INTRODUCTION

Air pollution has widespread impacts on the environment, on quality of life and on human health. The economic costs of air pollution have been studied for many years. We now have excellent data on the costs of industrial pollution controls, developing cleaner or substitute fuels, deposition on forests and vegetation, and repairing buildings from acid rain damage etc. It is increasingly apparent that the costs of air pollution are measured not only in monetary terms but also in human lives. Yet only recently we have started to quantify the health impacts.

In recent years there has been considerable concern regarding the possibility of adverse effects of toxic compounds in atmospheric environment on human health. Attention has focused particularly on chemical carcinogens in ambient air. Polycyclic Aromatic Hydrocarbons (PAHs) were one of the first atmospheric pollutants to be identified as being carcinogenic. These classes of compounds are ubiquitously present in the urban atmosphere and have therefore considerable scrutiny. PAH also known as Polynuclear Aromatic Hydrocarbons or polyarenes constitute a large class of organic compounds.

PAHs (which are well known for their strong mutagenic, carcinogenic and toxic properties) are composed of carbon and hydrogen atoms arranged in the form of fused aromatic rings (linear, cluster or angular arrangement) (Sims and Overcash, 1983). There are thousands of PAH compounds in the environment but in practice PAHs analysis is restricted to the determination of 6 to 16 compounds. Individual PAHs differ substantially in their physical and chemical properties (Maliszewska-Kordybach 1999; Sims and Overcash...
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1983). The best-known model compound from this group is highly carcinogenic Benzo(a)pyrene (BaP). The United State Environmental Protection Agency and the European Commission list PAHs as priority pollutants. US Environmental Protection Agency (EPA) has fixed 16 PAHs as priority pollutants, the latest being effective from 1997 (Mastral et al., 2000). These compounds are as follows: Naphthalene, Acenaphthylene, Acenaphthene, Fluorene, Phenanthrene, Anthracene, Fluoranthene, Pyrene, Chrysene, Benzo(a)anthracene, Benzo(b) fluoranthene, Benzo(k)fluoranthene, Benzo(a)pyrene, Indeno(1,2,3-c,d)pyrene, Benzo(g,h,i)perylene and Dibenzo(a,h)anthracene.

Human exposure to PAHs can occur through several environmental pathways including internal adsorption through food and water (Basu and Saxena, 1978). Their occurrence in ambient air has however, caused particular concern due to the continuous nature of exposure and the size of the population at risk, especially in urban, suburban and industrial area. The extent to which human beings are exposed to PAHs is a function of several parameters including the concentration in ambient air, the prevailing atmospheric conditions, their distribution between gaseous and particulate phases and the size of the particle with which the particulate fraction are associated.

In order to assess the significance of PAHs in ambient air it is necessary to evaluate the physical and chemical characteristics of airborne PAH as well as identify the major emission sources.

1.1. Physical and Chemical properties of PAHs

PAHs are composed of carbon and hydrogen atoms arranged in the form of fused aromatic rings and their physical and chemical properties are
<table>
<thead>
<tr>
<th>Compounds</th>
<th>Mol. Wt</th>
<th>Abbr.</th>
<th>Mol. Formula</th>
<th>Melting point (°C)</th>
<th>Boiling Point (°C)</th>
<th>Vap. Press. (Pa at 25°C)</th>
<th>n-Octanol/Water Partition Log Kow (μg/L)</th>
<th>Water solubility (25°C) (mg/L)</th>
<th>Henry's constant (25°C) KPa m³/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>Naphthalene</td>
<td>128</td>
<td>Nap</td>
<td>C₁₀H₈</td>
<td>81</td>
<td>217.9</td>
<td>1.4</td>
<td>3.4</td>
<td>3.17 x 10⁴</td>
<td>4.89 x 10⁻²</td>
</tr>
<tr>
<td>Acenaphthylene</td>
<td>152</td>
<td>Acl</td>
<td>C₁₀H₈</td>
<td>92-93</td>
<td>265-275</td>
<td>8.8 x 10⁻¹</td>
<td>4.07</td>
<td>-</td>
<td>1.14 x 10⁻³</td>
</tr>
<tr>
<td>Acenapthene</td>
<td>154</td>
<td>Acn</td>
<td>C₁₂H₁₀</td>
<td>85</td>
<td>279</td>
<td>2.9 x 10⁻¹</td>
<td>3.92</td>
<td>3.93 x 10³</td>
<td>1.48 x 10⁻²</td>
</tr>
<tr>
<td>Fluorene</td>
<td>166</td>
<td>Fl</td>
<td>C₁₂H₁₀</td>
<td>115-116</td>
<td>293-295</td>
<td>8.0 x 10⁻²</td>
<td>4.18</td>
<td>1.98 x 10³</td>
<td>1.01 x 10⁻²</td>
</tr>
<tr>
<td>Anthracene</td>
<td>178</td>
<td>Anth</td>
<td>C₁₄H₁₀</td>
<td>216.4</td>
<td>342</td>
<td>8.0 x 10⁻⁴</td>
<td>4.5</td>
<td>73</td>
<td>7.3 x 10⁻²</td>
</tr>
<tr>
<td>Phenanthrene</td>
<td>178</td>
<td>Phen</td>
<td>C₁₄H₁₀</td>
<td>100.5</td>
<td>340</td>
<td>1.6 x 10⁻²</td>
<td>4.6</td>
<td>1.29 x 10³</td>
<td>3.98 x 10⁻³</td>
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<tr>
<td>Fluoranthenne</td>
<td>202</td>
<td>Flan</td>
<td>C₁₆H₁₀</td>
<td>108.8</td>
<td>375</td>
<td>1.2 x 10⁻³</td>
<td>5.22</td>
<td>260</td>
<td>6.5 x 10⁻⁴</td>
</tr>
<tr>
<td>Pyrene</td>
<td>202</td>
<td>Pyr</td>
<td>C₁₆H₁₀</td>
<td>150.4</td>
<td>393</td>
<td>6.0 x 10⁻⁴</td>
<td>5.18</td>
<td>135</td>
<td>1.1 x 10⁻³</td>
</tr>
<tr>
<td>Benzo(a)Anthracene</td>
<td>228</td>
<td>BaA</td>
<td>C₁₈H₁₂</td>
<td>160.7</td>
<td>400</td>
<td>2.8 x 10⁻⁵</td>
<td>5.16</td>
<td>14</td>
<td>-</td>
</tr>
<tr>
<td>Chrysene</td>
<td>228</td>
<td>Chry</td>
<td>C₁₈H₁₂</td>
<td>253.8</td>
<td>448</td>
<td>8.4 x 10⁻⁵</td>
<td>5.91</td>
<td>2</td>
<td>-</td>
</tr>
<tr>
<td>Benzo(b)Fluoranthene</td>
<td>252</td>
<td>BbF</td>
<td>C₂₀H₁₂</td>
<td>168.3</td>
<td>481</td>
<td>6.7 x 10⁻⁵</td>
<td>6.12</td>
<td>1.2</td>
<td>5.1 x 10⁻⁵</td>
</tr>
<tr>
<td>Benzo(k)Fluoranthene</td>
<td>252</td>
<td>BkF</td>
<td>C₂₀H₁₂</td>
<td>215.7</td>
<td>480</td>
<td>1.3 x 10⁻⁸</td>
<td>6.84</td>
<td>2.5</td>
<td>4.4 x 10⁻⁵</td>
</tr>
<tr>
<td>Benzo(a)Pyrene</td>
<td>252</td>
<td>BaP</td>
<td>C₂₀H₁₂</td>
<td>178.1</td>
<td>496</td>
<td>7.3 x 10⁻⁷</td>
<td>6.5</td>
<td>3.8</td>
<td>3.4 x 10⁻⁵</td>
</tr>
<tr>
<td>Benzo(ghi)Perylene</td>
<td>276</td>
<td>BghiP</td>
<td>C₂₅H₁₂</td>
<td>278.3</td>
<td>545</td>
<td>1.4 x 10⁻⁸</td>
<td>7.1</td>
<td>0.26</td>
<td>2.7 x 10⁻⁵</td>
</tr>
<tr>
<td>Indeno(1,2,3-cd)Pyrene</td>
<td>276</td>
<td>IP</td>
<td>C₂₅H₁₂</td>
<td>163.6</td>
<td>536</td>
<td>1.3 x 10⁻⁸</td>
<td>6.58</td>
<td>62</td>
<td>2.9 x 10⁻⁵</td>
</tr>
<tr>
<td>Dibenzo(a,h)Anthracene</td>
<td>278</td>
<td>DBahA</td>
<td>C₂₅H₁₂</td>
<td>266.6</td>
<td>524</td>
<td>1.3 x 10⁻⁸</td>
<td>6.5</td>
<td>0.5 (27°C)</td>
<td>7 x 10⁻⁶</td>
</tr>
</tbody>
</table>

Source: Menichini (1994)
Figure 1.1. Structure of the PAHs

Acenaphthene  
Benz(a)Anthracene  
Benz(ghi)Perylene  
Dibenz(a,h)Anthracene  
Indeno(1,2,3-cd)Pyrene  
Pyrene

Acenaphthylene  
Benz(b)Fluoranthene  
Benz(a)Pyrene  
Fluoranthene  
Naphthalene  

Anthracene  
Benz(k)Fluoranthene  
Chrysene  
Fluorene  
Phenanthrene

Source: Menichini (1994)
a given in Table 1.1 and Figure 1.1. They vary quite regularly with the number of rings and the molecular mass. The general characteristics common to the class are high melting and boiling points, low vapour pressures and solubility in water. PAHs are soluble in many organic solvents (IARC, 1983).

Vapour pressure generally tends to decrease with the increase in molecular weight, varying more than an order of magnitude of ten from low to high molecular weight compounds. This affects the different percentages of individual PAHs which are adsorbed on particulate matter in the atmosphere and they are retained with the particulate matter during sampling on filters (Thrane and Mikalsen, 1981). Vapour pressure increases markedly with increase in ambient temperature (Murray et al., 1974), which then additionally affects the distribution coefficients between gas and particulate phase (Lane, 1989).

PAHs are chemically inert compounds. When they react, PAHs undergo two type of reactions, i.e. electrophillic substitution and addition reactions. The former is preferred since it does not destroy the aromatic character of PAHs, while addition is often followed by elimination resulting in a net substitution. Following photo-decomposition, in the presence of air and sunlight, a number of oxidative products have been identified particularly quinines and endoperoxides. Various experimental studies have revealed reactions of PAHs with nitrogen oxides and nitric acid to form nitro derivatives as well; with sulfur dioxide and sulfuric acid in solution to form sulfinic and sulfonic acids. PAHs may also be attacked by ozone and hydroxyl radicals which are present in the atmosphere.

The formation of nitro-PAH is particularly important owing to their biological impact, and to their mutagenic activity (Howard et al., 1990).

In general the mentioned reactions are of interest with regard to the
environmental fate of PAHs, but the results of experimental studies are
difficult to interpret because of complexity of interaction occurring in
environmental mixtures and difficulty in eliminating artifacts during analytical
determinations. These reactions are also considered for possible PAHs losses
during the ambient atmospheric sampling (Menichini et al., 1992a).

The incorporation of PAHs into particulates has been explained by a
general condensation and adsorption mechanisms. PAHs are initially
generated in the gas phase and then adsorbed on the pre-existing particles
while undergoing condensation during further cooling of the emission (Van
Vaeck et al., 1984). For the least volatile PAHs the gas particle conversion
step may be determined shortly after emission. A considerable fraction of
the more volatile PAHs will escape particle incorporation and persist in the
atmospheric gas phase (Broddin et al., 1980).

1.2. Formation of PAHs

PAHs are formed in all processes of incomplete combustion of organic
substances (Lenicek et al., 1997; Sims and Overcash 1983; Wild and Jones
1995). Their production is favoured by an oxygen deficient flame, temperatures
in the range of 650-900°C and fuels which are not highly oxidised. Natural
sources of pyrogenic PAHs such as volcanic activity and forest fires do not
significantly contribute for the present overall PAHs emission (Ramdahl et
al., 1982, 1984; Schuetzle et al., 1985; Simonich and Hites, 1994; Sims and
Overcash 1983; Subramanyam et al., 1994; Tremolada et al., 1996; Vaessen
et al., 1988; Valerio et al., 1984; Van Jaarsveld et al., 1997; Wania and
Mackay, 1996; Wild and Jones, 1995). Anthropogenic sources can be divided
into two categories viz. the combustion of materials for energy supply (e.g.
coal, oil, gas, wood, etc.) and combustion for waste minimisation (e.g. waste
incineration) (Ramdahl et al., 1982; Wild and Jones, 1995). The first category includes stationary sources like industries (mainly coke and carbon production, petroleum processing, aluminium sintering, etc.), residential heating (furnaces, fireplaces and stoves, gas and oil burners), power and heat generation (coal, oil, wood and peat power plants) and mobile sources like cars, lorries, trains, aeroplanes and sea traffic (gasoline and diesel engines). The second category covers incineration of municipal and industrial wastes. Other miscellaneous sources are unregulated fires such as agricultural refuse burning, recreational fires, crematoria etc., cigarette smoking as well as volatilisation from soils, vegetation and other surfaces (Ramdahl et al., 1982; Wild and Jones, 1995).

1.3. Sources of PAHs in the Environment

Naturally PAHs in the atmosphere arise from combustion processes such as forest fires and volcanic eruption (Nikolaou et al., 1984), but emissions from human activities are the predominant sources and motor vehicles contribute more than industrial processes. Motor vehicles are thought to be the major source of atmospheric PAHs in the United States accounting for approximately 36% of a year total (Benner et al., 1989). The results of studies like Tuomien et al. (1988), Westerholm et al. (1988a, b) and Pyyasalo et al. (1987) also showed that traffic was the major determinant for concentration of PAHs and the genotoxic activity in urban air.

1.3.1. Emission of PAHs from vehicular exhaust

Motor vehicles account for the majority of PAHs emissions in urban areas (Freeman and Cattell, 1990; Tuomien et al., 1988). In general, exhaust emissions of PAHs from mobile sources originate by three distinct mechanisms
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viz. (i) Synthesis from simpler molecules in fuel, particularly from aromatic compounds (ii) Storage in engine deposits and subsequent emissions of PAHs already in the fuel and (iii) Pyrolysis of lubricant. The emission rates of PAHs from vehicular exhausts are dependent upon a large number of factors including, engine type, operating conditions and composition of both fuel and lubricating oil (Candeli et al., 1983; Pederson et al., 1980).

The effect of engine type is largely determined by the design of the combustion system, the fuel/air mixture, the temperature within the combustion chamber and the manufacturing quality. It is established that different vehicles operating under the same conditions with the same fuel can emit significantly different amounts of PAHs (Handa et al., 1979; Lang et al., 1981).

The main engine operating parameters that affect exhaust PAHs content are engine load, air to fuel ratio (AFR) and engine coolant temperature. In general larger quantities of PAHs are emitted during acceleration, deceleration or when cruising at high speeds than when driving at steady average speeds. Of the various engine operating parameters changes in AFR are known to produce the largest effect on PAHs emissions. It has been found that the amount of PAHs in engine exhaust decreases with increasing AFR (i.e. leaner mixture) except for a sharp increase in the vicinity of the ‘lean misfiring limit’ (Pederson et al., 1980; Laity et al., 1973). Since leaner mixtures supply excess O₂, more complete combustion occurs, resulting in lower emission of PAHs.

The aromatic hydrocarbon content of fuel has been the main focus of concern since benzene and its derivatives produce more PAHs than aliphatic hydrocarbons (Hoffman et al., 1965). A number of investigations have shown that PAHs emission increases as the aromatic content increases (Candeli et
al., 1974; Begeman and Colucci, 1970; Laity et al., 1973). Not all aromatic compounds have the same effect, suggesting the importance of the individual aromatic constituents in the fuel (Candeli et al., 1974). The aromatic fraction in fuel for either petrol or diesel engine generally contains a broad spectrum of aromatic compounds ranging from C$_6$ to C$_{10}$ or C$_{10}^+$, although the heavier compounds (C$_{10}^+$) are present only in lower percentage (Candeli et al., 1974).

It was found that benzene derivatives such as ethyl benzene and xylene were better precursors for PAHs formation than benzene itself (Candeli et al., 1974, 1983). In general the greater the content of high boiling aromatic compounds in fuels the higher the PAHs content (Pederson et al., 1980, Badger, 1962).

An additional fuel parameter likely to affect PAHs emission is the content of alkyl Lead (Pb), which are added to petrol as anti-knocking additives. For a given octane number the Pb and aromatic content of fuel are not independent of one another, since the aromatic hydrocarbons also exert a marked anti-knock effect (Begeman and Colucci, 1970; Candeli et al., 1974; Gross, 1972; Lang et al., 1981). The Pb content in comparison with fuel aromatic content, exerts only a slight influence on particle bound PAHs emissions, both as a single variable and when the fuel aromatic content was changed simultaneously (Pederson et al., 1980).

During recent years, there has been a considerable change in fuel composition on a world wide basis, in particular there has been a decrease in the use of alkyl Pb, anti-knock additives, in petrol (Baek et al., 1992; Tims, 1983).

In order to maintain the octane quality of petrol while reducing Pb content, the aromatic content of petrol was increased in most of the countries.
In the FRG as a result of reducing Pb content from 0.4 to 0.15 g/L in 1976, the aromatic content increased by approximately 20% and a similar increase was predicted for other European countries which intended to reduce the Pb content in petrol to 0.15g/L. The same reduction of Pb in United Kingdom (UK) did not result in any significant increase in the aromatics mainly because the short chain aliphatic content of petrol was increased. In France and Italy high Pb content is associated with low aromatic content and conversely in Sweden and the FRG low Pb content is associated with high aromatic content. It has been shown that increase in the aromatic content of petrol significantly increases the PAHs content of the exhaust (Candeli et al., 1983). As a consequence the decision to reduce the Pb content of petrol has been a cause of much concern with respect to possible increase in PAHs emission. The decreased level of Pb in petrol has shifted attention to the use of certain PAH compounds as motor vehicle emission tracers (Benner et al., 1989).

Less attention has been paid to the content and type of aromatics in diesel fuel since the aromatic fraction can be lowered significantly without affecting quality which may even be improved when the percentage of aromatics is lowered (Candeli et al., 1983).

It is however uncertain whether the PAHs emitted are those which survive the combustion process or are produced by rearrangement of hydrocarbons present in the fuel (Handa et al., 1979; Pederson et al., 1980). Significant carry over effects of deposits formed during combustion of PAHs rich fuels were observed by Gross (1972). However, Westerholm et al. (1988) reported that up to 95% of the fuel PAH content was decomposed during combustion and emitted PAH being mainly formed by the combustion process. Pederson et al. (1980) reported that an approximate 23 times increase in the
BaP content of fuel resulted in only a 3-5 fold increase in BaP content in exhaust emission. Westerholm et al. (1988) reported that pyrene resists combustion and that 80% of Cyclopenta(cd)pyrene is formed during the combustion process.

PAHs are also produced by the combustion of lubricating oil. However, this source is relatively minor under normal operating conditions. The chemical structure of the lubricant controls the retention capacity for PAHs and also its emission characteristics on combustion. The accumulation of PAHs in the lubricant was explained largely by the presence of PAHs deposits in the combustion chamber (Begeman and Colucci, 1970).

1.4. Gas - particle distribution of PAHs

PAHs entering the atmosphere are derived from combustion and volatilisation. They are present in the ambient air as vapours or adsorbed into airborne particulate matter (Bodzek et al., 1993; Kamens et al., 1988, Martey et al., 1984, Neilsen et al., 1983). Gas to particle partition of PAHs depends on the molecular weight of the compounds, temperature, humidity and precipitation (Subramanyam et al., 1994; Van Jaarsveld et al., 1997). In general, low volatile PAHs with ≥ 5 rings, characterised by relatively high temperature of condensation, are adsorbed on the airborne particles (Subramanyam et al., 1994; van Jaarsveld et al., 1997). The lower molecular weight compounds with 2-3 rings, exhibiting low temperatures of condensation, are more abundant in the gas phase (Cautreels and Van Cawenbergh, 1978; Tuominen et al., 1988; Halkiewicz et al., 1987; Subramanyam et al., 1994, Valerio et al., 1984, Van Jaarsveld et al., 1997, Wania and Mackay, 1996, Wild and Jones, 1995). Semi-volatile 4 ring PAHs (like Pyrene or Phenanthrene) can be found in both phases and their gas to
particle partition coefficients are most susceptible to the influence of environmental factor (Subramanyam et al., 1994). Pyrene was estimated to be 50% gaseous at 30°C (Westerholm et al., 1988). De Raat et al. (1990) reported that volatility was more important than reaction in determining the PAH profile. With high summer temperatures, the concentrations of PAHs in the gas phase increase, whereas during winter particulate phase PAHs dominate (Bodzek et al., 1993, Subramanyam et al., 1994, Wania and Mackay, 1996). Baek et al. (1991a) reported that PAHs with molecular weight less than 234 are 50% or more of this group’s total concentration during summer, these values decrease by about half during winter. Gas phase PAHs above or equal to a molecular weight of 252 constitute less than 20% of the total for such weights, even during the summer (Baek et al., 1991a). On average 47% of the total PAHs were reported as gaseous by Baek et al. (1991a, b). Bodzek et al. (1993) found that the content of particulate phase PAHs in winter air samples from the Upper Silesia region in Poland is about 10-20 times higher than in summer samples. Lenicek et al. (1993) reported alike relationship between winter/spring air samples from the North Bohemia Region in the Czech Republic. Similar alterations were observed by other authors (Ramdhal et al., 1984). In the case of gas phase PAH the difference was much smaller.

Higher PAHs concentrations (in general measured in the particulate phase) in the winter months were also related to the higher emission of these pollutants from domestic heating sources (Bodzek et al., 1993; Wild and Jones 1995). The adsorption of PAHs onto particulate phases may be affected not only by temperature but by humidity as well, it was found (Subramanyam et al., 1994) that the gas to particle PAH ratio decreases with increasing humidity. The range of PAH adsorption on atmospheric
sorbents depends also on the quantity of the suspended particulates and their nature (soot, dust, fly ash, pyrogenic metal oxides, pollens, etc., of different particle size) (Subramanyam et al., 1994; Wania and Mackay, 1996). A significant correlation was found between the amount of dust in the air and PAH concentrations in the particulate phase (Valerio et al., 1984, Wild and Jones, 1995).

The dilution of gaseous and particulate phase emission during transport through the atmosphere can also cause a redistribution of gas-particle partition that can result in desorption of some constituent of the particulate matter to the gas phase, the so called 'aerodynamic dilution effect' (De Wiest and Della Fiorentina, 1975). The exchange between the gaseous and particulate phase represents an important feature of the ageing process of an aerosol (Van Veack and Van Cawenbergh, 1985; Van Veack et al., 1984). This exchange may superimpose on or interfere with the size distribution shift of PAH within the accumulation mode during long term transport (Van Veack et al., 1979).

A number of studies have demonstrated that atmospheric PAH concentrations are highly dependent upon the size of airborne particulate mater with the greatest concentration being in the respirable size range (Pierce and Katz, 1975). DeMaio and Corn (1966) found that more than 75% by weight of selected PAH from Pittsburgh air were associated with particle less than 5.0μm in aerodynamic diameter. Van Vaeck et al. (1984) reported that 90 to 95% of total PAH in both urban and suburban area of Belgium were associated with a size class less than 3 μm, with 60 to 70% being present on particles less than 1μm in diameter. Beak et al. (1991a) report a unimodal distribution for particulate PAH in contrast to the ambient aerosol with which they were associated. The peaks of the PAH distribution
appear to be exclusively localised between 0.4 and 1.1 μm. During winter Baek et al. (1991a) estimated that 63 to 82% of particulate PAH were associated with aerosols of aerodynamic diameter of less than 1.1 μm. Up to 95% were associated with particles under 3.3 μm diameter (Beak et al., 1991a). Pistikopoulos et al. (1990) reported two particle size distribution families for PAH. One group is associated with particles of less than 1 μm and corresponds to relatively non-volatile PAH, the other is associated with particles greater than 1 μm and corresponds to volatile PAH, except Fluoranthene. The first group being formed by adsorption, the second is being condensation (Pistikopolous et al., 1990).

1.5. Fate and transformation of PAHs during atmospheric processes

Once PAH are released into the atmosphere, they are subjected to a variety of atmospheric processes through which their distribution, removal, transport and degradation can occur. Thus the quantity and distribution of atmospheric PAH is dependent not only on the magnitude of the emission but also on the stability of PAH in the atmosphere. The atmospheric phenomena involve in the evolution of PAH can be summarised as follows (i) Physical removal by dry or wet deposition (ii) atmospheric transport and dispersion by the shift of air mass, turbulence and convection, (iii) atmospheric degradation or conversion either by chemical or photochemical reaction and (iv) exchange between the gaseous and particulate phase by shifting the phase equilibrium (Masclet et al., 1986).

1.5.1. Chemical reactions of PAHs

PAHs released into atmosphere are normally present in gaseous phase or adsorbed to particulates. During the residence time in atmosphere (half-
lives ~ 30 days) PAHs can undergo photochemical oxidation. A number of experimental studies have demonstrated that many PAH are susceptible to photochemical and/or chemical oxidation under simulated atmospheric conditions (Pitts et al., 1985a, b; Nielsen, 1984; Kamens et al., 1988). Although results from the laboratory simulation studies are difficult to extrapolate to the reactivities of PAH under real atmospheric conditions, there is however potential for chemical transformation of PAH by gas-particle interactions in emission plumes, exhaust systems or even during atmospheric transport (Neilsen et al., 1983; Daisey et al., 1986). Furthermore, the presence of direct mutagens in ambient aerosols which cannot be explained by PAH alone, may be at least in part due to the transformation products of PAH (Pitts, 1983). Oxy, hydroxy, nitro and hydroxynitro PAH are possible reaction products (Albeic-Juretic et al., 1990).

1.5.2. Photochemical Reactions of PAHs

Photochemical transformations have generally been considered to be the most important mode of atmospheric decomposition of PAH of both phases (Masclet et al., 1986; Kamens et al., 1984, 1990). Although the degradation rates by photolysis of different PAHs show a wide variation, it has become apparent that the extent of photochemical decay is strongly influenced by the nature of the substrate on which they are adsorbed (Korfmacher et al., 1980; Behymer and Hitess, 1988). PAH appear to be more stable when adsorbed on naturally occurring particles such as soot or fly-ash than when present in pure form or in solution or adsorbed on silica gel, alumina or coated on glass surface (Korfmacher et al., 1980). For example, benzo(a)pyrene, pyrene, anthracene are highly resistant to photo-degradation when adsorbed on fly ash but all photolyse efficiently in liquid solution.
However benzo(a)pyrene and anthracene photolyse with high efficiency when adsorbed to activated alumina. Also phenanthrene and fluoranthene are resistant to photo decomposition both in liquid and as adsorbates on fly ash (Korfmacher et al., 1980a).

The physical (colour) and chemical (carbon content) characteristics of the substrate are important in determining the reactivity of the adsorbed PAH (Behymer and Hites 1988). The reactivity of the PAH itself is however more important in determining reactivity than the substrate (Behymer and Hites, 1988). The available PAH on the substrate surface for reaction is also an important variable (Coutant et al., 1988; Albeic- Jureic et al., 1990). The suppression of photochemical degradation of PAH on soot or fly-ash has been tentatively explained by physical factors such as pore structure and colour of the particles, and more strongly by chemical factors involving the stabilising effects of transition metal ions present on the particle surface acting as quenchers of excited states of PAH molecules (Korfmacher et al., 1980; Behymer and Hites, 1988).

Although irradiation appears to play a major role in the degradation of airborne PAH (Valerio and Lazzarotto, 1985; Kamens et al., 1990), light is not necessarily required for the atmospheric decomposition of PAH. Various PAH may also degrade by non-photochemical pathways such as evaporative or oxidative reactions with gaseous pollutants (Korfmacher et al., 1981). Korfmacher et al. (1981) found that Fluorene and benzo(a/b)fluorene underwent oxidation without the presence of light. The non-photochemical degradation of PAH is of particular importance only because some PAH would be expected to decompose in the atmosphere without sunlight, but also that certain PAH compounds can be expected to degrade during sampling and storage in the absence of light (Korfmacher et al., 1981).
1.5.3. Thermal Degradation of PAHs

Observation of non-photochemical degradation of several PAHs implies that chemical transformation of adsorbed PAHs in the atmosphere may be determined largely by the rate of possible thermal reaction with photochemistry playing minor roles (Korfmacher et al., 1980). Authors have noted that several PAHs decomposed to a significant extent when vapour adsorbed on coal fly ash but not exposed to light. These results are significant for two reasons, firstly they indicate some PAHs adsorbed in fly ash would be expected to decompose in atmosphere even in the absence of sunlight, secondly during the sampling and storage process the PAHs would be expected to continue to decompose slowly even if protected from light (Korfmacher et al., 1981). A majority of the decomposition appears to occur during the adsorption implying that decomposition at elevated adsorption temperature is significantly faster than at room temperature (simulation studies) (Korfmacher et al., 1981).

1.5.4. Reaction of PAHs with Ozone

A number of experimental studies have shown that PAH can react readily with $O_3$ at ambient concentration (Brorstrom et al., 1983; Peters and Seifert 1980; Alebic-Juretic et al., 1990). Alebic-Juretic et al. (1990) identified quinones and epoxides as possible products of such reactions. The kinetics of the dark reaction of several PAH towards $O_3$ has been shown to be extremely fast under simulated atmospheric conditions. Lane and Katz (1977) reported a half-life of 0.62 hr for BaP exposed to an $O_3$ level of 190 ppb, irradiation appearing not to affect this reactivity significantly. Peters and Seifert (1980) investigated the effect of $O_3$ concentration on the loss of BaP under high volume sampling. They found the lifetime of BaP to be inversely
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correlated with the ambient $O_3$ concentration. The reaction of PAH adsorbed on diesel particulate with ppm levels of $O_3$ was investigated by Van Vaeck and Van Cauwenberghe (1984).

BaP and BaA were found to be the most reactive PAH investigated, with conversion yields of 60 and 50%, respectively. Pitts et al. (1986) demonstrated that five PAH, found at ng/m³ levels in ambient particulate organic matter, reacted with ozone in the range 50 to 300ppb, regardless of the relative humidity of the simulated system. These results implied that significant degradation of PAH might take place in $O_3$ polluted atmospheres; such as the Los Angeles air basin where ambient ozone levels of 200ppb are quite often exceeded at downwind smog receptors. Grosjean et al. (1983b) have however questioned the environmental relevance of PAH reactions with $O_3$ and other atmospheric pollutants. BaP, perylene and 1-nitropyrene showed no significant degradation when exposed to 100ppb of $O_3$ at 50% relative humidity (Coutant at al., 1988; De Raat at al., 1990).

1.5.5. Reaction of PAHs with NOx

Chemical reactions of PAH with NOx are particularly important since these compounds are usually emitted simultaneously with PAH from combustion sources (Pitts et al., 1978; Saik et al., 1985) and may result in the conversion of non-carcinogenic PAH to mutagenic nitro-PAH compounds (Pitts et al., 1985 a, b). The rate of reaction was found to be highly dependent upon the chemical structure of the individual PAH and the nature of the substrate on which the PAH are adsorbed (Nielsen et al., 1983). In addition, the reactions were facilitated by the acidity of the surface, particularly the presence of nitric acid (Nielsen, 1984; Grosjean et al., 1983b). Difference in the reactivity of individual PAH towards nitrating agents appeared to be
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generally in agreement with the order expected for electrophilic nitro substitution of aromatic systems (Nielsen, 1984; Butler and Crossley, 1981). There is a great deal of evidence for atmospheric nitration of PAH, the occurrence of nitro-PAH in samples collected in the atmosphere might however also be the result of artefact formation during the high volume sampling. A number of authors do however indicate the production of nitroarenes from the atmospheric reaction of PAH (Atkinson et al., 1985a; Pitts et al., 1985a, b; Arey et al., 1988; Sweetman et al., 1986). Pitts et al. (1987) report the atmospheric presence of 2-nitrofluoranthene (2-NO$_2$-FL) and 2-nitropyrene (2-NO$_2$-PYR). Atkinson et al (1987) indicate that BaP reacts with NO$_2$ to form nitro derivatives (6-nitrobenzo(a)pyrene; 1- nitro and 3- nitrobenzo(a)pyrene) which are direct mutagens according to Ames test. The nitration of BaP by ppm levels of NO$_2$ in air is catalysed by ppb levels of HNO$_3$. Although perylene is non-mutagenic, 3-nitroperylene was found to be a directly active mutagen (Pitts et al., 1978). The amount of nitrated PAHs present in urban atmosphere is most probably low, but is of great importance in air pollution questions because 1) they are or can be reduced to carcinogenic compounds and 2) if adsorbed on solid carriers, they may become highly concentrated locally whenever aerosol particles combine themselves with suitable adsorbates.

Atkinson et al. (1987) indicates that 2-nitrofluoranthene and 2-nitropyrene are not emitted from combustion sources, although Liberti and Coccioli (1986) report the production of both the compounds from the manufacture of carbon electrodes. The nitration of PAH can be initiated by homogeneous gas phase reaction with OH (at the site of highest electron density) followed by NO$_2$ addition and the loss of H$_2$O. The product nitro-PAH then condenses on the surface of the ambient particles (Pitts et al.,
1985a). Nitro-PAH may also be produced by the reaction of PAH with dinitrogen pentoxide ($N_2O_5$) (Pitts et al., 1985b; Kamens et al., 1990). The latter reaction is however believed to be of less significance with estimates of PAH lifetimes in the order of weeks compared to that of hours for reaction with OH (Pitts et al., 1987; Atkinson et al., 1987).

1.5.6. Reaction of PAHs with SOx

Atmospheric degradation of PAH may also occur by reaction with SOx or their acid derivatives, particularly in aerosols or when adsorbed on particles. It is uncertain whether PAH react with SOx in the atmosphere, even at a very much higher concentration than normally found in ambient air (Nielsen et al., 1983; Lienster and Evans, 1986). Little is known about the products from the reactions of PAH with SOx in environmental samples. PAH related sulphonic acids have been found in laboratory experiments, but no evidence is yet available for their presence as atmospheric particulates. One of the reasons for this may be that the sulfonic acids are water-soluble and hence they may not appear in organic solvent extracts of the particulate matter (Sortland Olufsen and Bjorseth, 1983).

1.5.7. Deposition and Transport of PAHs

Since PAH in the atmosphere are mostly associated with particulate matter their atmospheric residence time is closely related to the behaviour of the carrier particles (Chaung et al., 1987; Baker and Eisenreich, 1990). The physical removal or transport of airborne particles is a function of particle size and meteorological conditions. It has been established that both coarse particles (larger than 3 to 5μm) and nuclei range particles (below 0.1μm) are similarly limited in their atmospheric residence times and
consequently in their effects although their removal mechanisms are different. The former tend to be removed from the atmosphere by simple sedimentation, such as dry or wet deposition, while the latter are removed predominately by coagulation with each other and or larger particles (Whitby and Sverdrup, 1980). Particles in the size range between 0.1 and 3μm with which airborne PAH are predominately associated are known to diffuse only slowly and have little inertia and can be expected to remain airborne for a few days or longer (Lodge et al., 1981). Particles of this size class are not removed efficiently by rain ad may be transferred over long distance dependent upon atmospheric conditions (Grover et al., 1977).

The presence of PAH in precipitation appears to be the result of both in-cloud and below cloud scavenging of atmospheric PAH (Georgii and Scmitt, 1982; Van Noort and Wondergem, 1985). In general PAH concentration in precipitation were found to be higher in winter than in summer, reflecting seasonal variation of the atmospheric levels. In addition snowfall appears to be a more effective sink for PAH than rainfall (Gerogii and Schmitt, 1982). PAH in the gas phase enters the rain through gas water partitioning mainly below cloud scavenging whereas those associated with particles are more efficiently removed within clouds as a result of diffusion, impaction and interception (Van Noort and Wondergem, 1985; Ligocki et al., 1985; Masclet et al., 1986; Tuominen et al., 1988). Gas phase PAH are however prone to re-volatalise once deposited, especially from water bodies (Baker and Eisenreich, 1990; McVeety and Hites, 1988). Masclet et al. (1986) report that wet scavenging can remove upto 60% of PAH concentration during precipitation events.

Dry deposition can be classified into three mechanisms, diffusion, impaction and sedimentation. Estimates of concentration fluxes to wet and particularly dry deposition are however uncertain mainly due to the number
of chemical and physical variables involved (Behymer and Hites, 1988). For PAHs in particle phase the removal rates are a function of the physical parameters of the carrier particle, of which particle size is the most important (Masclet et al., 1988, Valerio et al., 1984; Van Jaarsveld et al., 1997); e.g. mean dry deposition velocity for particle class with median aerodynamically diameter of $0.2 \mu m$ was calculated to be $0.000065 \mu m/sec$ while for the particles with diameter of $40 \mu m$ - $0.067 \mu m/sec$ (Van Jaarsveld et al., 1997). Higher molecular weight PAHs, like BaP, are supposed to be emitted with substantial fraction on large particle (Van Jaarsveld et al., 1997).

The association of PAH with the fine fraction of airborne particulate matter is of importance in terms of their persistence in the atmosphere where they can undergo chemical reactions as well as be transported over long distances. Lunde and Bjørseth (1977) identified 20 different PAH in aerosol sample with different trajectories collected in southern Norway. High levels of PAH were generally associated with trajectories collected from the European continent and the UK (Daisey and Lioy, 1981). The occurrence of some PAH in remote pristine areas such as the Arctic and marine atmosphere was explained mainly by aerial transport from distant anthropogenic sources (Marty et al., 1984; Mcveety and Hites, 1988). The similarity of sediment and air PAH profiles as well as ubiquitous occurrence lead to the conclusion that the transport of PAH is extensive (McVeety and Hites, 1988; Freeman and Cattell, 1990). PAH will however be depleted by reaction during transport prior to deposition (Masclet et al., 1986).