2. REVIEW OF LITERATURE

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Historical background:

Polycyclic aromatic hydrocarbons are a group of compounds composed of two or more fused aromatic (benzene) rings. They are found throughout the environment in water, air and soil. These PAH originate from both anthropogenic sources (mainly incomplete combustion processes) and natural sources (volcanoes, forest fires, etc.). Since some of these multi-ring compounds have been found to be carcinogenic, there is increasing concern about their presence and their occupational and environmental health impacts. While extensive experimental animal studies are being pursued by many research groups, the carcinogenicity of some PAHs, particularly benzo pyrene, has been clearly established.

The suspicion of some aromatic hydrocarbons causing cancer is about 100 years old. Thus, in the late 19th century unusually high rates of skin cancer were reported for workers in paraffin refinery, shale oil and coal tar industries (Phillips, 1983).

Passey in 1922, discovered the occupational hazard of coal tar. The organic extracts of this coal tar soot proved to be carcinogenic to experimental animals. The tumorogenic nature of the PAH derivatives was shown in 1930, by Kenaway and Heiger. Benzo (a) pyrene was identified by Cook, et al. and branded as a carcinogen in the year 1933. In 1949 Benzo
(a) pyrene was identified in domestic soot by Goulden and Tipler while in 1952 it was reported by Waller that BaP was found in the extracts of ambient particulates collected in Great Britain.

Sawicki, et al (1965, 1967), identified the PAH associated compounds like nitrogen analogues, the aza-arenes etc. which were identified in motor vehicle exhaust, smoke from residential wood combustion, and from coal fired electric generating plants.

In 1971, the World Health Organisation recommended that the total concentration of six specific PAH should not exceed 200 ng/l for domestic drinking water. The six specified PAH are fluoranthene, benzo (b) fluoranthene, benzo (k) fluoranthene, benzo (a) pyrene, benzo (ghi) perylene and indeno (1,2,3 - cd) pyrene, which were subsequently known as "WHO SIX" (Kieth & Telliard, 1979).

It was observed by Tokiwa, et al, 1976 that organic extracts of fine particles collected from ambient air contained not only the expected promutagens such as BaP, but direct acting mutagens and subsequently extracts of respirable particles collected from primary combustion sources, such as diesel engines (Huisingsh, et al, 1979) coal fired power plants (Chrisp, et al, 1978) and wood burning stoves (Lofroth, 1978;
Rudling, et al, 1982) were also found to contain large quantity of particulate matter which are carcinogenic in nature.

**OCCURRENCE:**

Until the mid sixties the evidence available seemed to indicate that PAH are formed only in high temperature pyrolytic processes involving compounds of carbon and hydrogen. Since then, however a number of investigations have suggested the endogenic formation of PAH in plants and microorganisms. The PAH originating from man-induced and or man controlled combustion processes are, quantitatively, by far the most significant and more easily accountable. Their sources consists of various industrial processes, including coke production in iron and steel industry and catalytic cracking in petroleum industry, carbon black, coal tar pitch, asphalt hot road mix processes, general chemical processes, as well as heating and power generation, controlled refuse incineration, open burning and internal combustion engines used for various means of transportation.

However, it is the natural sources which provide the natural background concentration of PAH in our environment. The bio-synthesis of Benzo (a) pyrene and a variety of other PAH has been demonstrated in plants, wheat and rye seedlings, bacterial like Clostridium putrifice and Escherichia coli, and
in fresh water algae like Chlorella vulgaris. More over carcinogenic PAH have been extracted from large variety of fresh plants, including root and leaf vegetables, fruits, grains and edible mushrooms, where they appear to be concentrated mainly in active tissues. Pytoplankton and marine organism also contain this PAH compounds (Suess, 1975).

The concentration of PAH in surface water is due to the domestic wastes and industrial effluents, urban and river runoff, transportation. The petroleum hydrocarbons entering the oceans is a major contributor for the PAH in marine waters and marine sediments.

The concentrations of PAH have been detected in waste water, in many instances. Domestic effluents have higher PAH concentrations than factory effluents. The PAH levels in domestic sewage increase during periods of heavy rain, due to increased runoff, primarily from high ways.

The concentration of PAH in the upper layers of earth is in the range of 100-1000 μg/kg. This results from the activity of soil bacteria and from decayed plants. This PAH occurs in water, air, soil (Pucknat, 1981)

There are about 500 types of PAH compounds which have been identified. The PAH observed in the atmosphere range from bi cyclic species such as naphthalene, present largely
in gas phase, to PAH containing seven or more fused rings such as coronene which are present, solely adsorbed on particles (NAS, 1983). The importance of studying the PAH adsorbed on suspended particles results from the fact that the majority of PAH are in particle form (70-90%) and that the PAH are found on the particles in the range of less than 5 μm that is in the respirable fraction (Nikolaou, et al., 1984).

The various important sources of PAH are as follows:

**Natural Sources:**
1. Forest fires (NAS, 1972; Youngblood and Blumer, 1975).

**Anthropogenic Sources:**
1. Industrial emissions.
2. Emissions from working environment.
3. Domestic heating emissions.
4. Refuse burning emissions.
5. Tobacco smoking.
6. Automobile emission.

The main contribution from anthropogenic sources with special reference to automobile exhaust is given later.

**CHEMISTRY FORMATION OF PAH**

The majority of PAH in the environment is derived during incomplete combustion of organic matter at high temperature.

Several mechanisms have been proposed for the formation of PAH by pyrolysis and pyrosynthesis. In pyrolysis, complex organic molecules are partially cracked to lower molecular weight free radicals. Pyrosynthesis of PAH then proceeds by the rapid combination of free radicals containing one, two or many carbons. Pyrolysis of Styrene-like compounds similar to caffeic acid found in tobacco smoke yields PAH which could be formed from a biphenyl cyclobutane intermediate, which is a dimerization product of Styrene (Schmeltz and Hoffman, 1976).

Cyclic compounds, both saturated and unsaturated are excellent PAH precursors. Schmeltz and Hoffman, 1976, proposed a scheme for the pyrosynthesis of naphthalene and higher molecular weight PAH from benzene. At high temperatures in
the presence of air, benzene is converted to phenol which upon loss of water would be converted to 'benzyne'. The latter, through a 1, 4 addition across benzene, gives rise to benzo bi-cyclo (2, 2,2) octatriene which spontaneously decomposes to acetylene and naphthalene. Similarly, naphthalene could give rise to naphthalynes and ultimately to higher PAH.

Nearly all the air borne PAH produced by flame pyrolysis are associated with particulate fraction produced during combustion. Soot can be thought of as an agglomerate of peri condensed PAH. The fundamental chemical unit of a soot particle is thought to be a C_{150}H_{30} molecule of 61 fused rings or C_{216}H_{36} molecule of 91 fused rings. The highly condensed aromatic system in the particle are essentially inert. PAH of environmental concern are primarily adsorbed on the surface of soot through hydrogen bonding.

The pyrolysis of organic matter produces a variety of polybenzenoid radicals, continued polymerization of these radicals results in soot. Early termination of this polymerization by hydrogen atoms results in enhanced PAH production.

Several factors affects the yield and molecular weight distribution of PAH formed by pyrolysis. These include chemical composition of the fuel, pyrolysis temperature, duration of exposure to elevated temperature, and the presence in
the pyrolysis mixtures of C, H - radical scavengers. Pyrolysis of substances displaying chain branching or unsaturation results in a substantial increase in the production of PAH.

Commins (1969), studied the effects of temperature between 550°C and 1000°C on the pyrosynthesis of 12 PAH from Styrene. Maximum yields of all PAH ranging in molecular weight from naphthalene to coronene were highest at 780°C, decreasing at higher and lower temperatures. A great many domestic and industrial activities results in pyrosynthesis of PAH. Resulting PAH may be released to the environment in airborne particulates or in solid or aqueous by products of pyrolytic process (Neff, 1979).

**Physical & chemical properties of PAH:**

PAH are composed of two or more fused aromatic (benzene) rings. Two aromatic rings are said to be fused when a pair of carbon atoms is shared. The resulting structure is a molecule with all carbon and hydrogen atom lying in a single plane. Naphthalene, which consists of two fused aromatic rings is the lowest molecular weight member. The ultimate fused ring aromatic system is graphite, an allotropic form of elemental carbon. Of primary environmental concern are mobile compounds ranging in molecular weight from naphthalene
to coronene. Within this range is an extremely large number of PAH compounds differing in the number and position of aromatic rings and in the number, chemistry and position of substituents on the basic ring system.

Physical and chemical characteristics of PAH vary in a more or less regular fashion with molecular weight. Resistance to oxidation and reduction tends to decrease with increasing molecular weight. Vapor pressure and aqueous solubility decrease almost logarithmically with increasing molecular weight. As a consequence of these differences, PAH of different molecular weights vary substantially in their behaviour and distribution in the environment and their effects on biological systems.

The low molecular weight PAH (2-3 ring aromatics) have significant acute toxicity to aquatic organisms, whereas the high molecular weight (4-7 ring aromatic) PAH do not. On the other hand, all of the proven PAH carcinogens are in the high molecular weight PAH group.

PAH undergo three types of chemical reactions characteristic of aromatic hydrocarbons—electrophilic substitution, oxidation and reduction. The oxidation and reduction reactions destroy the aromatic character of the affected benzene ring but electrophilic substitution does not. (Neff, 1979).
Carcinogenicity:


PAH are readily adsorbed to very small particles i.e. those particles having a diameter less than 0.04 μ, but are not readily eluted from them. PAH detected in the atmosphere is associated exclusively with particulate matter, especially soot. More than 75% of BaP is associated with particles less than 5 μm in diameter. (Katz & Chan, 1980). Within the limits of 0.01 to 100 μ, a fraction of the mass of an inhaled particulate cloud is deposited in the nose, tracheobronchial and pulmonary compartments.

Iron oxide particulate matter appears to have properties that contribute to cancer production. BaP when attached to iron oxide (Fe₂O₃) particles induced an unexpected high incidence of bronchogenic – carcinomas. Iron oxide has no extremely irritating or toxic effects (Pucknat, 1981).

PAH are highly lipid soluble and readily adsorbed from gastro intestinal tract of mammals. They are rapidly distributed to a wide variety of tissues, with a particular tendency for localisation in body fat. PAH can cross the placenta and may be toxic or carcinogenic to the foetus (Enzminger, Ahlert, 1987).
The metabolism of PAH is via the cytochrome P-450 mediated mixed function oxidase system with oxidation or hydroxylation as the first step. The resultant epoxides or phenols may then go through a detoxification reaction to produce glucuronides, sulphates, or glutathione conjugates. Some of the epoxides, however, may be metabolised to dihydrodiols, which in turn may undergo conjugation to form soluble detoxification products or oxidation to diol-epoxides. These latter compounds are thought to be the ultimate carcinogens in cases where carcinogenicity has been demonstrated. The metabolites of PAH are primarily eliminated in the urine and faeces as water soluble compounds. (Fawell & Haunt, 1988).

PAH can induce the synthesis of enzymes for their own metabolism. This in turn means that the efficiency of metabolism of PAH will increase with continued exposure. However, the effects of various exogenous and endogenous inducers, genetic factors, age, sex and nutritional status, which have been shown to influence these enzyme systems, make it difficult to predict whether the carcinogenicity of PAH will be increased or decreased with time (Loc cit).

ANTHROPOGENIC SOURCES

(i) Industrial emission:

The major direct petroleum industry source of PAH is
the catalytic cracking process by which organic molecules in crude oil are broken down into the higher components used in the manufacture of gasoline, heating oil, aviation fuel. The cracking takes place in the presence of a catalyst, which can become deactivated through deposition of carbon or coke on active sites. It is in the regeneration of the catalyst, through the combustion of coke on the catalyst surface, that Benzo (a) pyrene and other PAH are formed (NAS, 1972).

The coal combustion and conversion are accompanied by the possible production of PAH. PAH are implicated as primary carcinogens in coal derived materials by virtue of their carcinogenicity and common occurrence in coal tar. The experimental carcinogenicity of coal derived materials increases with increasing boiling point and is correlated with process conditions which favor the formation of PAH. The urban and non urban areas further emphasize the importance of coal combustion as a source of atmospheric polycyclic aromatic hydrocarbons. Coal fired power plants contribute relatively little to the natural particulate BaP burden. (Pucknat, 1981).

(ii) Emission from working environment:

Occupational health control in environments containing PAH is a major objective of PAH measurements. The critical parameter is understanding the relationship of PAH exposures to human cancer. The characterization of workplace PAH will
be considered from the viewpoint of mutagenecity and carcinogenicity as well as individual PAH composition and its measurements. (Bjronseth, 1983).

If adequately refined mineral oils, which contain various PAH with four to six or more condensed rings, are used for lubricating the spindles and this oil contaminates the skin and clothing of the operators, this may give rise to the cancer of the hands and arms (Nikolaou, et al, 1984).

Stocks and his co-workers studies PAH and smoke in garages and offices and reported high concentrations of certain PAH compounds found higher than ambient air (Stocks, 1958).

(iii) Domestic heating:

Oil and gas burning units used for institutional and home heating, as well as steam for process heating have been shown to be a source of low PAH emissions.

In the soot from the chimney of a residence heated by oil, the alkylated members of lower molecular weight PAH series predominate, and the unsubstituted hydrocarbons are in the minority. Higher ring number series are present at low concentration or altogether absent. This soot sample reflects compositional features that are characteristic for crude oil and its distillates (Blumer, et al, 1977).
(iv) Refuse burning emissions:

The intentional combustion of solid wastes as a method of disposal as well as accidental or naturally occurring uncontrollable combustion processes, can contribute significantly to overall PAH emissions. The emissions include those resulting from the municipal and commercial incineration of such wastes as those collected from households, businesses and restaurants as well as the burning of municipal and agricultural refuse and scrap automobile parts (NAS, 1972).

(v) Tobacco smoking:

A major source of non industrial indoor PAH pollution is tobacco smoking. Cigarette smoke condensate contains N-PAH (indoles, carbozoles and azaarenes) and O-PAH (Benzo-furans, dibensofurans) in amounts equal to or greater than PAH, (Snook, et al, 1978 a, NAS, 1972). Cellulose acetate and charcoal cellulose acetate filters effectively decreased the PAH levels in the smoke (Severson, et al, 1976 b).

(vi) Automobile emission:

In general the atmospheric levels of polycyclic aromatic hydrocarbons are of higher magnitude in urban areas than in rural areas. The main part of the carcinogenic poly-nuclear aromatic hydrocarbons in air has been associated with particles. In areas close to congested roads and streets,
automobile emissions can be a dominant source (Candeli, et al, 1974).

The diesel engines produce 30 - 100 times more particulate matter than equivalently sized spark ignition engines, and this particulate matter is composed primarily of carbon. Diesel particulate extracts contain aliphatic hydrocarbons, polycyclic aromatic hydrocarbons, oxygenated polycyclic aromatic hydrocarbons and few oxygen and sulfur heterocyclic and nitro PAH. Oxy-PAH have not been reported in spark-ignition engines. The diesel particulate concentrations are 3-4 times higher than spark engine particulate concentrations. Although diesel engines produce, on average 0.5 g of particulates/mile the spark-ignition engines produce only 0.0008 g of particulates per mile. (Behymer, et al, 1984).

The research on automotive polynuclear aromatic hydrocarbons emissions has established that these emissions are influenced greatly by many factors including fuel composition and operating conditions of the engine; with fuel-rich operation particularly favouring high PAH emissions. It appears that PAH occurs in exhaust due to following two mechanisms.

1. Survival of small amounts of PAH present in the fuel or lubricating oil.
2. Synthesis of PAH from light hydrocarbons and hydrocarbon fragments.
Survival of PAH in an engine occur at the flame quench zones near the surfaces of combustion chamber. PAH synthesis presumably involves bimolecular and higher order reactions of hydrocarbon fragments to form large compounds. Such chemical reactions would be expected to occur only in regions which are rich in hydrocarbons such as at the surface of the combustion chamber. The both PAH survival and PAH synthesis could take place at the walls and in deposits of the combustion chamber. Advancing the spark timing also caused an immediate increase in the PAH emitted in the exhaust of the vehicle (Laity, et al, 1973).

The fuel aromatic content was found to influence particle bonded PAH emission. The type of fuel aromatic fraction was found to have a strong influence on the particle bonded PAH emission rate and profile. (Candeli, et al, 1974).

The lubricants influence particle - bonded PAH emissions mainly because of their PAH content and consumption rate. The unused lubricant is found to be almost without PAH and lubricant PAH is found to increase linearly with time of use. This causes particle - bonded PAH emissions to increase significantly. (Pedersen, et al, 1980).

The PAH have not been detected in new crankcase oils;
however, the concentrations of PAH compounds increased rapidly with usage in the gasoline engine of an automobile.

The PAH distributions have been found to be dominated by alkylated two and three ring compounds which were detected in the oil after the automobile had been driven a little distance (212 miles). Four - ring compounds were measurable after three weeks of driving (728 miles). The concentrations of four - ring compounds were generally higher in oils that were used longer. Benzo (a) pyrene was only detectable in oil that was used for long distances (5817 miles). These PAH compounds are produced due to incomplete combustion (Pruell & Quinn, 1988; Pasquini & Nononarea, 1983).

The addition of anit-knock lead to gasoline had variable effects on PAH emission. The world wide trend to reduce lead addition to gasoline in order to reduce lead emission to the atmosphere is likely to have the effect of increasing the content of aromatic hydrocarbons, in order to maintain the knock resistance of the fuel; a number of investigations have shown that this leads to increased PAH emission. (Newhall, et al, 1973; Begeman and Colucci, 1970; Zaghini, et al, 1973).

Air: fuel ratio and engine load also effects the PAH emission to a great extent. The PAH particulates profile varies with the air : fuel ratio. The higher PAH constitute
a larger fraction of the PAH formed during combustion as the air : fuel ratio increases (Commins, 1969). Generally, the particle bonded PAH emissions varied with air:fuel ratio in a manner similar to that of particulate matter; this gave high emission rates at very rich and very lean mixtures (Pedersen, et al, 1980).

The increased engine load promotes PAH formation more than particle formation. (Pedersen et al, 1980). The lubricant concentration in the upper cylinder increases and the heavy lubricant molecules provide convenient intermediates for PAH formation (NAS, 1972). The PAH emissions from automobiles are closely related to the car age i.e. car mileage. (Handa, et al, 1979. a.). The emission rates of gasoline and diesel automobiles are similar and they are six times higher with cold starts. The emission of diesel engines are higher than those of gasoline when a warm engine is started (Williams & Swarin, 1979). The emission of PAH increases with the increase of car speed.

The carcinogenic PAH is also associated with highway traffic, coal tar based road asphalt, tyre particles, lubricants, asbestos and components of automobile exhaust (Blumer, et al, 1977). These are some of the factors affecting the PAH emission from automobiles.

The naphthalenes observed in what is certainly the best
characterized combustion emission, namely diesel POM, have been expected from electrophilic nitration of PAH. Presumably being formed after the combustion process but before extensive dilution after emission occurs. (Schustzlo, 1983, Kittelson, et al, 1985).

The specific isomers and the relative abundance of the nitroarenes present in diesel POM can be rationalized on the basis of the abundance of the parent PAH and their reactivity towards electrophilic nitration. 1-nitro pyrene is the primary nitroarene observed in diesel POM, together with much lower amounts of 3 and 8-nitro fluoranthenes. (Paputapeck, et al, 1983; Liberti and Cicciolio, 1986; Robbat, et al, 1986 b; Gibson, 1982, Nishioka, et al, 1982).

Most of the research work has been carried out on the PAH derivatives like Nitro-PAH, Oxygenated PAH in diesel particulate matter. By using high-resolution gas chromatography, high resolution mass spectrometry and high performance liquid chromatography various derivatives of PAH have been identified in diesel exhaust, viz., hydroxy, ketone, quinone, carbonyl, aldehyde, acid anhydride, dihydroxy derivatives of PAH. There are about 60 poly cyclic aromatic ketones present in diesel exhaust (Ramdahl, 1983 b).

These PAH derivatives showed significant mutagenicity (Bayona, et al, 1988; Henderson, et al, 1984; Choudhury, 1982).
Polynuclear aromatic hydrocarbons are emitted into the environment by these diverse sources.

THE FATE OF PAH IN THE ENVIRONMENT:

The degradation of PAH in the atmosphere by photodegradation and by reactions with nitrogen and sulfur-oxides will also continue to some extent when they have to settle back on earth and water faces, and as long as they are exposed to sunlight. However, some PAH will be degraded by soil bacteria and aquatic organisms. Moreover, some of the aquatic organisms may take up and concentrate PAH before metabolically degrading them, if degradation takes place at all. PAH, while adsorbed on particles or in solution, may eventually reach the bed of the various water bodies and be taken up by bottom organisms, or remain there stable for extremely long periods, in the absence of light and in anaerobic conditions (Suess, 1976).

(i) Fate in water:

In natural stream systems, PAH will be transported to the oceans, decomposed or removed. Removal consists of consumption by biota, adsorption on biological material, or adsorption on suspended or bottom mineral matter. Decomposition depends on biological metabolism or chemical oxidation, whereas physical transport usually occurs in the absence of
the other mechanisms. Transient storage compartments for hydrocarbons include water and organisms, whereas sediments probably constitute the most significant long term storage site. Losses from an aqueous system include evaporation, tidal and riverine flushing and microbiological decomposition (Di Salvo, et al. 1975).

(ii) Fate in soil:

The decomposition of hydrocarbons in soil is by soil micro organisms. The decomposition of saturated, unsaturated alicyclic, aliphatic and aromatic hydrocarbons undergo various types of reactions in soil and in culture of micro organisms: (1) oxidation of terminal carbon atom, (2) Oxidation of C₂ - carbon atom, and (3) dehydrogenation (Meikle, 1972). Microbiological degradation of the aromatic nucleus accomplished with relative ease, resulting in destruction of the ring and leading to the ultimate use of the fragments by the micro organisms as a source of carbon for growth e.g., soil pseudomonas degrade naphthalene in a degradative path way. (Enzlinger and Ahlert, 1987).

(iii) Fate in air:

The PAH observed in the atmosphere, range from gas phase to solid phase. Naphthalene exists virtually 100% in the gas phase, while BaP and other PAH with five and six
rings are predominantly adsorbed on particulate matter. The intermediate PAH are distributed in both phases. However, that their vapor pressures can be significantly reduced by their adsorption on various types of substrates. The concentrations of three or four ring PAH in ambient air or in vehicle exhaust exists either in gas phase or in solid phase.

PAH have strong absorption in ultraviolet radiation at wave lengths 300 - 420 nm (present in solar radiation at ground level) and most are very readily photo oxidized. (NAS, 1972). PAH also reacts with various gas like oxides of nitrogen, ozone and oxides of sulphur.

(iv) Photo chemical degradation:

Polycyclic aromatic hydrocarbons present in atmospheric aerosols is highly susceptible to photo chemical transformation in presence of sunlight. There is ample evidence that most PAH will undergo photo oxidation in solution, as pure solids, and when adsorbed on certain solid substrates such as alumina. It has been inferred that similar processes take place when these compounds are adsorbed on air borne particulates.

The diagramatic representation of the degradation of PAH is given by Valerio, et al, 1984, Fig 2.1.

PAH degrade quickly at moderate ambient temperatures
Fig 21. Fate of PAH in the atmosphere.
when exposed to natural mid day sunlight. (Kamens, et al., 1988). The PAH decay is slower in cool temperatures than at moderate temperatures.

There are two schools of thought concerning the ultimate environmental fate of PAH. One school which we call the "fast school" says that PAH degrade quickly in the atmosphere. Some laboratory studies have found that PAH degrade with lifetime as short as a few hours. The other school, which we call the "slow school" says that PAH degrade slowly, if at all in the atmosphere and eventually deposit on soil or water. This idea is supported by studies of marine and lacustrine sediments the ultimate environmental sinks of PAH. (Behmér and Hites, 1988).

When PAH solution is exposed to 300 W mercury lamps, a series of compounds have been identified. They are 5-phenoxy 3, 4 - BaP, along with series of quinones of BaP. These are relatively stable compounds.

Photo oxidation involves energy transfer from the triplet stage of the aromatic compound, yielding singlet oxygen which reacts with the compound yielding peroxide. (Foote, 1968). The more water soluble bicyclic and tricyclic PAH are not carcinogenic, but exposure to ultra violet radiation transform some of these chemicals into products that are acutely toxic for a variety of aquatic organisms (Larson, et al., 1977).
The PAH present in urban and suburban atmospheres are primarily associated with aerosol soot particles in the submicron size range. Particles of this size range will have atmospheric life times of weeks rather than hours or days and if, in addition, strong sunlight is absent, then photochemical degradation of these compounds will not occur. Under these conditions long range transport of aerosol becomes feasible without adsorbed material undergoing significant chemical change (Butler and Crossley, 1981). The photo oxidation products of PAH also includes, quinones, epoxides, phenols and dihydrodiols. (Jones, 1982).

(v) Thermal decomposition:

Some PAH adsorbed on fly ash would be expected to decompose in the atmosphere even in the absence of sunlight. During sampling and storage process, these PAH would be expected to decompose slowly even if they are protected from the light.

A major portion of the decomposition appears to occur during adsorption, implying that decomposition at the elevated adsorption temperatures is significantly faster than at room temperature (Korfmacher, et al, 1981).

(vi) Reaction with oxides of Nitrogen:

The particle associated PAH transforms to nitro-PAH
in presence of relatively low concentrations of nitrogen
dioxide and nitric acid. It is reasonable to assume that
transformation of PAH in the environment and during sampling
caused by reaction with nitrogen dioxide and sulfurtrioxide
and/or species derived from these are electrophilic reactions
and that the reactivity scale is relevant for these decompo-
sition reactions. It should be added that reactions of PAH
with NO₂, N₂O₄, HNO₂ and HNO₃ may lead to products other
than nitro-PAH e.g. hydroxy derivatives and quinones. One
should, therefore be cautious when reactivity scale is used
for predicting relative concentration of nitro-PAH in en-

It is possible that prolonged exposure to oxidizing
species would degrade any nitro-PAH compounds. The 9-
nitro anthracene on photolysis forms 9-10-anthraquinone both
in solution. This suggests the fate of nitro-PAH in the
ambient atmospheres, where several quinones, including the
three quinones derived from Benzo (a) pyrene have been iden-
tified. Thus photo oxidation of nitro-derivatives should be
considered as an alternative path way, besides direct oxida-
tion of PAH by Ozone or by sunlight in air for the formation

(vii) Reaction with Ozone:

Ozone reacts readily with PAH. Several modes of reac-
tions have been identified. The half life of BaP has decreased considerably with increasing ozone level (Grosjean, 1983).

The oxidation by sunlight or Ozone will have significance when it is related to the actual oxidation products formed in the atmosphere. The pioneering work by Pitts, (1978) have demonstrated the presence of directly active mutagens such as 4-5 epoxides. Three of the oxidation products are found to be the quinones of BaP. The oxidation rates for BaP seem to depend very much on the surface area of exposure. The actual oxidation rates by sunlight and Ozone can be enhanced by more exposure of BaP when it is in the form of aerosols (Raja Gopalan, et al, 1983; Grosjean, 1983; Coutant, et al, 1988).

(viii) Reaction with oxides of Sulphur:

PAH react readily with sulfuric acid at room temperature to form polycyclic aromatic sulfonic acids. These sulfonic acids along with other sulfur containing products were obtained, when BaP and pyrenes are exposed to sulphur dioxide. At lower sulphur dioxide concentration more relevant to atmospheric plume conditions, PAH do not appear to react with sulphur dioxide (Butler & Crossley, 1981; Grosjean, 1983).

METHODOLOGICAL FACTORS AFFECTING PAH CONCENTRATIONS:

Temperature, humidity and seasonal variation in rain-
fall and sunlight affects the PAH concentrations in the atmosphere to a great extent.

(i) **Temperature**:

The PAH decay depends on the temperatures. The coolest temperatures have exhibited the slowest rates of PAH decay. During day time at higher temperatures higher amount of loss of PAH has been reported (Kamens, et al, 1986).

**Particle heating**: Fiocco and co workers (1978) showed particle heating in the atmosphere, based on analysis on the energy balance for a given particle, which was taken from the sum of -

1. absorbed energy from incoming radiation,
2. absorbed energy from the earth's surface infrared radiation,
3. energy exchanged through collisions with surrounding gas molecules and
4. re radiated energy from the particle.

Their computations predicted that the maximum mid day values for the temperature difference between particles and ambient air were smaller than 0.01 k at altitudes below 10 km. Hence particle heating and subsequent vaporization losses of PAH are not consequential (Kamens, et al, 1986).
(ii) **Humidity:**

Lower water vapor concentrations have also been associated with lower rates of PAH decay. (Kamens, et al, 1986, 1988).

(iii) **Sunlight:**

The rate of loss in the presence of sunlight for a given PAH may also differ from substrata to substrata.

Slow rates of decay for PAH adsorbed on air borne particles, carbon particles, and very rapid decays on wood soot, gasoline soot silica particles have been observed (Saucy et al, 1986; Kamens, et al, 1985 b). PAH decay rate is directly proportional to the absorbed light energy or solar intensity. (Muel & Sagun, 1985).

(iv) **Rainfall:**

The distribution of PAH, released into atmosphere, as a consequence of human activities, is transport by air or clouds, and either dry fallout or wet deposition by rain. Maximum amounts and concentrations of PAH were reached during the winter period, mainly due to household heating. Rain plays an important role in transport and distribution of pollutants over a wide area. (Quaghebeur, et al, 1983; Paul, 1985).
(v) **Seasonal variation:**

The PAH levels were generally higher in winter periods when compared to summer seasons, although higher ratios were observed for volatile PAH and highly reactive PAHs. The atmospheric reactivity of PAH establishes a characteristic equilibrium profile. In light of the fact that one would anticipate the summer atmosphere to be much more chemically active than winter atmosphere, (Greenberg, et al, 1985; Chakraborti, et al, 1980; Harkov, et al, 1984).

(vi) **Long range transport of PAH:**

PAH are exclusively of anthropogenic origin and constitute one of the principal families of organic compounds present in trace amounts in all media: water, air and soil. The lifetime of these compounds can range from a few hours to several weeks. Many measurements have been taken in the urban areas of industrialized countries, showing that the relative PAH abundance, described by the characteristic profile, differs little from one town to another if the type of industry is similar. This is true at least for European towns, as significant differences are noted for American towns because different combustibles are used, especially for cars. (Cretney, et al, 1985).

When the concentrations are measured in a zone which is not polluted by a nearby source, it is possible to deter-
mine, from characteristic ratios, the age of the contamination of air mass and eventually the source zone (Masclet, et al, 1986 a).

The concentration ratio between the tracer and non tracer PAH gives information about the origin of the air mass and therefore about the source area, while the ratio between reactive and non reactive PAH indicates the transport time between the source area and the receptor site. The latter ratio diminishes with the age of air mass, since the concentration of the reactive species decreases much more quickly than that of the non reactive species (Masclet, et al, 1988; Masclet, et al, 1986).

The total PAH concentrations are also very informative. The total amount of PAH is hardly affected by very reactive species since at emission the non reactive species are already the most abundant. There is a direct correlation between concentrations measured far from the source and at source itself (Masclet, et al, 1988).

Bjorseth, et al. (1978, 1983) considered the transport PAH containing aerosols and showed that PAH originating in Great Britain could be collected, in winter, in far away Norway and Sweden. These studies were essentially qualitative but demonstrated clearly that PAH can be transported over long distances. This result seems to indicate
the life times of all PAH are long (> 1 day).

The PAH gas/particle phase distribution varies with seasons and depends more on the variations of the emissions than on the meteorological variations. Local rain and precipitation produces scavenging of particles and the concentration of particulate PAH decreases, increasing the gas particle ratio. Rain has no effect on the gaseous PAH concentrations. The most reactive PAH compounds disappear almost completely during prolonged transport across a non polluted zone; this depletion is undoubtedly due to photochemical degradation during the day, probably by OH radical. (Ligocki, et al, 1985; Masclet, et al, 1988).

**SAMPLING OF PAH:**

The collection of suspended particulate matter and vapor phase PAH compounds has been performed most frequently by active sampling methods in which collection takes place on a filter. Solid sorbents or impregnated filters have been used behind the filter to capture vapor phase material. (Davis, et al, 1987).

Active sampling methods that relay on integration of the sample, requires pumping the air stream through a medium filter or sorbents which will retain the target compounds. In general, sampling rates in the range 300-1500 l/min are
designated as high volume sampler and for lower flow rates up to 300 l/min as low volume sampler (Davis, et al, 1987).

An ultra high volume sampler operates at 18000 l/min with an inlet allowing only particles less than 20 μm aerodynamic diameter. Four identical Teflon coated glass fibre filters are used simultaneously and the linear face velocity is typically four times that of normal high volume sampler. (Fitz, 1983).

In addition, readily available vacuum pumps are also used. The usual flow rates in these samplers are 1-3 l/min. through filter holders or cassettes housing 37 mm or 47 mm filters. For particle size measurement in which particles are fractionated into specific size ranges based on aerodynamic particle diameters, cascade impactors designed as addition to high vol samplers. The separate units typically employ flow rates in the range of 30 - 90 l/min. (Handa, et al, 1980).

Impregnated filters, impingers, solid sorbents and cryogenic traps are used to collect vapor phase PAH. The adsorption media includes charcoal, Tenax or polyurethane foam, and XAD-2 Resin. These can be used for collection of gas phase PAH. (Chuang, et al, 1987).

(i) Choice of Filters:

Several types of filter material have been used to
collect PAH and other organics. Two types of filters - glass fibre and silver membrane have been utilized most often in the sampling of airborne PAH with high volume sampler and low volume samplers.

There are five types of filters -
(1) glass fibre (Gelman A),
(2) Silica quartz,
(3) Micro glass fibre with Teflon binder on fibres,
(4) Teflon membrane bonded to poly ethylene net and
(5) Teflon membrane supported by Teflon fibres (Lee, 1980).

Glass fibre filter are comparatively insensitive to changes in relative humidity. The collection efficiency is 100%.

(ii) Exhaust sampling:

To obtain a representative sample of exhaust gases from vehicles operating on the road under normal traffic conditions, Smith described a proportional sampler in which a laminar flow meter was used to measure the air intake to the engine and similar matter was used to monitor the sample flow of exhaust gases extracted from the exhaust system which was controlled with motorised valve. (Smith, 1964).

The PAH compounds are collected from the total raw exhaust gas generated during a test run. In order to provide a
good efficiency the sampling is done in two steps. In the first one the exhaust gas is condensed using a glass heat exchanger. The second step involves the collection on a special micron filter of impregnated fibre glass material at the top of the cooling system. After the test the sampling system is cleaned up by employing a distillation with acetone (Kraft, et al, 1981).

Constant volume sampler was also used for exhaust sampling. This was achieved by attaching a miniature constant volume sampler to one tube of a flow splitter which was attached to the tail pipe of the engine exhaust system (Pott, 1987).

Vehicle emissions are important source of polycyclic aromatic hydrocarbons. The test was done in a cold chamber of high cooling capacity capable of absorbing the heat loses from test engine down to temperature - 30°C. The particulate filter was situated in exhaust line below the test chamber after the heat exchanger and the gas flow meter. The average temperature of the exhaust gas in the filter was between 18°C and 20°C.

The test engine was a carburetted automotive gasoline engine and was loaded with a computer controlled dynamometer. After a cold start and an idle period of 20 sec., the
load cycle was repeated six times to give a total test time of 30 minutes. Gasoline exhaust particulate samples were gathered on glass fibre filters. (Tuominen, et al, 1987).

These particulates are collected either on Teflon coated glass fibre filter paper or glass fibre filter papers (2 μm porosity) (Ming - Li Yu and Hites, 1981; Vanvaek & Vandevenberghe, 1984; Behymer, et al, 1984).

**EXTRACTION OF PAH FROM FILTER MEDIA**

The filter material is extracted in a soxhlet apparatus for 10-12 hours. A variety of solvents have been used for extraction of PAHs from filtered particulate matter, including, cyclohexane, methanol, methylene chloride, tetrahydrofuran, chloroform, pentane, acetone, dichloromethane and benzene.

Acetone, dichloromethane and benzene were efficient in extracting mutagenic components from particulate matter by soxhlet extraction. Of all these solvents Benzene is found to be best for extraction of the PAH in particulate matter. (De Raat, et al, 1987; Bozicevig, et al, 1987; Lazaridis and Lofroth, 1987; Viras, et al, 1987; Ang, et al, 1986).

Normally it was found 12 hrs extraction time with solvent cycling rate of 2-4 cycles/hr is able to extract on an average of more than 85% to 90% of PAH. The concentration of the sample is done by Buchi rotavapor. The concentrated samples
are used for analysis.

The modern method of extraction is to use ultrasonic and mechanical stirring in the extraction of PAHs from particulate matter. This has also been reported for the determination of total PAHs (Miguel & De Andrade, 1988).

**ANALYSIS OF PAH.**

After the recovery of the sample, it is first necessary to determine whether its complexity is amenable to the technique selected for quantitative analysis. High-resolution, high-specificity techniques such as cap-GC-MS can achieve facile analysis of PAHs in relatively gross mixtures of organic species. Low resolution, low specificity techniques, such as liquid chromatography thin layer chromatography, flame ionization detection and u.v. detection, require higher degree of sample clean up and prefraction. Extracts are cleaned up by passage through micro-columns of alumina with hexane eluent. (Readman and Mantoura, 1987).

The resolution of thin layer chromatography is too low to have realistic applicability to measurement of large number of individual PAH in complex environmental mixtures.

Numerous studies of PAHs by TLEC have been undertaken, including the use of silica (Candeli, et al, 1975; Liberti, et al, 1975, Hunter 1975) alumina and cellulose acetate (Tomingas, et al, 1977). Highest resolution has been achie-
ved using two dimensional development of 2:1 alumina - 40% acetylated cellulose (Pierce & Katz, 1975) when the majority of PAH have had recoveries of 85% to 95%. The photo decomposition on large surface areas may lead to quantitation errors. (Jones, 1982).

The most commonly used grade is silica gel for liquid chromatography is 100-200 mesh, the usual sample adsorbent ratio is similar to alumina. The elution of PAH is most commonly accomplished by using benzene (Chakraborty & Long, 1967). The recovery of PAHs from silica gel has been reported to average about 80% (Liberti, et al, 1975).

High performance liquid chromatography is a very powerful separation technique whose application is essential to the separation of very complex mixtures. The most useful detector systems are presently fluorescence, uv and refractive index.

When mixtures of very highly polar species are to be separated, HPLC is the only analytical technique available.

HPLC analysis schemes that achieve separation of benzopyrenes isomers have been described. Using HPLC-sorbpolyamide - 6 - column with various polar solvents, good separations were obtained.

It is necessary to clean up the sample on an aluminium
oxide LC column prior to HPLC procedures to remove anthracene which would interfere with the benzpyrene detection. The uv detector was used for quantification and identification, the method is sensitive for submicrogram quantities. A sensitive HPLC method using a fluorimetric detector for PAH analysis, with a detection limit of 0.01 ng was achieved. (Jones, 1982, Futoma, et al., 1981).

Gas chromatography offers the highest reported resolution of complex PAH mixtures attainable in a single pass. Mass spectrometry presently offers the greatest selectivity for PAHs in complex organic mixtures, although it fails to distinguish between PAH structural isomers. Ms demonstrates excellent sensitivity for PAHs, similar to that exhibited by the fluorescence detection for HPLC. In consequence, GC-MS presently offers the highest resolution selectivity, and sensitivity that is attainable in a single pass for PAHs in complex organic mixture. (Jones, 1982).

Sellstrom, et al, 1987, identified PAH in a complex organic mixture using a gas chromatogram equipped with a DB-5 fused silica capillary column fitted into chemical ionisation source. High purity helium gas was used as a carrier gas,
Methane was used as a reagent gas. With this technique picogram levels could be easily detected. (Bayona, et al, 1987).

UV absorption spectrophotometry is a well-established analytical technique used almost exclusively for quantitative analysis. This technique takes advantage of the fact that aromatic compounds exhibit strong absorption in ultraviolet region (Barttle, et al, 1981). It offers a fast and convenient alternative to other methods, which normally require extensive sample cleanup to avoid or limit interference from other materials during analysis. In contrast, this method requires only a basic column chromatography for cleaning up the sample (Lee, et al, 1988).

**FLUORESCENCE ANALYSES**

In the present study, this method was mainly used.

Fluorescence spectra of solutions of poly cyclic aromatic hydrocarbons used for the identification of such compounds in rather complex mixtures.

A potentially important advantage of fluorescence over UV-visible absorption analysis is the inherent involvement of two wave lengths in the fluorescence process. If two compounds absorb at the same wave lengths but fluoresce at different wave lengths, then an emission spectrum differentiates between them. Like wise, two compounds whose fluorse-
Scence spectra over lap but which absorb at different wave lengths can be distinguished by the corresponding difference in their fluorescence excitation spectra or, more simply, by setting the excitation wave length such that the compound of interest is selectively excited and measuring the emission signal at the wave length of maximum fluorescence.

The probability that a molecule which has been promoted to an excited singlet state will decay back to ground state by fluorescence is termed the fluorescence quantum yield $\Phi_F$. The fluorescence power $F$ produced by a particular molecule is proportional to the rate at which excited states are produced by absorption of light and to the fluorescence quantum yield. Fluorescence methods are capable of detecting much lower concentrations of analyte species than are absorption techniques.

Most PAH are intensely fluorescent. Perhaps the most serious difficulty in quantitative analysis by fluorometry is the tendency for $\Phi_F$ for a given compound to vary as a function of the solvent and in presence of other solutes.

Quenching is defined as any process where in the fluorescence quantum efficiency of a particular compound is decreased by interactions with other constituents of a sample.
The quenching can proceed by both collisional and "long range" processes. Molecular oxygen is a notorious fluorescense quencher of many organic molecules, including most 'PAH' and procedures for quantitative fluorometric analysis of PAH therefore usually include a deoxygenation step. (Wehry, 1983; Bjorseth, 1983).