggarwal et al., 1982). Concentration of the 16 US EPA PAHs measured over a cooking period of 45–60 min were 2.0 μg m⁻³ (wood), 3.5 μg m⁻³ (wood/dung), and 3.6 μg m⁻³ (dung-cake) for respective combustion activities (Raiyani et al., 1993a). Low-temperature bio-fuel combustion has the potential to result in higher emissions of PAHs than high-temperature industrial sources. PAHs emission factors from wood combustion in small-scale space heating stoves exceeded those from furnace-oil combustion by a factor of 100 on an energy equivalent basis (Smith, 1987). Venkataraman et al. (2002) also reported the emission factors of total PAH from wood, briquette, and dung-cake combustion and they ranged from 2.0 to 3.2 mg kg⁻¹, 2.8 to 3.0 mg kg⁻¹, and 3.1 to 5.5 mg kg⁻¹, respectively. The PAH emission factors from open burning of agricultural biomass in wind tunnel experiments were also studied and ranged from 5 to 683 mg kg⁻¹ (Jenkins et al., 1996). Recently, Oanh et al. (2005) estimated PAH emissions (16 US EPA plus B[e]P) from 12 selected cook-stoves burning wood fuel, rice husk briquettes and anthracite coal. The emission factors of the 17 PAHs were 24–114 and 140 mg kg⁻¹ from wood fuel and rice husk briquettes fuel, respectively. The majority of PAHs in the biomass fuel smoke were of low molecular weight and mostly volatile, with more than 86% of total PAHs found in vapor phase. For anthracite coal, the PAHs were found only in particulate phase with a lower emission rate (2 mg kg⁻¹).

Rogge et al. (1993c) quantified the PAHs emission from natural gas home appliances and found that they can contribute nearly half of the total elutable organic mass with an emission rate from a few up to 2000 pg kJ⁻¹ of natural gas burned. Gupta et al. (1998) reported emission factors of B[a]P in respirable particles (<5 μm aerodynamic diameter) in the range of 5.3–13.2 mg kg⁻¹ for wood and root-fuel combustion. Total emission factors of 18 PAHs in particulate phase (by filtration) and vapor phase (adsorption onto an XAD-2 resin) were found to be highest from wood, followed by coal briquettes and charcoal (Oanh et al., 1999) and ranged from 25 to 100 mg kg⁻¹.

The partial combustion of coal, which has a hydrogen-to-carbon ratio <1, is a major source of PAH compounds. Domestic combustion of solid fuels makes a significant contribution to the total PAHs emission. In Sweden, wood burning has been estimated to contribute 430 kg B[a]P in 1994, whereas gasoline and diesel vehicles together were estimated to contribute up to 320 kg B[a]P (Boström et al., 1999). Similar results have been reported for Los Angeles city, and specifically during winter, with a higher PAH to organic carbon ratio resulting from wood combustion than those from vehicular emission (Schauer and Cass, 2000).

In urban areas where coal, wood, and peat burning are predominant, a high proportion of the PAH ambient air concentration is associated with these sources (Li and Kamens, 1993). The burning of wood, coal, and peat in open fireplaces is often conducted for decorative effects in addition to providing heating. These systems are often hand-fed with a low thermal efficiency and potentially generate high PAH emissions. The PAHs emission from domestic sources is mainly associated with a range of particle size <2 μm (Raiyani et al., 1993b; Gupta et al., 1998, Boström et al., 1999). The emissions rate in domestic heating are greatly influenced by the nature of fuel (wood type, presence of foliage) and combustion conditions such as temperature, moisture, and availability of oxygen (Standley and Simonetz, 1987; Jenkins et al., 1996). Further, it has also been noticed that smoldering combustion emit 4–5 times more PAHs than flaming combustion (Jenkins et al., 1996).

However, it has to be noticed that there are large geographic variations in the domestic emissions of.
PAHs due to the climatic differences and due to the domestic heating systems in use. But PAH emissions from these sources may be of major health concern because of their prevalence in indoor environment.

5.2. Mobile emissions

Mobile sources include the emission from vehicles such as aircraft, shipping, railways, automobiles, off-road vehicles, and machinery. The emission of PAHs from these sources is a function of engine type, load and age, fuel type and quality (e.g. aromaticity), PAH accumulation in lubricant oil, lubricant oil combustion, and driving mode, including cold starting and emission control. Paturel et al. (1996) found that the start conditions of vehicles, hot or cold engine, have only a little influence on the mass repartition of the PAHs in gaseous or particulate phase. Further, the study suggests that there are very high emissions of PAHs under cold start, particularly with gasoline cars at low speed. Similarly, Devos et al. (2006) found that cold start PAHs emission are around 10 times higher for gasoline vehicles than for diesel vehicles. Most of the studies show that the emissions from vehicle exhaust (diesel, leaded and unleaded gasoline) are the largest contributors of PAHs in urban areas (Rogge et al., 1993a; Khalili et al., 1995; Miguel et al., 1998; Marchand et al., 2004; Ravindra et al., 2006a, b; Marr et al., 2006). Diesel fueled vehicles have higher particulate emissions than gasoline fueled vehicles. These particles consist of combustion-generated soot, a solvent extractable hydrocarbon fraction, and a mineral fraction. The PAHs are found within the solvent extractable fraction.

A strong correlation between chemical composition and PAHs emission rate for gasoline-powered light vehicles was reported by Marr et al. (1999). Furthermore, the study indicates the importance of unburnt fuel as a significant PAH source. Schauer et al. (2002) also found that the composition of the fuel also influences PAH emissions for diesel vehicles. For diesel vehicles, an additional source of PAHs in the exhaust emissions is the PAHs content in the fuel (Westerholm and Li, 1994; Ravindra et al., 2006b).

The production of PAHs from gasoline automobiles depends on the air/fuel ratio. It has been found that the amount of PAHs in engine exhaust decreases with a leaner mixture. For example, Jones et al. (2004) found that as the air/fuel combustion ratio increased, the high molecular weight PAHs (> 202 amu) diminished rapidly. The use of catalytic converters has also been shown to have a significant effect on the reduction of the PAHs concentration in the exhaust gases. A study by Rogge et al. (1993a) showed that the total PAH emission rate was 25-fold lower for vehicles fitted with catalytic converters. Duran et al. (2001) simulated atmospheric PAHs emission from diesel engines. Their study showed that engine speed was a more decisive factor for PAHs emission than torque. Further, an increase in aromatic content beyond 25wt% also causes a significant increase in PAHs emission at high engine speed. All internal combustion engines have varying PAH emission characteristics dependent on engine temperature (particularly cold-start), load, fuel quality, and speed (Westerholm and Li, 1994). Urban areas with congested traffic conditions with vehicles often only traveling short journeys promote the emission of PAHs. Engine deterioration and high mileage also increase emissions.

Two-stroke engines are relevant in the motor scooter and motor cycle sector of transportation. Two-stroke fuel is a mixture of gasoline and oil. The engines are generally small and not equipped with additional emission control systems. Recent research has estimated that unabated PAH emissions whilst performing the ECE R40 simulation are 1.6 mg km\(^{-1}\) for the sum of 29 PAHs with 2–6 rings and 20.8 µg kg\(^{-1}\) for 6 carcinogenic PAHs (B[a]P, benzo[b+j+k]fluoranthene, benzo[a]anthracene, dibenz[a,h]anthracene, see Gambino et al., 2000). The same test cycle carried out with a catalytic converter fitted led to tailpipe emissions of 0.89 mg km\(^{-1}\) (29 PAH) and 14.2 µg kg\(^{-1}\) of the carcinogenic PAHs (Gambino et al., 2000). Wingfors et al. (2001) studied correlation between PAH concentration and traffic composition. They found significant correlation between tricyclic PAHs and heavy-duty vehicles (HDVs) and naphthalene; and heavy PAHs and light-duty vehicles (LDVs). However, the total amount of PAHs associated with particles did not increase with an increasing percentage of HDVs. The emission factors from HDVs were found to be significantly larger than LDVs (Staehelin et al., 1998).

Measurements in tunnels have been used to derive PAH emission factors and to estimate the contribution of traffic to PAH content of the ambient air. This approach is considered to yield more realistic emission estimates than measurements using dynamometer tests (Gertler and Pierson, 1996; Oda et al., 2001; Wingfors et al., 2001). In a laboratory...
only a selection can be tested, whereas in a tunnel, all types of fuel and real world fleet vehicles can be studied. Furthermore, by repeated tunnel studies it is possible to trace improvements or changes following the use of new fuels or emission control systems.

Trains, aircrafts, and ships also contribute significantly to the mobile sources of PAHs. The main source of PAHs emissions in rail transportation is the use of diesel and diesel/electric locomotives. Coal-fired steam locomotives in developing countries may also contribute but no measurement data or very little are available. Further Kohler and Kunniger (2003) also estimated that around 139 tons of US EPA PAHs are emitted by the creosoted ties of the Swiss railway network, every year. The PAHs emission from aircraft exhaust might be significant as approximately 227 billion liters of jet fuels are consumed worldwide every year (Chen et al., 2006). The PAH emissions from aircrafts are dependent on fuel composition (volatility) and on the power setting of the engine and tend to decrease as the power setting increases. Average emission factors for an aircraft gas turbine engine have been given as 1.24 mg per landing-take off (LTO) cycle for B[a]P. As air travel increases the proportion of total PAH emissions which are attributable to air transport could increase (EPAQS, 1998). The PAHs fingerprints from aircraft exhaust were compared with diesel exhaust by Krahl et al. (1998). Recently, Chen et al. (2006) characterized the emission of PAHs from a helicopter turbo-shaft engine and a 843 μg m⁻³ of mean total PAH concentration measured in engine exhaust. Two and three benzene ring PAHs dominate the total PAH emission (98%). The total emission levels of B[a]P during one LTO cycle was found to be higher than the European Commission standard (1.24 mg LTO⁻¹).

There are a limited number of publications focusing on PAH emissions from shipping (Lloyds, 1995; Cooper et al., 1996; Cooper, 2001, 2003). Westerholm and Li (1994) measured PAH emissions from an onboard marine diesel engine (6600 kW, maximum continuous rating) burning marine diesel fuel with a sulfur content of 1.9% (w/w). The emissions of PAHs of 500 μg kg⁻¹ fuel (sum of 25 PAH, fluorene to coronene), B[a]P < 2.2 μg kg⁻¹ fuel and sulfur PAHs 93 μg kg⁻¹ fuel were reported. Within the Lloyds Marine Exhaust Emissions Research programme, (Lloyds, 1995) individual PAHs from several different ships using marine distillates and heavy bunks were measured. Lloyds have reported emissions of PAHs (phenanthrene to 6-ring PAHs) in the range 21–244 μg m⁻³, and for B[a]P in the range of 0.02–0.65 μg m⁻³, respectively. Furthermore, the genotoxic dibenzo[a,l]pyrene is reported to occur in the exhaust at concentrations ranging from <0.01 μg m⁻³ to as large 3.20 μg m⁻³. Cooper et al. (1996) reported emissions of total PAHs (23 species) and B[a]P were in the range of 73–360 μg Nm⁻³ (or 410–2300 μg kWh⁻¹) and <0.02–0.2 μg Nm⁻³ (or <0.1–0.9 μg kWh⁻¹), respectively. Furthermore, higher PAH levels were measured from auxiliary engines operating at low engine load during harbor stops and they were in agreement with Cooper (2001). In this study the engine investigated had a 6400 kW maximum continuous rating running on fuel oil containing 0.48% sulfur. Cooper (2003) also estimated the exhaust emission from a ship during normal real world operation (hotelling, unloading, and loading activities). The total PAH (29 species) emissions were mostly in the range of 0.15–2 mg kWh⁻¹ except for a ship using heavier residual oils (9.5–11 mg kWh⁻¹). Additional PAH emissions from shipping result from the generation of electrical power by smaller diesel engines (Cooper, 2003). It is expected that PAH emissions from larger ships/ferries may contribute significantly to PAHs in air concentrations depending on geographical conditions of the local harbor and the route, but further investigations would be needed.

In addition to the combustion emissions related to transportation, there are additional emissions of PAHs due to abrasion of rubber tires, asphalt road surfaces, and brake linings (Marchesani et al., 1970; Rogge et al., 1993d; Boulter, 2005). The magnitude of these emissions is hard to quantify. However, high PAH emissions from these sources have been estimated (Ahlbom and Duus, 1994), but have been disputed [Baumann and Ismeier, 1997]. It is estimated that over 2,500,000 tons of tires were produced per year in European Union and with a similar estimation for the USA. Larnesjö (1999) has indicated that the dominant PAHs in the tire tread are fluoranthene, pyrene, benz[ghi]perylene, and coronene. The PAHs content of tires is dependent on the manufacturer and the year of manufacture.

5.3. Industrial emissions

The most important industrial sources of PAHs include primary aluminum production (in particular
plants using Soderberg process), coke production (e.g. as part of iron and steel production), creosote and wood preservation, waste incineration, cement manufacture, petrochemical and related industries, bitumen and asphalt industries, rubber tire manufacturing, and commercial heat/power production (PAHs Position paper, 2001).

Pisupati et al. (2000) studied the emission of PAHs from bench-scale and small industrial, water tube boilers. Only acenaphthene, fluoranthene, and naphthalene were detected and the emission factors ranged from 85 to 320 mg kg\(^{-1}\) of fuel fired. Interestingly no significant differences were found in the emissions for different fuel types/forms and firing conditions. The PAH emissions showed an increase with a decrease in the firing rate. Li et al. (1999) also investigated the PAHs emission from 25 industrial boilers. The emission factors of total PAHs were 13,300, 2900, 2880 and 208 mg kg\(^{-1}\) for heavy oil, diesel, co-combustion of heavy oil and natural gas, and co-combustion of coke oven gas and blast furnace gas boiler, respectively. The PAHs in the stack flue gas were primarily dominated by the lower molecular weight PAHs and specifically by the naphthalene.

The emissions from various industrial stacks (blast furnace, basic oxygen furnace, coke oven, electric arc furnace, heavy oil plant, and cement plant), including an industrial waste incinerator, a diesel engine and a gasoline-powered engine were investigated by Yang et al. (1998). The measured total PAHs emission factor of eight stationary sources were between 77 and 3970 mg kg\(^{-1}\) feedstock, while B[a]P emission factor were between 2 and 16 mg kg\(^{-1}\) feedstock (coke, liquid steel, coal, waste steel, fuel oil, bituminous coal, cement raw material, and kiln feed). Out of these sources the heavy oil plant has the highest total PAHs and B[a]P emission factor. The indicatory PAHs of the cement plant were acenaphthylene, acenaphthene and anthracene (3 benzene ring PAHs), while for the industrial waste incinerator indeno[1,2,3-cd]pyrene and chrysene were identified. Whereas, 4- and 5-benzene ring PAHs (B[a]P, benzo[a]anthracene, perylene, benzo[e]pyrene, cyclopenta[c,d]pyrene, and dibenz[a]anthracene) were marked for eight industrial stacks. The PAH emission factors were affected by incoming fuel, the manufacturing process, and the air pollution control devices.

The emission of PAHs from furnaces burning recycled paper and virgin bamboo were quantified (Yang et al., 2005) and the individual PAH emission factors varied from <1 mg kg\(^{-1}\) fuel to several tens of mg kg\(^{-1}\) fuel. Chen et al. (2007) investigated the PAHs generated in a waste-tire pyrolysis process and the mean content of total PAHs was 77 mg kg\(^{-1}\) dominated by indeno[1,2,3-cd]pyrene, dibenz[ah]anthracene and B[a]P. Further, the emission rate of gaseous, particulate, and residual PAHs in the flare exhaust were 25, 1.6, and 3.0 mg min\(^{-1}\), respectively, and the corresponding emission factors of 3.4, 0.2, and 0.4 mg kg\(^{-1}\) for tires. The PAHs emission rate and factor estimated for a scrap tire pyrolysis plant were 42 g day\(^{-1}\) and 4.0 mg kg\(^{-1}\) tire, respectively. These results indicate the importance of improving the technologies to remove the PAHs from the scrap tires pyrolysis process.

### 5.4. Agricultural sources

Open burning of biomass is a common method for crop and forest residue disposal and land preparation. Burning of agricultural waste, however, is a source of atmospheric PAHs. Agricultural sources include the stubble burning, open burning of moorland heather for regeneration purposes, and open burning of brushwood and straw. All of these activities involve the burning of organic materials under sub-optimum combustion conditions. Thus, it can be expected that a significant amount of PAHs is produced (e.g. Freeman and Catell, 1990; Godoi et al., 2004). Recently, Godoi et al. (2004) studied the particulate PAHs emission during sugarcane burning and the levels were found to be comparable with some urban centers. Similar results were also found by Fang et al. (1999) in Indonesia and the levels varied from 7 to 46 ng m\(^{-3}\). Larkin et al. (1986) estimated that 1.26 million ha of land was burnt in UK during 1884, resulting in emission of 18,000 tons of black smoke. Based on this and the Freeman and Catell (1990) study, an estimation of 6.3 tons of total particulate PAHs emission was calculated by Wild and Jones (1995).

Jenkins et al. (1996) studied the emission factor for the 19 PAH species under wind tunnel simulation of open burning for agricultural and forest biomass fuels including cereals grasses, agricultural tree pruning, and fir and pine wood. They varied from 5 to 683 mg kg\(^{-1}\), depending mainly on burning condition and to a lesser extent on fuel type. Excluding naphthalene and 2-methylnaphthalene, the total PAH emission factor varied from 1.4 to 100 mg kg\(^{-1}\) for all fuels. The total PAH emission rates increases with increasing particulate matter
emission rate and decreasing combustion efficiency. The higher PAHs emissions were found at higher wind speed, lower flaming rate, and smoldering of wood fuels. However, the PAHs emission estimation of open burning by Kakareka and Kukharchyk (2003) were found highest (Table 2) with significant content of phenanthrene. Recently, Hays et al. (2005) also simulated the agricultural fires of surface residuals of rice and wheat and found that n-alkane, PAHs, and lignan dimmer molecules predominate in the organic carbon fraction of the PM$_{2.5}$ emissions. In particular, the wheat and rice straw aerosol were enriched by eight-fold of high molecular weight PAHs (> 178 amu). Recently, Kumata et al. (2006) also estimated that biomass burning contributes 17–45% of PAHs burden of fine particles in Tokyo and the increase in the biomass-PAH accounts for approximately 27% and 22% of winter-time elevation of 3–4 ring PAHs and 5–6 ring PAHs, respectively.

In some countries there are policies to regulate these activities but not in developing countries; where biomass burning seems to be dominate. Due to uncertainty in emission factors and the occurrence of these activities, the emissions of PAHs from agricultural sources are difficult to quantify. Nevertheless, they may contribute significantly to PAH levels at certain locations and will be subject to long range transport processes.

5.5. Natural sources of PAHs

5.5.1. Terrestrial origin

Terrestrial sources of PAHs include the non-anthropogenic burning of forests, woodland, and moorland due to lightning strikes (Baumard et al., 1999). Volcanic eruptions may also emit PAHs, but no data regarding these emissions in atmosphere were found. Wild and Jones (1995) have estimated that the contribution from these sources to over all PAHs emission may be negligible.

In nature, PAHs may be formed in three ways: (1) high-temperature pyrolysis of organic materials; (2) low to moderate temperature diagenesis of sedimentary organic material to form fossil fuels; and (3) direct biosynthesis by microbes and plants (Neff, 1979). A number of PAHs are generated by biogenic precursors which are common constituents of terrestrial higher plants, through diagenetic process (Bouloubassi and Saliot, 1993). Some authors suggest that PAHs can be synthesized by unicellular algae, higher plants or bacteria, but at the same time others conclude that organisms accumulate PAHs rather than synthesize them (Wilcke, 2000). It is commonly accepted that predators accumulate non-metabolized pollutants and thus have higher levels than their food supply (Cripps, 1992).

Meteorological conditions (such as wind, temperature, and humidity) and fuel type (e.g. moisture content, green vs. seasoned wood) may play an important role in the degree of natural PAH production. There was no recent inventory found for the global estimation of natural sources of PAHs emission and hence this appears to be a gap in our knowledge of air pollutant emissions.

5.5.2. Cosmic origin

Among the cosmic source of PAHs are carbonaceous chondrites, which originate in the main asteroid belt and are not associated with life (Sagan et al., 1993; Clemett et al., 1993; Halasinski et al., 2005). The PAHs in chondrites appear to be the product of a high-temperature synthesis. However they may be the thermal alteration of pre-existing aliphatic compounds. Thermal alteration requires the presence of low-temperature mineral phases such as magnetite and hydrated phyllosilicates for their formation.

6. Source identification of PAHs

6.1. Source markers

Specific PAHs have been suggested as being indicators for certain processes that release PAHs into the environment. These PAHs are called source markers, tracers, or signatures. The PAH concentration profile and ratio can be used to determine the contribution of different sources to their concentrations in air.

Li and Kamens (1993) characterized PAH signatures for three combustion sources, i.e. residential wood combustion, gasoline spark ignition emissions, and diesel engine emissions. Normalization is a general statistical approach to reduce the anomalies in large data sets and Li and Kamens (1993) found that the normalized PAH signatures gave better results than un-normalized signatures. Furthermore, it was possible to distinguish between the above-mentioned sources when a smaller source contributed more than 10% of the total. Khalili et al. (1995) determined the chemical composition (source finger prints) of the major sources of
airborne PAHs in the Chicago metropolitan area, from 1990 to 1992. They found that 2- or 3-ring PAHs were responsible for 92%, 65%, 74%, 99%, and 80% of the total concentration of the measured 20 PAHs from highway tunnels, diesel engine, petrol engines, coke oven, and wood combustion samples, respectively (Table 3). Six-ring PAHs such as indeno[1,2,3-cd]pyrene and benzo[ghi]pyrene were mostly below the detection limit in the highway tunnels, diesel and petrol engine samples (Khalili et al., 1995). The following individual PAH or group of PAHs have been suggested as source markers in the literature:

(a) Dominance of chrysene and benzo[k]fluoranthene were suggested for their origin from coal combustion (Khalili et al., 1995; Smith and Harrison, 1998; Ravindra et al., 2007, 2008).

(b) The significantly higher level of benzo[ghi]pyrene, coronene, and phenanthrene were proposed for motor vehicle emissions (Smith and Harrison, 1998; Ravindra et al., 2006a). Miguel et al. (1998) found that diesel trucks were the major source of lighter PAHs, whereas light-duty gasoline vehicles were the dominant sources of higher molecular weight PAHs such as B[a]P and dibenz[a,h]anthracene. Similarly, Marr et al. (1999) found LDVs contribute significantly to 4- and 5-benzene ring PAHs, whereas HDVs (diesel) were the dominant source of 3-benzene ring PAHs, such as fluoranthene and pyrene.

(c) Phenanthrene, fluoranthene, and pyrene are associated with salt particles (from salting road during winter), which appear to adsorb volatile PAH emissions from motor vehicles (Harrison et al., 1996).

(d) Pyrene, fluoranthene, and phenanthrene shows reasonably high levels in emission from incineration (Smith and Harrison, 1998; Ravindra et al., 2006a).

(e) Oil combustion was reported to be associated with the high concentration of the more volatile PAHs such as fluorene, fluoranthene, and pyrene, along with moderate levels of the higher molecular weight compounds, i.e. benzo[b]fluoranthene and indeno[1,2,3-cd]pyrene (Harrison et al., 1996; Ravindra et al., 2006a).

(f) A significant enrichment is the ratio of unsubstituted PAHs to their methyl- and dimethyl-substituted homologues which have been observed in tailpipe emission relative to the fuel used (Schauer et al., 1999, 2002).

(g) Yang et al. (1998) also suggested indicatory PAHs for cement plants, waste incinerator and for industrial stacks, which are already discussed in details in Section 5.3.

Krahl et al. (1998) also suggested a non-PAH compound (p-quaterphenyl) as tracer for PAH pollution from aerospace and to distinguish this from diesel emission. However, it has to be noticed that these markers imply some degree of overlap between the profiles from different emission source categories.

6.2. PAH diagnostic ratio (DR)

The binary ratio method for PAH source identification involves comparing ratios of pairs of frequently found PAH emissions. For example, PAHs resulting from the use of coal, oil, and wood are low in coronene relative to B[a]P, while mobile source combustion emissions from diesel and petroleum use are high in benzo[ghi]perylene and coronene relative to B[a]P (Stenberg et al., 1979). The ratio of these PAHs can be used to distinguish between traffic dominated PAH profiles and other sources (Brasser, 1980; Mainwaring and Stirling, 1981; Hooper et al., 1993). PAHs profiles have been used to identify vehicle emission following the use of

<table>
<thead>
<tr>
<th>Table 3</th>
<th>Source distribution of percentage PAHs to total mass</th>
</tr>
</thead>
<tbody>
<tr>
<td>PAH</td>
<td>Highway tunnel</td>
</tr>
<tr>
<td>---------</td>
<td>----------------</td>
</tr>
<tr>
<td>2-Ring</td>
<td>76.2</td>
</tr>
<tr>
<td>3-Ring</td>
<td>16</td>
</tr>
<tr>
<td>4-Ring</td>
<td>4.3</td>
</tr>
<tr>
<td>5-Ring</td>
<td>3.1</td>
</tr>
<tr>
<td>6-Ring</td>
<td>0.4</td>
</tr>
<tr>
<td>7-Ring</td>
<td>Bdl</td>
</tr>
</tbody>
</table>

Bdl (below detection limit); from Khalili et al. (1995).
unleaded gasoline in many countries and the unsuitability of lead as a vehicle sources marker (Venkataraman et al., 1994). The PAH profile was also seen to perform as reliably as inorganic compound profiles in a multivariate PAHs source apportionment study in Birmingham, UK (Harrison et al., 1996).

The diversity in PAH sources could also be characterized from diagnostic ratios. The concentrations of specific PAHs or group have been used to identify the emission sources (Ravindra et al., 2006a, b). As shown in Table 4 many studies have developed and used a specific value of PAH diagnostic ratio for a source category. Studies reported in Table 4 also indicate that it is further possible to differentiate the traffic emission in to gasoline or diesel exhaust as shown by Khalili et al. (1995), Guo et al. (2003), Fang et al. (2004), and Ravindra et al. (2006a). Grimmer et al. (1983) suggested indeno[1,2,3-cd]pyrene/(indeno[1,2,3-cd]pyrene + benzo[ghi]perylene) ratio of 0.62 for wood burning, whereas Kavouras et al. (2001) used a ratio between 0.35 and 0.70 indicating diesel emission. Hence, it would be difficult to differentiate diesel emission from biomass emission based only on one proposed diagnostic ratio (indeno[1,2,3-cd]pyrene/indeno[1,2,3-cd]pyrene + benzo[ghi]perylene). However, source identification can be improved using various other ratios proposed in Table 4 and performing their relative comparison.

However, the diagnostic ratios method should be used with caution because it is often difficult to discriminate between some sources (Ravindra et al., 2006a). The ratio can be altered due to the reactivity of some PAH species with other atmospheric species, such as ozone and/or oxides of nitrogen.

### Table 4

<table>
<thead>
<tr>
<th>Diagnosis ratio</th>
<th>Value</th>
<th>Sources</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Indeno[1,2,3-cd]pyrene/(indeno[1,2,3-cd]pyrene + benzo[ghi]perylene)</td>
<td>0.18</td>
<td>Cars</td>
<td>Grimmer et al. (1983); Ravindra et al. (2006a, b) Kavouras et al. (2001)</td>
</tr>
<tr>
<td></td>
<td>0.37</td>
<td>Diesel</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.56</td>
<td>Coal</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.62</td>
<td>Wood burning</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.35-0.70</td>
<td>Diesel emissions</td>
<td></td>
</tr>
<tr>
<td>Fluorene/(fluorene + pyrene)</td>
<td>&gt;0.5</td>
<td>Diesel</td>
<td>Rogge et al. (1993a,b); Mandalakis et al. (2002); Fang et al. (2004); Ravindra et al. (2006a, b)</td>
</tr>
<tr>
<td></td>
<td>&lt;0.5</td>
<td>Gasoline</td>
<td></td>
</tr>
<tr>
<td>B[a]P/(B[a]P + chrysene)</td>
<td>0.5</td>
<td>Diesel</td>
<td>Khalili et al. (1995); Guo et al. (2003)</td>
</tr>
<tr>
<td>Benzo[b]fluoranthene/benzo[k]fluoranthene</td>
<td>0.73</td>
<td>Diesel</td>
<td>Pandey et al. (1999); Park et al. (2002)</td>
</tr>
<tr>
<td></td>
<td>&gt;0.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>B[a]P/benzo[ghi]perylene</td>
<td>0.5–0.06</td>
<td>Traffic emission</td>
<td>Pandey et al. (1999); Park et al. (2002); Pandey et al. (1999)</td>
</tr>
<tr>
<td></td>
<td>&gt;1.25</td>
<td>Brown coal</td>
<td></td>
</tr>
<tr>
<td>Indeno[1,2,3-cd]pyrene/benzo[ghi]perylene</td>
<td>&lt;0.4</td>
<td>Gasoline</td>
<td>Caricchia et al. (1999)</td>
</tr>
<tr>
<td>CPAHs/TPAHs&lt;sup&gt;a&lt;/sup&gt;</td>
<td>~1</td>
<td>Diesel</td>
<td>Pandey et al. (1999); Park et al. (2002); Pandey et al. (1999)</td>
</tr>
<tr>
<td></td>
<td>~1</td>
<td>Combustion</td>
<td>Prahl et al. (1984); Takada et al. (1990); Mantis et al. (2005) Ravindra et al. (2006a, 2008); Gogou et al. (1996)</td>
</tr>
</tbody>
</table>

<sup>a</sup> Sum of major non-alkylated compounds (fluorene + pyrene + benzo[a]anthracene + chrysene + benzo[b]fluoranthene + benzo[k]fluoranthene + B[a]P + indeno[1,2,3-cd]pyrene + benzo[ghi]perylene)/total concentration of PAHs.

<sup>b</sup> Used for residential heating and industrial operation.
(Robinson et al., 2006a, b). In addition to the atmospheric reactivity, degradation that may occur during the sampling process and can also modify the atmospheric PAHs levels and thus the ratios between PAHs, as shown by Tsapakis and Stephanou (2003) and reference therein. The other limitation of diagnostic ratio is that their interpretation greatly depends on the ratio considered and on the source profile chosen. This may be a case, when the sampling is carried out in the vicinity of sources of particulate PAHs and for highly reactive compounds (Goriaux et al., 2006). Furthermore, the difference in chemical reactivity, volatility, and solubility of PAH species may introduce bias but to minimize this error, the diagnostic ratio with similar physicochemical properties of PAHs should be used.

6.3. Principal components analysis (PCA)

PCA is the oldest and most widely used multivariate statistical technique in atmospheric sciences. It simplifies the interpretation of complex systems and transforms the original set of variables into a smaller set of linear combinations that accounts for most of the variance of the original set. The primary function of this analysis is the reduction of the number of variables while retaining the original information as much as possible. Variables with similar characteristics are grouped into factors. These factors can be interpreted either as an emission source, or a chemical interaction. In practice many of these factors, however, indicate more than one possible cause. In general, each factor from PCA is associated with a source characterized by its most representative chemical marker, PAH compound(s) in this case.

In most applications, mathematical and statistical software are used for source grouping by using PCA with varimax rotation and the retention of principal components having eigenvalue $> 1$ of complete data set of PAH concentrations. The principal components that show the maximum percentage of total variance of the data set are used as factors. Loading determines the most representative PAHs compounds in each factor and generally a value $> 0.5$ is selected. The following conclusions have been drawn from various studies, which have used PCA methods to enhance the accuracy of emission source identification:

(a) A high factor loading of fluoranthene, pyrene, and especially of benzo[ghi]perylene and coronene has been suggested for gasoline-powered vehicles (Duval and Friedlander, 1981; Maselet et al., 1986; Khalili et al., 1995), whereas Guo et al. (2003) also include benzo[a]anthracene, B[a]P, benzo[b]fluoranthene, benzo[ghi]perylene, and indeno[1,2,3-cd]pyrene as source markers for gasoline emission.

(b) Diesel emission has a high factor loading for fluoranthene, phenanthrene, anthracene, and pyrene (Caricchia et al., 1999; Yang et al., 1998; Ho et al., 2002; Omar et al., 2002; Fang et al., 2004; Ravindra et al., 2006a, b). Other studies also suggest that fluoranthene, pyrene with high factor loading of benzo[b]fluoranthene and benzo[k]fluoranthene indicates diesel-powered vehicles (Duval and Friedlander, 1981; Khalili et al., 1995).

(c) According to Daisey et al. (1986), volatile compounds such as fluoranthene and species of high molecular weight such as indeno[1,2,3-cd]pyrene, are probably generated together by the combustion of lubricating oil and also might be emitted by industrial sources.

(d) A high factor loading of acenapthylene,acenaphthene, chrysene, benzo[b]fluoranthene, and benzo[ghi]pyrene, points to stationary emission sources (Yang et al., 1998; Kulkarni and Venkataraman, 2000; Ravindra et al., 2006a).

(e) A high level of anthracene, phenanthrene, B[a]P, benzo[ghi]perylene, and chrysene has been suggested for steel industry emissions (Ravindra et al., 2006a).

Most studies, conducted to identify the potential sources of PAHs, have used total (vapor plus particulate phase) PAH levels for PCA. However, it is suggested that by using PCA separately for both vapor and particulate phase PAHs, a clearer indication about the local and regional emission sources of these compounds would be found (Ravindra et al., 2006a). This consideration is also true for the statistical analysis of other material systems existing in more than one phase in the atmosphere.

7. Emission inventories for PAHs

In recent years, inventories of potential emission sources of PAHs have been developed in several countries and have shown that combustion is a major contributor to the environmental concentration of these toxic pollutants. The PAHs emission...
sources and PAH emission rates into the environment have been reviewed in the Environmental Health Criteria Monogram on PAHs by WHO International Program on Chemical Safety (IPCS, 1998). Some emissions data reported by IPCS are summarized in Tables 5 and 6. The processing of coal and petroleum products, power plants using fossil fuels, incineration, aluminum production, iron and steel production are major industrial processes, which are known to be sources of PAHs. Yang and Chen (2004) calculated emission inventories of the sum of 21 PAHs for heavy oil combustion, natural gas combustion, coal combustion, diesel combustion, vehicles, and municipal solid waste incinerator and the emissions were 10.2, 2.0, 5.7, 0.003, 28.5, and 0.06 kg day\(^{-1}\), respectively, in Taiwan.

Recently, Breivik et al. (2006) discussed the existing inventories of persistent organic pollutants including PAHs. Based on their study, the relative contribution of major sources and temporal changes to total PAHs emission in Europe are shown in Table 7. Their study suggests that around 47% reduction has occurred in PAHs emission during the last decades and the residential sector was identified as a major source of PAHs emission. Fig. 3 depicts collective B[a]P emission in Europe (total of 43 countries) based on nationally reported data and some estimates from Mantseva et al. (2004). It shows that B[a]P emission has fallen by 26% from 1990 to 2001. High emissions seem to originate from Lithuania, Belgium, Spain, Czech Republic, Slovakia, Bosnia and Herzegovina, Serbia and Montenegro, and from some regions of Germany and Poland (Supplementary Table S1).

|-----------------------|

Table 6 PAH emission due to incomplete combustion from industrial process

<table>
<thead>
<tr>
<th>Emissions source</th>
<th>Typical emissions/profiles</th>
</tr>
</thead>
<tbody>
<tr>
<td>Power plants using fossil fuel</td>
<td>Naphthalene (Nap), phenanthrene and derivatives: 69–92% of PAHs emitted</td>
</tr>
<tr>
<td></td>
<td>Nap: 31–25% of PAHs emitted</td>
</tr>
<tr>
<td></td>
<td>B[a]P: 0.02 mg kg(^{-1}) coal burnt</td>
</tr>
<tr>
<td></td>
<td>B[e]P: 0.03 mg kg(^{-1}) coal burnt</td>
</tr>
<tr>
<td></td>
<td>B[a]P: 0.1 tpa (ton per annum) (Germany)</td>
</tr>
<tr>
<td>Incinerators (refuse burning)</td>
<td>PAH: 0.1 tpa Norway, PAH: 11 tpa Canada</td>
</tr>
<tr>
<td></td>
<td>B[a]P: 0.001 tpa (Germany)</td>
</tr>
<tr>
<td>Aluminum production (vertical process)</td>
<td>PAH: 50 tpa (USA)</td>
</tr>
<tr>
<td></td>
<td>PAH: 2.4 tpa (Canada)</td>
</tr>
<tr>
<td>Iron and steel production</td>
<td>PAH: 4.4 kg tons(^{-1}) aluminum</td>
</tr>
<tr>
<td></td>
<td>1000 tpa (USA)</td>
</tr>
<tr>
<td></td>
<td>930 tpa (Canada)</td>
</tr>
<tr>
<td>Foundries</td>
<td>PAH: 34 tpa (Norway)</td>
</tr>
<tr>
<td>Sinter process</td>
<td>PAH: 19 tpa (Canada)</td>
</tr>
<tr>
<td>Phosphorus production</td>
<td>0.2 tpa (the Netherlands)</td>
</tr>
</tbody>
</table>


Table 7 Relative contribution of various sources to total PAHs emission in Europe

<table>
<thead>
<tr>
<th>Source categories</th>
<th>Relative contribution (%) to total PAHs emission</th>
</tr>
</thead>
<tbody>
<tr>
<td>Residential sector</td>
<td>3.2</td>
</tr>
<tr>
<td>Commercial/institutional plants</td>
<td>2.1</td>
</tr>
<tr>
<td>Solvent and other product use</td>
<td>17.9</td>
</tr>
<tr>
<td>Other industrial process</td>
<td>1.6</td>
</tr>
<tr>
<td>Metal production</td>
<td>9.3</td>
</tr>
<tr>
<td>Iron and steel</td>
<td>8.6</td>
</tr>
<tr>
<td>Passenger cars</td>
<td>4.0</td>
</tr>
<tr>
<td>Heavy-duty vehicles</td>
<td>2.8</td>
</tr>
<tr>
<td>Light-duty vehicles</td>
<td>1.7</td>
</tr>
<tr>
<td>Non-ferrous metals</td>
<td>2.3</td>
</tr>
<tr>
<td>Agriculture burning</td>
<td>1.4</td>
</tr>
<tr>
<td>Waste incinerator</td>
<td>2.2</td>
</tr>
<tr>
<td>Other waste</td>
<td>9.9</td>
</tr>
<tr>
<td>Public electricity and heat production</td>
<td>25.1</td>
</tr>
<tr>
<td>Other sources</td>
<td>6.4</td>
</tr>
<tr>
<td>Total emission</td>
<td>2.4 ktons year(^{-1})</td>
</tr>
<tr>
<td></td>
<td>1.3 ktons year(^{-1})</td>
</tr>
</tbody>
</table>

Please cite this article as: Ravindra, K., et al., Atmospheric polycyclic aromatic hydrocarbons: Source attribution, emission factors and regulation. Atmospheric Environment (2008), doi:10.1016/j.atmosenv.2007.12.010
8. Atmospheric transport, residence time, and reactions

PAHs are widespread harmful compounds generated by different sources as discussed in Section 5. Concerns over the carcinogenic and mutagenic properties of PAHs have led to efforts to understand their formation and atmospheric chemistry (Bjorseth and Ramdahl, 1985; Fraser et al., 1998a, b; Yassaa et al., 2001). The concentration of PAHs in air can range from trace to significant levels (Ravindra et al., 2001, 2006a).

The transport, deposition, and chemical transformation of these compounds depends on their gas/particle phase partitioning (Harner and Bidleman, 1998). The gas/particle partitioning of PAHs depends on the molecular weight of the compounds, temperature, humidity, and precipitation (Subramanyam et al., 1994; Van Jaarsveld, 1997; Lee and Jones, 1999). Baek et al. (1991) also noticed that (i) vapor pressure of the PAHs, (ii) ambient temperature, (iii) PAH concentration/amount, and (iv) type of fine particles present in the atmosphere, can influence partitioning. PAHs with >5 benzene rings are characterized by a relatively high temperature of condensation and are sorbed on airborne particles. These PAHs are classified in the low mobility category of PAHs and deposited rapidly close to the sources (Wania and Mackay, 1996). The lower molecular weight compounds (2–3 benzene rings) are more abundant in the gas phase (Subramanyam et al., 1994; Lee and Jones, 1999). These PAHs can undergo world wide atmospheric dispersion and preferential accumulation in polar regions (Wania and Mackay, 1996; Van Jaarsveld, 1997).

While reviewing levels and seasonal trends of particulate PAHs in some major cities of the world, Ravindra et al. (2001 and references therein) found comparatively higher concentrations occurring during the winter season. The higher concentrations in winter are most likely due to (a) reduced vertical dispersion due to inversion; (b) lower mixing layer and less intensive atmospheric reactions; (c) enhanced sorption to particles at lower temperature (as a result of reduced vapor pressure and/or shifting in the gas/particle distribution induced by ambient temperature variation Subramanyam et al., 1994); and (d) increased emissions from domestic heating and power plants during winter with low temperature (Lee et al., 2005; Ravindra et al., 2006a).

Organic substances brought to the atmosphere by evaporation from the earth’s surface or emissions from human activities may be subsequently transported by air masses over long distances. Water in clouds becomes saturated with these substances and precipitation contaminates surface water and land, sometimes far away from the emission sources (Rogge et al., 1993b). Removal of PAHs from the atmosphere can be accomplished by dry or wet deposition of particles and vapors. The dry or wet deposition of PAHs from the atmosphere prevails in the removal of particulate compounds and depends on their physico-chemical properties (solubility in water, Henry’s law constant, vapor pressure), its vapor-to-particle partitioning and meteorological parameters (rain height, intensity, and temperature). In general, PAHs present in the gas phase dissolve within clouds and into raindrops (Golomb et al., 2001; Offenberg and Baker, 2002), whereas PAHs bound to particles are washed out from the
atmosphere by precipitation (Ravindra et al., 2003). Baek et al. (1991) show that dry deposition results from the direct fallout of PAHs adsorbed to large particles and this mechanism is greatly dependent on the size of these particles. For instance, B[a]P, which is predominantly bound to fine particles, is expected to be removed mainly by particle wash-out and dry particle deposition, while naphthalene, which occurs mainly in vapor phase, is removed by vapor wash-out and/or dry vapor deposition (Rogge et al., 1993b).

It was found that dry deposition dominates in the case of the PAHs which are hydrophobic and may be easily bound to particles suspended in air (Golomb et al., 1997). Up to 70% of B[a]P in wet precipitation was found adsorbed on aerosol particles <0.3 μm (Kiss et al., 1997), while naphthalene, due to its solubility in water (31.7 mg l⁻¹), is present in the precipitation predominantly as a solute (Manoli and Samara, 1999). Although most combustion-derived (pyrogenic) PAHs are deposited close to their source, atmospheric transport can carry significant amount of these compounds to remote locations, and may be found in high-altitude lake sediments, deep sea sediments, and arctic ice and snow.

Combustion related PAHs tend to be associated with fine mode vehicle emissions. The concentration of PAHs may vary due to meteorological conditions but high concentrations with high temperature and high solar intensity are considered favorable to photochemical and/or chemical reaction in the atmosphere (Harrison et al., 1996). Photochemical transformations are also considered significant processes for the removal of atmospheric PAHs. Studies suggest that PAHs in the vapor phase are more susceptible to such reactions than particulate phase (Valerio and Lazzarotto, 1985; Kamens et al., 1988; Wild and Jones 1995). Kamens et al. (1988) found that at moderate temperatures the rate of PAH photo-decomposition may decrease with increased PAH particle loading. Thus, adsorption on highly porous, carbonaceous particle like soot or fly ash may provide some protection from photo-oxidation (see also Nielsen et al., 1983). The study also suggested that in the absence of sunlight, some PAHs may react with molecular oxygen but these reactions appear to be very slow and are likely to be insignificant as a degradation mechanism. Table 8 shows the half-life of selected PAHs under laboratory experiments. Further, there are many recent lab studies showing the photo-oxidation of PAHs (e.g. Esteve et al., 2006; Perraudin et al., 2007) but for the better understanding of these processes, there is still a need exist to examine these process in field experiments.

Light PAHs with 2–3 benzene rings are mostly found in gas phase while the heavy ones are mainly associated with airborne particles. The majority of PAHs (70–90%) are adsorbed on suspended particles at ambient temperature. Moreover, PAHs are mostly adsorbed on small inhalable particles with a high concentration on airborne particles of sub-micron diameter (Van Vaecck and Van Cauwenberghhe, 1978; Nicolaou et al., 1984), which can be deposited in the respiratory tract, hence increasing the potential health effects. It is also reported that the water-soluble ions (e.g. Na⁺, NH₄⁺, K⁺, Mg²⁺, Ca²⁺, Table 8

<table>
<thead>
<tr>
<th>PAHs</th>
<th>Half life in hours</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Simulated sunlight</td>
</tr>
<tr>
<td>Anthracene</td>
<td>0.20</td>
</tr>
<tr>
<td>Benzo(a)anthracene</td>
<td>4.20</td>
</tr>
<tr>
<td>Dibenzo(a,h)anthracene</td>
<td>9.60</td>
</tr>
<tr>
<td>Dibenzo(a,c)anthracene</td>
<td>9.20</td>
</tr>
<tr>
<td>Pyrene</td>
<td>4.20</td>
</tr>
<tr>
<td>Benzo(a)pyrene</td>
<td>5.30</td>
</tr>
<tr>
<td>Benzo(e)pyrene</td>
<td>21.10</td>
</tr>
<tr>
<td>Benzo(b)fluroanthene</td>
<td>8.70</td>
</tr>
<tr>
<td>Benzo(k)fluroanthene</td>
<td>14.10</td>
</tr>
</tbody>
</table>

Source: Katz et al. (1979); see also Baek (1991); Perraudin et al. (2007).
Ca^{2+}, F^-, Cl^-, NO_3^-, and SO_4^{2-}), which form a part of airborne particles may increase the solubility of toxic organic compounds, such as n-alkanes and PAHs by acting as surface active agents (Jacobson et al., 2000).

PAHs in air also exhibit thermal oxidation and can react with a number of atmospheric chemicals to produce derivatives. Sasaki et al. (1997) reported that the transformations of PAHs on particles have the potential to affect the particles toxicity through the formation of more toxic species than the original compounds, e.g. nitro-PAH (Nicolaou et al., 1984). Several other PAHs are neither very volatile nor very soluble and will adsorb on almost any solid surface with a strong affinity for organic matter (Onuska, 1989; Kennish, 1997).

Heterogeneous reactions of particulate PAHs (Bertram et al., 2001; Esteve et al., 2003, 2004, 2006) may serve as surrogates for heterogeneous chemistry of many types of organics; such reactions could change the particles hydrophilicity and thus their potential to act as cloud condensation nuclei (Jones et al., 2004). A second mechanism of transformation is coating of freshly emitted particles by condensation of secondary aerosol components formed by gas-phase reactions. Through this type of transformation, PAHs that are initially present on the surface of particles may become less accessible for heterogeneous reactions and less bioavailable. PAHs are associated with black carbon, and the coating of such particles has significant implications for radiative forcing and climate change (Jacobson, 2001; Conant et al., 2003; Chandra et al., 2004; Marr et al., 2006; Ramanathan et al., 2007).

9. Regulation and control of PAHs emissions

As discussed in Section 5, vehicle pollution contributes significantly to the global PAHs emissions. The catalytic converters for gasoline engines have a marked effect on the reduction of PAHs. Studies have shown that the reduction achieved by catalytic converters was usually between 80% and 90% but for B[a]P a reduction of 94% has been observed (Rogge et al., 1993a; Paturel et al., 1996; Schauer et al., 2002). Catalytic converters for diesel engines also reduce total PAH emissions; however the reductions are not as high as for gasoline engines (CONCAWE, 1998). In heavy-duty diesel engines the use of turbo-charging and inter-cooling reduces diesel particulate emission and catalytic converters are very efficient at reducing particle-bound organic emissions. Other technologies, such as trap oxidizers and filters, are currently being developed and improved for heavy-duty diesel engines.

The implementation of trap oxidizers and filters in automobiles is complex due to several factors including considerations of weight, fuel consumption, maintenance, and operating cycles. Fuel composition also influences the PAH emissions from a modern diesel motor. It has been reported that the aromatic content has an influence on the PAH levels in the exhaust gases (Van Borstel et al., 1999; World Fuel Charter, 2000; CONCAWE, 1998; Ravindra et al., 2006b). Fuels with 7–11% mass/mass (2 benzene ring) and 1–3% (3 benzene ring) content give significantly higher PAH emissions than fuels containing virtually no 2 or 3 benzene rings. Within the EU, the PAH content of diesel fuels is regulated to 11% (m/m) within the Directive 98/70/EC. In this context, PAHs are defined as the total aromatic hydrocarbon content less the mono-aromatic hydrocarbon contents. The maximum content of aromatic compounds for fuels to be used for vehicles equipped with positive ignition fuels was set as 42% but has been reduced to 35%. A reduction in the sulfur content has been reported to decrease PAH emissions (Tanaka et al., 1988) by enabling the catalytic converter to function more efficiently.

The reformulation of diesel fuels, such as lowering the sulfur content, lowering the aromatic or potentially the addition of oxygen within the fuel, could achieve substantial reductions in emissions (Ying et al., 2006). Further, it has been shown that many oxygenates (alcohols, esters, and ethers) are effective in reducing particulate emissions from diesel engines (Neeft et al., 1996; Choi and Reitz, 1999). Dimethyl ether (DME) is regarded as one of the promising alternative fuels with the advantages of a high cetane number and another alternative is oxygen additives for diesel engines. Furthermore, its cetane number and ignition temperature are close to that of diesel fuel, and hence DME is thought to be an excellent substitute for use in compression ignition engines. The addition of some oxygenated compounds to fuels to reduce engine emissions without engine modification seems practical. An additional source for PAHs in the exhaust of gasoline/diesel fuelled vehicles is PAHs in the fuel (Westerholm et al., 1988). Consequently a reduction of exhaust gas PAHs emission can be achieved by
reducing fuel PAHs content. Fig. 4 shows some of the current standards to reduce total aromatics and PAHs from diesels (Ravindra et al., 2006b).

The emissions of PAHs from agriculture sources are difficult to quantify and control because of the uncertainty in the emission factors and the wide occurrence of these activities. However, the open burning of the agricultural residue/waste can be regulated. Industrial source, on the other hand, are comparatively well understood and increasingly being regulated in developed countries. Indeed, improved energy management can lead to improved combustion, which in turn leads to lower emissions.

Domestic sources of PAHs are geographically widespread, and the PAH emissions are largely unregulated. Some countries have regulations controlling the general emission from some domestic heating systems. Modern gas and oil burners, used for circulatory heating systems and hot water systems, have relatively low PAH emissions. Similarly, solid fuel systems (wood, coal, and peat), which are automatically controlled and fed, are thermally more efficient (and have lower PAH emissions) than those which are hand-fed. Abatement measures can be adopted, such as catalytic devices, which will lead to a reduction of PAH emissions.

10. Implementation of standards and current ambient levels of PAHs

10.1. Air quality standards of PAHs

Many countries have added PAHs to their hazardous air pollutants lists but till date there is no strict ambient air quality standard for PAHs (Table 9). The EPA (1994) has classified PAHs with BaP indicator species as a B-2 pollutant, that means a probable human carcinogen with sufficient evidence from animal studies but inadequate evidence from human studies and hence PAHs are among the list of hazardous air pollutants to be regulated under the US Clean Air Act Amendment, 1990. The Occupational Safety and Health Administration (OSHA) has set a limit of 0.2 mg m⁻³ of PAHs (ATSDR, 1995). European union directive has proposed a target value of 1 ng m⁻³ BaP for the total content in the PM₁₀ fraction averaged over a calendar year (EUD, 2004). Furthermore, this directive also suggest to assess the contribution of BaP in ambient air, each Member State shall monitor other relevant PAHs, i.e. benzo(a)anthracene, benzo(b)fluoranthene, benzo(j)fluoranthene, benzo(k)fluoranthene, indeno(1,2,3-cd)pyrene, and dibenz(a,h)anthracene. Monitoring sites for these PAHs should be selected in such a way that

<table>
<thead>
<tr>
<th>Countries</th>
<th>Limit valuea (ng m⁻³)</th>
<th>Guide value (annual average) (ng m⁻³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Australia</td>
<td>–</td>
<td>1.0</td>
</tr>
<tr>
<td>Belgium</td>
<td>1.0</td>
<td>0.5</td>
</tr>
<tr>
<td>Croatia</td>
<td>2.0</td>
<td>0.1</td>
</tr>
<tr>
<td>Germany</td>
<td>–</td>
<td>10.0</td>
</tr>
<tr>
<td>India</td>
<td>–</td>
<td>5.0</td>
</tr>
<tr>
<td>Netherlands</td>
<td>1.0</td>
<td>0.5</td>
</tr>
<tr>
<td>France</td>
<td>0.7</td>
<td>0.1</td>
</tr>
<tr>
<td>Italy</td>
<td>1.0</td>
<td>–</td>
</tr>
<tr>
<td>Sweden</td>
<td>–</td>
<td>0.1</td>
</tr>
<tr>
<td>UK</td>
<td>–</td>
<td>0.25</td>
</tr>
<tr>
<td>WHO</td>
<td>–</td>
<td>1.0</td>
</tr>
<tr>
<td>EUc</td>
<td>6.0</td>
<td>–</td>
</tr>
<tr>
<td>EU</td>
<td>1.0b</td>
<td></td>
</tr>
</tbody>
</table>

aLimit value may not be exceeded and exceeding the guide value should be avoided.
bReducing 1 ng m⁻³ every year from 2005 till 2010 to met 1 ng m⁻³ in 2010.
cTo be met in 2010.
dTarget value for the total content in the PM₁₀ fraction.

Please cite this article as: Ravindra, K., et al., Atmospheric polycyclic aromatic hydrocarbons: Source attribution, emission factors and regulation. Atmospheric Environment (2008), doi:10.1016/j.atmosenv.2007.12.010
geographical variation and long-term trends can be identified (EUD, 2004).

In Europe, the Netherlands introduced an interim goal of reducing the annual average B[a]P concentration to below 5 ng m\(^{-3}\) (Smith and Harrison, 1998), while a guideline of 10 ng m\(^{-3}\) for the annual average B[a]P has been proposed by the German Federal Environmental Agency. The Dutch National Institute of Public Health and the Environment (DNIPHE) has determined values of maximum permissible concentrations (MPCs) and negligible concentrations (NCs) for about 200 toxic compounds including some PAHs (RIVM, 1999a). The MPCs and NCs represent risk limit of the substances in different compartments of the environment-surface water, soil, air, groundwater, and sediments, and are calculated from available ecotoxicological data. These risk limits are used to derive environmental quality standards in the Netherlands (RIVM, 1999b). However, eco-toxicological data available for only B[a]P out of the 7 PAHs has been reported. These MPCs and NCs for air were not available for the other 6 PAHs (anthracene, benz[a]anthracene, benzo[k]fluoranthene, fluoranthene, naphthalene, and phenanthrene) but DNIPHE has assigned a critical concentration value for each of these compounds. Critical concentrations are normally calculated for air and/or rainwater. They are theoretically derived steady state concentrations of the pollutants in air and/or rainwater that will not lead to exceedance of MPCs value for soil (RIVM, 1999a, b).

10.2. Comparison of ambient levels with standards

In Europe, the B[a]P inventory shows the highest loading is in Eastern Europe (e.g. Poland, parts of Russia, and the Czech Republic), and the more populated and industrialized areas of western Europe, e.g. parts of United Kingdom and The Netherlands (Jaward et al., 2004). Breivik et al. (2006) demonstrated that the emissions of selected PAHs showed a decline in 10 European countries from 1990 to 2003 (from 2.4 to 1.3 ktons year\(^{-1}\)). Fig. 5 depicts the calculated levels of B[a]P over Europe during 1990, 2001, and 2005 (EMEP, 2007). Based on the EMEP model assessment, Mantseva et al. (2004) reported that the annual average values of B[a]P over the European countries were 0.4 and 0.3 ng m\(^{-3}\) for the years 1990 and 2001, respectively (Fig. 5). Furthermore, the study reports that levels of B[a]P in air vary from 0.2 to 2 ng m\(^{-3}\) in most of the European countries and the regions with the high levels of concentrations, such as in some parts of France, Germany, Poland, and Lithuania, exceed 2 ng m\(^{-3}\).

The UK expert panel recommends 0.25 PAHs ng m\(^{-3}\) measured as an annual average, using B[a]P as an indicator of the PAHs mixture. At present this value is exceeded in most urban areas and near industrial facilities, which emit PAHs. However, the concentrations monitored at three national rural sites do not exceed the recommended standards (NAQIA, 1999). Similarly, Prevedouros et al. (2004) reported that urban centers in the UK have concentrations 1–2 orders of magnitude higher than in rural regions of Europe and up to 3 orders of magnitude higher than Arctic Canada. Marchand et al. (2004), suggest that the current levels of PAHs show that it will be difficult to meet new EU standards with a target 1 ng m\(^{-3}\) for B[a]P on an annual average in two French alpine valleys. However, B[a]P target values are met on an annual basis in Belgium but the levels were
significantly high during winter (Ravindra et al., 2006a).

It is likely that the overall annual average B[a]P target value will be met in some countries but it seems more challenging in urban centers and/or near the proximity of the emissions sources. Further, it has to be noticed that most of the air quality standards are based on B[a]P but it would be more appropriate to include probable human carcinogenic PAHs and report a value based on seasonal as well on annual ambient levels of PAHs. It might be interesting to transform such information into an index to assess the likely human health risks.

11. Conclusions

The European Directive (1999/30/EC) frames the inhalable and fine particle fraction according to the negative impact on health. Organic compounds form a major fraction of airborne particles and hence it is important to measure and identify the organic contaminants and especially the PAHs proportion. The control and abatement of PAH contamination requires the knowledge of the nature, source, and extent of pollution and hence existing literature has been reviewed to synthesize the available information on the formation, sources and emission rates of PAHs. This review identifies the vehicular, wood/coal burning, and industrial emission as significant sources of PAHs although it is recognized that this will vary from region to region. Furthermore, the emission factors should be updated from various sources after a certain period of time.

The levels of individual PAHs can be associated with their origin sources through the use of specific PAH species which provide more unique markers for the sources. The applications of correlation, diagnostic ratio, and PCA to improve the emission source identification have been discussed. Furthermore, the emission inventories, atmospheric transport, residence time and reactions, regulation and control of PAHs emission, and air quality standards for PAHs have also been examined. However, during the last decades the emission of PAHs have fallen 50% in Europe but it is still a challenge to comply the new EU standard in urban centers. The review also highlights the need to include not only B[a]P but also other probable human carcinogenic PAHs when developing a new air quality index.

Acknowledgments

The authors thank to two anonymous referees for their constructive comments. This review is also part of a wider program of air quality and health research funded by the EU Commissions through the FP6 projects CAIR4HEALTH and ENVIRISK.

Appendix. Supplementary materials

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.atmosenv.2007.12.010.

References


Boström, C.E., Gerde, P., Hanberg, A., Jernström, B., Johansson, C., Kyrklund, T., Rannug, A., Tornqvist, M.,


source reconciliation and evaluation of sampling artifacts. Atmospheric Environment 33, 4977–4986.


NAQIA (National Air Quality Information Archive), 1999. United Kingdom.


Ravindra, K., Wauters, E., Taygi, S.K., Mor, S., Van Grieken, R., 2006b. Assessment of air quality after the implementation of CNG as fuel in public transport in Delhi, India. Environmental Monitoring and Assessment 115, 405–417.


