We are IntechOpen, the world’s leading publisher of Open Access books
Built by scientists, for scientists

4,300
Open access books available

116,000
International authors and editors

125M
Downloads

154
Countries delivered to

TOP 1%
Our authors are among the most cited scientists

12.2%
Contributors from top 500 universities

WEB OF SCIENCE™
Selection of our books indexed in the Book Citation Index in Web of Science™ Core Collection (BKCI)

Interested in publishing with us?
Contact book.department@intechopen.com

Numbers displayed above are based on latest data collected.
For more information visit www.intechopen.com
Sources, Distribution and Toxicity of Polycyclic Aromatic Hydrocarbons (PAHs) in Particulate Matter

Byeong-Kyu Lee and Van Tuan Vu
Department of Civil and Environmental Engineering, University of Ulsan
Korea

1. Introduction
Polycyclic aromatic hydrocarbons (PAHs) are a group of organic compounds consisting of two or more fused aromatic rings. PAHs originate mainly from anthropogenic processes, particularly from incomplete combustion of organic fuels. PAHs are distributed widely in the atmosphere. Natural processes, such as volcanic eruptions and forest fires, also contribute to an ambient existence of PAHs. PAHs can be present in both particulate and gaseous phases, depending upon their volatility. Light molecular weight PAHs (LMW PAHs) that have two or three aromatic rings are emitted in the gaseous phase, while high molecular weight PAHs (HMW PAHs), with five or more rings, are emitted in the particulate phase. In the atmosphere, PAHs can undergo photo-degradation and react with other pollutants, such as sulfur dioxide, nitrogen oxides, and ozone.

Due to widespread sources and persistent characteristics, PAHs disperse through atmospheric transport and exist almost everywhere. Human beings are exposed to PAH mixtures in gaseous or particulate phases in ambient air. Long-term exposure to high concentrations of PAHs is associated with adverse health problems. Since some PAHs are considered carcinogens, inhalation of PAHs in particulates is a potentially serious health risk linked to an excess risk of lung cancer. Thus, studies on PAHs in particulate matter (PM), such as PM10 and PM2.5 in ambient air, have become attention greater focus of research in recent years.

2. Physical and chemical characteristics of PAHs
PAHs are a group of several hundred individual organic compounds which contain two or more aromatics rings and generally occur as complex mixtures rather than single compounds. PAHs are classified by their melting and boiling point, vapor pressure, and water solubility, depending on their structure. Table 1 shows physical and chemical characteristics of 16 priority PAHs, listed by the US EPA. Most PAHs, especially as molecular weight increases, are soluble in non-polar organic solvents and are barely soluble in polar water. Most PAHs are persistent organic pollutants (POPs) in the environment. Many of them are chemically inert. However, PAHs can be photochemically decomposed under strong...
ultraviolet light or sunlight, and thus some PAHs can be lost during atmospheric sampling. Also, PAHs can react with ozone, hydroxyl radicals, nitrogen and sulfur oxides, and nitric and sulfuric acids, which affect the environmental fate or conditions of PAHs.

3. Sources and Emission of PAHs

PAHs are mainly derived from anthropogenic activities related to pyrolysis and incomplete combustion of organic matter. Emission sources of PAHs affect their characterization and distribution, as well as their toxicity. In this book, the major sources of PAH emissions may be divided into four classes: stationary sources (including domestic and industrial sources), mobile emissions, agriculture activities, and natural sources.

3.1 Stationary sources

3.1.1 Domestic sources

Heating and cooking are dominant domestic sources of PAHs. The burning and pyrolysis of coal, oil, gas, garbage, wood, or other organic substances are the main domestic sources. Domestic sources are important contributors to the total emissions of PAHs in the environment. Differences in climate patterns and domestic heating systems produce large geographic variations in domestic emissions. PAH emissions from these sources may be a major health concern because of their prevalence in indoor environments (Ravindra et al., 2006). According to a recent World Health Organization (WHO) report, more than 75% of people in China, India, and South East Asia and 50-75% of people in parts of South America and Africa use combustion of solid fuels, such as wood, for daily cooking. Main indoor PAH sources are cooking and heating emissions and infiltration from outdoors. PAHs emissions from cooking account for 32.8% of total indoor PAHs (Zhu et al., 2009). LMW PAHs which originate from indoor sources are the predominant proportion of the total PAHs identified in residential non-smoking air. Toxicity of PAH mixtures from indoor sources is lower than mixtures which contain large amounts of HMW PAHs. Cigarette smoke is also a dominant source of PAHs in indoor environments. In many studies, PAHs in the indoor air of smoking residences tend to be higher than those of non-smoking residences.
ultraviolet light or sunlight, and thus some PAHs can be lost during atmospheric sampling. Also, PAHs can react with ozone, hydroxyl radicals, nitrogen and sulfur oxides, and nitric and sulfuric acids, which affect the environmental fate or conditions of PAHs.

3. Sources and Emission of PAHs

PAHs are mainly derived from anthropogenic activities related to pyrolysis and incomplete combustion of organic matter. Emission sources of PAHs affect their characterization and distribution, as well as their toxicity. In this book, the major sources of PAH emissions may be divided into four classes: stationary sources (including domestic and industrial sources), mobile emissions, agriculture activities, and natural sources.

3.1 Stationary sources

3.1.1 Domestic sources

Heating and cooking are dominant domestic sources of PAHs. The burning and pyrolysis of coal, oil, gas, garbage, wood, or other organic substances are the main domestic sources. Domestic sources are important contributors to the total emissions of PAHs in the environment. Differences in climate patterns and domestic heating systems produce large geographic variations in domestic emissions. PAH emissions from these sources may be a major health concern because of their prevalence in indoor environments (Ravindra et al., 2006). According to a recent World Health Organization (WHO) report, more than 75% of people in China, India, and South East Asia and 50-75% of people in parts of South America and Africa use combustion of solid fuels, such as wood, for daily cooking. Main indoor PAH sources are cooking and heating emissions and infiltration from outdoors. PAHs emissions from cooking account for 32.8% of total indoor PAHs (Zhu et al., 2009). LMW PAHs which originate from indoor sources are the predominant proportion of the total PAHs identified in residential non-smoking air. Toxicity of PAH mixtures from indoor sources is lower than mixtures which contain large amounts of HMW PAHs. Cigarette smoke is also a dominant source of PAHs in indoor environments. In many studies, PAHs in the indoor air of smoking residences tend to be higher than those of non-smoking residences.

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>Chemical formula</th>
<th>Chemical structure</th>
<th>Molecular weight</th>
<th>Melting point</th>
<th>Boiling point</th>
<th>Vapor pressure</th>
<th>Log Kow</th>
<th>Log Koc</th>
</tr>
</thead>
<tbody>
<tr>
<td>Naphthalene (naphthalin Naphthaline)</td>
<td>C10H8</td>
<td><img src="image" alt="Naphthalene" /></td>
<td>128.17</td>
<td>80.26°C</td>
<td>218°C</td>
<td>0.087 mmHg</td>
<td>3.29</td>
<td>2.97</td>
</tr>
<tr>
<td>Acenaphthene (1,8-dihydroacenaphthalene 1,8-ethylenenaphthalene 1,8-dihydroacenaphthaline 1,2-dihydroacenaphthylene)</td>
<td>C12H10</td>
<td><img src="image" alt="Acenaphthene" /></td>
<td>154.21</td>
<td>95°C</td>
<td>96°C</td>
<td>4.47x10^-3 mmHg</td>
<td>3.98</td>
<td>3.66</td>
</tr>
<tr>
<td>Acenaphthylene (cycopenta(de)naphthalene)</td>
<td>C12H8</td>
<td><img src="image" alt="Acenaphthylene" /></td>
<td>152.20</td>
<td>92-93°C</td>
<td>265-275°C</td>
<td>0.029 mmHg</td>
<td>4.07</td>
<td>1.40</td>
</tr>
<tr>
<td>Fluorene (ortho-biphenylene methane diphenylene methane 2,2-methylene biphenyl 2,3-benzidene)</td>
<td>C13H10</td>
<td><img src="image" alt="Fluorene" /></td>
<td>166.2</td>
<td>116-117°C</td>
<td>295°C</td>
<td>3.2x10^-4 mmHg</td>
<td>4.18</td>
<td>3.86</td>
</tr>
<tr>
<td>Anthracene (anthracin green oil paranaphthalene)</td>
<td>C14H10</td>
<td><img src="image" alt="Anthracene" /></td>
<td>178.2</td>
<td>218°C</td>
<td>340-342°C</td>
<td>1.75x10^-6 mmHg</td>
<td>4.45</td>
<td>4.15</td>
</tr>
<tr>
<td>Phenanthrene (phenantrin)</td>
<td>C14H10</td>
<td><img src="image" alt="Phenanthrene" /></td>
<td>178.2</td>
<td>100°C</td>
<td>340°C</td>
<td>6.8x10^-4 mmHg</td>
<td>4.45</td>
<td>4.15</td>
</tr>
<tr>
<td>Compound</td>
<td>Molecular Formula</td>
<td>Boiling Point</td>
<td>Flash Point</td>
<td>Melting Point</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>----------------------------------</td>
<td>-------------------</td>
<td>---------------</td>
<td>-------------</td>
<td>---------------</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fluoranthene (benzo(j,k)fluorine 1,2-(1,8-naphthylene) benzene 1,2-benzacenaphthene)</td>
<td>C16H10</td>
<td>202.26°C</td>
<td>110.8°C</td>
<td>375°C</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pyrene (benzo(d,e,f)phenanthrene)</td>
<td>C16H10</td>
<td>202.3°C</td>
<td>156°C</td>
<td>393-404°C</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Benzo(a)anthracene (benz(a)anthracene 1,2-benzanthracene benzo(b)phenanthrene 2,3-benzophenanthrene Tetraphene)</td>
<td>C20H12</td>
<td>228.29°C</td>
<td>158°C</td>
<td>438°C</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Chrysene (benzo(a)phenanthrene 1,2-benzphenanthrene)</td>
<td>C18H12</td>
<td>228.28°C</td>
<td>254°C</td>
<td>448°C</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Benzo(b)fluoranthene (2,3-Benzfluoranthen 2,3-benzofluoranthene 3,4-benz(e)acephenanthrylene 3,4-benzfluoranthene benz(e)fluoranthene)</td>
<td>C20H12</td>
<td>252.3°C</td>
<td>168.3°C</td>
<td>No data</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Compound</td>
<td>Molecular Formula</td>
<td>Molecular Weight</td>
<td>Melting Point</td>
<td>Boiling Point</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>----------</td>
<td>-------------------</td>
<td>------------------</td>
<td>--------------</td>
<td>---------------</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fluoranthene</td>
<td>C16H10</td>
<td>202.26</td>
<td>110.8°C</td>
<td>375°C</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pyrene</td>
<td>C16H10</td>
<td>202.3</td>
<td>156°C</td>
<td>393-404°C</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Benzo(a)anthracene</td>
<td>C20H12</td>
<td>228.29</td>
<td>158°C</td>
<td>438°C</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Chrysene</td>
<td>C18H12</td>
<td>228.28</td>
<td>254°C</td>
<td>448°C</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Benzo(b)fluoranthene</td>
<td>C20H12</td>
<td>252.3</td>
<td>168.3°C</td>
<td>No data</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Benzo(k)fluoranthene</td>
<td>C20H12</td>
<td>252.3</td>
<td>215.7°C</td>
<td>480°C</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Benzo(a)pyrene</td>
<td>C20H12</td>
<td>252.3</td>
<td>179-179.3°C</td>
<td>495°C</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dibenzo(a,h)anthracene</td>
<td>C22H14</td>
<td>278.35</td>
<td>262°C</td>
<td>No data</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Benzo(g,h,i)perylene</td>
<td>C22H12</td>
<td>276.34</td>
<td>273°C</td>
<td>550°C</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ideno(1,2,3-c,d)pyrene</td>
<td>C22H12</td>
<td>276.3</td>
<td>163.6°C</td>
<td>530°C</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 1. Physical and chemical characteristics of some popular PAHs (US EPA, 1995; ATSDR, 1995)
Liu et al. (2008) reported that coal stoves are still widely used for cooking and heating in rural North China. Total emission factors (EFs) for 15 PAHs ranged from 52.8 to 1434.8 mg/kg, depending on the drying status and compositions of raw coals used for cooking and heating. Chen et al. (2004) found a large decrease in the EFs of PAHs from residences with coal stoves that burned honeycomb coal briquettes. Emission factors of 17 PAHs and 10 genotoxic PAHs, based on a coal-weight basis were 111.65 and 18.41 mg/kg, respectively. This indicates a twenty-fold decrease in EFs, as compared to those from cooking and heating with raw coal. Oanh et al. (1999) investigated EFs from wood fuel, charcoals, and coal briquettes in a stove for domestic combustion. They found that wood fuel burning released the highest emissions of 18 PAHs and 11 genotoxic PAHs in terms of EFs, accounting for energy (mg/MJ) emission rates and based on the pollutant concentrations in smoke. Charcoal released the lowest amount of PAH emissions. On a fuel-weight basis, wood fuel burning has the same EF as coal briquette burning (110 mg/kg). However, emissions of genotoxic PAHs from wood burning were twice as high as those from charcoal burning.

### 3.1.2 Industrial sources

PAH emissions from industries are produced by burning fuels such as gas, oil, and coal. PAHs can also be emitted during the processing of raw materials like primary aluminum. Sources of PAHs include emissions from industrial activities, such as primary aluminum and coke production, petrochemical industries, rubber tire and cement manufacturing, bitumen and asphalt industries, wood preservation, commercial heat and power generation, and waste incineration.

Chen et al. (2007) studied emissions of PAHs from the pyrolysis of scrap tires. Total PAH emissions from a scrap tire plant via pyrolysis were 42.3 g/day with an EF of 4 mg/kg. To study the thermal degradation of organic materials, Fabbri et al. (2006) investigated PAH emissions from pyrolysis products. EFs of PAHs from thermal decompositions of organic materials ranged from 0.4 ± 0.13 mg/g for cellulose to 9.0 ± 0.5 mg/g for tyre. Yang et al. (2005) reported that EFs average 71.0 mg/g from joss paper furnaces. With applied air pollution control devices, such as adsorption towers, removal efficiencies of total PAHs are 42.5% and 11.7% for particulate and gaseous PAHs, respectively.

Yang et al. (1998) reported emissions of PAHs from various industrial stacks: a blast furnace, a basic oxygen furnace, a coke oven, an electric arc furnace, a heavy oil plant, a power plant, and a cement plant. The coke oven, electric arc furnace, and heavy oil combustor produced large amounts of HMW PAH emissions. EFs of PAHs from these industrial stacks ranged from 0.08 to 3.97 mg/kg feedstock, while EFs for BaP ranged from 1.87 to 15.5 µg/g feedstock. The highest EFs of total PAHs and BaP were found from the combustion of heavy oils.

Recently, PAH emissions from waste incineration have been investigated in many studies. According to the Italia Agency for Environmental Protection, total EFs of PAHs ranged from 91 to 414 µg/g of waste burned in incinerators of municipal and industrial wastes. Lee et al. (2002) estimated that EFs from two batch-type medical waste incinerators: a mechanical grate (MG-MWI) and a fixed rate (FG-MWI). EFs of total PAHs were 252 and 856 mg/kg-waste for MG-MWI and FG-MWI, respectively. EFs for medical waste incinerators were consistently much higher than those for municipal waste incinerators (871 µg/kg-waste) operated in the same city. Air pollution control devices remove PAHs with efficiencies higher than 78% for PAHs with four or more rings, but had efficiencies lower than 5% for LMW PAHs with two or three rings.
3.2 Mobile sources

Mobile sources are major causes of PAH emissions in urban areas. PAHs are mainly emitted from exhaust fumes of vehicles, including automobiles, railways, ships, aircrafts, and other motor vehicles. PAH emissions from mobile sources are associated with use of diesel, coal, gasoline, oils, and lubricant oil. Exhaust emissions of PAHs from motor vehicles are formed by three mechanisms: 1) synthesis from smaller molecules and aromatic compounds in fuel; 2) storage in engine deposits and in fuel; and 3) pyrolysis of lubricant (Back et al., 1991). One of the major influences on the production of PAHs from gasoline automobiles is the air-to-fuel ratio. It has been reported that the amount of PAHs in engine exhaust decreases with leaner mixtures (Ravindra et al., 2006).

A main contributor to PAH concentrations in road dust as well as urban areas is vehicle exhaust. Abrantes et al. (2009) reported that total emissions and toxicities of PAHs released from light-duty vehicles using ethanol fuel are less than those using gasohol. For example, in ethanol vehicles, total EFs of PAHs ranged from 11.7 to 27.4 µg/km. In gasohol vehicles, total EFs ranged from 41.9 to 612 µg/km. EFs for BaP toxicity equivalence varied from 11.7 to 21.8 ng TEQ/km for ethanol vehicles and from 9.84 to 4,610 ng TEQ/km for gasohol vehicles. LMW PAHs are the dominant PAHs emitted from light-duty vehicles. According to the report of PAH emissions from vehicles by Abrantes et al. (2004), total EFs of PAHs from the exhaust of light-duty diesel vehicles ranged from 1.133 to 5.801 mg/km with emissions dominated by LWM PAHs. EFs reported for heavy-duty vehicles (MSC-E, 2001) and light-duty vehicles were 11.4–82.1 µg/km and 28.2 µg/km, respectively.

Yang et al. (2005) reported that EFs of total PAH emissions from a 2-stroke carburetor (2-Stk/Cb), 4-stroke carburetor (4-Stk/Cb), and 4-stroke fuel injection (4-Stk/FI) motorcycles were 8.320, 5.990 and 3.390 mg/kg, respectively. The EFs of total BaP equivalent are 10.8 µg/kg, indicating that most of the PAHs exhausted from the 2-Stk/Cb motorcycle are carcinogenic. Spezzano et al. (2008) reported that EFs of total PAHs (18 PAHs) ranged from 1.790 to 15.059 mg/kg, and EFs of benzo(a)pyrene equivalent (BaPeq) ranged from 4.7 to 86.3 µg/kg for two-stroke 50-cm³ mopeds. Two-stroke mopeds with small engines emit comparable or even more PAHs than emissions reported from gasoline- and diesel-powered passenger cars and light- and heavy-duty vehicles.

Chen et al. (2006) reported that EFs of total PAHs and total BaPeq for the UH-1H helicopter turboshaft engine (63.4 and 0.509 mg/L-fuel) are 1.65-23.4 and 1.30-7.54 times higher, respectively, than those for the motor vehicle engine, heavy-duty engine, and F101 aircraft engine. LMW PAHs are the dominant PAHs emitted from helicopter engines, accounting for 97.5% of the total PAH emissions. Fuel type has a substantial effect on EFs and toxicity of PAHs from vehicle engines. He et al. (2010) indicated that diesel engines using diesel/biodiesel and their blends can greatly reduce total emissions of PAHs by 19.4 and 13.1%, respectively. The BaP TEQ of PAHs emitted also decreased 15% with the use of biodiesel.

3.3 Agricultural sources

Open burning of brushwood, straw, moorland heather, and stubble are agricultural sources of PAHs. All of these activities involve burning organic materials under suboptimum combustion conditions. Thus, it is expected that a significant amount of PAHs are produced from the open burning of biomass.
Emission factors of PAHs from wood combustion ranged from 16.4 to 1,282 mg/kg wood (Jenkins et al., 1996; Oanh et al., 1999; Schauer et al., 2001). PAH concentrations released from wood combustion depend on wood type, kiln type, and combustion temperature. 80-90% of PAHs emitted from biomass burning are LMW PAHs, including naphthalene, acenaphthylene, phenanthrene, fluoranthene and pyrene. Lu et al. (2009) reported that PAHs emitted from the open burning of rice and bean straw are influenced by combustion parameters. Total emissions of 16 PAHs from the burning of rice and bean straw varied from 9.29 to 23.6 µg/g and from 3.13 to 49.9 µg/g, respectively. PAH emissions increased with increasing temperatures from 200 to 700 °C. Maximum emissions of PAHs were observed at 40% O₂ content in supplied air. However, emissions of PAHs released from the open burning of rice straw negatively correlate with the moisture content in the straw.

3.4 Natural sources
Accidental burning of forests, woodland, and moorland due to lightning strikes are natural sources of PAHs. Furthermore, volcanic eruptions and decaying organic matter are also important natural sources, contributing to the levels of PAHs in the atmosphere. The degree of PAH production depends on meteorological conditions, such as wind, temperature, humidity, and fuel characteristics and type, such as moisture content, green wood, and seasonal wood.

3.5 Emission factors and inventory
Emission factors (EFs) of PAHs from different sources are given in Table 2. The EF data of PAHs are useful for estimating the amount of PAHs released from processes, including combustion, open burning, and pyrolysis. Atmospheric emission inventories of PAHs from certain sources or processes are obtained from an emission estimate using PAH EFs of various sources, using the following formula:

\[
\text{Emission of PAHs} = \Sigma (\text{Activity Level}_i) \times \text{EF}_i \times \left(1 - \frac{\text{Control Efficiency}_i}{100}\right)
\]

Thus, the difference between measured values and reported or estimated values of EFs is a major limitation of PAH inventory construction. Recently, PAH emission inventories have been developed in several countries and have shown that combustion is a major source of PAHs. Combustion of biofuel contributed to 56.7% of total sixteen priority PAHs on a global basis in 2004 (Yang and Tao, 2009). Table 3 shows emission inventories of PAHs on a global scale and for some countries based on emissions in 2003 and 2004.
Emission factors of PAHs from wood combustion ranged from 16.4 to 1,282 mg/kg wood (Jenkins et al., 1996; Oanh et al., 1999; Schauer et al., 2001). PAH concentrations released from wood combustion depend on wood type, kiln type, and combustion temperature. 80-90% of PAHs emitted from biomass burning are LMW PAHs, including naphthalene, acenaphthylene, phenanthrene, fluoranthene and pyrene. Lu et al. (2009) reported that PAHs emitted from the open burning of rice and bean straw are influenced by combustion parameters. Total emissions of 16 PAHs from the burning of rice and bean straw varied from 9.29 to 23.6 µg/g and from 3.13 to 49.9 µg/g, respectively. PAH emissions increased with increasing temperatures from 200 to 700°C. Maximum emissions of PAHs were observed at 40% O2 content in supplied air. However, emissions of PAHs released from the open burning of rice straw negatively correlate with the moisture content in the straw.

### 3.4 Natural sources
Accidental burning of forests, woodland, and moorland due to lightning strikes are natural sources of PAHs. Furthermore, volcanic eruptions and decaying organic matter are also important natural sources, contributing to the levels of PAHs in the atmosphere. The degree of PAH production depends on meteorological conditions, such as wind, temperature, humidity, and fuel characteristics and type, such as moisture content, green wood, and seasonal wood.

### 3.5 Emission factors and inventory
Emission factors (EFs) of PAHs from different sources are given in Table 2. The EF data of PAHs are useful for estimating the amount of PAHs released from processes, including combustion, open burning, and pyrolysis. Atmospheric emission inventories of PAHs from certain sources or processes are obtained from an emission estimate using PAH EFs of various sources, using the following formula:

\[
\text{Emission of PAHs} = \sum (\text{Activity Level}_i) \times \text{EF}_i \times \text{Control Efficiency}_i \times 100
\]

Thus, the difference between measured values and reported or estimated values of EFs is a major limitation of PAH inventory construction. Recently, PAH emission inventories have been developed in several countries and have shown that combustion is a major source of PAHs. Combustion of biofuel contributed to 56.7% of total sixteen priority PAHs on a global basis in 2004 (Yang and Tao, 2009). Table 3 shows emission inventories of PAHs on a global scale and for some countries based on emissions in 2003 and 2004.

<table>
<thead>
<tr>
<th>Emissions source</th>
<th>Emission Factor (mg/kg)</th>
<th>PAHs</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wood combustion</td>
<td>16.4-1,282</td>
<td>total PAHs</td>
<td>Schauer et al., 2001</td>
</tr>
<tr>
<td>Rice burning</td>
<td>9.29-23.6</td>
<td>16 PAHs</td>
<td>Lu et al., 2009</td>
</tr>
<tr>
<td>Bean burning</td>
<td>3.13-49.9</td>
<td>16 PAHs</td>
<td>-</td>
</tr>
<tr>
<td>Wood and root fuel</td>
<td>5.3-13.2</td>
<td>B[a]P</td>
<td>Gupta et al., 1998</td>
</tr>
<tr>
<td>Two-stroke fuel-no catalyst</td>
<td>0.021</td>
<td>6 PAHs</td>
<td>Gambino et al., 2000</td>
</tr>
<tr>
<td>Two-stroke fuel-with catalyst</td>
<td>0.014</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Oil-burner-boiler combination</td>
<td>0.005</td>
<td>B[a]P</td>
<td>IPCS, 1998</td>
</tr>
<tr>
<td>Barbecue briquettes</td>
<td>2.5-13</td>
<td>total PAHs</td>
<td>-</td>
</tr>
<tr>
<td>Soot open fire</td>
<td>3-240</td>
<td>B[a]P</td>
<td>-</td>
</tr>
<tr>
<td>Boilers using heavy oil</td>
<td>0.013</td>
<td>total PAHs</td>
<td>Li et al., 1999</td>
</tr>
<tr>
<td>Boilers using diesel</td>
<td>0.3</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Feed-stock</td>
<td>0.077-3.970</td>
<td>total PAHs</td>
<td>Yang et al., 1998</td>
</tr>
<tr>
<td>Feed-stock</td>
<td>0.002-0.016</td>
<td>B[a]P</td>
<td>-</td>
</tr>
<tr>
<td>Coal charged</td>
<td>15</td>
<td>Total PAHs</td>
<td>IPCS, 1998</td>
</tr>
<tr>
<td>-</td>
<td>0.02</td>
<td>B[e]P</td>
<td>-</td>
</tr>
<tr>
<td>Aluminum production</td>
<td>4.4 kg/tons</td>
<td>total PAHs</td>
<td>-</td>
</tr>
<tr>
<td>-</td>
<td>0.11 kg/tons</td>
<td>B[a]P</td>
<td>-</td>
</tr>
<tr>
<td>Bituminous coal</td>
<td>70.2</td>
<td>total PAHs</td>
<td>Chen et al., 2005</td>
</tr>
<tr>
<td>Scrap tire pyrolysis plant</td>
<td>4</td>
<td>-</td>
<td>Chen et al., 2007</td>
</tr>
<tr>
<td>Honeycomb briquette</td>
<td>56.94</td>
<td>-</td>
<td>Oanh et al., 1999</td>
</tr>
</tbody>
</table>

Table 2. The emission factors (EFs) of PAHs from the different sources

Major emissions of PAHs in developing countries, such as China, India, Brazil, and Sudan, are associated with biomass burning, including use of biofuel and wild savanna fire. In particular, total emissions of PAHs from China and India were almost 40% of the global total emissions. However, emission features in developed countries, such as USA and UK, are quite different from those in developing countries. For example, PAH emissions in the USA are mainly associated with emissions from the use of consumer products, vehicles exhaust, and waste incinerators. The largest emissions of PAHs in UK are from traffic, followed by wood burning.
4. Sampling and analytical methods

4.1 PAH sampling equipment

Due to the volatility of PAHs, released PAHs can be associated with the particulate and/or vapor phase. LMW PAHs are released in a vapor phase into the environment, while HMW PAHs containing five or more rings are adsorbed onto suspended particulate matter. These physical states of PAHs influence collection efficiency and selection of the sampling apparatus of PAHs. PAHs in the atmosphere are mainly collected by two sampling models: active sampling and passive sampling.

Active samplers include high-volume, low-volume, and impingement cascade samplers. A sorbent, filter, and plug are among the implements usually used to collect PAHs in the active sampling mode. Active sampling utilizes deposition or adsorption of target PAH compounds on filters or sorbent materials, through the collection of air particulates onto filters or into sorbent tubes, using a pump. PAHs accumulated on filters or sorbent materials are returned to the laboratory for analysis. In many applications, filters such as quartz fiber filters, glass fiber filters and cellulose filters are used to collect PAHs associated with particulate matter. These filters are highly vulnerable to losing the collected PAHs via volatilization and thus precautions need to be taken to minimize the loss of LMW PAHs. For these disadvantages can be alleviated by using passive sampling methods, which are based on free flow of analyte molecules from the sampled medium to a collecting medium as a result of differences in chemical potentials (Caslavsky et al., 2004).

Passive sampling has been widely applied for ambient monitoring over broad areas. There are many sampling devices which have been successfully used for passive sampling. Semi permeable membrane devices (SPMDs) have been reported as the most used devices for passive sampling.

Table 3. The emission inventories of PAHs for global and some countries (Yang & Tao, 2009)

<table>
<thead>
<tr>
<th>Sources</th>
<th>Global</th>
<th>USA</th>
<th>China</th>
<th>India</th>
<th>Brazil</th>
<th>Sudan</th>
<th>UK</th>
</tr>
</thead>
<tbody>
<tr>
<td>Biofuel</td>
<td>56.7</td>
<td>9.1</td>
<td>66.4</td>
<td>92.5</td>
<td>17.7</td>
<td>28.1</td>
<td></td>
</tr>
<tr>
<td>Wild fire</td>
<td>17</td>
<td>3.3</td>
<td></td>
<td>66</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Savanna fire</td>
<td>4.5</td>
<td></td>
<td>69.7</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Firewood</td>
<td></td>
<td></td>
<td>15.5</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Open straw burning</td>
<td></td>
<td>2</td>
<td>3.2</td>
<td>1.2</td>
<td>4.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Consumer products</td>
<td>6.9</td>
<td>35.1</td>
<td>0.9</td>
<td>0.6</td>
<td>2.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Traffic oil</td>
<td>4.8</td>
<td>23</td>
<td>2</td>
<td>3</td>
<td>58.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Other oil</td>
<td></td>
<td></td>
<td>1.9</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Domestic Coal</td>
<td>3.7</td>
<td></td>
<td>10.7</td>
<td>1.3</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Industrial Coal</td>
<td></td>
<td>1.7</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Coke Industry</td>
<td>3.6</td>
<td>14.4</td>
<td>0.6</td>
<td>3.8</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Petrol refining</td>
<td>2.4</td>
<td>8.7</td>
<td>1</td>
<td>1.7</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Waste incineration</td>
<td>1.9</td>
<td>9.5</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Gasoline distribution</td>
<td>3</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Areospace industry</td>
<td>2.5</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Al electron</td>
<td>1.4</td>
<td>1.9</td>
<td>2.2</td>
<td>4.8</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Other industry</td>
<td>1.5</td>
<td>3.9</td>
<td>2.7</td>
<td>2.3</td>
<td>0.7</td>
<td>2.2</td>
<td>5.2</td>
</tr>
<tr>
<td>Total (gigatons)</td>
<td>530</td>
<td>32</td>
<td>114</td>
<td>90</td>
<td>19</td>
<td>5</td>
<td></td>
</tr>
</tbody>
</table>

www.intechopen.com
volatilization and thus precautions need to be taken to minimize the loss of LMW PAHs. For collecting gaseous PAHs, commonly used sorbents include XAD-2 resin and polyurethane foam (PUF) due to their high collection efficiencies, chemical stability, easy extractability and low cost.

However, drawbacks for active sampling include very high costs of samplers and the loss or volatilization of PAHs during the sampling and handling process. “These disadvantages can be alleviated by using passive sampling methods, which are based on free flow of analyte molecules from the sampled medium to a collecting medium as a result of differences in chemical potentials” (Caslavsky et al., 2004). Passive sampling has been widely applied for ambient monitoring over broad areas. There are many sampling devices which have been successfully used for passive sampling of PAHs. Semipermeable membrane devices (SPMDs) have been reported as the most used devices for passive sampling.

There are three basic active sampling models of PAHs associated with particulate collection equipment:

1. PUF samplers: used for sampling PAHs in both total suspended particulate (TSP) and vapor phases.
2. High-volume samplers (Tisch sampler, PQ 200 sampler): used for sampling PAHs in PM$_{10}$ and PM$_{2.5}$.
3. Cascade impactor (3, 4 and 9-stages): used for sampling PAHs in different size particles.

Sampling times are restricted to 24 h to minimize degradation and loss (volatilization) of collected PAHs. Reduced sampling times and flow rates in the collection of vapor PAHs is important. The use of an annular diffusion denuder, such as an oxidant denuder, with the filter systems minimizes PAH losses during sampling.

### 4.2 Pretreatment of air samples

Before sampling, filters must be wrapped separately in aluminum foil and baked in a muffle furnace at a temperature of 450°C for 6 h. After sampling, they are kept under refrigeration at low temperatures to protect them from thermal degradation or loss by volatilization. Sorbents also need to be preserved carefully. XAD-2 resins and PUF plugs need to be cleaned by Sohxlet or ultrasonic methods before they are used for sampling (Lee and Lee, 2004).

### 4.3 Extraction, concentration and analysis of PAHs

After sampling, PAHs are extracted using organic solvents such as mixtures of n-hexane and dichloromethane. The extracted PAHs solutions need to be concentrated for analysis because PAHs are not as easily detected at low concentrations. To get sufficient detection and concentration analyses of PAHs from the collection medium, this chapter is limited to the following four major types of sample extraction techniques:

1. Soxhlet extraction
2. Ultrasonic extraction
3. Supercritical fluid extraction (SPE)
4. Accelerated solvent extraction (ASE)

Concentration methods popularly used to concentrate extracted PAH samples are rotary evaporators and K-D evaporators. For qualitative and quantitative analysis of extracted

---

**Table 3. The emission inventories of PAHs for global and some countries (Yang & Tao, 2009)**

<table>
<thead>
<tr>
<th>Source</th>
<th>Total (gigatons)</th>
<th>USA</th>
<th>China</th>
<th>India</th>
<th>Brazil</th>
<th>Sudan</th>
<th>UK</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wild fire</td>
<td>56.7</td>
<td>9.1</td>
<td>66.4</td>
<td>92.5</td>
<td>17.7</td>
<td>28.1</td>
<td>2.4</td>
</tr>
<tr>
<td>Open straw burning</td>
<td>2.4</td>
<td>8.7</td>
<td>1.7</td>
<td>4.3</td>
<td>3.8</td>
<td>6.9</td>
<td>0.9</td>
</tr>
<tr>
<td>Firewood</td>
<td>3.6</td>
<td>14.4</td>
<td>0.6</td>
<td>15.5</td>
<td>4.5</td>
<td>2.5</td>
<td>3.7</td>
</tr>
<tr>
<td>Savanna fire</td>
<td>1.4</td>
<td>1.9</td>
<td>2.2</td>
<td>1.2</td>
<td>4.8</td>
<td>3.6</td>
<td>10.7</td>
</tr>
<tr>
<td>Gasoline distribution</td>
<td>1.9</td>
<td>1.9</td>
<td>2.5</td>
<td>3.2</td>
<td>4.8</td>
<td>1.9</td>
<td>69.7</td>
</tr>
<tr>
<td>Waste incineration</td>
<td>4.8</td>
<td>23</td>
<td>2</td>
<td>3</td>
<td>58.2</td>
<td>6.9</td>
<td>35.1</td>
</tr>
<tr>
<td>Petrol refining</td>
<td>6.9</td>
<td>35.1</td>
<td>0.9</td>
<td>0.6</td>
<td>2.5</td>
<td>0.9</td>
<td>0.6</td>
</tr>
<tr>
<td>Other oil</td>
<td>3.7</td>
<td>10.7</td>
<td>1.3</td>
<td>4.5</td>
<td>2.5</td>
<td>3.6</td>
<td>14.4</td>
</tr>
<tr>
<td>Traffic oil</td>
<td>1.4</td>
<td>1.9</td>
<td>2.2</td>
<td>4.3</td>
<td>3.8</td>
<td>6.9</td>
<td>0.9</td>
</tr>
<tr>
<td>Consumer products</td>
<td>1.4</td>
<td>1.9</td>
<td>2.2</td>
<td>1.2</td>
<td>4.8</td>
<td>3.6</td>
<td>10.7</td>
</tr>
<tr>
<td>Coke Industry</td>
<td>3.7</td>
<td>10.7</td>
<td>1.3</td>
<td>4.5</td>
<td>2.5</td>
<td>3.6</td>
<td>14.4</td>
</tr>
<tr>
<td>Industrial Coal</td>
<td>1.4</td>
<td>1.9</td>
<td>2.2</td>
<td>1.2</td>
<td>4.8</td>
<td>3.6</td>
<td>10.7</td>
</tr>
<tr>
<td>Domestic Coal</td>
<td>3.7</td>
<td>10.7</td>
<td>1.3</td>
<td>4.5</td>
<td>2.5</td>
<td>3.6</td>
<td>14.4</td>
</tr>
<tr>
<td>Other industry</td>
<td>1.4</td>
<td>1.9</td>
<td>2.2</td>
<td>1.2</td>
<td>4.8</td>
<td>3.6</td>
<td>10.7</td>
</tr>
<tr>
<td>Al electron</td>
<td>1.4</td>
<td>1.9</td>
<td>2.2</td>
<td>1.2</td>
<td>4.8</td>
<td>3.6</td>
<td>10.7</td>
</tr>
<tr>
<td>Others</td>
<td>5.7</td>
<td>5.7</td>
<td>5.7</td>
<td>5.7</td>
<td>5.7</td>
<td>5.7</td>
<td>5.7</td>
</tr>
</tbody>
</table>

---

Sources, Distribution and Toxicity of Polycyclic Aromatic Hydrocarbons (PAHs) in Particulate Matter

www.intechopen.com
PAHs, gas chromatography, combined with mass spectrometry (GC-MS) or high performance liquid chromatography (HPLC), are often used. Recent studies of extraction, concentration, and analysis of PAHs in particulates are summarized in Table 4.

5. Typical urban and rural concentrations of PAHs

In general, concentrations of total PAHs are easily affected by locational and seasonal variations. Table 5 shows concentrations of total PAHs in urban and rural areas of different regions based on a recent literature survey. Average PAH concentrations (both gaseous and particle-bound PAHs) were highest in winter and lowest in summer due to higher energy consumption for heating and engine operation of vehicles and facilities during the cold seasons. Traffic exhaust and domestic coal combustion are main contributors of PAHs in urban areas, while biomass and domestic coal combustion are the predominant PAH sources in rural areas. Sources of PAHs in both urban and rural areas can be derived from industrial areas by the transport of PAHs through the atmosphere.

Liu et al. (2008) reported that urban PAH emissions (motor vehicle and coke production) are higher than rural emissions (primarily firewood and straw burning for cooking and heating) in spring, summer, and fall. However, winter PAH emissions in rural areas were much higher than those in urban areas due to of the abundance of coal, straw, and firewood burning for indoor heating in rural residences and for disposal of agricultural residues.

<table>
<thead>
<tr>
<th>Country</th>
<th>Area</th>
<th>ΣPAHs</th>
<th>PAHs conc. ng/m³</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>North Chinese Plain</td>
<td>urban</td>
<td>10</td>
<td>870 ± 330</td>
<td>Liu et al., 2008</td>
</tr>
<tr>
<td>-</td>
<td>rural</td>
<td>-</td>
<td>710 ± 330</td>
<td>-</td>
</tr>
<tr>
<td>Flanders, Belgium</td>
<td>rural</td>
<td>16</td>
<td>114</td>
<td>Ravindra et al., 2006</td>
</tr>
<tr>
<td>Seoul, Korea</td>
<td>urban</td>
<td>16</td>
<td>89 ± 74.3</td>
<td>Park et al., 2002</td>
</tr>
<tr>
<td>Chicago, USA</td>
<td>urban</td>
<td>16</td>
<td>13-1865</td>
<td>Li et al., 2005</td>
</tr>
<tr>
<td>New Delhi, India</td>
<td>urban</td>
<td>12</td>
<td>668 ± 399</td>
<td>Sharma et al., 2007</td>
</tr>
<tr>
<td>-</td>
<td>-</td>
<td>-</td>
<td>672 ± 388</td>
<td>-</td>
</tr>
<tr>
<td>London, UK</td>
<td>urban</td>
<td>15</td>
<td>166</td>
<td>Halsal et al., 1994</td>
</tr>
<tr>
<td>Cardiff, UK</td>
<td>urban</td>
<td>15</td>
<td>59</td>
<td>-</td>
</tr>
<tr>
<td>Campo Grande, Brazil</td>
<td>Campus</td>
<td>14</td>
<td>8.94-62.5</td>
<td>Poppio and Silva, 2005</td>
</tr>
<tr>
<td>Tai Chung, Taiwan</td>
<td>urban</td>
<td>21</td>
<td>220 ± 520</td>
<td>Fang et al., 2004</td>
</tr>
<tr>
<td>-</td>
<td>rural</td>
<td>-</td>
<td>831± 427</td>
<td>-</td>
</tr>
<tr>
<td>-</td>
<td>industry</td>
<td>-</td>
<td>1650 ±1240</td>
<td>-</td>
</tr>
<tr>
<td>Brisbane, Australia</td>
<td>urban</td>
<td>16</td>
<td>0.4 - 19.73</td>
<td>Lim et al., 2005</td>
</tr>
</tbody>
</table>

Table 5. Concentration of PAHs in various cities
PAHs, gas chromatography, combined with mass spectrometry (GC-MS) or high performance liquid chromatography (HPLC), are often used. Recent studies of extraction, concentration, and analysis of PAHs in particulates are summarized in Table 4.

5. Typical urban and rural concentrations of PAHs

In general, concentrations of total PAHs are easily affected by locational and seasonal variations. Table 5 shows concentrations of total PAHs in urban and rural areas of different regions based on a recent literature survey. Average PAH concentrations (both gaseous and particle-bound PAHs) were highest in winter and lowest in summer due to higher energy consumption for heating and engine operation of vehicles and facilities during the cold seasons. Traffic exhaust and domestic coal combustion are main contributors of PAHs in urban areas, while biomass and domestic coal combustion are the predominant PAH sources in rural areas. Sources of PAHs in both urban and rural areas can be derived from industrial areas by the transport of PAHs through the atmosphere.

Liu et al. (2008) reported that urban PAH emissions (motor vehicle and coke production) are higher than rural emissions (primarily firewood and straw burning for cooking and heating) in spring, summer, and fall. However, winter PAH emissions in rural areas were much higher than those in urban areas due to the abundance of coal, straw, and firewood burning for indoor heating in rural residences and for disposal of agricultural residues.

<table>
<thead>
<tr>
<th>Analyte</th>
<th>Pretreatment method</th>
<th>Analytical method</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>15-PAHs</td>
<td>Soxhlet- Warm extraction method, rotary evaporation</td>
<td>HPLC-FLD</td>
<td>Okuda et al., 2010</td>
</tr>
<tr>
<td>15 EPA- AHS</td>
<td>RS- fluorescence detection</td>
<td></td>
<td></td>
</tr>
<tr>
<td>16 EPA-PAHs</td>
<td>ASE extraction (hydrometric), evaporate concentration</td>
<td>GC-MS</td>
<td>Li et al., 2009</td>
</tr>
<tr>
<td>16 EPA-PAHs</td>
<td>dichloromethane/n-hexan (1:1)</td>
<td>HPLC</td>
<td>Lee and Dong, 2009</td>
</tr>
<tr>
<td>32-PAHs</td>
<td>Ultrasonic extraction with methanol</td>
<td>GC-MS</td>
<td>Saanio et al., 2008</td>
</tr>
<tr>
<td>20 PAHs</td>
<td>Rotary evaporator and nitrogen concentration</td>
<td></td>
<td></td>
</tr>
<tr>
<td>16 EPA-PAHs</td>
<td>Soxhlet extraction (dichloromethane, &gt;40 cycles), column chromatography on Active silica gel. elute with mixture (n-hexan/dichloromethane =3:1)</td>
<td>GC-MS</td>
<td>Lee et al., 2008</td>
</tr>
<tr>
<td>16 EPA-PAHs</td>
<td>Ultrasonic extraction with dichloromethane/acetone (3:1), SPE extraction</td>
<td>GC-MS</td>
<td>Li et al., 2007</td>
</tr>
<tr>
<td>16 EPA-PAHs</td>
<td>Accelerated Solvent Extractor with dichloromethane/acetone (1:1), Turbo Vap 500 concentration, UV and fluorescence detection. Soxhlet extraction by dichloromethane for 8 h, evaporate concentration</td>
<td>HPLC</td>
<td>Ravindra et al., 2006</td>
</tr>
<tr>
<td>22 PAHs</td>
<td>Ultrasonic extraction with dichloromethane, centrifugation, evaporate concentration</td>
<td>HPLC-UV</td>
<td>Kameda et al., 2005</td>
</tr>
<tr>
<td>16 EPA-PAHs</td>
<td>Ultrasonic extraction with dichloromethane, rotary evaporation</td>
<td>GC-MS</td>
<td>Gou et al., 2003</td>
</tr>
<tr>
<td>16 EPA-PAHs</td>
<td>Mass selective detection HP 5972 Ultrasonic extraction with dichloromethane and supercritical fluid extraction</td>
<td>GC-MS</td>
<td>Park et al., 2002</td>
</tr>
<tr>
<td>16 EPA-PAHs</td>
<td>Dialysis in hexane for 48 h, silica gel/alumina column clean-up, elute with dichloromethane/hexane, GPC clean-up Ultrasonic extraction with dichloromethane</td>
<td>GC-MS</td>
<td>Lohmann et al., 2001</td>
</tr>
<tr>
<td>16 EPA-PAHs</td>
<td>rotary evaporation</td>
<td>RP-HPLC-FLD</td>
<td>Li and Ro, 2000</td>
</tr>
</tbody>
</table>
6. Toxicity

6.1 Exposure

In ambient air, human beings are exposed to PAH vapor or PAHs contained in dust and other particulate matter outdoors or indoors at the home or workplace. Sources of human exposure to PAHs include cigarette smoke, vehicle exhaust, residential heating, agriculture burning, waste incineration, and emissions from industrial processes. According to the United States Agency for Toxic Substances and Disease Registry (ATSDR), main exposures of the U.S. population to PAHs include the inhalation of tobacco smoke, wood smoke, and ambient air with PAHs from traffic emissions and consumption of food containing PAHs. Predominant sources of PAH pollution at home include residential heating, tobacco smoking, and cooking. Vehicle emissions are also main sources of PAHs in many cities. For some people, the primary exposure to PAHs occurs in the workplace. For example, workers in a coke manufacturing factory receive high exposures to PAHs produced in their workplace.

The inhalation of air containing PAHs can lead to human exposure to PAHs. The exposure of traffic policemen to ambient PAHs is mainly from inhalation of vehicle exhaust and road dust containing PAHs. PAHs can also enter the body via food and water consumption or skin contact. PAHs are transported into all tissues of the human body containing fat. They can be stored in fat, liver and kidneys and can accumulate by repeated and long-term exposures. Smaller amounts are also stored in the spleen, adrenal glands, and ovaries.

6.2 Carcinogenicity and risk assessment

Air with high concentrations of PAHs causes many adverse effects on different types of organisms, including plants, birds, and mammals. Some studies reported that there is a significant positive correlation between mortality by lung cancer in humans and exposure to PAHs from exhaust from coke ovens, roofing-tar, and cigarette smoke. Some PAHs have been demonstrated to be carcinogenic in humans and experimental animals, and they are classified as carcinogenic materials by many organizations, including the United States Agency for Toxic Substances and Disease Registry (ATSDR), the International Agency for Research on Cancer (IARC), the Department of Health and Human Services (DHHS), the National Occupation Safety and Health Administration (OSHA), and the US-EPA. Table 6 shows the carcinogen classification of 17 priority PAHs by the IARC, compared to classifications by the DHHS and the US-EPA.

Table 7 shows the relative toxicity of priority PAHs selected by the US-EPA. LMW PAHs, except naphthalene, usually are associated with relatively lower toxicity (cancer risk) than HMW PAHs with 5 or 6 aromatic rings. Many toxicity studies reported that benzo[a]pyrene (BaP) has the highest carcinogenic potency with long-term persistency in the environment. Shulte et al. (1993) found a significant increase in all lung tumors and a dose-dependent increase in malignant lung tumors for mice exposed to PAH-enriched exhausts containing...
0.05 or 0.09 mg/m³ BaP. BaP is often used as an indicator of human exposure to PAHs, and the toxicity of other PAHs is converted into toxicity equivalency factors (TEFs) to BaP to evaluate their relative toxicities. Methods using TEFs and the BaP as a surrogate are more or less similar to each other, except for not requiring expensive monitoring. However, comparative potency methods are quite different from the previous two methods.

<table>
<thead>
<tr>
<th>PAHs</th>
<th>EPA</th>
<th>IARC</th>
<th>DHHS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acenaphthene</td>
<td>Not classifiable</td>
<td>Not classifiable</td>
<td></td>
</tr>
<tr>
<td>Acenaphthylene</td>
<td>Not classifiable</td>
<td>Not classifiable</td>
<td></td>
</tr>
<tr>
<td>Anthanthrene</td>
<td>Probable Carcinogen</td>
<td>Probable Carcinogen</td>
<td>Animal Carcinogen</td>
</tr>
<tr>
<td>Benz(a)anthracene</td>
<td>Probable Carcinogen</td>
<td>Probable Carcinogen</td>
<td>Animal Carcinogen</td>
</tr>
<tr>
<td>Benzo(a)pyrene</td>
<td>Probable Carcinogen</td>
<td>Possibly Carcinogen</td>
<td>Animal Carcinogen</td>
</tr>
<tr>
<td>Benzo(b)fluoranthene</td>
<td>Probable Carcinogen</td>
<td>Not classifiable</td>
<td></td>
</tr>
<tr>
<td>Benzo(e)pyrene</td>
<td>Probable Carcinogen</td>
<td>Possibly Carcinogen</td>
<td>Animal Carcinogen</td>
</tr>
<tr>
<td>Benzo(gi)perylene</td>
<td>Not classifiable</td>
<td>Not classifiable</td>
<td></td>
</tr>
<tr>
<td>Benzo(j)fluoranthene</td>
<td>Not included</td>
<td>Possibly Carcinogen</td>
<td>Animal Carcinogen</td>
</tr>
<tr>
<td>Benzo(k)fluoranthene</td>
<td>Probable Carcinogen</td>
<td>Possibly Carcinogen</td>
<td>Animal Carcinogen</td>
</tr>
<tr>
<td>Chrysene</td>
<td>Probable Carcinogen</td>
<td>Not classifiable</td>
<td>Animal Carcinogen</td>
</tr>
<tr>
<td>Dibenzo(ah)anthracene</td>
<td>Probable Carcinogen</td>
<td>Not classifiable</td>
<td>Animal Carcinogen</td>
</tr>
<tr>
<td>Fluoranthene</td>
<td>Not classifiable</td>
<td>Not classifiable</td>
<td></td>
</tr>
<tr>
<td>Fluorene</td>
<td>Not classifiable</td>
<td>Not classifiable</td>
<td></td>
</tr>
<tr>
<td>Ideno(1,2,3-cd)pyrene</td>
<td>Probable Carcinogen</td>
<td>Possibly Carcinogen</td>
<td>Animal Carcinogen</td>
</tr>
<tr>
<td>Phenanthrene</td>
<td>Not classifiable</td>
<td>Not classifiable</td>
<td></td>
</tr>
<tr>
<td>Pyrene</td>
<td>Not classifiable</td>
<td>Not classifiable</td>
<td></td>
</tr>
</tbody>
</table>

Table 6. 17 priority PAHs were classified by the IARC in comparing those by the DHHS and the US-EPA.
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Acenaphthene</td>
<td>0.001</td>
<td>0.001</td>
<td></td>
<td></td>
<td>0.001</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Acenaphthylene</td>
<td>0.001</td>
<td>0.001</td>
<td></td>
<td></td>
<td>0.01</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Anthanthrene</td>
<td>0.32</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Benzo(a)anthracene</td>
<td>0.145</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
</tr>
<tr>
<td>Benzo(a)pyrene</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Benzo(b)fluoranthene</td>
<td>0.141</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
</tr>
<tr>
<td>Benzo(e)pyrene</td>
<td>0.004</td>
<td></td>
<td></td>
<td></td>
<td>0.01</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Benzo(ghi)perylene</td>
<td>0.022</td>
<td>0.01</td>
<td>0.01</td>
<td></td>
<td></td>
<td></td>
<td>0.01</td>
</tr>
<tr>
<td>Benzo(phenanthrene)</td>
<td>0.01</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Benzo(k)fluoranthene</td>
<td>0.061</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
</tr>
<tr>
<td>Chrysene</td>
<td>0.0044</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
</tr>
<tr>
<td>Coronene</td>
<td>0.001</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cyclopenta(cd)pyrene</td>
<td>0.023</td>
<td>0.1</td>
<td>0.1</td>
<td></td>
<td>0.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dibenzo(a,e)pyrene</td>
<td>1</td>
<td>1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dibenzo(a,c)anthracene</td>
<td>0.1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dibenzo(ah)anthracene</td>
<td>1.11</td>
<td>1</td>
<td>1</td>
<td>0.4</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Dibenzo(a,e)pyrene</td>
<td>100</td>
<td>10</td>
<td></td>
<td></td>
<td>100</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dibenzo(a,h)pyrene</td>
<td>10</td>
<td>10</td>
<td></td>
<td></td>
<td>1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dibenzo(a,i)pyrene</td>
<td>0.1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.1</td>
</tr>
<tr>
<td>Dibenzo(a,j)pyrene</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fluoranthene</td>
<td>0.001</td>
<td>0.001</td>
<td></td>
<td></td>
<td>0.01</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fluorene</td>
<td>0.001</td>
<td>0.001</td>
<td></td>
<td></td>
<td>0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ideno(1,2,3-cd)pyrene</td>
<td>0.232</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
</tr>
</tbody>
</table>
Table 7. Proposed TEFs for individual PAHs (Modified from Knafla et al., 2006)

<table>
<thead>
<tr>
<th>PAH</th>
<th>Route Not Specified</th>
<th>Dermal Not Specified</th>
<th>Inhalation</th>
<th>Multiple</th>
<th>Subcutaneous</th>
<th>Inhalation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Naphthalene</td>
<td>0.001</td>
<td>0.001</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Perylene</td>
<td>0.001</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Phenanthrene</td>
<td>0.001</td>
<td>0.001</td>
<td>0</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pyrene</td>
<td>0.81</td>
<td>0.001</td>
<td>0.001</td>
<td>0.001</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
6.3 Toxicity equivalency factors (TEFs)
TEF evaluation is the most popular method used to identify the toxicity of PAHs. TEFs of individual PAHs have been reported by many researchers (Table 7). Toxicity equivalency concentrations (TEQs) are calculated as the product of summing up the values obtained by TEF values and concentrations of PAHs, as follows:

\[ \text{TEQ} = \sum (C_i \times TEF_i) \]

Where,

- TEQ: toxic equivalent concentration
- \( C_i \): concentration of PAH \( i \)

Petry et al. (1995) used TEFs in assessing occupational and environmental health risks associated with exposure to airborne mixtures of PAHs. They used information of the ratio between airborne concentrations of BaP equivalents to the concentrations of BaP alone, which can indicate the variation of risk for the different environments. Individual PAH-based BaP\(_{eq}\) toxicity estimates were up to one order of magnitude higher than estimates based on BaP concentration measurements and BaP-risk from risk assessment of lung cancer related to occupational exposure (Vyskocil et al., 2004; Yanjual et al., 2007). Yajuan et al. (2008) reported that 1.73% of the cancer sufferers of Beijing inhabitants in 2007 were related to inhalation of PAHs in ambient air. There is an increasing trend of the cancer risk of residents by inhalation of ambient air containing hazardous air pollutants (HAPs), such as PAHs.

Halek et al. (2008) estimated that the annual number of lung cancer cases attributable to carcinogenic PAH compounds in 2005 was 58 persons per million. The BaP is the highest carcinogenic contributor, followed by DahA, Ind and BbF (Pufulete et al., 2004). However, DahA was suggested as a new surrogate compound to measure the toxicity of particle phase-PAHs because its toxicity is almost equal to that of BaP. While estimating the toxicity of PAHs in road dust of Ulsan, Korea, Dong and Lee (2009) found a significant correlation coefficient between TEQ and total PAH concentrations.

7. Introduction of Nitro-PAHs
Nitrated polycyclic aromatic hydrocarbons (N-PAHs) are an important category of derivations of PAHs and are of special interest because they include potential mutagens and carcinogens. They have been recognized as direct-acting mutagens and carcinogens to mammalian systems and are, thus, considered to have far greater toxicity than unsubstituted PAHs (Pedersen et al., 1998; Atkinson and Arey, 1994). Nitro-PAHs are formed mainly from incomplete combustion processes or by the reaction of PAH with atmospheric oxidants, such as dinitrogen pentoxide, nitrogen trioxide, and oxygen radicals in the presence of nitrogen oxides (Atkinson et al., 1990; Fan et al., 1995; Enya et al., 1997; Environmental Health Criteria-EHC, 2003). Nitro-PAHs occur as a mixture with parent PAHs in the vapor phase or adsorbed onto particulate matter in the atmosphere. Two-ring N-PAHs, such as nitronaphthalenes, are the dominant N-PAHs in the vapor phase. However, N-PAHs, which include nitro derivatives of pyrene, fluoranthene, anthracene, chrysene, and others, tend to condense on particle surfaces because of their low vapor pressure. Atmospheric lifetimes of N-PAHs are affected.
by photolysis and gas-phase reactions with hydroxyl and nitrate radicals and with ozone under atmospheric conditions. Photolysis is the dominant loss process for N-PAHs (e.g. 1-and 2-nitronaphthalene). “Particle oxidation of nitro-PAHs by ozone may be the main loss process at night” (EHC, 2003).

N-PAHs in the environment originate from direct emissions from combustion sources and nitration of unsubstituted PAHs. Main sources include vehicle exhaust (particularly diesel), industrial emissions, and domestic emissions (residential heating/cooking and wood burning), as with unsubstituted PAHs. In urban areas, N-PAH pollution is predominantly caused by diesel engine vehicle traffic and residential heating. Indoor human exposure to nitro-PAHs is from kerosene heating and use of cooking oil. Effects of N-PAHs on human health have been estimated based on the data of carcinogenic effects for 28 N-PAHs. Tokiwa et al. (1998 and 2000) reported that N-PAHs have been detected in samples of resected lung tissue from patients in Japan.

Sampling methods of nitro-PAHs are similar to those of unsubstituted PAHs. Most nitro-PAH samples are collected on sorbent (PUF) or XAD-2 resins and filters by high-volume samplers. Then, nitro-PAH samples undergo extraction, clean up, and analysis. However, there are problems which affect atmospheric sampling and measurement of N-PAHs. These issues include: 1) N-PAHs are emitted in a very complex matrix; 2) concentrations of N-PAHs are very low and only detected using highly sensitive analytical methods; and 3) formation of N-PAHs is strongly influenced by meteorological conditions, such as sunlight radiation, humidity, and concentrations of ambient contaminants, such as ozone, nitrogen oxides, and photooxidants.

8. References


Although the climate of the Earth is continually changing from the very beginning, anthropogenic effects, the pollution of the air by combustion and industrial activities make it change so quickly that the adaptation is very difficult for all living organisms. Researcher’s role is to make this adaptation easier, to prepare humankind to the new circumstances and challenges, to trace and predict the effects and, if possible, even decrease the harmfulness of these changes. In this book we provide an interdisciplinary collection of new studies and findings on the score of air pollution.

How to reference
In order to correctly reference this scholarly work, feel free to copy and paste the following:
