# CHAPTER II

# LITERATURE REVIEW

## 2.1 Definition of PNAs

*Polycyclic organic compounds* (POCs) comprise a complex class of compounds. The parent homocyclic species, which contain only carbon and hydrogen, are the familiar PAHs. In addition to the PAHs, there are thousands of substitutent PAHs that could have various substitute groups, such as alkyl, amino, chloro, cyano, hydroxy, oxo, or thio groups. Also, there is a wide spectrum of PAH heterocyclic derivatives that contain one or several heteroatoms such as nitrogen, oxygen, or sulfur in the aromatic structure.

Over the past few decades, the family of POCs has been known by various names. Historically, the term "PAHs" has been most widely used because the early interest was devoted to carcinogenic activities of the basic homocyclic system.

Nomenclature problems arise when other groups of POCs, which contain heterocyclic substituents or derivatives, are described. The use of different names by various research groups has often led to confusion. Some investigators have referred to POCs whereas others have preffered the term *polycyclic organic matter* (POM). The term of polynuclear aromatic (PNA) compounds has also been frequently used. (Vo-Dinh,T., 1992)

## 2.2 Main Sources of PNAs Emission (quoted in Rathore,H.S.,1993)

### 2.2.1 Coal- Fired Residential Heating Stoves

The amount of PNA emitted depends on the type of fuel, e.g., nut-size anthracite briquettes, various qualities of coal, as well as on the type of stove used. This has led to the widespread presence of PNA in industrial and ambient atmospheres. For example, 2.2 mg benzo[a]pyrene (BaP) per kilogram, a potent carcinogen, is emitted during the combustion of nut-size anthracite briquettes in a universal continuous burner, whereas 380 mg/kg is emitted from a bottom-firing stove. Additionally, the emission of PNA from the burning of coal or wood for residential space heating is several orders of magnitude greater than that from gas or oil burning.

### 2.2.2 Oil-Fired Residential Heating Units

In contrast to PNA emission from coal-burning stoves, household burners do not depend on the type of oil. An extra light heating oil installation, however, emits < 0.1 μg BaP per kilogram of oil, if the burner dose not produce soot.

### 2.2.3 Coal-Fired Industrial Plants

Most of the fly ash from large firing plants is precipitated in separators, and the final emission of smoke particles is low compared to that from household heating. Urban and highly industrialized environments contain higher levels of PNA than do rural locations. The order of magnitude of the BaP burden has been estimated in several investigations carried out in the US.

### 2.2.4 Forest Fires

During forest fires, PNA are released into the atmosphere. McMahon and Tsoukalas , reported the emission of BaP at 238 to 345 ng/g for wood burned in backing fires and 38 to 97 ng/g for wood burned in heading fires.

### 2.2.5 Volcanic Activity

It has been reported that volcanic activity can also be a source of PNA pollution; however, samples of volcanic ash and of soil and plants in an area near a volcano have not been found to contain more BaP than that occurring in the background.

### 2.2.6. Automobile Traffic

About 150 different PNA have been detected in automobile exhaust, and 73 of these have been identified by comparison of gas chromatography (GC) retention times and mass spectra (MS) with those of authentic samples. Investigations of the influence of motor condition, fuel, and lubricating oil have shown that only the ratio of fuel to air and the temperature of the engine determine the amount of PNA emitted.

### 2.2.7 Cigarette Smoke

The epidemiological evidence implicating cigarette smoking as the major cause of lung cancer is overwhelming. As many as 150 PNA have been detected by means of GC/MS in cigarette smoke, 60 compounds were identified by comparison with authentic samples. Ultraviolet (UV) spectrometric investigation of the separated PNA mixture suggested that several hundred methyl and alkyl derivatives are present in tobacco smoke, in addition to the parent PNA.

The carcinogenic activity of PNAs in this case correlates well with the BaP content, when the smoke condensates are assayed on mouse skin.

The composition of PNA emissions varies with the combustion source. For example, emissions from residential wood combustion contain more acenaphthylene than other PNA(Perwak *et al.* 1982), whereas auto emissions contain more benzo[g,h,i]perylene and pyrene (Santodonato,1981). Phenanthrene was the most abundant and frequently detected PNA in samples of fly ash and bottom ash collected from municipal refuse incinerators in the United States (Shane *et al.* 1990),whereas benzo[g,h,i]perylene was the most abundant and frequently detected PNA in samples of fly ash and bottom ash collected from municipal solid waste incinerators in the United Kingdom(Wild *et al.* 1992). In coal tar pitch emissions, concentrations of phenanthrene and pyrene are 20-80 times greater than concentrations of benzo[g,h,i]perylene (Sawicki 1962).[quote in Draft public comment, 1994]

## 2.3 Physical and Chemical Properties of PNAs

Commonly PNA that are found in ambient air are benzo[a]pyrene, and their nitrogen analogs, aza- and imino arenes. Other related compounds such as carbonyl arenes and dicarbonyl arenes (quinones) are less commonly detected.

Most of the PNA are high melting/high boiling point solids that are very insoluble in water. At 25°C, the available vapor pressures of the pure compounds vary for the individual compounds from $10^{-4}$ torr (3-rings) to $10^{-12}$ torr (7-rings). The PNA are strong absorbers of ultraviolet light of wavelengths from 200 to 400 nm.

Most PNA compounds are associated with suspended particle matter, with a large portion found with particles smaller than 1 μm. However, two- or three- ring compounds may be found partially in the vapor phase. Whether PNA are condensed into discrete particles after cooling or are adsorbed on surfaces of existing particles is still unknown.

Urban aerosols appear to have a residence time without precipitation of 4 to 40 days for particles less than 1 μm in diameter and 0.4 to a days for particles 1 to 10 μm in diameter.Thus, the atmospheric lifetime of a PNA particle will be closely related to its particle size.Atmospheric residence time and transport distance depend on the size of the particles to which PNA are sorbed. Larger particles emitted from urban sources tend to settle onto streets and become part of urban runoff. PNA in urban air are primarily associated with submicron-diameter soot particles that have residence times of weeks and are subject to long-range transport (Butler and Crossley 1981quote in Baek *et al.,*1991)].

The NAS report states that the lifetime of PNA in air depends on the carrier aerosol and on the chemical alteration of the matter itself. In dry atmospheric conditions, residence times of particles < 5 μm in diameter exceed 100 hr, but in the presence of sunlight, chemical reactivity may lead to transition of PNA adsorbed on soot to other material in several hours. (ORNL, 1977 quote in Pucknat,1981)

Chemical and Photochemical reactivities of PNA on particulate matter vary considerably from half-lives of less than a day to several days. Reaction rates of compounds on smaller particle sizes are likely to be faster than those of larger particles. Light irradiation considerably accelerates the reactions of some compounds, but not others. However, monitoring data suggest that at least 20 PNA are stable enough in the form found in the atmosphere that they can travel long distances and times with particulate matter. Although the smaller particles will have a longer atmospheric residence time, they will probably also react faster because of the greater surface area exposure to oxidants and light. (Pucknat,1981)

### 2.4 PNA in Atmosphere

Airborne particulate matter consists of a complex mixture of solid and liquid particles that contain PNA and are emitted to the atmosphere from a variety of sources, such as the products of the combustion of fossil fuels, automotive engine exhausts, and emissions from industrial operations. PNA, which are potently carcinogenic in nature, are liberally spread throughout the environment. For example, BaP is present at low levels, $< 1$ to $100\ \mu g/1000\ m^3$ in air. Due to methodological limitations, air samples are usually analyzed only for BaP content, which is used to indicate the presence of the total PNA in an environmental sample, but not to measure its carcinogenic activity. Numerous measurements show that BaP concentrations in ambient air are considerably highly during winter than during summer.

In extracts of suspended particulate matter, about 130 PNA have been detected by GC and characterized by MS, 56 of these were identified by comparison with authentic samples. Lee *et al.* have characterized 120 PNA by means of GC,MS, and nuclear magnetic resonance (NMR) studies in airborne particulate samples.

### 2.4.1 Levels Monitored or Estimated in the Air (quoted in Draft for Public Comment,1994)

Some data are available that suggest that there are higher concentrations of PNA in urban air than in rural air. Pucknat(1981) summarized 1970 data from the U.S. National Air Surveillance Network and reported that benzo[a] pyrene concentrations in 120 U.S. cities were between 0.2 and 19.3 ng/m$^3$. Ambient benzo[a]pyrene concentrations in nonurban areas ranged between 0.1 and 1.2 ng/m$^3$. Table 2-1 presents the concentration of Mean BaP concentration in various cities. More recently, Greenberge *et al.* (1985)quote in studied PNA levels in New Jersey over two summer and winter seasons and found that urban areas had PNA levels approximately 3-5 times higher than those in a rural site. Geometric mean concentrations of eight PNA(benzo[a] pyrene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]anthracene, indeno[1,2,3,-cd]pyrene, chrysene, benzo[g,h,i]perylene, and pyrene) ranged from 0.15 to 0.62 ng/m$^3$ in urban areas and from 0.02 to 0.12 ng/m$^3$ in rural areas.

Several studies provide evidence that atmospheric PNA levels are higher in the winter than in the summer. Individual PNA concentrations in the Los Angeles atmosphere (1981-1982) ranged from 0.1 to 1.5 ng/m$^3$ (with an average of 0.43 ng/m$^3$ ) during the summer and from 0.4 to 4.5 ng/m$^3$ m$^3$ (with an average of 1.26 ng/m$^3$ ) during the winter(Baek *et al.*1991).

Table 2-1 Comparison of Mean BaP Concentrations (ng/m$^3$) Various Cities

| City | Winter | Summer |
|---|---|---|
| Paris (France)<br>(Coviaux et al., 1980; Masclet te al., Nikolaou et al., 1982; Mouvier et al., 1983) | 2.8-15 | 0.25-1.8 |
| Prague (Czechoslovakia)<br>(Jager, 1980) | 24.0 | 1-7 |
| Los Angeles (U.S.A.)<br>(Colucci and Begeman,1971) | 11.0 | 0.08 |
| Birmingham (U.S.A.)<br>(Sawicki et al., 1962) | 25.0 | 6.4 |
| Sydney (Australia)<br>(Cleary and Sullivan,1965) | 7.7 | 0.8 |
| London (England)<br>(during the 1956 air pollution episode)(Commins and Waller,1967) | 2200 | |
| Ontario (Canada)<br>(during the 1962 air pollution episode)(Moore et al., 1966) | 40-50 | |
| Karlsruhe (W.Germany)<br>(Romanowski,1981) | 1.7 | |

A similar seasonal variation in PNA levels in the Los Angerles atmosphere was seen in an earlier study(1974-1975); individual PNA concentrations ranged from 0.1 to 3.7 ng/m$^3$ during the summer (average of 0.62 ng/m$^3$ ) and from 0.5 to 10.9 ng/m$^3$ (average of 2.09 ng/m$^3$ ) during the winter(Gordon 1976quote in ). Possible factors contributing to these seasonal variations in PNA levels include the following: changes in emission patterns, change in meteorological conditions(i.e., daylight hours and temperature), and changes in space heating emissions, volatilization, and photochemical activity.

In a study that characterized air levels for a variety of PNA, Gordon, (1976 quote in ) reported median ambient levels of individual PNA in Los Angerles ranging from 0.18 ng/m$^3$ for benzo[a]anthracene to 3.27 ng/m$^3$ for benzo[g,h,i]perylene. Most individual PNA had a median concentration of less than 0.6 ng/m$^3$ . The relatively high levels of benzo[g,h,i]perylene were probably related to high levels of automobile emissions, which are known to contain high levels of benzo[g,h,i]perylene relative to other PNA (Santodonato 1981quote in ). During the same time period, Fox and Stanley (1976)quote in reported average concentrations of PNA in the range of 3.2 ng/m$^3$ for benzo[a] pyrene. Reported average ambient levels of individual PNA in Denver range between 0.83 ng/m$^3$ for benzo[k]fluoranthene and 39 ng/m$^3$ for phenanthrene (Freeman and Bidleman 1990). Higher concentrations were reported in the Baltimore Harbor Tunnel where the average concentrations of individual PNA ranged from 66 ng/m$^3$ for benzo[a]pyrene to 120 ng/m$^3$ for pyrene.

## 2.5 Fate of PNAs in Air

In atmospheric particulate matter, a wide variety of parent PNA and alkyl PNAs have been identified, as have many oxygenated PNAs and PNA ketones, nitro PNAs, and aza-arenes.

The emission of PNA s to the atmosphere is of concern, principally because many of the compounds are known carcinogens and/or mutagens. During their migration through the environment, the PNA may be transformed, by interaction with oxidants and sunlight, into products which, in some cases, are much more mutagenic than the compounds from which they were derived.

At 25 °C, the three-ring PNAs were found primarily in the vapor phase, the four- and five-ring PNAs were found distributed between the particle and the vapor phase, and the six- and higher PNAs were found almost exclusively in the particle phase.

### 2.5.1 Physical Reactivity

During the summer months, 6 to 23 % of the total atmospheric PNA were associated with particles having diameter ≤ 1.0 μm, whereas particles having a diameter ≤ 3.0 μm contained 56 to 70 % of the total PNA content.

Pierce and Katz noted that particles having a diameter ≤ 5.0 μm are in the respirable size range, that is, the size range most likely to be deposited in the pulmonary portion of the respiratory tract. DeMaio and Corn (1966) found that aerosol particles < 5.0 μm in diameter contained more than 75 % of the weight of selected PNAs (quoted in Baek *et al.*,1991)

### 2.5.2 Gas Particulate Distribution (quoted in Baek *et al.*,1991)

Pistikopoulos *et al.*,1990 report two particle size distribution families for PNA. One group is associated with particles of less than 1 μm and corresponds to volatile PNA, except fluoranthene. The first group being formed by adsorption, the second by condensation. PNA are present in the atmosphere in the gaseous phase and sorbed to particulates. NRC reported the ratio of particulates to gaseous PNA in air samples collected in Antwerp, Belgium, was 0.03 for anthracene, 0.49 for pyrene. 3.15 for summed benzo[a]anthracene and chrysene, and 11.5 for summed benzo[a]fluoranthene, benzo[b]fluoranthene.

### 2.5.3 Atmospheric Processes

Atmospheric phenomena involving the evolution of PNA can be summarized as follow: (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 reactions, and (iv) exchange between the gaseous and particulate phase by shifting the phase equilibrium ( US National Academy of Sciences 1972 and Masclet *et al.*,1986 quoted in Pucknat, 1981).

### 2.5.4 Chemical and Photochemical Reactions of PNA

#### Singlet Molecular Oxygen

The existence of the oxidation product of numerous PNAs in atmospheric particulate master has been taken to indicate that the PNAs react with oxygen or ozone in the atmosphere.(Vo-Dinh,T.1989)

NAS reported that PNA also react with ozone, peroxides, nitrogen oxides, and sulfur oxides and undergo one- electron oxidation . They react with ozone in one of four ways:

(1) Cleavage of phenanthrene-link double bonds, which results in diacid formation under oxidative conditions;

(2) Oxidation at anthracene-9,10-link positions to yield quinones

(3) A more complex nuclear oxidation; and

(4) A side chain oxidation.

A typical example is the ozonolysis of benz[a]anthracene, BaA, which undergoes cleavage of the phenanthrene-link double bonds to yield a cleavage product, a quinones, and a phthalic acid(Pucknat,1981).

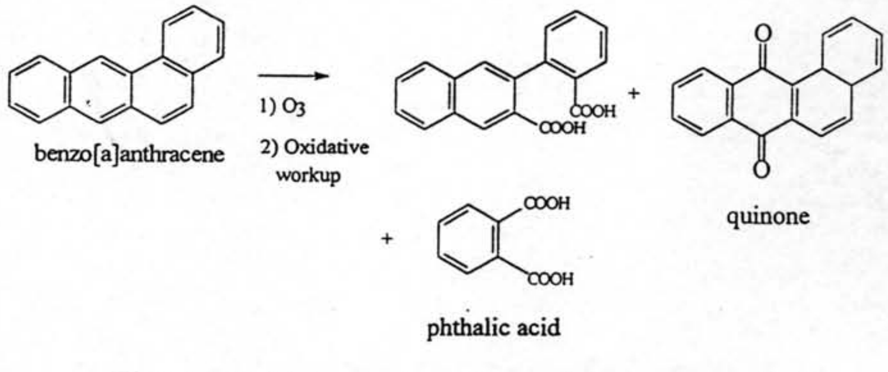

Figure 2-1 Ozonolysis of Benzo[a]anthracene, BaP

OH Radical reactions

The reaction of hydroxyl radicals with organic molecules in the atmosphere during daylight conditions is considered to be the major reaction of these molecules leading to their removal from the atmosphere. (Vo-Dinh,T.1989)

The peroxide reaction involves the interaction of benzoyl peroxide [$(C_6H_5CO_2)_2$] with the PNA, in this case BaP, to yield the 6-benzoyloxy derivatives.

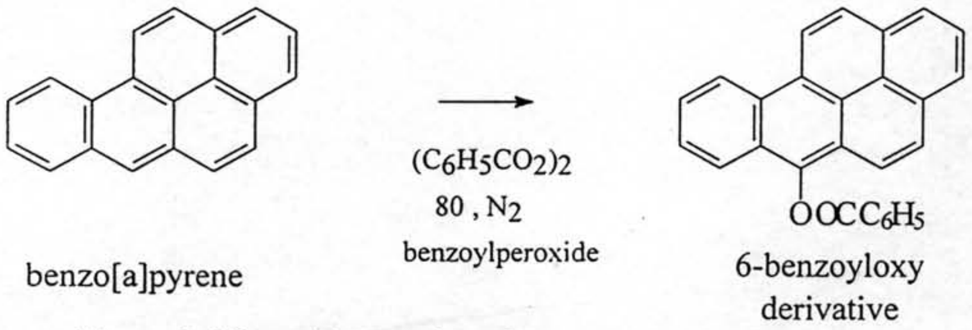

Figure 2-2 Peroxide reaction of Benzo[a]pyrene

In the presence of oxygen, this peroxide reaction could lead to further oxidation (Pucknat,1981).

Reactions with Oxide of Nitrogen and Nitric Acid

The reactions of PNAs with the nitrogen oxide and nitric acid to from the nitro-PNA are of considerable interest because many of the resulting products have been shown to be direct-acting mutagens.(Vo-Dinh,T.1989)

Nitrogen oxides or dilute aqueous $HNO_3$ oxidizes anthracene to anthraquinone(Pucknat,1981) :

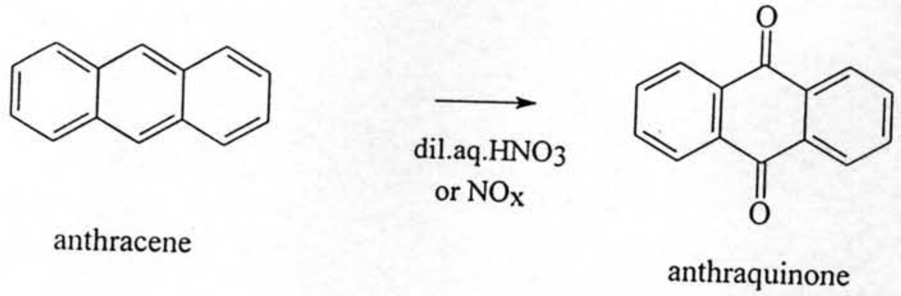

Figure 2-3 Oxidation of Anthracene by $NO_x$ or $NHO_3$

Specifically, the addition and substitution of $NO_2$ in anthracene yields an oxidation product by loss of $HNO_2$ from the intermediate compound (Pucknat,1981):

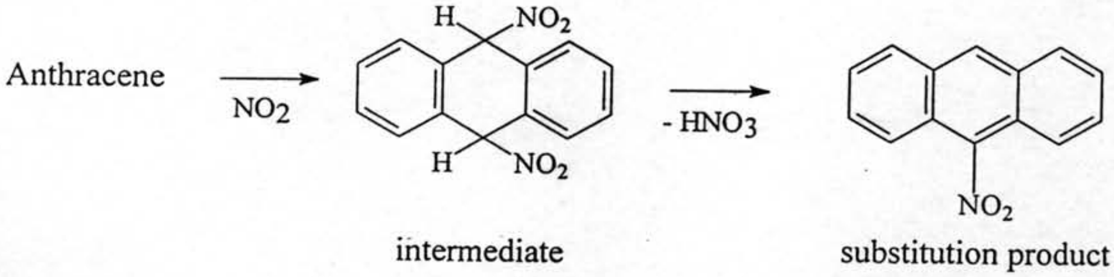

Figure 2-4 Addition and substitution of $NO_2$ in Anthracene

Reaction with Sulphur Oxides

The concentrations of $H_2SO_4$ commonly have found in the atmosphere are sufficient to result in chemical reactions with the PNAs. If such reactions do, in fact, occur, the product would not be detected in the normal extraction procedures used for the PNAs and their derivatives.(Vo-Dinh,T.1989)

PNA also react with sulfur oxides, yielding sulfuric and sulfonic acids as products; these sulfur compounds will no longer appear in the benzene-solution fraction because they are water-soluble. (Pucknat,1981)

Atmospheric suspended particles evolve by the following mechanisms (NAS,1972quote in )(Pucknat,1981) :

(1) Growth or Change in particles by homogeneous or heterogeneous chemical reaction of gases on the surface of particles;

(2) Change in particles by attachment and adsorption of trace gases and vapors to aerosol particles;

(3) Net change by collision between particles undergoing Brownian motion or differential gravitational settling;

(4) Net change by collision between particles in the presence of turbulence in the suspending gases;

(5) Gain or loss in concentration by diffusion or convection from neighboring air volumes;

(6) Loss by gravitational settling;

(7) Removal at the earth's surface on obstacles by impaction, interception, Brownian motion and turbulence diffusion ;

(8) Loss or modification by rainout within clouds; and

(9) Loss by washout below cloud level.

These mechanisms can influence aerosol chemical composition, as a function of size, and can affect the observed size distribution of aerosols.

NAS reported the major mode of PNA removal from the atmosphere is through chemical reactions; for example, photooxidation is probably one of the most important processes in atmospheric removal of PNA. Thomas, Mukai and Tebbens indicate that BaP and other arenes are primarily adsorbed on the surface of soot through hydrogen bonding. Chemisorption is appearently not feasible because of the rapid rate of photomodification, indicating that BaP must be primarily in an exposed position on the surface(quoted in Pucknat,1981).

Tebbens, Thomas and Mukai quote in Pucknat,1981 demonstrated a 15 to 50 % loss of BaP in smoke on filters with 6 hr of sunlight exposure. Another study shows a 10 % destruction of BaP adsorbed on soot or a filter after a 48 hr exposure to light of unstated intensity and a 50 % destruction after a 1 hr exposure to light and synthetic smog.

Products of photooxidation of adsorbed PNA (anthracene , A .,and pyrene, Py.,)adsorbed on silica gel and alumina)are given in the NAS report:

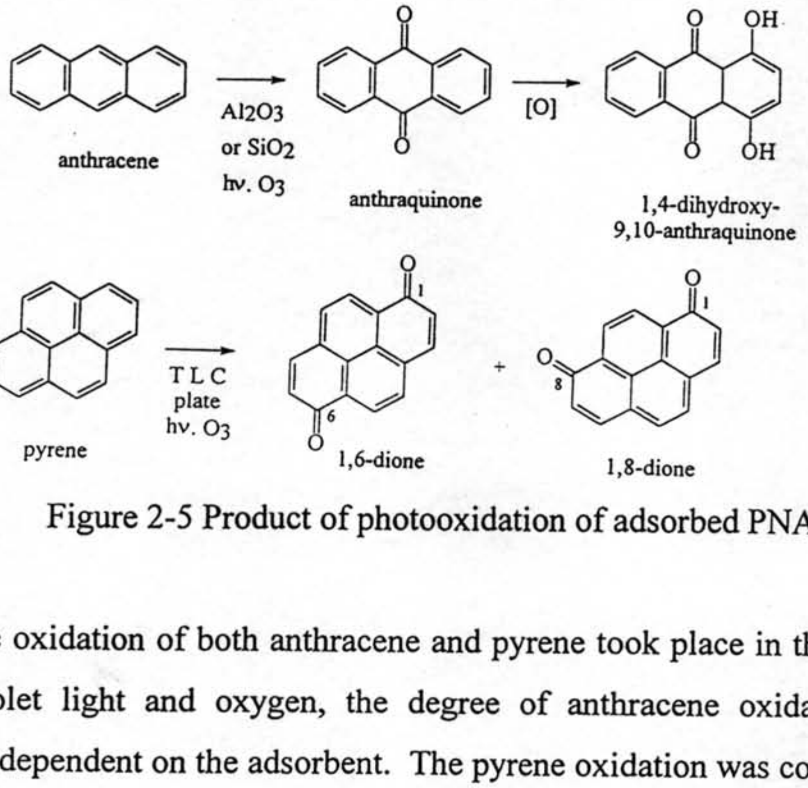

Figure 2-5 Product of photooxidation of adsorbed PNA

The oxidation of both anthracene and pyrene took place in the presence of ultraviolet light and oxygen, the degree of anthracene oxidation being somewhat dependent on the adsorbent. The pyrene oxidation was conducted on thin-layer chromatography plates(Pucknat,1981).

The one-electron oxidation of PNA results in the formation of radical cations as the primary products; these react rapidly with water or other nucleophiles or with oxygen. The complete reaction leads to formation of quinones (with water and oxygen), nucleophiles adducts, or dimeric hydrocarbons. One-electron oxidation of BaP illustrates the formation of quinones and dimers :

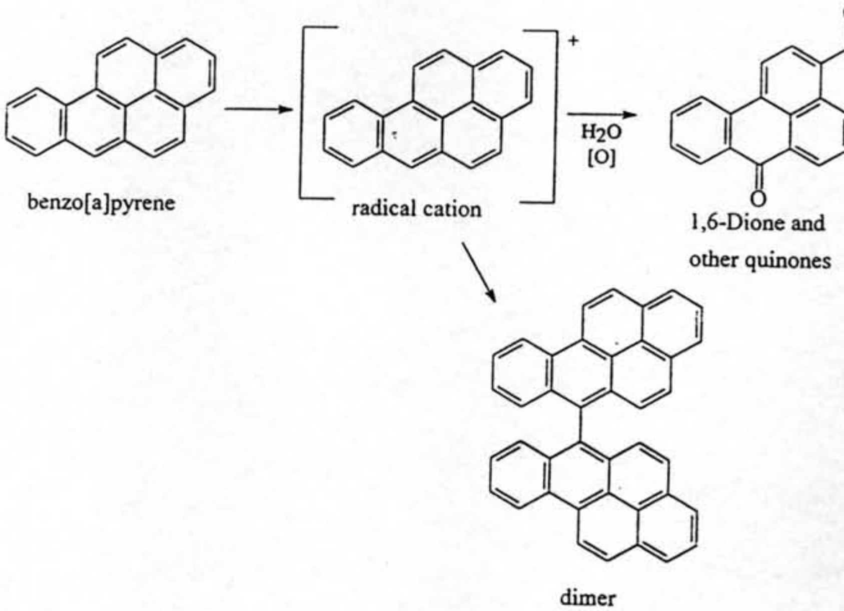

Figure 2-6 Formation of Quinones from Benzo[a]pyrene

## 2.6 Health Hazard of PNA (quoted in Draft for Public Comment,1994)

There are more than 100 known different PNAs compounds. Although the health effects of the individual PNA are not exactly alike, the following 17 PNAs are considered as a group in this study :

- acenaphthene
- anthracene
- benzo[a]pyrene
- benzo[b]fluoranthene
- benzo[j]fluoranthene
- acenaphthylene
- benzo[a]anthracene
- benzo[e]pyrene
- benzo[g,h,i]perylene
- benzo[k]fluoranthene

- chrysene
- fluoranthene
- indeno[1,2,3,-cd]pyrene
- pyrene
- dibenzo[a,h]anthracene
- fluorene
- phenanthrene

These 17 PNAs were chosen to be included in this profile because (1) more information is available on these than on the others; (2) they are more harmful than many or most of the others; (3) there is a greater chance of exposure to these PNA than to the others.

Background levels of some representative PNA in the air are reported to be 0.02 - 1.2 ng/m$^3$ in rural areas and 0.15 - 19.3 ng/m$^3$ in urban areas .

The primary sources of exposure to PNA for most of the US population are inhalation of the compounds in tobacco smoke, and ambient air, and ingestion of PNA in food. Food that was grown in contaminated soil or air may also contain PNA.

PNA can enter the body through the as they can be contained in air,Usually stuck to particles or dust. This is one of the routes of exposure for people living near roadway sites. However, it is not known how rapidly or completely uptake by the lung occurs.

PNA can enter all the tissues of the body that contain fat and tend to be stored mostly in the kidneys, liver, and fat, with smaller amounts in the spleen, adrenal glands, and ovaries. PNA are changed by all tissues in the body into many different substances. Some of these substances are more harmful and some are less harmful than the original PNA. Results from animal studies show that they leave the body within a few days, primarily in the feces and urine.

PNA can be harmful to health. Several of the PNA, including benzo[a] anthracene, benzo[a]pyrene, benzo[b]fluoranthene, benzo[j]fluoranthene, benzo [k]fluoranthene, chrysene, dibenzo[a,h]anthracene, and indeno[1,2,3,-cd] pyrene, have caused tumors in laboratory animals when absorbed via the air, food, or through long term skin contact. It has been reported that humans, exposed by breathing or skin contact for long periods to mixtures containing PNA and other compounds, can also develop cancer.

Studies in animals have also shown that PNA can cause harmful effects on skin, body fluid, and the immune system after both short- and long-term exposure. These effects have not been reported in humans.

The Department of Health and Human Services (DHHS) of the USA has determined that benzo[a]anthracene, benzo[b]fluoranthene, benzo[j] fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, dibenzo[a,h]anthracene, and indeno[1,2,3,-cd]pyrene may reasonably be anticipated to be carcinogens. The International Agency for Research on Cancer (IARC) has determined the following: benz[a]anthracene and benz[a]pyrene are probably carcinogenic to humans; benz[b]fluoranthene, benz[j]fluoranthene, benz[k]fluoranthene, and indeno[1,2,3,-cd]pyrene are possibly carcinogenic to humans; and anthracene, benz[g,h,i]perylene, benz[e]pyrene, chrysene, fluoranthene, fluorene, phenanthrene, and pyrene are not classifiable as carcinogen to humans. EPA has determined that benz[a]anthracene , benz[a]pyrene , benz[b]fluoranthene, benz[k]fluoranthene, chrysene, dibenz[a,h]anthracene, and indeno[1,2,3,-cd] pyrene are probable human carcinogens and that acenaphthylene, anthracene, benz[g,h,i]perylene, fluoranthene, fluorene, phenanthrene, and pyrene are not classifiable as having humans carcinigenicity. Acenaphthene has not been classified for carcinogenic effects by the DHHS, IARC, or EPA.

The EPA has suggested that the following amounts of individual PNA are not likely to cause any significant (noncancer) harmful health effects:
0.3 mg of anthracene, 0.06 mg of acenaphthene, 0.04 mg of fluoranthene, 0.04 mg of fluorene, and 0.03 mg of pyrene per kilogram of your body weight.

The history of PNA exposured to human health and show the health effects in Table 2-2.

Table 2-2 History of the Epidemiological Basis for Concern about Human PAH Exposure.

| Researcher | Year | Workers exposed | Cancer type |
|---|---|---|---|
| Pott | 1775 | Chimney sweeps | Scrotum |
| Volkmann | 1875 | Tar/paraffin workers | Scrotum |
| Rehn | 1895 | Synthetic dye workers | Bladder |
| Luehe | 1907 | Carbon workers | Skin |
| Kennaway | 1947 | Asphalt and coal gas workers | Lung |
| Doll | 1952 | Coal gasification workers | Lung |
| Sexton | 1960 | Coal liquefaction workers | Bladder |
| Soy/Redmond/ Maxemdar/Lloyd | 1968-1975 | Coke producers or workers | Lung |

Yang and Bauman ,1995, found that , PNA in street dust in winter was 2-12 times that in summer of Germany. Fluoranthene, Pyrene, Phenanthrene always exhibited the highest concentrations, independent of the total PNA concentration, and thus may be used as indicators of PNA pollution in street dusts.

Allen *et al.,*1996 studied PNA in atmospheric aerosols (Kenmore Square, Massachusetts) by GC/MS analysis. The atmospheric temperature during the sampling periods was 21 - 29 °C (June,1994). He quantified fifteen PNA species, Phenanthrene, Fluoranthene and Pyrene were more highly concentrated than other PNAs. They are illustrated in Table 2-3.

Venkataraman *et al.,*1994 investigated PNA and Elemental carbon (EC) size distributions in the Caldecotle Tunnel, California are unimodal in vehicular emissions with over 85 % of the mass in particles smaller than 0.12 μm aerodynamic diameter. Ambient air intrusion into the Sepulveda Tunnel, which is only 0.5 kilometer along, results in small secondary peaks in the PNA distributions in the 0.5 - 1.0 μm size range.

Gardner *et al.,*1995 found that vehicular emissions probably make a greater contribution in non-winter periods of UK, while heating production sources dominate in winter. In summer, air concentrations were more heavily influenced by temperature than precipitation rates. These is evidence of a significant source of low molecular weight PNA in the vapor phase in summer months.

Aceves and Grimalt,1993.found that the seasonal fluctuations of hydrocarbons reflect a strong decrease in the warm period. The changes in the fine particulate (< 1.5 μm) content of *n*-alkanes and PNA show that these fluctuations are due to atmospheric dilution and , in the case of PNA, photochemical degradation.

Takada *et al.,*1990 investigated PNA in street dust on heavily trafficked streets in the Tokyo metropolitan area. These were strongly affected by automobile exhausts. Those in residential areas have a somewhat more significant contribution from combustion products in stationary sources. With both types of dusts, asphalt is thought to contribute only a minor part of their PNA.

TABLE 2-3 PNA Identified in Kenmore Square, Massachusetts Samples

| **PNA** | **mol wt** | **conc with aerosol [ ng / m$^3$ ]** |
|---|---|---|
| naphthalene | 128 | identified |
| acenaphthylene | 152 | identified |
| acenaphthane | 154 | identified |
| fluorene | 166 | identified |
| phenanthrene | 178 | 13.28 ± 0.62[a] |
| anthracene | 178 | 1.28 ± 0.08 |
| fluoranthene | 202 | 14.70 ±0.41 |
| pyrene | 202 | 8.07 ±0.21 |
| benzo [*ghi* ]fluoranthene | 226 | 0.90 ± 0.04 |
| cyclopenta[*cd*]pyrene | 226 | identified |
| benz[*a*]anthracene | 228 | 1.66 ±0.08 |
| chrysene/ triphenylene | 228 | 1.78 ±0.10 |
| benzofluoranthenes | 252 | 3.22 ± 0.10 |
| benzo[*e*]pyrene | 252 | 1.34 ± 0.03 |
| benzo[*a*]pyrene | 252 | 1.17 ± 0.02 |
| perylene | 252 | 0.22 ± 0.01 |
| indeno[1,2,3-*cd*]pyrene | 276 | 1.03 ± 0.05 |
| dibenzanthracenes | 278 | 0.15 ±0.01 |
| benzo[*b*]chrysene | 278 | identified |
| picene | 278 | identified |
| benzo[*ghi*]perylene | 276 | 0.82 ±0.05 |
| dibenzo[*a,l*]pyrene / dibenzo[*b,k*]fluoranthene | 302 | identified |
| coronene | 300 | 0.11±0.01 |

[a] One standard deviation.

[Allen et al.,1996.Chemical Engineering Department, Massachusetts Institutute of Technology,Cambridge, Massachusetts.quoted in Allen *et al.,*1996)

Harkov *et al.,*1984 stidied variations in the summertime concentrations of selected PNA collected by using inhalable particulate samplers(IPM-$D_{50} <$ 15 μm), at four sites in New Jersey. The levels of PNA found in this study were consistent with other urban values. While day-to-day trends in PNA concentrations at four sites were influenced by regional meteorology, it appears that local sources had the greatest influence on ambient levels.

Smith *et al.,*1995 found a high correlation between airborne particulate matter and soil concentrations in Birmingham (UK), which suggests that atmospheric deposition is the dominant sources of PNA in soils. A high correlation was also found between PNA concentrations in soils and road tunnel dust. This illustrates the impact of vehicle emissions as the major sources of PNA in urban areas. PNA levels in soils from Lahore(Pakistan) were considerably lower than those collected in Birmingham despite far higher atmospheric concentrations. This is most likely to be due to Pakistan's climate enhancing the effects of photo-oxidation and volatilization. A high correlation was found between PNA in airborne particles and soils in Lahore.

Westerholm *et al.,*1988 showed that 2-4 ring PNA originating from gasoline-fueled exhausts are mainly in the gas phase in the urban street environment of Stockholm, Sweden. In the case of diesel vehicles, a substantial part of the low molecular weight PNA are adsorbed on the exhaust particles.

Blumer *et al.,*1977 found low values in town close to industry but remote from the highway, and high PNA values outside of town but near the highway, suggesting a correlation between automobile traffic and PNA content of soils. These results indirectly suggest a correlation between the automobile traffic and the observed mortality from cancer.

Table 2-4 Total PNA Concentration from Other Studies

| Researchers | Year | No.of Samples | $\sum$ PNA (mean, ng/m$^3$) | Location | Remark |
|---|---|---|---|---|---|
| Foreman and Bidleman[a] | 1990 | MW≥166 | 93 | Denver, CO | |
| Baker and Eisenreich | 1990 | 13 | 3.8 | Continantal | Background |
| Niehaus *et al.* | 1990 | 16 | 0.1 - 10 | Germany | Nonurban |
| Broman *et al.*[b] | 1991 | 15 | 2.5 - 11(4.1) | Sweden | Background |
| Cothman and Bidleman[a] | 1992 | MW≥166 | 57 | Portland, OR | |
| Jone *et al.*[c] | 1992 | | 164<br>134<br>125<br>98 | London<br>Manchester<br>Cardiff<br>Stevenage | |
| Ngabe *et al.*[a] | 1992 | MW≥166 | 43 - 56 | Columbia, SL | |
| Gardner *et al.* | 1995 | 10<br>10 | 6 - 254<br>9 - 52 | Esthwaite water<br>Castleshaw | Rural<br>Semiurban |

[a] quote in Cotham and Bidleman, 1995.

[b] quote in Harkov *et al.* , 1995.

[c] quote in Gardner *et al.* , 1995.

Other studies found that total PNA concentrations in other cities have differences and are influence by location . They are illustrated in Table 2-4.

Emission characteristic of PNA from diesel and gasoline engine were studied by LARC (1983) and Daisey *et al* (1986) found that gasoline exhaust has more species of PNA than diesel exhaust with phenanthrene, fluoranthene and pyrene predominanting. They are illustrated in Table 2-5.(Baek *et al.*,1991)

Table 2-5 Emission Characteristics PNA (ng/m$^3$) from Gasoline and Diesel Exhaust relative to BeP

| | Automobile Exhausts | | |
|---|---|---|---|
| | Gasoline engine[a](1) | | Diesel engine[b] |
| | Air-cooled | Water-cooled | |
| PHEN | 49.7 | 63.7 | 1602.2 |
| ANTHR | 9.1 | 17.4 | - |
| FLUR | 18.0 | 44.9 | 63.0 |
| PYR | 36.4 | 78.0 | 11.8-87.0 |
| BcPH | - | - | - |
| CcdP | 16.7 | 20.3 | - |
| BaA | 1.4 | 1.4 | 01.4-08.8 |
| CHRY | 2.1 | 0.5 | 00.9-05.4 |
| BNTH | - | - | - |
| BeP | 1.0 | 1.0 | 1.0 |
| BbF | 0.8 | 0.5 | - |
| BkF | 0.3 | 0.2 | - |
| BaP | 1.4 | 1.4 | 01.0-05.5 |
| DahA | - | - | - |
| BghiP | 5.6 | 3.1 | 00.6-01.8 |
| In123P | 1.5 | 0.9 | - |
| ANTHN | 0.3 | 0.7 | - |
| COR | 4.6 | 2.9 | - |

[a] IARC(1983)

[b] Daisey et al. (1986)

(1) No emission control device equipped

(2) Side draft burning mode