

POLYCYCLIC AROMATIC HYDROCARBONS

IN

SYDNEY, PORT KEMBLA AND NEWCASTLE AIR

1984-1985

BY

Narayan K. Pradhan

TECHNICAL SERVICES AIR BRANCH  
STATE POLLUTION CONTROL COMMISSION

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SUMMARY

A report on polycyclic aromatic hydrocarbon (PAH) levels in the ambient airborne particulate matter of Sydney and Port Kembla, measured for a period of twelve months during 1984 is presented. PAH levels in the inner city of Sydney have declined by a factor of at least two to three times those found 20 years ago, and are less than those reported for major overseas cities.

Results obtained from a special study carried out in the vicinity of coke oven furnaces at the Newcastle BHP Steel Works, during May - August, 1985, are also included in this report. The preliminary data indicates the coke oven furnaces to be major sources of PAH emissions. A further study is recommended to investigate the PAH emissions from other existing coke ovens in New South Wales.

CONTENTS

	Page
SUMMARY	(i)
1. INTRODUCTION	1
1.1 Polycyclic Aromatic Hydrocarbons (PAHs) and their Structures	2
1.2 Chemical Reactivity of PAHs.	4
1.3 Carcinogenicity of PAHs.	8
1.4 Sources of PAHs in the Atmosphere.	10
1.5 Mechanism of PAHs Formation	13
1.6 PAHs in Ambient Air.	13
1.7 Analytical methods for Monitoring PAHs.	17
2. EXPERIMENTAL METHODOLOGY	19
2.1 Sampling Method for Airborne Particulate Matter	19.
2.2 Sample Extraction and Concentration.	19
2.3 Separation of PAHs by HPLC	20
2.4 Percentage Recovery and Precision Studies	23
2.5 Detection limits of HPLC for PAHs	25
2.6 Monitoring Program	26
3. RESULTS AND DISCUSSION	30
3.1 Annual Average PAHs at Rozelle, Sydney and Port Kembla	31
3.2 Seasonal Variation of PAHs	33
3.3 PAHs levels around the BHP Steel Works, Newcastle	39
4. CONCLUSIONS AND RECOMMENDATIONS	42

5.	ACKNOWLEDGEMENTS	44
6.	REFERENCES	45
7.	APPENDICES	51
7.1	Monthly Average PAHs concentration - Sydney	52
7.2	Monthly Average PAHs concentration - Rozelle	54
7.3	Monthly Average PAHs concentration - Port Kembla	56
7.4	Determination of PAHs in Ambient Air - Method	58

## 1. INTRODUCTION

An investigation of polycyclic aromatic hydrocarbons (PAHs) in the ambient atmosphere of Sydney, Port Kembla and Newcastle has been carried out. The aims of the study were:

- to establish suitable air sampling and analytical methods for the estimation of PAHs in ambient air.
- to measure PAH levels in ambient air from selected sites representative of residential, industrial and inner city areas.
- to identify possible sources of PAHs and compare the findings with other industrialized cities.

Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous pollutants of ambient air. These compounds are of particular interest due to the fact that several are known animal carcinogens and some are suspected carcinogens to man. The main sources in the atmosphere are the airborne particles formed by the incomplete combustion of fossil fuels, vegetation, refuse etc. The concentrations of PAHs in the environment vary significantly depending on the geographic location, the presence of nearby sources of pollution such as traffic, highways or industries, and the season.

To date PAHs are extensively studied components in airborne particulate matter in many industrialized cities. However, our knowledge of these compounds in Australian cities is very limited in spite of the improvement of analytical instrumentation and techniques in recent years. The study of PAHs in the inner city of Sydney was first carried out by Cleary and Sullivan in 1962-63. However, the rapid growth of industry in NSW over the last twenty years has required more critical evaluations of environmental health hazards associated with these compounds. The changing pattern in the utilization of energy sources places even greater emphasis on these evaluations.

In carrying out this study, a method of high performance liquid chromatography (HPLC) for the determination of polycyclic aromatic hydrocarbons (PAHs) containing three or more arene rings in air particulate samples was established. Ambient air particulates collected on a glass fibre filter by means of a high volume sampler were extracted with cyclohexane, cleaned up using column chromatography and finally analysed by means of a high performance liquid chromatograph (HPLC).

The PAH levels measured at Rozelle (residential area), Sydney City (commercial inner city area) and Military Road, Port Kembla (industrial area near Electrolytic Refining and Smelting Company) for a period of 12 months during 1984 are presented and compared with those published for other similar cities in the northern hemisphere. A special study was also made to measure the PAH levels in the surrounding atmosphere of coke ovens at the BHP Steel Works, Newcastle.

### 1.1 POLYCYCLIC AROMATIC HYDROCARBONS (PAHs) AND THEIR STRUCTURES

Polycyclic aromatic hydrocarbons are made up of three or more fused benzene rings in linear, angular or cluster arrangements and contain only carbon and hydrogen (Fig. 1). They are formed whenever organic substances are exposed to high temperatures and may also be synthesized by some plants and bacteria.

Most PAHs are practically insoluble in water. All these compounds are solid at ambient temperature and are the least volatile of the aromatic hydrocarbons. Those most studied melt over the range 101°C (phenanthrene) to 439°C (coronene) and boil over the range 293°C (fluorene) to 525°C (coronene). Molecular weights of 40 PAHs listed by the National Academy of Science (1972) range from 178 to 300.

The structure of some of the more widely studied PAH compounds, and those which have been found most frequently in airborne particulate samples are presented in Fig. 1.



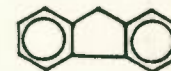
Naphthalene  
(128)



Acenaphthylene  
(152)



Acenaphthene  
(154)



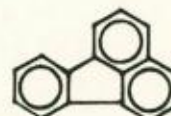
Fluorene  
(166)



Phenanthrene  
(178)



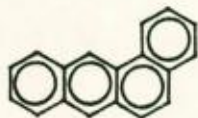
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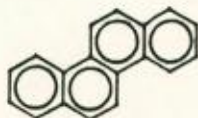
Fluoranthene  
(202)



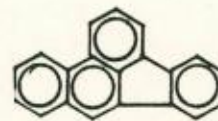
Pyrene  
(202)



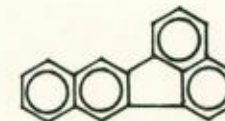
Benz [a] anthracene  
(228)



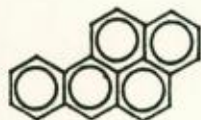
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(228)



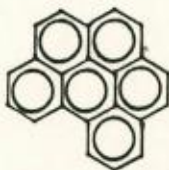
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(240)



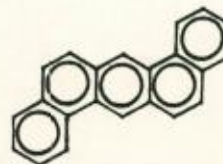
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(240)



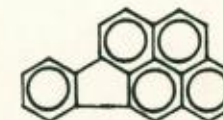
Benzo [a] pyrene  
(252)



Benzo [ghi] perylene  
(276)



Dibenz [ah] anthracene  
(278)



Indeno [1,2,3-cd] pyrene  
(290)



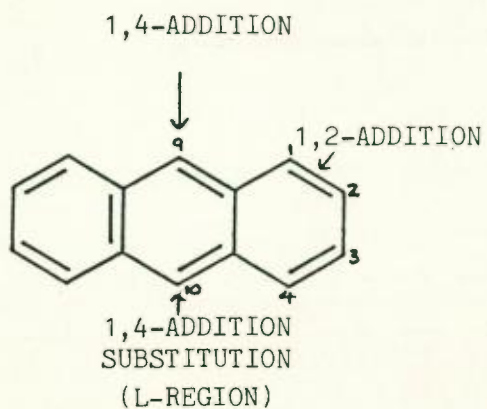
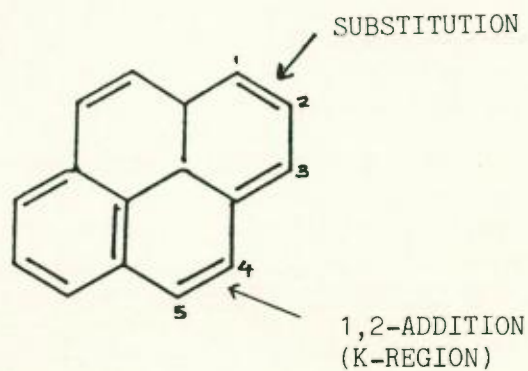
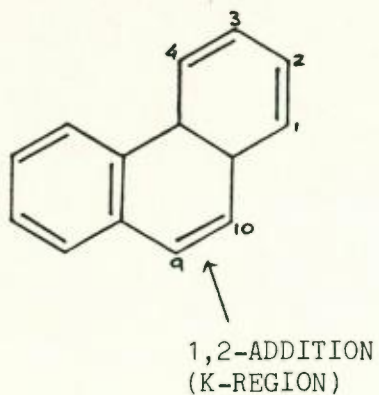
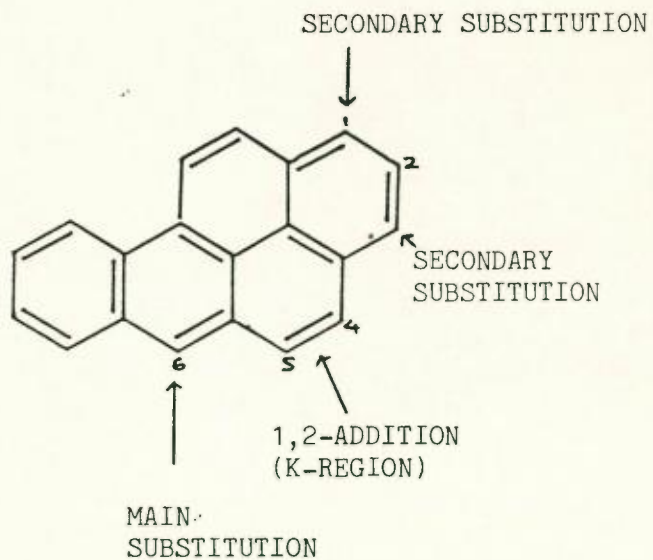
## 1.2 CHEMICAL REACTIVITY OF PAHs.

Chemical reactions of PAHs in the atmosphere are important because some of the products of the reactions may be health hazards themselves. PAHs have some highly reactive sites within the molecules which readily undergo addition and substitution reactions. The type of reaction depends both on the reagent and on the compounds. Generally, reactions of linear hydrocarbons tend to take place at the anthracene 9,10- like position (1,4-addition or substitution, L-region) or the 1,2 position (1,2-addition, K-region). Reactions of angular PAHs tend to take place at the anthracene 9,10-like position (1,4-addition or substitution) or the phenanthrene 9,10-like double bonds (1,2-addition, K-region). Reactions of more condensed ring systems tend to take place at positions adjacent to ring fusions. The tendencies are illustrated in Fig 2.

Photo-oxidation of polycyclic aromatic hydrocarbons is one of the most important reactions that must be avoided during the analysis. This process is often important in the destruction of PAHs in the atmosphere. The photo-sensitivity of many aromatic hydrocarbons in liquid solution is well known (Bowen 1963). The photo-oxidation of PAHs can produce oxygenated compounds, some of which can exist in the atmosphere and several of which appear to be carcinogenic (Epstein et al. 1968, Fatadi 1967, Masuda and Kuratsune 1966).

Products of photo-oxidation are often peroxides, as in the case of 9,10-dimethyl anthracene, or diones or quinones, as in the case of benzo[a]pyrene (Fig 3). Such products may have properties which may account for the extra carcinogenicity of air particulate in comparison with that of the identified PAHs.

PAHs are readily attacked by ozone, particularly in the K-region, to give ultimately carboxylic acids, or may undergo 1,4-addition in the L-region to give compounds which normally proceed to quinones (Figure 3A) (Katz 1979).

ANTHRACENEPYRENEPHENANTHRENEBENZO [a] PYRENEFIG. 2 NOTABLY REACTIVE SITES IN PAHs.

6.

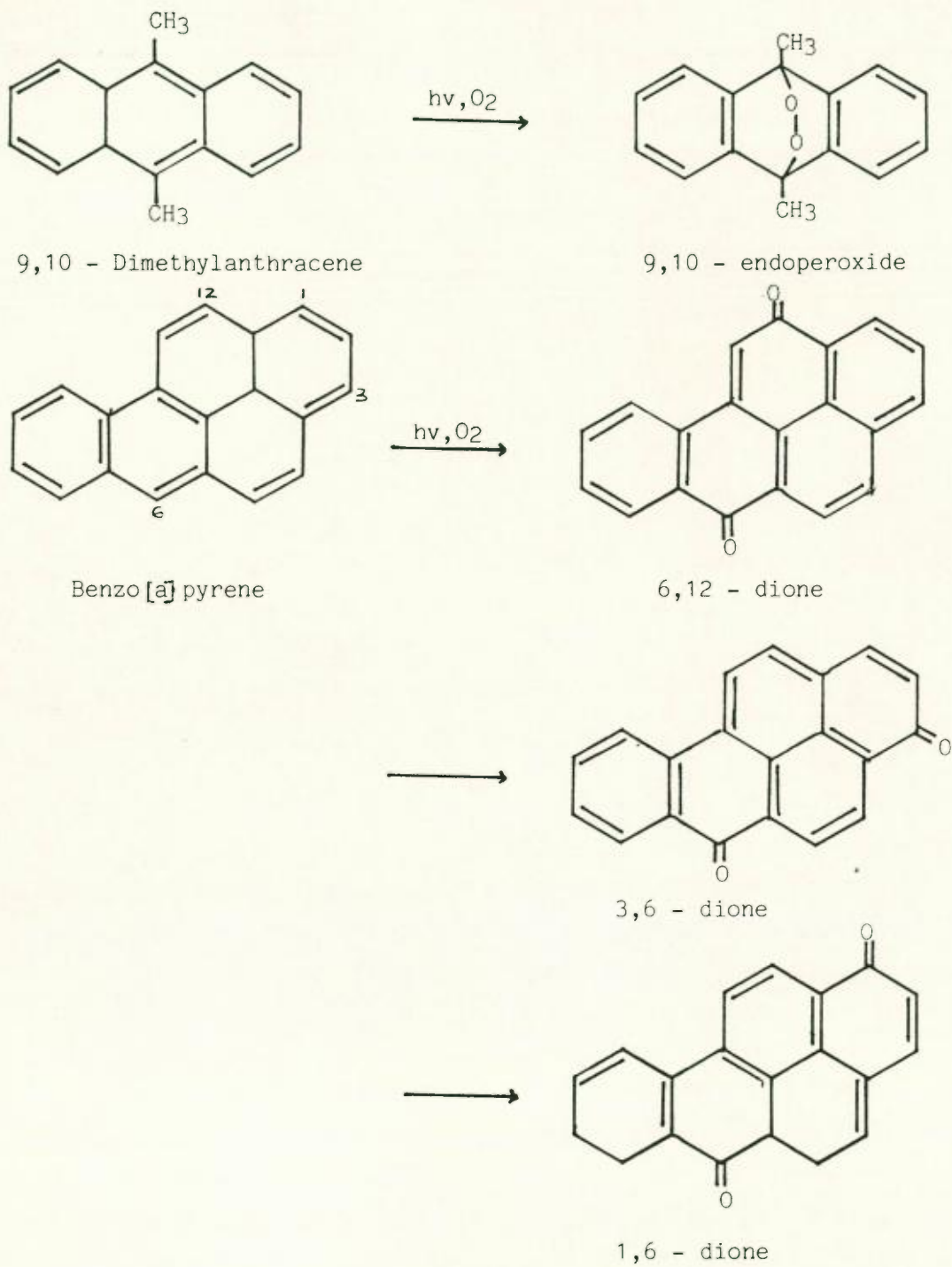


FIG. 3. PHOTO-OXIDATION PRODUCTS OF 9,10-DIMETHYLANTHRACENE AND BENZO[a]PYRENE

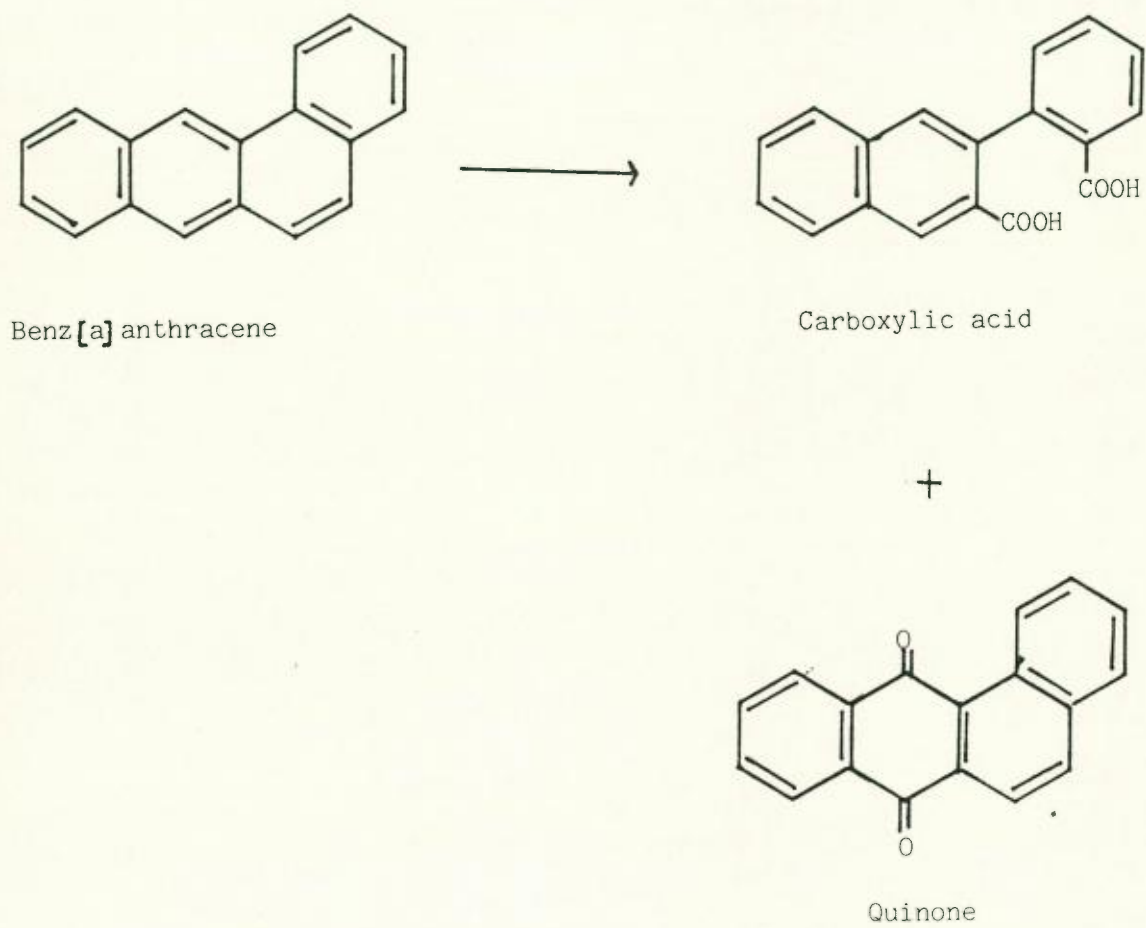


Fig. 3A. OXIDATION OF BENZ [a] ANTHRACENE BY OZONE

Fox and Olive (1979) have reported that anthracene added by sublimation to filter collected atmospheric particulate matter, underwent photo-decomposition upon exposure to sunlight. Several oxygen-containing photo products were identified. Peter and Seifert (1980) have demonstrated that benzo[a]pyrene deposited from solution onto dust-coated glass fibre filters under-went rapid photodegradation when exposed to the output of a unfiltered 400W halogen lamp. They concluded that oxidative degradation phenomena may be a significant loss mechanism in high volume sampling. Barofsky and Baum (1976) exposed several PAHs, adsorbed on carbon needle field desorption emitters, to ultraviolet radiation (Hg lamp); benzo[a]pyrene, anthracene, benz[a]anthracene and pyrene all underwent photo-oxidation to carbonyl compounds.

Nitration and sulphonation of polycyclic aromatic hydrocarbons occur readily at the position indicated in Fig 2. Nitrogen oxides or dilute  $\text{HNO}_3$  can either add to, substitute, or oxidize PAHs. Anthracene is oxidised by dilute aqueous  $\text{HNO}_3$  or nitrogen oxides to anthraquinone (National Academy of Science, 1972). Sulphonation reactions of adsorbed pyrene and benzo[a]pyrene with  $\text{SO}_2$  have been reported (Jager and Rakovic 1974).

### 1.3 CARCINOGENICITY OF PAHs

Polycyclic aromatic hydrocarbons can be environmental carcinogens in heavily populated or industrialized areas. The potential health hazards associated with these compounds in the atmosphere are of concern because many PAH species have been found to be carcinogenic in laboratory animal tests (Searle 1976). The relation between cancer and PAHs was best documented in epidemiological studies of coke oven workers by Lever (1974) and Lloyd (1971).

Several numerical scales of carcinogenicity have been proposed and are based on the statistics of cancer induced in animals, as detected by pathological assay. A list of 16 polycyclic aromatic

hydrocarbons that were identified by the Environmental Protection Agency (EPA) in the United States as priority pollutants (1979) and tested for carcinogenic activity, is presented in Table 1. In this table, a listing is presented of these compounds with their activities based on the percentage of treated animals which developed tumors, i.e., non-carcinogenic (0%), up to 33%, weakly carcinogenic (+); and above 33%, strongly carcinogenic (++) . The information in the table was compiled from a number of sources (Hartwell 1951 and IARC Monographs 1984).

The carcinogenic activity of an individual PAH is dependent on its molecular structure (Searle 1976). Many of the carcinogenic PAHs contain the benz[a]anthracene, B[a]A, nucleus. Addition of another benzene ring to the B[a]A nucleus in select positions usually results in compounds with powerful carcinogenic potential. Alkyl substituents such as a methyl group on specific carbon atoms of the ring can enhance carcinogenicity. The electronic structure of PAHs suggests that the K-region is specifically related to the carcinogenic potential of a given compound while substitution in the L-region will enhance its carcinogenicity. This consideration allow fairly reliable prediction of the carcinogenicity of various PAHs. However it is not useful in predicting the structure - carcinogenicity relationships with larger ring systems (Das, 1984).

TABLE. 1 CARCINOGENIC ACTIVITY OF SOME PAH COMPOUNDS

<u>COMPOUND</u>	<u>CARCINOGENIC ACTIVITY</u>
Naphthalene	0
Acenaphthylene	0
Acenaphthene	0
Fluorene	0
Phenanthrene	0
Anthracene	0
Fluoranthene	0
Pyrene	0
Benz[a]anthracene	+
Chrysene	+
Benzo[b]fluoranthene	++
Benzo[k]fluoranthene	++
Benzo[a]pyrene	++
Benzo[ghi]perylene	+
Dibenz[a,h]anthracene	++
Indeno[1,2,3-cd]pyrene	+

#### 1.4 SOURCES OF PAHs IN THE ATMOSPHERE

The sources of environmental PAHs are due to a variety of processes - both natural and man-made. Forest and prairie fires, volcanoes and even synthesis by plants and micro-organism are the major contributors to production of PAHs by natural processes. Suass (1976) and Shabad (1980) emphasized that the quantities of PAHs formed by natural processes are very small in comparison with those from anthropogenic sources. The average concentration of the sum of 11 PAHs in remote sites of the northern hemisphere reported by Daisey (1981) was very low (0.16ng/m<sup>3</sup>) compared to that found in most industrialized cities.

Anthropogenic sources of PAHs such as the burning of fossil fuels, refuse and agricultural material are the major contributors (more than 90%) of PAHs in the atmosphere. These can be broadly

separated into mobile and stationary sources.

Mobile sources contribute relatively small amounts of PAHs, although they are the most important contributors in many large cities. It has been reported (Handa et al. 1984) that the average emission rates of PAHs per vehicle from light-duty gasoline engine cars were about 2-3 times higher than those from heavy duty diesel engine vehicles, but the rates of PAH derivatives (mostly nitro-derivatives) and particles from diesel exhaust were higher than those from the former, by a factor of 10 for nitro-PAHs and 14 for particles. A series of nitro-aromatic compounds were identified in diesel exhaust particles (Gibson, 1982 and Newton et al. 1982). It was reported that the nitro-derivatives of PAHs are more carcinogenic than their parent compounds (Ames et al. 1975).

Other mobile sources such as locomotives, aircraft and farm machinery tend to be of less concern to public health because most of the emissions result in little public exposure (for an example, in the case of aircraft, their emissions are dispersed above the boundary layer). Shabad (1980) reported that a jet aircraft engine emits 2-4mg benzo[a]pyrene/min when cruising and up to 40,000mg/min during take off. Thus, vegetation and soil near airports often contain relatively high concentration of PAHs.

Stationary fuel combustion is the major source of PAHs in the atmosphere. The most common large scale stationary sources of PAHs are as follows:

- Industrial emissions
- Domestic heating emissions
- Refuse burning emissions

Of all the stationary sources of air pollution, industrial processes and power generation bear the brunt of present air pollution control regulations and environmental concern.

Industrial processes such as coke ovens, some types of aluminium smelters, and coal gasification plants are mostly noted (IARC



Monograph 1984) for atmospheric PAH emissions. Bjorseth and Eklund (1979) identified about 100 PAH compounds in the particulate matter of atmospheric samples taken from a coke plant and an aluminium production plant. Lloyd (1971) reported a 2.5-fold increase of respiratory cancer in coke oven employees, and a 10-fold increase in lung cancer for coke oven battery top workers who had been employed five or more years. Several studies of PAHs and coal tar pitch volatiles (CTPV) in and around coke manufacturing facilities have been reported (Searl et al. 1970; Seim et al. 1974; Bjorseth et al. 1978).

Another stationary source of PAHs is domestic heating emissions. Coal, oil, gas and wood are burned in a variety of installations. Hangebrauck et al. (1967) concluded that the most important source of benzo[a]pyrene of these four fuels was the inefficient combustion of coal in hand-fired residential fires. Oil and gas burning units used for domestic heating, as well as steam for process heating, have been shown to be relatively low sources of PAH emissions. Recently, residential wood combustion has become a significant air pollution source contributing to ambient particulate levels in many communities during winter months. Consumption of wood appears to be steadily increasing, judging from the dramatic increase in sales of wood burning stoves and homes constructed with fire places. Several studies in the U.S.A. have documented that residential wood combustion (RWC) can cause high concentrations of respirable particulates (RSP), benzo[a]pyrene and other pollutants in ambient air (Cooper 1980; Core et al. 1984; Faoro et al. 1981; and Imhoff 1985).

The combustion of solid wastes as a method of disposal as well as backyard burning, popular in Australian cities, can contribute significantly to overall PAH emissions. These emissions may arise from the municipal and commercial incineration of wastes collected from households, business and restaurants, agricultural and municipal activities and scrap automobile tyres (Hangebrauck 1967). The current philosophy is that open burning should be abolished and that incineration should be restricted to

well-designed multiple chamber incinerators. This will result in a significant improvement in air quality.

### 1.5 MECHANISM OF PAHs FORMATION

The mechanism of formation of PAHs during incomplete combustion of organic materials is not completely understood. It is believed that two distinct reaction steps are involved, pyrolysis and pyrosynthesis. At high temperature, organic compounds are partially cracked down to smaller, unstable molecules (pyrolysis). These fragments, mostly radicals, recombine to form larger, stable aromatic hydrocarbons (pyrosynthesis) (Hoffman and Wynder 1968).

The hypotheses that were proposed for the formation of PAHs have generally been founded upon the results of pyrolysis experiments. The most widely accepted classical stepwise synthesis of benzo[a]pyrene from acetylene, proposed by Badger et al. (1958), is shown in Figure 4. Badger also showed conclusively that specific aromatic and diolefinic compounds serve as precursors for other polycyclic organic products. The mechanism in Fig. 4 is a pathway to benzo[a]pyrene formation, but similar routes could be devised, with somewhat different intermediates, to lead to most of the known PAHs produced in combustion processes.

### 1.6 PAHs IN AMBIENT AIR

PAHs are widespread contaminants of the environment. They have been detected in a wide variety of environmental samples including air, water sediments and soils, as well as foodstuffs, oils and tars (NAS 1972). The concentrations in the atmosphere are connected to the large number of technological activities and other factors such as geographical location, traffic conditions, meteorological conditions and the time of the year. The concentration range of benzo[a]pyrene, one of the indexes used for PAHs in unpolluted nonurban air varies between 0.1 and 0.5ng/m<sup>3</sup> while the concentration in polluted air reached 74ng/m<sup>3</sup>, approximately 150 times higher (NAS 1972).

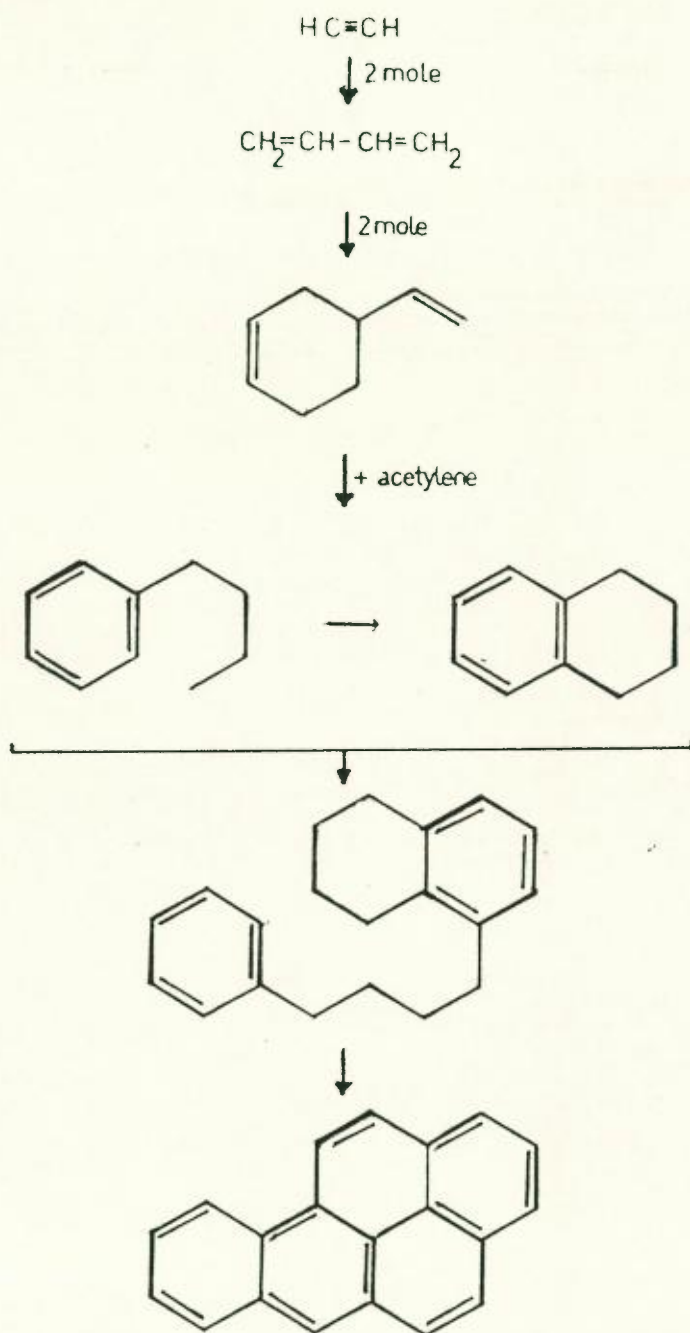


Fig. 4. MECHANISM OF BENZO[a] PYRENE FORMATION FROM ACETYLENE

The U.S Environmental Protection Agency (1974) conducted a comparative study of benzo[a]pyrene in the atmosphere of coke oven cities vs. non-coke oven cities over the period 1966-1972. The coke oven cities were found to show consistently higher benzo[a]pyrene levels in every year, the ratios of coke-oven/non-coke oven ranging from 1.42 to 3.34 and generally about 2.

Generally, the concentrations of PAHs in ambient air are higher in winter seasons than those found in summer seasons (Pierce & Katz 1975 and Katz & Chan 1980). Data compiled by Sawicki et al. (1962) shows that average (seven U.S cities) winter and summer benzo[a]pyrene concentrations were 14.3 and 2.6 ng/m<sup>3</sup> respectively, during 1958 - 1959. Similar results were reported by Cleary and Sullivan (1965) in the airborne particulate samples taken in Sydney in 1963.

Published data containing concentrations of some of these PAH compounds in the air of Los Angeles (Gorden and Bryan 1973), Birmingham, U.S.A. (Baum 1978), Sydney (Cleary and Sullivan 1965) and Osaka, (Matsumoto et al. 1982) are presented in Table 2. Highest concentrations were found in Birmingham and Osaka which are mostly associated with heavy coal burning industries. Many large urban areas experience comparatively low PAH levels - among these are Los Angeles and Sydney, where the major PAH contributors are motor vehicles and the oil refinery industry (Gordon 1976).

## 1.7 ANALYTICAL METHODS FOR MONITORING PAHs

Various analytical methods have been used for the determination of PAHs in environmental samples. Methods have included column, paper and thin layer chromatography, and more recently capillary gas chromatography (GC) - mass spectrometry (MS) and high performance liquid chromatography (HPLC). Before the development of HPLC and GC-MS, the classical techniques of column adsorption, paper and thin layer chromatography provided the most powerful means of analysis. Recently, the superior performance of HPLC techniques has almost completely replaced the use of classical column adsorption chromatography for the analysis of PAHs except for the separation and purification of the total PAHs fraction from other classes of compounds.

HPLC has many distinct advantages over other forms of chromatography. Recent developments in microparticulate column technology have produced highly efficient analytical HPLC columns with stationary phases capable of providing unique selectivity for the separation of isomeric PAHs that are often difficult to detect by other forms of chromatography (Lao et al. 1973).

HPLC is a method of separation which depends on the equilibrium distribution of the solute molecules between two phases, one stationary over which the second mobile phase flows. Those solutes preferentially distributed in the mobile phase will pass rapidly through the system while those preferentially distributed in the stationary phase will pass more slowly. The stationary phase is contained in a column and the mobile phase is pumped through the column. The sample is placed before the column using a suitable sample introduction system, and after passage through the column the separated components are detected using an appropriate detector whose output is usually displayed on a strip chart recorder.

It is often necessary to use a gradient elution system; ie, a mixture of two or more solvents, as the mobile phase to separate

a complex sample. The rate of addition of the solvents may be varied in either a linear fashion or exponentially by either a concave or convex manner. The majority of liquid chromatographs now available allow two or even three solvents to be mixed to form the gradient system and this is achieved using two or more pumping heads. A block diagram illustrating the various parts of the chromatograph is shown in Fig 5.

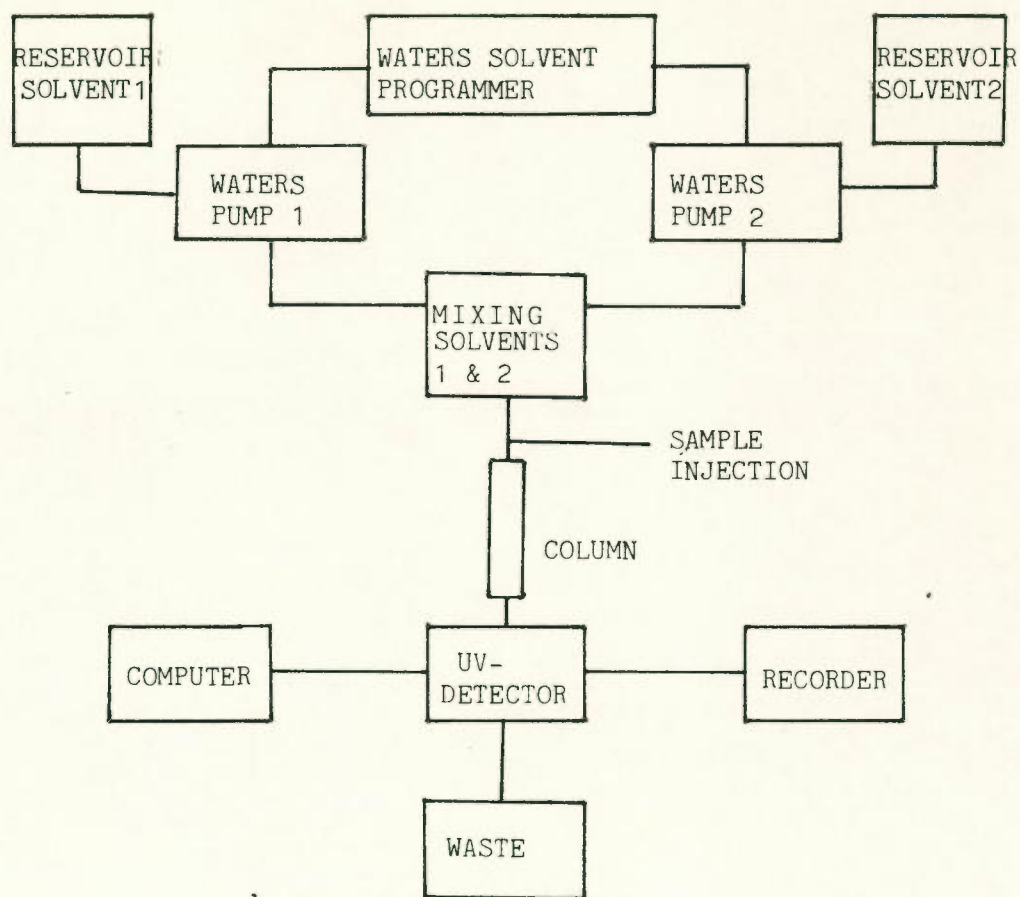


FIG. 5 BLOCK DIAGRAM OF HPLC SYSTEM

## 2. EXPERIMENTAL METHODOLOGY

### 2.1 Sampling Method for Airborne Particulate Matter

Airborne particulate matter was collected for 24 hrs periods using high volume samplers with glass fibre filters in accordance with the procedure described in AS 2724, Part 3, for total suspended particulates. Glass fibre filters were equilibrated at 20-22° C and 40-50% relative humidity and weighed before and after air sampling to determine the mass of the total suspended particles before PAH analysis. The filters were carefully stored in polythene bags in order to avoid exposure to air before and after the sampling. To reduce losses of PAHs from the glass fibre filters, the samples were immediately analysed after sampling. Other sampling methods such as the uses of Tenax (Zlatkis et al. 1973) or glass fibre filters with polyurethane foam backup (Thrane et al. 1981) are often useful to improve the collection efficiencies of volatile organic compounds. However, these are not considered essential for the collection of non-volatile PAHs (with higher molecular weight) which are reportedly carcinogenic (see Table 1.). To date, virtually all available information concerning ambient levels of PAH is derived from analysis of samples collected on glass fibre filters (eg Sawicki et al. 1960; Pierce and Katz, 1975; Matsumoto et al 1985; Gordon, 1976; Cleary et al. 1965).

### 2.2 Sample Extraction and Concentration

PAHs are soluble in many organic solvents and a variety have been recommended for the Soxhlet extraction of solid environmental samples (Chalot et al. 1971, Stanley et al. 1967). Solvents include acetone, benzene, cyclohexane, chloroform, methanol and other alcohols, dichloromethane, and tetrahydrofuran. Among these, the first three have all been shown (Stanley et al. 1967) to be nearly 100% efficient in Soxhlet extraction of benzo[a]pyrene from filters. Broddin et al. (1977) found 99% extraction with benzene after only 2 hr, or 20 Soxhlet cycles. However, as suggested by the World

Health Organization (WHO 1969) and Moore et al. (1969), it was found that the use of cyclohexane was as good as benzene and considerably less hazardous. As mentioned by Griest et al. (1980), ultrasonification of air particulates with cyclohexane was found unsuitable for extracting all PAH components, particularly the recoveries of PAHs with four or more rings, found to be incomplete.

One quarter of the glass fibre filter loaded with airborne particulate matter was cut into small pieces, placed into an extraction thimble, and extracted with 200 ml of cyclohexane in a Soxhlet apparatus for 16 hrs. The solvent volume was then reduced to 2 ml in a Kuderna-Danish evaporating flask (see Appendix 7.4).

During the initial investigation, the crude cyclohexane extracts were directly injected onto the HPLC system to compare with the standard. However, it was found that the extracts contained substantial quantities of materials other than PAHs which interfered with subsequent analysis. It was, therefore, found essential to clean up the extract prior to HPLC analysis.

The concentrated extract was subsequently partitioned using a 10mm id chromatographic column filled with activated silica gel (ca 10g) by sequential elution of n-pentane (25 ml), and a mixture of 40% dichloromethane and 60% pentane (40 ml) at a rate of approximately 2 ml/min. The pentane fraction containing non-polar compounds was discarded and the dichloromethane/pentane fraction containing the polycyclic aromatic hydrocarbons was collected and reduced down to 1 ml using a Kuderna-Danish apparatus. The fraction was further evaporated to dryness with a stream of dry nitrogen and the residue was dissolved in acetonitrile (0.5 ml) (see Appendix 7.4).

### 2.3 Separation of PAH by High Performance Liquid Chromatography (HPLC)

A HPLC system (Water Associates) consisting of two Model 510 solvent delivery pumps, a Model U6K septumless injector, a Lambda-Max Model 48 UV-Vis detector and a Model 660 solvent programmer



was used for the separation and analysis of polycyclic aromatic hydrocarbons. A Radial - PAK, PAH cartridge (Water Associates) was used. Peak areas were quantified using a Waters Data Module which prints out the retention time of individual peaks and their respective areas.

Conditions used for the HPLC were as follows:

Mobile phase: acetonitrile in water

Segment 1: 50% - 90%, 15 min

Segment 2: 90% - 90%, 15 min

Flow rate: 2 ml/min.

Temperature: room temperature (22 °C)

Detector: UV - at 254 nm

Sample volume injected: 20ul.

A typical chromatogram of a standard PAH mixture (NBS Reference Material 1649) containing 16 PAH components is presented in Fig 6. With the above solvent systems, the PAHs were gradually eluted in order of increasing molecular weight, the retention time increased with the number of benzene rings. Isomeric compounds such as phenanthrene and anthracene (molecular weight 178), fluoranthene and pyrene (molecular weight 202), benz[a]anthracene and chrysene (molecular weight 228), and benz[b]fluoranthene and benzo[k]fluoranthene (molecular weight 240), which are difficult to separate by most of other chromatographic methods, were clearly resolved. Approximate retention times of the 16 PAH compounds are given in Table 3.

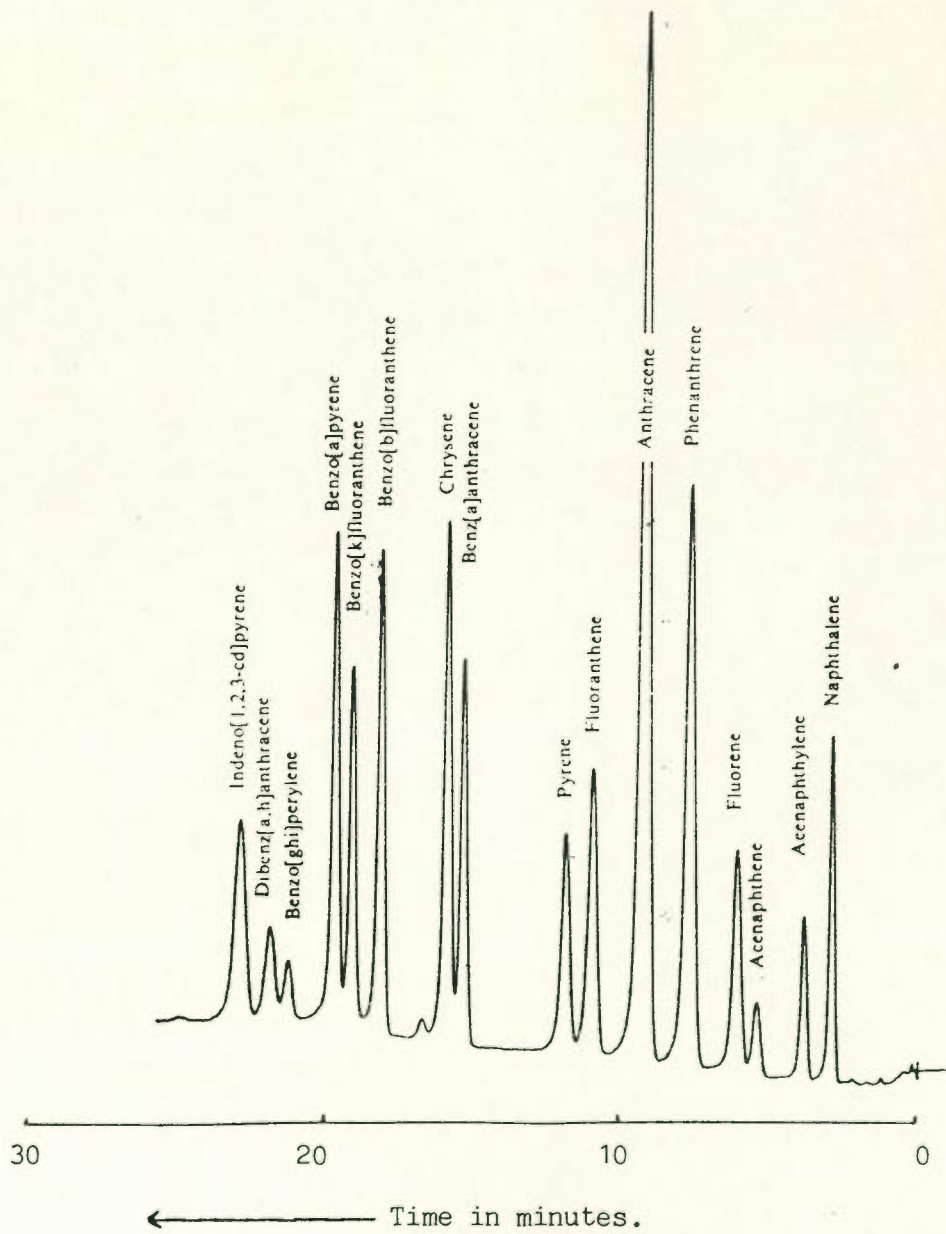


Fig. 6. TYPICAL CHROMATOGRAM OF STANDARD PAH MIXTURE (NBS STANDARD)

Table 3 APPROXIMATE RETENTION TIME OF PAH COMPONENTS

<u>PAHs</u>	<u>RETENTION TIME (min)</u>
Naphthalene	3.1
Acenaphthylene	4.2
Acenaphthene	5.2
Fluorene	6.6
Phenanthrene	8.2
Anthracene	9.6
Fluoranthene	11.2
Pyrene	12.2
Benz[a]anthracene	15.6
Chrysene	16.2
Benzo[b]fluoranthene	18.4
Benzo[k]fluoranthene	19.4
Benzo[a]pyrene	20.0
Benzo[ghi]perylene	21.5
Dibenz[a,h]anthracene	22.5
Indeno[1,2,3-cd]pyrene	23.0

#### 2.4 Percentage Recovery and Precision Studies

Recovery studies were carried out with blank filters spiked with known amounts of the PAH calibration mixture containing 16 components. The results are listed in Table 4. The recovery of the most volatile components with low molecular weight i.e., naphthalene, acenaphthylene, acenaphthene and fluorene were very poor, ranging from only 10 percent for naphthalene to 52 percent for fluorane. No further attempts were made to improve the recoveries of these four volatile components which have been reported as non carcinogenic (see Table 1). Recoveries of the other 12 PAH compounds were within the ranges of 70-100 percent with an average overall recovery of about 90 percent.

TABLE 4. PERCENTAGE RECOVERY OF PAHs

<u>PAHs</u>	<u>RECOVERY</u>
	%
Naphthalene	10
Acenaphthylene	37
Acenaphthene	42
Fluorene	52
Phenanthrene	90
Anthracene	81
Fluoranthene	91
Pyrene	95
Benz[a]anthracene	87
Chrysene	89
Benzo[b]fluoranthene	84
Benzo[k]fluoranthene	85
Benzo[a]pyrene	83
Benzo[ghi]perylene	77
Dibenz[a,h]anthracene	80
Indeno[1,2,3-cd]pyrene	82

Relative standard deviations (RSD) ranged from 4.1 percent for Chrysene to 11.7 percent for anthracene are listed in Table 4A.

The precision study was carried out by combining five normal glass fibre filters all loaded with airborne particulate matter and dividing into ten equal parts for ten repeated determinations. Because of the mass of the particulate matter collected in the glass fibre filter (24 hrs sampling period), it is often impracticable to carry out more than two determinations from a single glass fibre filter.

TABLE 4A RELATIVE STANDARD DEVIATION OF THE TEST METHOD

<u>Compounds</u>	<u>Range</u> ng/m <sup>3</sup>	Mean n = 10 ng/m <sup>3</sup>	Standard Deviation ng/m <sup>3</sup>	R.S.D %
Phenanthrene	0.63 - 0.75	0.69	0.06	8.1
Anthracene	0.16 - 0.22	0.18	0.02	11.7
Fluoranthene	2.65 - 3.00	2.89	0.23	7.9
Pyrene	3.60 - 4.10	3.92	0.24	6.1
Benz[a]anthracene	0.70 - 0.90	0.80	0.07	9.2
Chrysene	3.82 - 4.20	4.09	0.17	4.1
Benzo[b]fluoranthene	2.00 - 2.40	2.24	0.17	7.5
Benzo[k]fluoranthene	0.75 - 0.95	0.82	0.10	10.8
Benzo[a]pyrene	2.00 - 2.35	2.22	0.15	6.6
Benzo[ghi]perylene	4.00 - 4.40	4.23	0.15	3.3
Dibenz[a,h]anthracene	2.30 - 2.75	2.48	0.19	7.9
Indeno[1,2,3-cd]pyrene	2.20 - 2.60	2.49	0.15	5.7

### 2.5 Detection Limits of HPLC for PAHs

Detection limits of 12 PAH compounds are listed in Table 5. These are calculated from the minimum detectable HPLC response being equal to 5 times the background noise, assuming an equivalent of 1 ml final extract from one half of the glass fibre filter and assuming an HPLC injection of 20 ul. The volume of sample injection can be increased accordingly if an improvement in detection limit is required.

Table 5. HPLC DETECTION LIMITS FOR PAHs

<u>Compounds</u>	<u>Detection limit</u> ng/m <sup>3</sup>
Phenanthrene	0.05
Anthracene	0.02
Fluoranthene	0.2
Pyrene	0.2
Benz[a]anthracene	0.1
Chrysene	0.1
Benzo[b]fluoranthene	0.1
Benzo[k]fluoranthene	0.1
Benzo[a]pyrene	0.1
Benzo[ghi]perylene	0.4
Dibenz[a,h]anthracene	0.2
Indeno[1,2,3-cd]pyrene	0.1

A complete analytical method for the determination of polycyclic aromatic hydrocarbons in airborne particulate matter, which has been submitted to the Standards Association of Australia for publication as a standard method, is presented in Appendix 7.4.

## 2.6 Monitoring Program

Initially, three sampling sites were studied over a period of 12 months, starting from 6th January, 1984 to 31st December, 1984. Particulate matter in the air at these sites was collected once every six days with a collection time of 24 hrs. The sites investigated were:

- Sydney city (corner of George and Market Streets)
- Rozelle (Rozelle Hospital compound)
- Port Kembla (Military Road, near ER&S)

Sydney City - This site is located in the heart of the central business district of Sydney city (on the corner of George Street

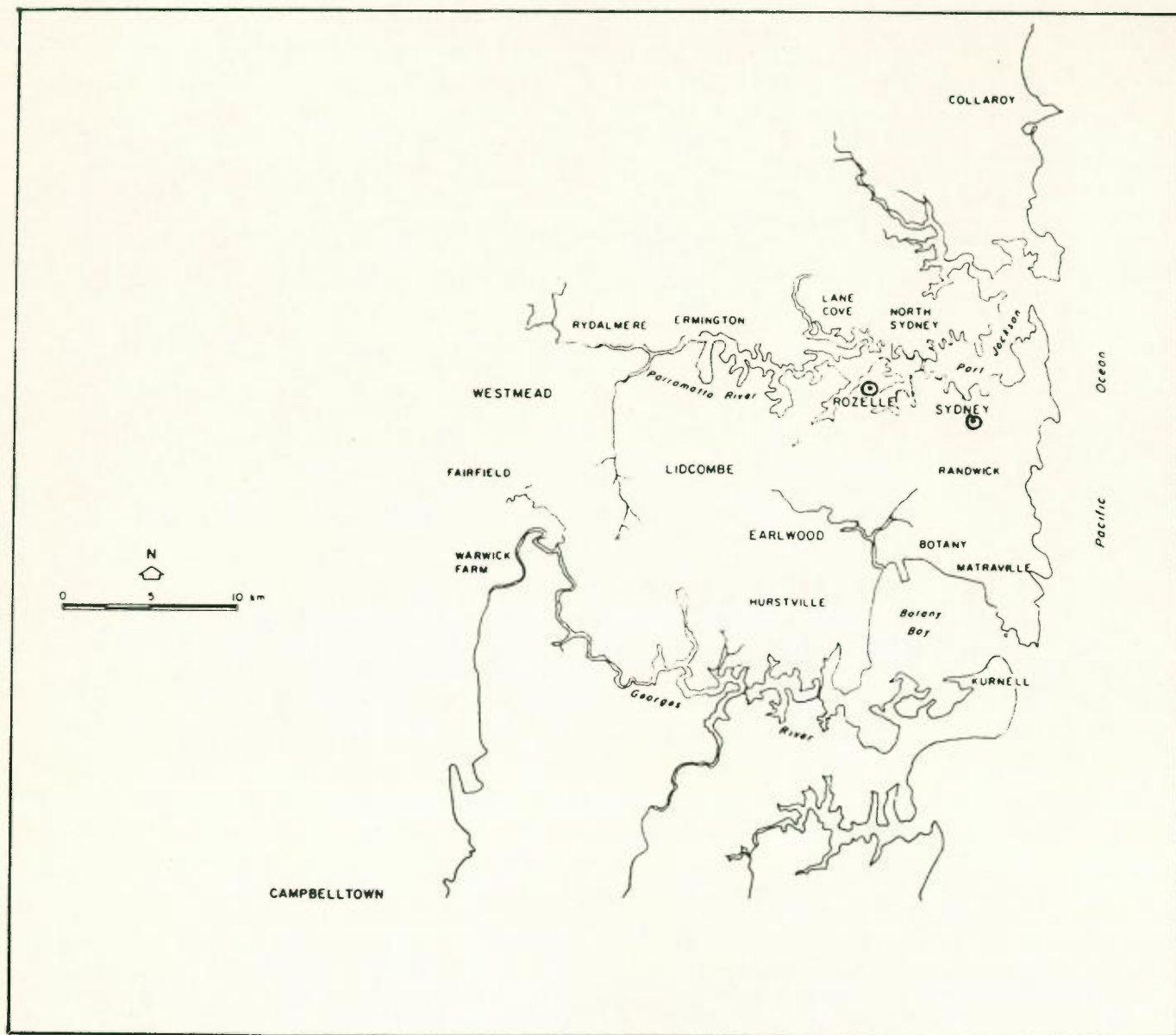
FIG. 7. SAMPLING LOCATIONS AT SYDNEY CITY AND ROZELLE

FIG. 8. SAMPLING LOCATION AT PORT KEMBLA

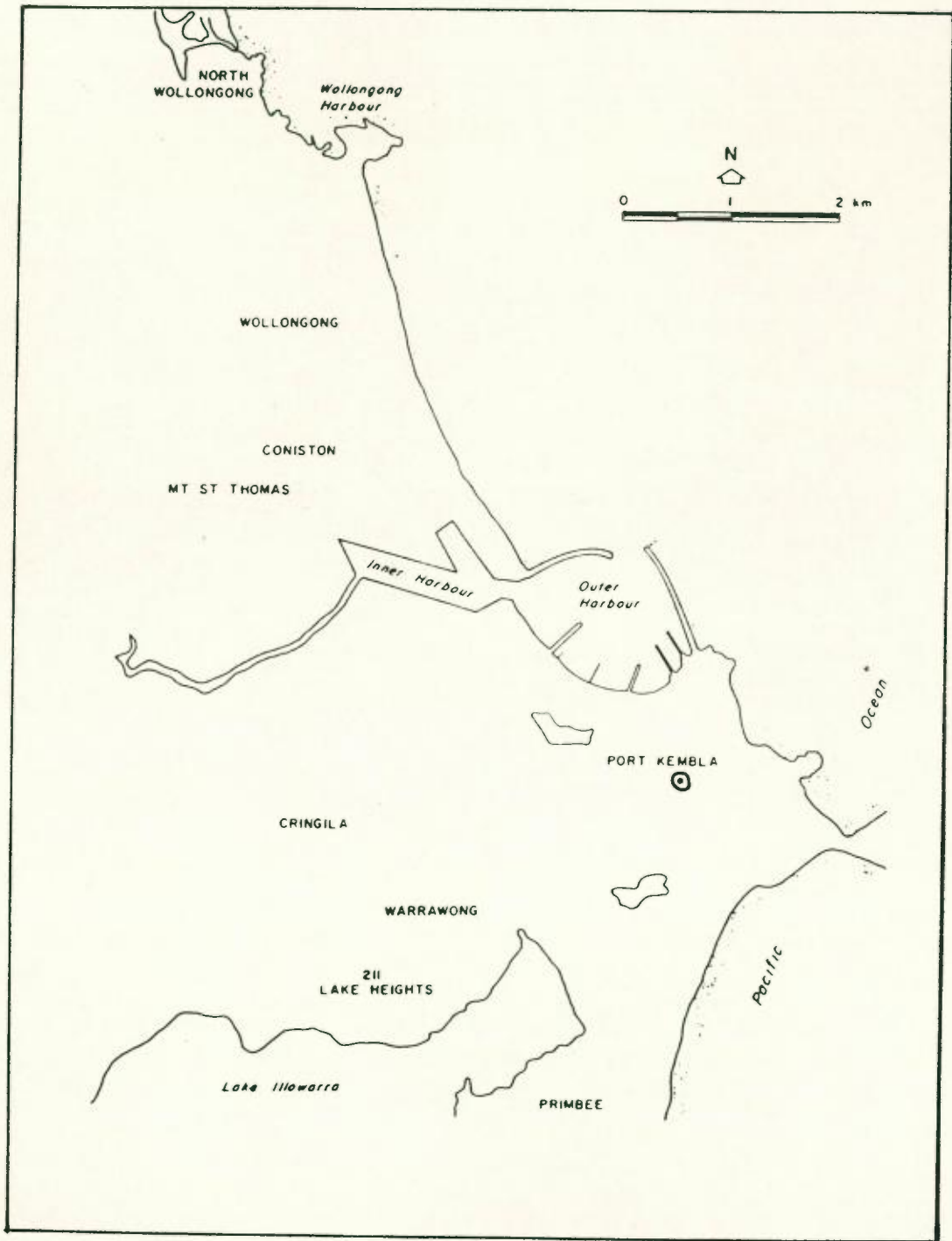
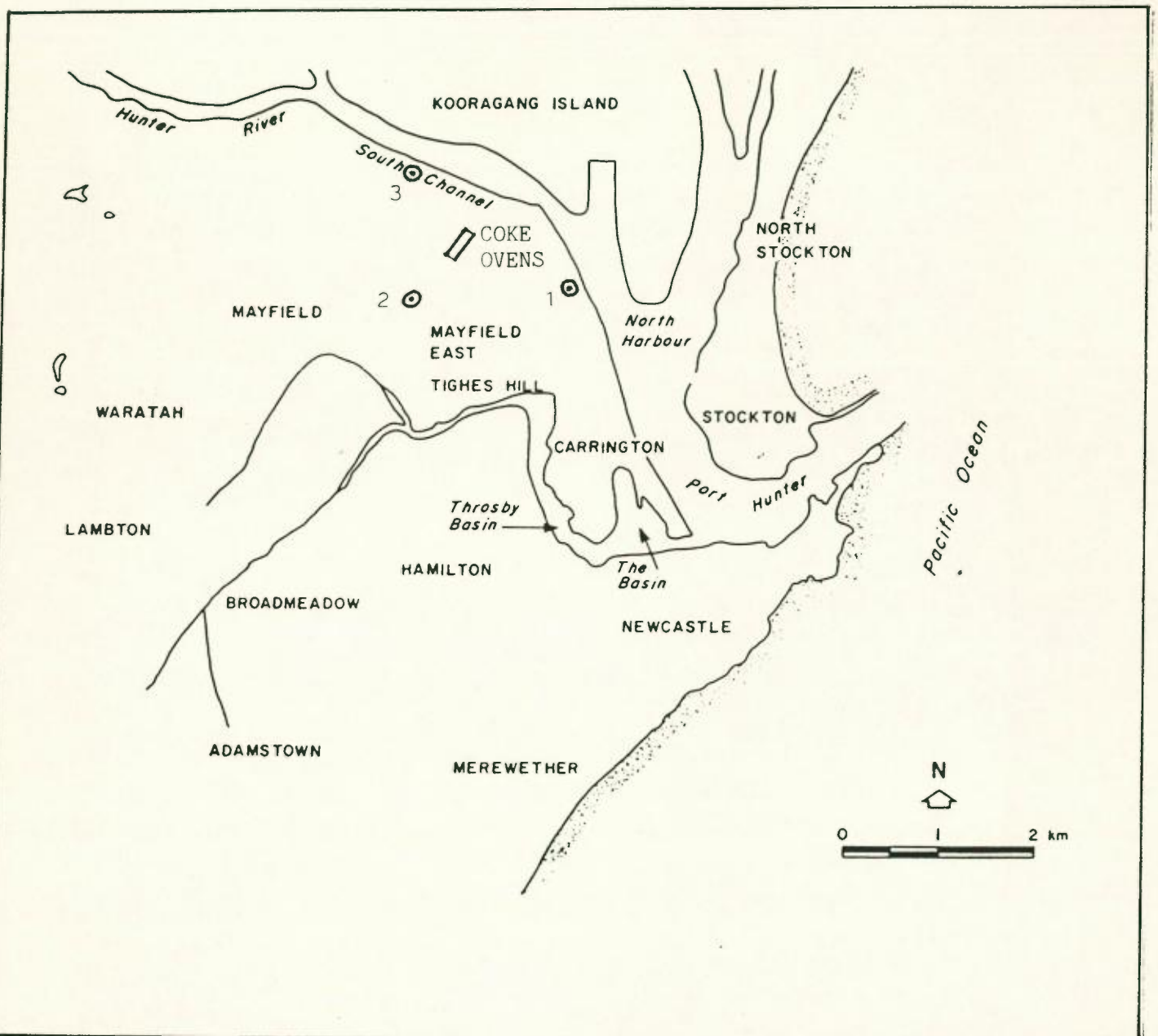




FIG. 9. SAMPLING LOCATIONS AT THE BHP STEEL WORKS NEWCASTLE

- (1) Carrington Gate
- (2) Folly Park
- (3) Oxygen Plant

and Market Street (see Fig 7)). The high volume sampler was placed in Myer's building facing towards the main road at a height of about 5m from the ground. The site is surrounded by high rise, multi-storeyed buildings mainly used for commercial purposes. The main source of pollution in this area is motor vehicle exhaust identified from the Commission's lead and carbon monoxide monitoring programme.

Rozelle - This site is a residential area with less traffic density than the Sydney site and less industrialisation compared to the Port Kembla site. It is located inside the grounds of Rozelle Hospital (see Fig. 7).

Port Kembla - This site is located near the fire station which is on the corner of Church Street and Military road (see Fig 8). It is in a residential area adjacent to an industrial area mostly affected by the emissions from the nearby Electrolytic Refining and Smelting Co and, to a lesser extent, by Australian Iron and Steel Ltd. and British Australian Cables Ltd.

Newcastle - The concentration of heavy industry in the area has resulted in considerable air pollution. There is much evidence from overseas work that industries such as coke production, aluminium production, coal-gasification, and iron and steel foundries are the main stationary sources of PAH emissions in the atmosphere. A detailed study of PAH emissions from these industries is not possible here. However, some areas affected by coke ovens in the BHP Steel Works at Newcastle were investigated. Three sampling sites located around the BHP Steel Works were considered: 1. Carrington gate, approximately 1200 metres east from the coke oven, 2. Folly Park, approximately 650 metres south west from the coke oven and 3. Oxygen plant, approximately 600 metres north west from the coke oven (see Fig 9). Air particulate samples from these three sites were collected for 24 hrs periods using high volume samplers on 1-2 May 1985, 4-5 June 1985 and 26-27 August 1985. Average wind directions during the sampling period were recorded. In order to confirm

the source of PAH emissions, one of the samples was analysed for lead using the method described in Australian Standard 2800-1985 (Ambient Air - Determination of Particulate Lead).

### 3. RESULTS AND DISCUSSION

#### 3.1 Annual Average PAH concentrations at Rozelle, Sydney City and Port Kembla

Annual average PAH concentrations for Rozelle, Sydney and Port Kembla during the year 1984 are presented in Table 6. The highest annual average PAH concentration (Total of 12 PAHs) found in this study was at Sydney city ( $14.7 \text{ ng/m}^3$ ), followed by Port Kembla ( $10.2 \text{ ng/m}^3$ ). The lowest was at Rozelle ( $7.0 \text{ ng/m}^3$ ). It should be noted that the concentrations of PAHs in Sydney in 1984 were generally less than those reported for Los Angeles (USA) in 1971-72 (see Table 2) before catalyst equipped motor vehicles were introduced.

Identification of the sources of PAHs absorbed in air particulate matter has been attempted by a number of workers using selected PAHs as source indicators (Sawicki et al. 1960 and Hangebrauck et al. 1967). The ratio of benzo[a]pyrene to benzo[ghi]perylene, one of the most commonly used source indicators, indicates that the source of PAHs emission in this study was generally due to automobile exhaust products. This was also found to be the case in Los Angeles. The average ratios of benzo[a]pyrene to benzo[ghi]perylene found in this study for Rozelle, Sydney and Port Kembla were 0.49, 0.42 and 0.48 respectively. These figures are lower than 0.76 reported for Sydney city in 1962 (calculated from Table 2). The dramatic increase in the motor vehicle population over the last 20 years, accompanied by the rapid decline of coal as fuel source for industry and domestic heating, are the likely factors responsible for this change.

TABLE 6. ANNUAL AVERAGE CONCENTRATIONS OF POLYCYCLIC AROMATIC HYDROCARBONS (ng/m<sup>3</sup>) IN SYDNEY AND PORT KEMBLA - 1984

PAHs	Rozelle	Sydney	Port Kembla
Phenanthrene	0.14	0.24	0.17
Anthracene	0.02	0.04	0.04
Fluoranthene	0.43	0.81	0.84
Pyrene	0.50	0.95	1.10
Benz[a]anthracene	0.16	0.36	0.41
Chrysene	0.45	0.93	0.87
Benzo[b]fluoranthene	0.77	1.45	1.22
Benzo[[k]fluoranthene	0.22	0.34	0.39
Benzo[a]pyrene	0.70	1.26	0.84
Benzo[ghi]perylene	1.41	3.00	1.72
Diben[a,h]anthracene	1.18	3.35	1.27
Indeno[1,2,3-cd]pyrene	1.00	1.96	1.25
<u>TOTAL (12 PAHs)</u>	<u>6.98</u>	<u>14.69</u>	<u>10.2</u>

In this study, 60 samples were collected from each site throughout 1984. The highest concentrations of PAHs in the air particulate samples at all the sites occurred on 26th June, 1984 (Table 7) when the recorded ambient temperature and the atmospheric dispersion rate were at a minimum (Hawke). The reasons were probably due to high consumption of fossil fuel and a low rate of atmospheric dispersion.

TABLE 7      PAH LEVELS (ng/m<sup>3</sup>) MEASURED ON 26.6.84

<u>PAHs</u>	<u>Rozelle</u>	<u>Sydney</u>	<u>Port Kembla</u>
Phenanthrene	0.1	0.2	0.5
Anthracene	-	0.1	0.1
Fluoranthene	1.4	2.7	7.3
Pyrene	-	2.7	3.1
Benz[a]anthracene	3.1	2.1	4.2
Chrysene	6.6	5.6	5.3
Benzo[b]fluoranthene	15.5	11.9	8.2
Benzo[k]fluoranthene	3.6	3.0	3.1
Benzo[a]pyrene	14.7	14.6	7.8
Benzo[ghi]perylene	20.5	15.7	9.9
Dibenz[a,h]anthracene	19.5	17.1	6.7
Indeno[1,2,3-cd]pyrene	19.6	14.6	7.2
Total PAHs	106.6	89.3	63.4

### 3.2 Seasonal Variation of PAHs

Ambient PAH levels measured during this study exhibited marked seasonal variations. Typical HPLC chromatograms of Sydney city air samples extracted during winter and summer days are shown in Figs. 10 and 11 respectively. Monthly average concentrations of total PAHs for Sydney, Rozelle and Port Kembla, measured during 1984, are shown in Fig. 12. The variations are more significant in the inner city and residential areas than for those observed in the industrial area. It should be noted that the sampling location for the industrial area (Military Road) selected in this study is mostly affected by the nearby Electrolytic Refining and

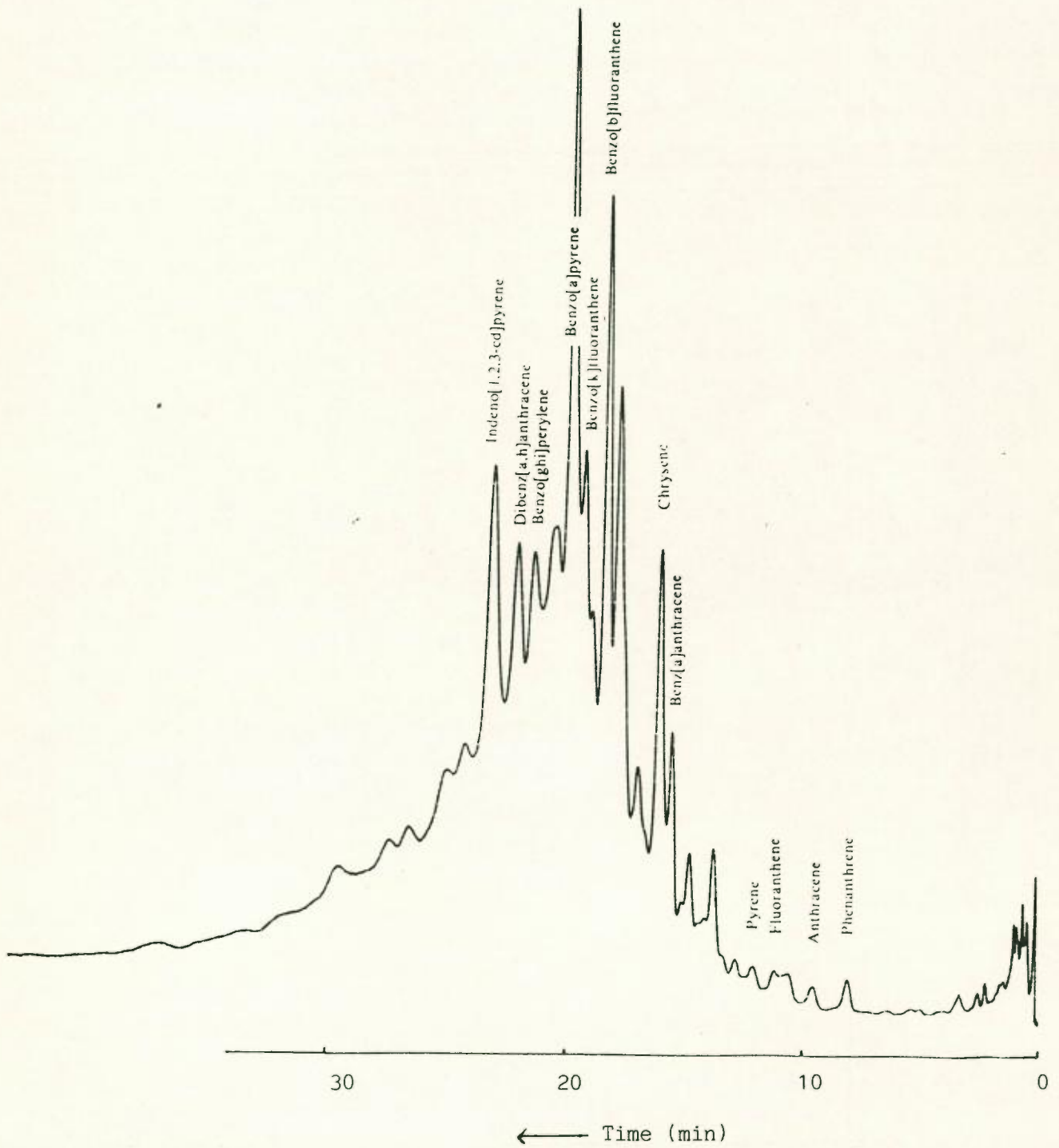


Fig. 10. TYPICAL WINTER TIME CHROMATOGRAM OF SYDNEY CITY AIR SAMPLE EXTRACT

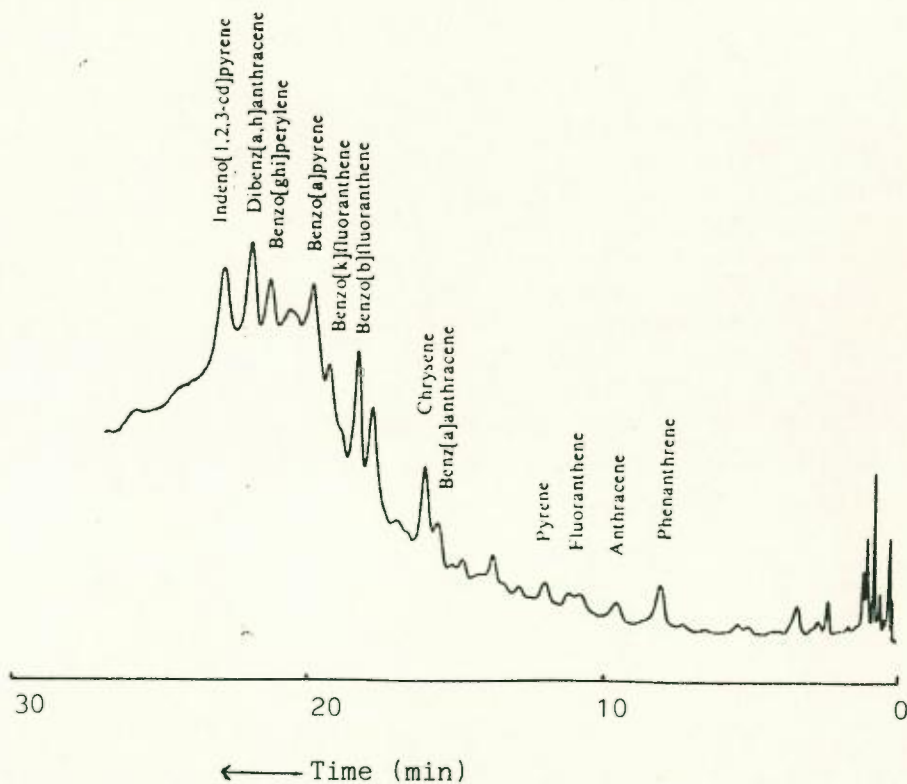


Fig. 11. TYPICAL SUMMER TIME CHROMATOGRAM OF SYDNEY AIR SAMPLE EXTRACT

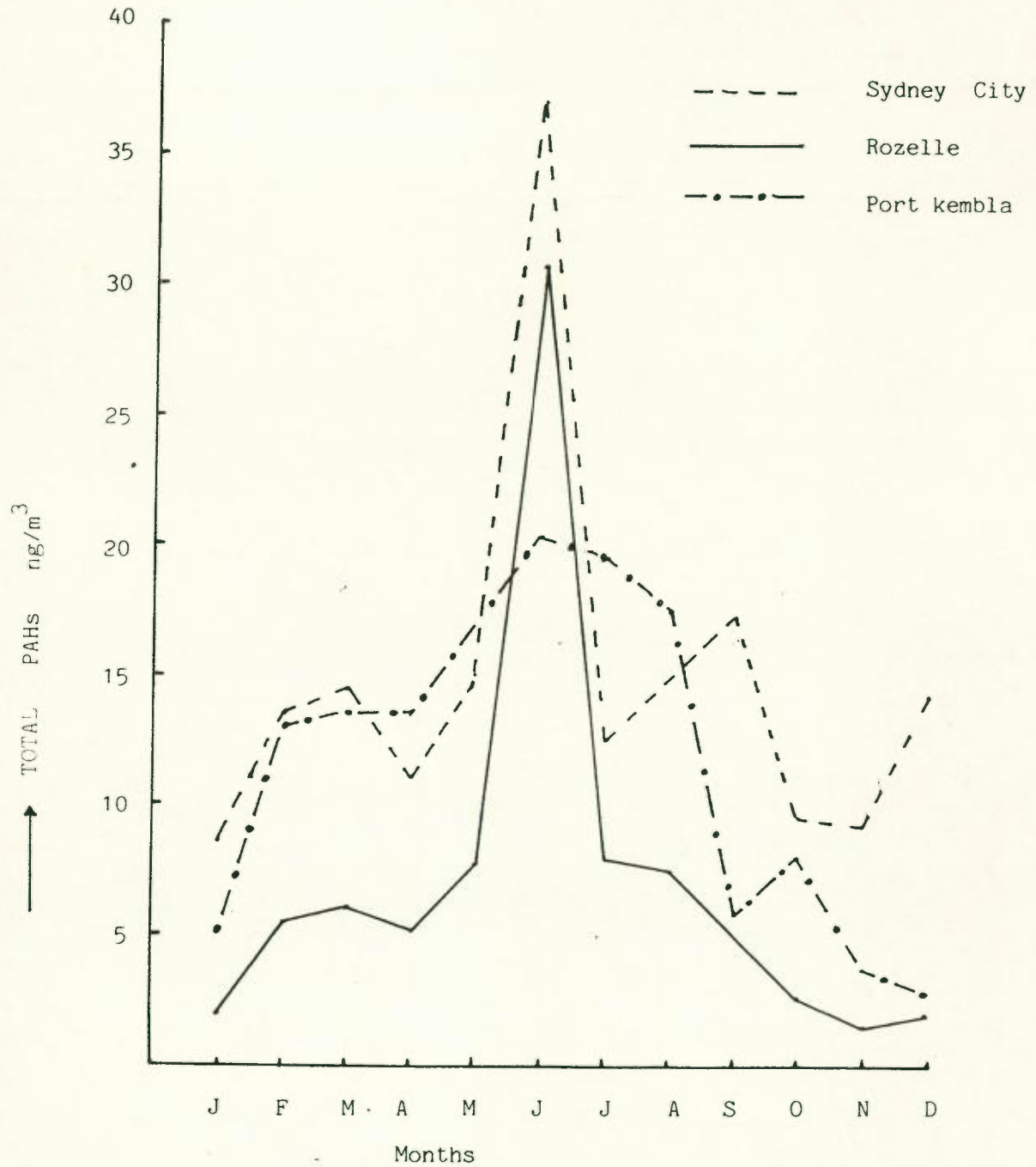


Fig. 12 Monthly Average PAHs ---- 1984



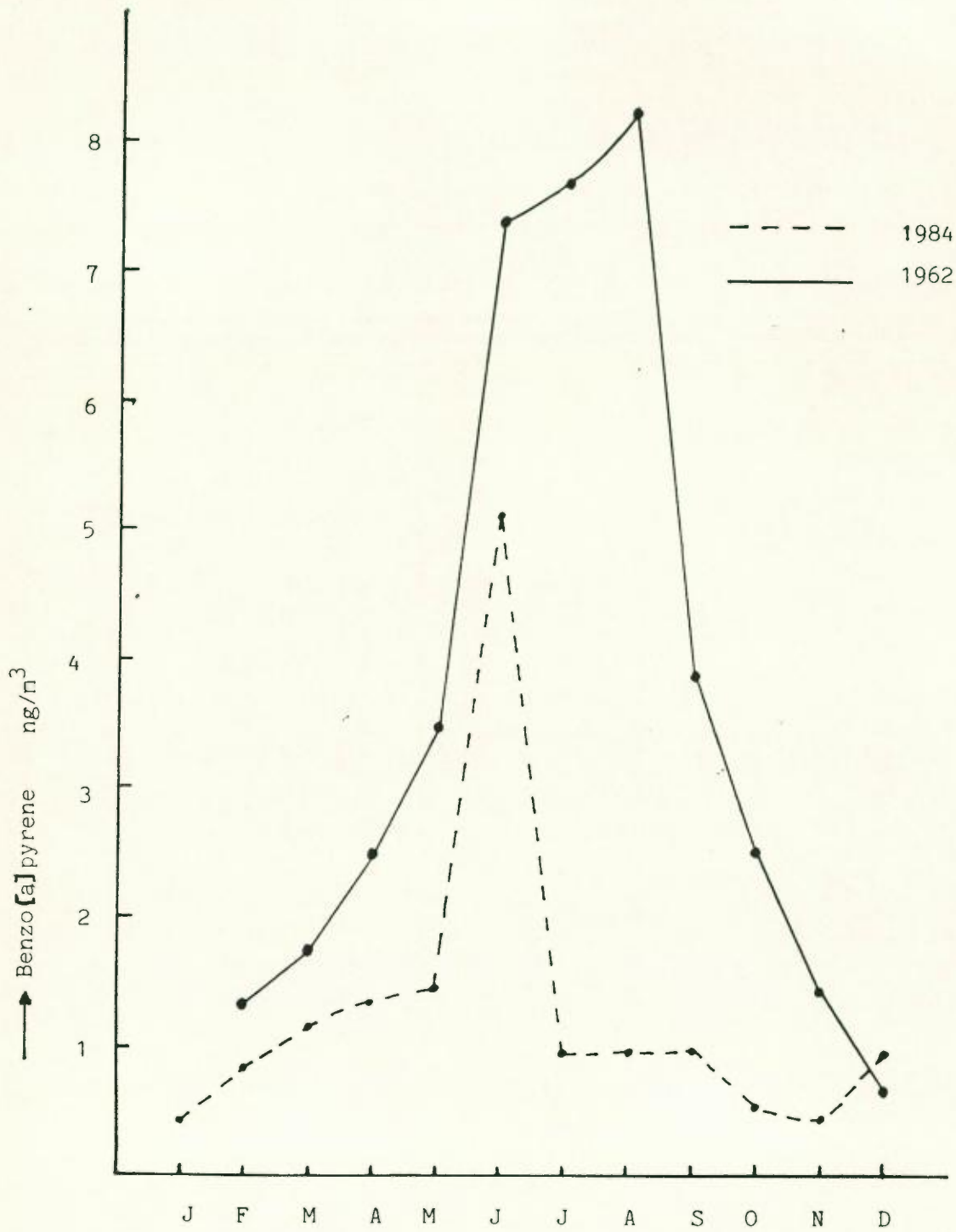


Fig. 13 Monthly Average Benzo[a]pyrene in Sydney City.

1984 and 1962

Smelting Company. Table 8 shows the winter and summer average concentrations of PAHs measured in Sydney city in 1984 and those reported for 1962 by Cleary and Sullivan (1965). Accurate comparisons cannot be made as the 1962 study did not produce precision data. The average PAHs concentrations during the winter season (June-August) are lower than those for the summer season (Dec-Feb), with summer-to-winter ratio ranging typically from 0.3 to 1. The winter average benzo[a]pyrene level is much lower in 1984 than for 1963, however, there is no significant change observed during the summer season (see Fig. 13). As mentioned earlier, the rapid decline of the use of coal for industrial and domestic purposes is partly responsible for this change.

Several factors may be involved in the seasonal variations in ambient PAH levels. It is reasonable to assume that fossil fuel consumption for domestic heating is higher in winter than in summer but there is little doubt that the reduced atmospheric dispersion in winter is the major factor.

Further details of the PAHs results measured at Rozelle, Sydney and Port Kembla are tabulated and presented graphically in the Appendices 7.1, 7.2 and 7.3 respectively. For comparison, monthly average concentrations of total suspended particulate matter (TSP) are also included.

TABLE 8 SEASONAL VARIATION OF AMBIENT PAH LEVELS (ng/m<sup>3</sup>) IN SYDNEY CITY PAST AND PRESENT

PAHs	SYDNEY 1984		SYDNEY 1962	
	WINTER	SUMMER	WINTER	SUMMER
	JUNE-AUG	DEC-FEB	JUNE-AUG	DEC-FEB
Phenanthrene	0.21	0.32		
Anthracene	0.04	0.04		
Fluoranthene	1.29	0.73	2.04	0.21
Pyrene	1.05	1.01	3.4	0.68
Benz[a]anthracene	0.52	0.4	5.3	0.74
Chrysene	1.23	0.91	4.07	0.56
Benzo[a]fluoranthene	2.42	0.91		
Benzo[k]fluoranthene	0.60	0.26		
Benzo[a]pyrene	2.35	0.74	7.70	0.83
Benzo[ghi]perylene	4.40	2.34	8.60	1.50
Diben[a,h]anthracene	4.43	2.68		
Indeno[1,2,3-cd]pyrene	2.91	1.55		
Total (12 PAHs)	21.45	11.89		

### 3.3 PAH Levels in the Vicinity of Coke Ovens, Newcastle

The concentrations of 12 PAHs which were measured at three sites; Carrington gate, Folly Park and Oxygen plant around the BHP Steel Works at Newcastle (see Fig. 9) during May, June and August 1985, are presented in Table 9. The concentrations of PAHs vary significantly depending on the sampling sites and the wind directions. On 4-5 June, 1985, the highest total PAH level measured was 359.8 ng/m<sup>3</sup> at Carrington gate when the wind direction was westerly, whereas on 1-2 May, 1985, when the wind direction was east and south easterly, the highest PAHs level

TABLE 9

## POLYCYCLIC AROMATIC HYDROCARBONS (PAHs)

## B.H.P. NEWCASTLE

Sampling Date	4 - 5 June 1985			1 - 2 May 1985			26 - 27 August, 1985		
Wind direction	Westerly			E & S Easterly			S & Westerly		
Site	1	2	3	1	2	3	1	2	3
Total PAHs	359.8	48.1	24.7	34.6	3.4	434.4	19.7	12.3	77.3
Phenanthrene	5.2	1.2	2.7	2.1	0.2	2.3	1.8	1.0	4.3
Anthracene	1.8	0.3	0.4	0.3	0.03	1.5	.2	0.1	0.5
Fluoranthene	42.5	6.1	5.1	6.6	0.6	45.2	4.1	2.9	10.6
Pyrene	18.7	4.6	2.5	4.8	0.4	17.1	4.6	2.9	8.6
Benz[a]anthracene	37.9	2.8	1.1	1.9	0.4	47.7	0.7	0.5	5.4
Chrysene	46.6	3.8	2.3	2.0	0.4	32.1	1.4	0.6	8.0
Benzo[b]fluoranthene	46.6	6.1	2.7	3.5	0.4	67.5	1.7	0.9	9.1
Benzo[k]fluoranthene	32.9	3.7	1.2	1.7	0.1	26.5	0.6	0.3	3.3
Benzo[a]pyrene	41.7	4.0	1.9	2.8	0.18	59.4	1.1	0.4	7.9
Benzo[ghi]perylene	35.8	6.8	2.4	3.0	0.36	58.3	1.0	1.0	7.0
Diben [a,h]anthracene	22.3	4.9	0.2	3.1		33.3	1.1	0.9	5.7
Indeno[1,2,3-cd]pyrene	28.2	3.8	2.2	2.8	0.3	43.5	1.4	0.8	6.9
Benzo(a)pyrene/Benzo(ghi)perylene	1.16	0.58	0.8	0.9	0.5	1.02	1.1	0.4	1.2

All the results are expressed in ng/m<sup>3</sup>

Site No. 1 - Carrington Gate (approximately 1200 m east from Coke Ovens)  
 Site No. 2 - Folly Park (approximately 650 m south west from Coke Ovens)  
 Site No. 3 - Oxygen Plant. (approximately 600 m north west from Coke Ovens)

measured was 434.4 ng/m<sup>3</sup> at the Oxygen plant. On 26-27 August 1985, when the wind direction was south and westerly, the highest PAHs level was 77.3 ng/m<sup>3</sup> at the Oxygen plant (see Fig 9).

The ratios of benzo[a]pyrene to benzo[ghi]perylene for all samples collected from Carrington gate and Oxygen plant were in the range of 0.8 to 1.2 which indicate the PAHs emissions were mainly due to the combustion of coke and coal. The wind directions also support this finding. The low PAH levels and the ratios of benzo[a]pyrene to benzo[ghi]perylene, which was in the range of 0.4 to 0.58 at sampling point 2 (Folly Park) for the entire sampling period, indicate that the source of PAH emissions was mostly due to motor vehicle exhausts from nearby roads and highways. Lead, which is an indicator of motor vehicle exhaust emissions, was determined in the airborne particulate samples collected on 1-2 May, 1985. The results obtained were 95 ng/m<sup>3</sup>, 236 ng/m<sup>3</sup> and 300 ng/m<sup>3</sup> for Carrington gate, Folly park and Oxygen plant respectively and the ratios of lead to total PAHs were 2.7, 69.4 and 0.7 respectively. The high lead/PAHs ratio at Folly park supports the view that automobiles are the main source of PAHs measured.

The occurrence of PAHs in the work atmospheres of coke oven furnaces is well established. The American Conference of Government Industrial Hygienists has established a threshold limit value (TLV) for coal tar pitch volatiles (benzene-soluble fraction of total particulates) of 0.2 mg/m<sup>3</sup> of air, for an 8 hours daily exposure. However, there are, as yet, no environmental standards for PAHs. The benzene soluble method has been shown to be inaccurate (Seim et al. 1974) and does not correlate well with the analytical determination of PAHs. Under the conditions of sampling on glass fibre filters, as used in this study, it should also be stated that the results presented here are somewhat conservative due to vapour losses of some of the low molecular weight PAHs during sampling.

4. CONCLUSIONS AND RECOMMENDATIONS

- High performance liquid chromatography provides a method with both sufficient sensitivity and selectivity for the determination of twelve individual PAHs in extracts of airborne particulate matter. The method established offers an attractive alternate for the routine monitoring of PAHs, in terms of cost and ease of operation.
- The annual average concentrations of total PAHs during 1984 for Sydney city, Port Kembla and Rozelle were  $14.7 \text{ ng/m}^3$ ,  $10.2 \text{ ng/m}^3$  and  $7.0 \text{ ng/m}^3$  respectively. Maximum levels of PAHs, ie  $106.6 \text{ ng/m}^3$  at Rozelle site,  $89.3 \text{ ng/m}^3$  at Sydney city site and  $63.4 \text{ ng/m}^3$  at Port Kembla, were recorded on 26.6.85
- Several variations were observed in PAH concentrations, with the highest levels found during the winter season. For instance, the average level of total PAHs in Sydney city was about two times higher during winter ( $21.5 \text{ ng/m}^3$ ) than that found during summer ( $11.9 \text{ ng/m}^3$ ). This variation was more significant in residential and commercial areas than in industrial areas, possibly because of increased fossil fuel burning during winter in the residential and commercial areas.
- PAH levels measured in the inner city of Sydney are generally less than those reported for Los Angeles (USA) in 1971-72, before catalyst equipped motor vehicles were introduced. In both these cities motor vehicles are the major contributors of PAHs. These levels are much lower than those reported for the industrial coal burning cities of Birmingham (USA) and Osaka (Japan).
- PAH levels in Sydney city appear to be at least two to three times less than those found 20 years ago. With the recent introduction of catalyst equipped motor vehicles

these levels are further expected to decrease. The past trends for residential and industrial areas are not yet known as these areas were not included in the previous survey. Future work at an interval of at least five years should be continued in order to obtain the PAHs trends in N.S.W.

- Coke ovens in BHP Newcastle are contributing significantly to atmospheric pollution. The preliminary data (Table 8) is a cause for concern about the impact of the emissions on air quality in the Newcastle area. Studies aimed at the identification of the mutagenic activity of the ambient air in the city of Newcastle would be enlightening.
- Further sampling and analysis of airborne particulate matter in the vicinity of coke ovens should be conducted in order to establish long term residential exposures.

## 5. ACKNOWLEDGEMENTS

Thanks are especially due to the following people who made important contributions throughout this project; Dr R. Goldsack, Mr J. Shortland and Dr. G. Hawke for valuable discussions, Mr E. Pender and Mr J. Kostiw for ambient air particulate sampling and finally Ms. K. Preston for technical assistance.



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## 7. APPENDICES

- 7.1 Monthly Average Airborne PAHs concentration for Sydney city - 1984..
- 7.2 Monthly Average Airborne PAHs concentration for Rozelle - 1984
- 7.3 Monthly Average Airborne PAHs concentration for Port Kembla (Military Road) - 1984.
- 7.4 Determination of PAHs in Ambient Air - Method.

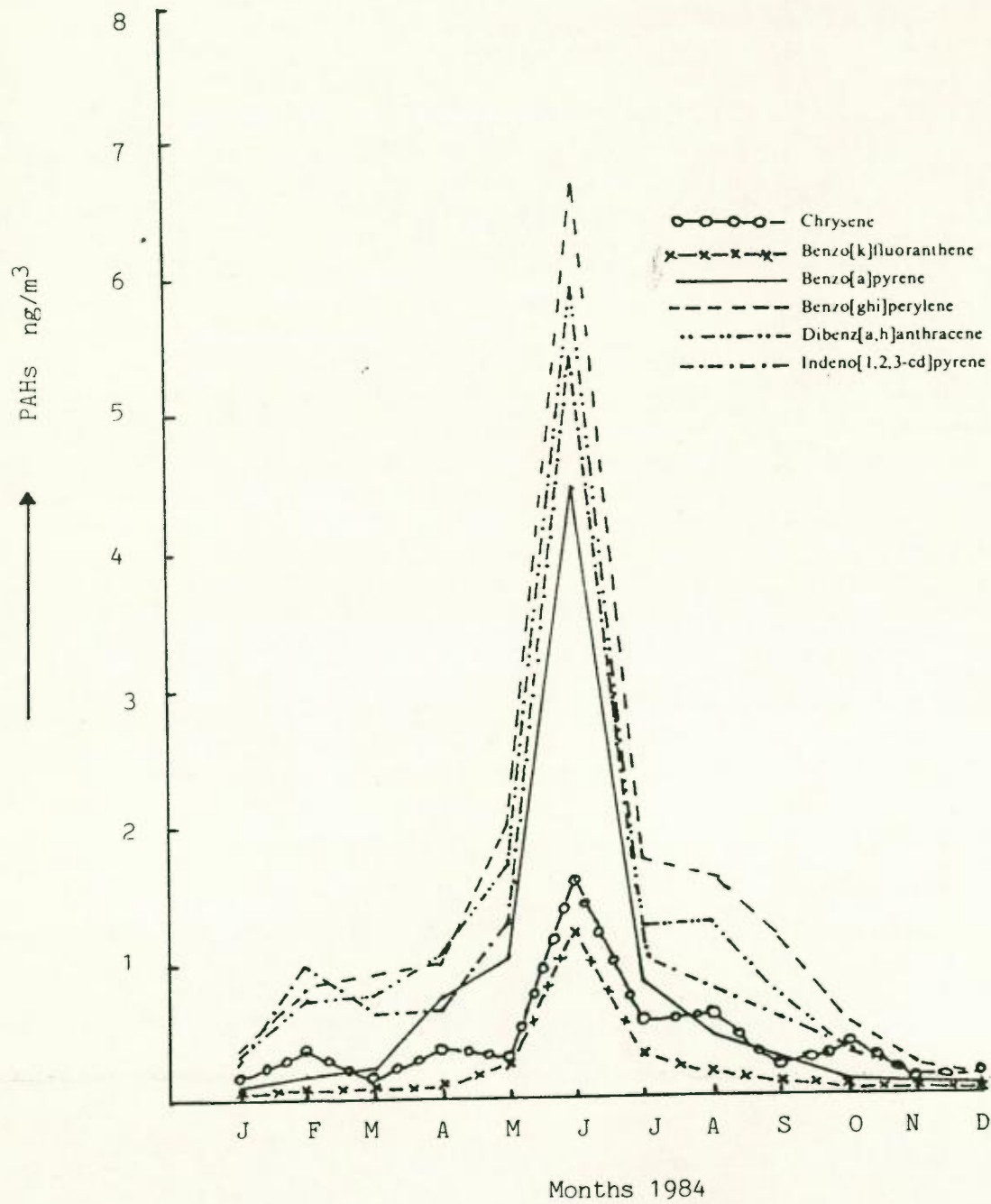
APPENDIX 7.1 MONTHLY AVERAGE AIRBORNE PAH CONCENTRATION FOR SYDNEY CITY - 1984

Month	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec	Annual Average
Phenanthrene	0.24	0.34	0.15	-	0.12	0.25	0.09	0.03	0.62	0.19	0.20	0.39	0.24
Anthracene	-	0.02	0.03	0.04	0.04	0.050	.03	0.05	0.10	0.02	0.02	0.08	0.04
Fluoranthene	0.23	0.63	0.71	0.78	0.57	1.94	0.62	1.28	0.80	0.30	0.56	1.33	0.81
Pyrene	0.31	1.10	0.58	0.83	0.42	0.85	0.85	1.44	1.65	0.65	1.06	1.62	0.95
Benz[a]anthracene	0.11	0.3	0.27	0.04	0.31	0.65	0.35	0.56	0.62	0.17	0.13	0.79	0.36
Chrysene	0.47	0.75	1.06	0.61	0.80	1.91	0.77	1.00	1.26	0.52	0.56	1.51	0.93
Benzo[b]fluoranthene	0.53	0.80	1.40	1.17	1.41	4.60	1.34	1.33	1.54	0.87	1.10	1.28	1.45
Benzo[k]fluoranthene	0.15	0.27	0.38	0.11	0.31	1.02	0.29	0.48	0.30	0.21	0.25	0.36	0.34
Benzo[a]pyrene	0.43	0.84	1.14	1.36	1.41	5.16	0.92	0.98	0.98	0.51	0.41	0.96	1.26
Benzo[ghi]perylene	2.13	2.96	2.75	1.82	3.45	7.41	3.02	2.79	3.50	2.27	1.75	1.93	3.00
Diben[a,h]anthracene	2.54	2.62	3.71	2.84	3.59	7.52	2.71	3.06	3.61	2.57	2.14	2.26	3.35
Indeno[1,2,3-cd]pyrene	1.48	1.91	2.15	1.45	1.93	5.51	1.55	1.68	2.10	1.31	1.18	1.27	1.96
Total PAHs (ng/m <sup>3</sup> )	8.62	13.54	14.33	11.05	14.33	36.9	12.54	14.95	17.08	9.59	9.36	13.78	14.69
Particulate Conc.(ug/m <sup>3</sup> )	80	83	137	93	113	133	73	104	103	112	123	197	113



## Appendix 7.1

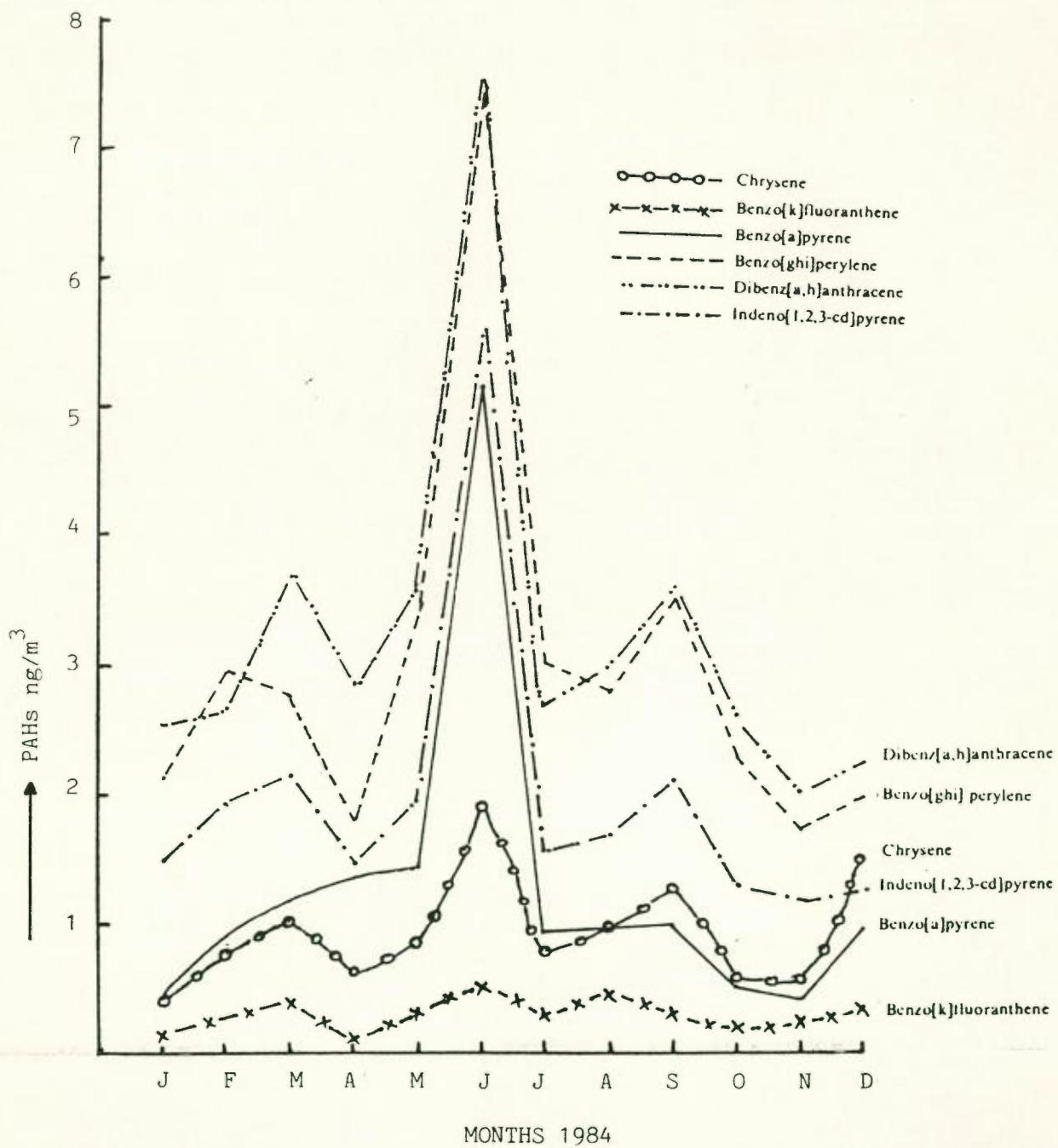
## MONTHLY AVERAGE PAHs - SYDNEY CITY 1984



APPENDIX 7.2 MONTHLY AVERAGE AIRBORNE PAH CONCENTRATION FOR ROZELLE - 1984

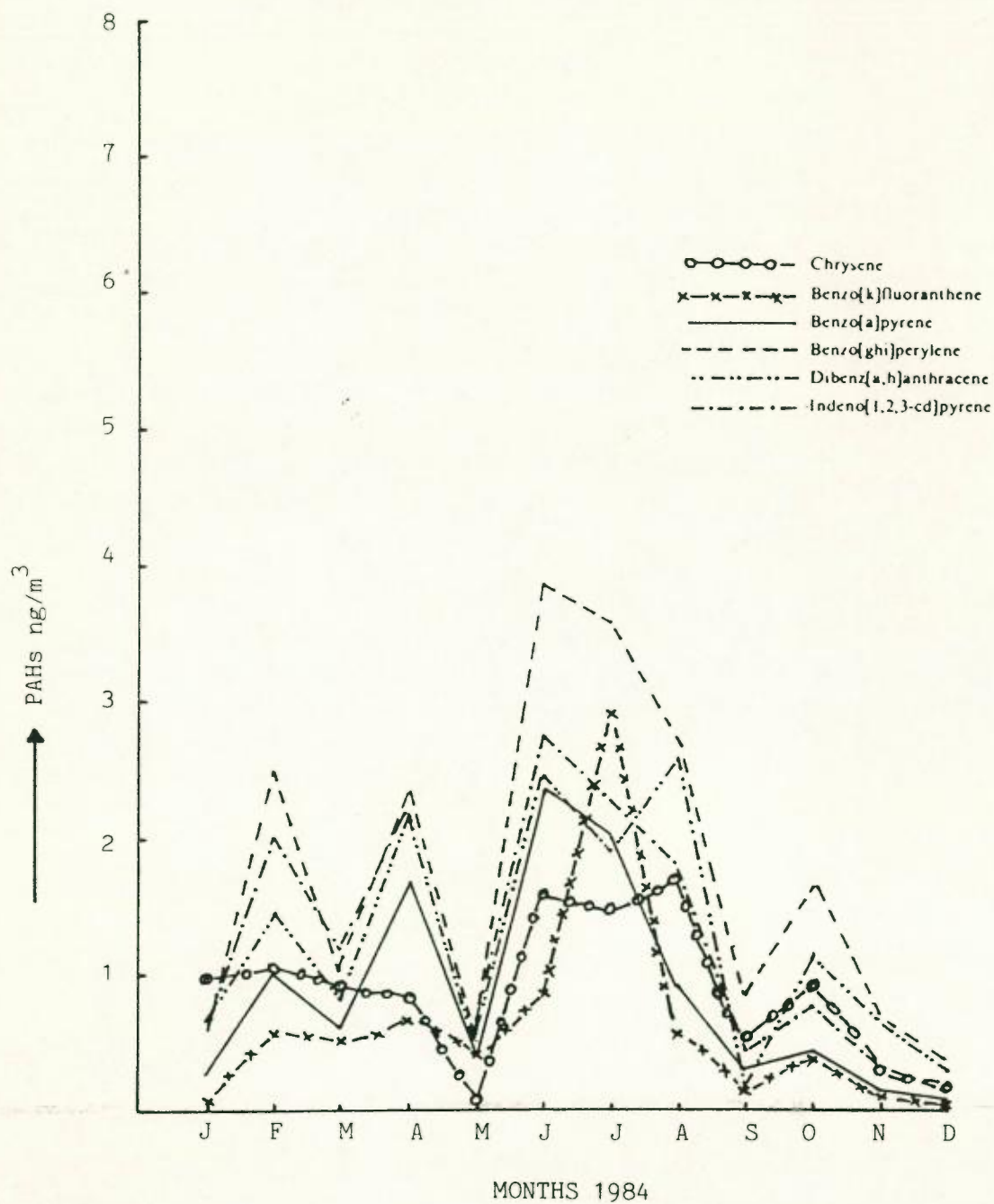
Month	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec	Annual Average
Phenanthrene	0.12	0.27	0.25	0.01	0.19	0.05	0.04	0.22	0.28	0.16	0.02	0.05	0.14
Anthracene	0.01	0.04	0.04	0.03	0.03	0.01	0.01	0.02	0.03	0.02	-	0.01	0.02
Fluoranthene	0.18	0.57	0.74	0.40	-	0.43	0.47	0.83	0.70	0.35	0.12	0.35	0.43
Pyrene	0.22	1.01	0.99	0.29	0.04	0.04	0.10	0.96	0.50	0.45	0.43	0.98	0.50
Benz[a]anthracene	0.04	0.14	0.27	0.06	-	0.72	0.44	0.09	-	0.03	0.08	0.12	0.16
Chrysene	0.14	0.36	0.17	0.37	0.30	1.58	0.55	0.57	0.26	0.36	0.09	0.16	0.45
Benzo[b]fluoranthene	0.16	0.22	0.46	0.40	1.02	4.29	0.17	0.56	0.44	0.25	0.08	0.20	0.77
Benzo[k]fluoranthene	0.04	0.07	0.17	0.12	0.33	1.18	0.29	0.19	0.09	0.10	0.07	0.04	0.22
Benzo[a]pyrene	0.09	0.17	0.20	0.72	1.01	4.46	0.83	0.46	0.25	0.07	0.06	0.02	0.70
Benzo[ghi]perylene	0.37	0.81	0.83	1.00	2.00	6.68	1.74	1.60	1.18	0.51	0.22	0.05	1.41
Diben[a,h]anthracene	0.33	0.75	0.74	1.07	1.69	5.90	1.24	1.28	0.74	0.30	0.11	0.05	1.18
Indeno[1,2,3-cd]pyrene	0.27	0.99	0.67	0.64	1.22	5.43	1.00	0.75	0.53	0.24	0.13	0.05	1.00
Total PAHs (ng/m <sup>3</sup> )	1.99	5.39	6.08	5.10	7.81	30.76	7.89	7.54	5.01	2.84	1.47	2.08	6.98
Particulate Conc. (ug/m <sup>3</sup> )		36	55	51	40	48	60	35	42	35	49	31	40

Appendix 7.2 MONTHLY AVERAGE PAHs - ROZELLE 1984



APPENDIX 7.3 MONTHLY AVERAGE AIRBORNE PAH CONCENTRATION FOR PORT KEMBLA - 1984.

Month	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec	Annual Averag
Phenanthrene	0.17	0.39	0.36	0.01	-	0.11	0.22	0.32	0.28	0.13	0.04	0.04	0.17
Anthracene	0.01	0.03	0.08	0.02	0.01	0.04	0.07	0.13	0.05	-	0.01	0.03	0.04
Fluoranthene	0.56	1.10	1.44	1.05	-	1.96	1.70	0.87	0.17	0.57	0.35	0.35	0.84
Pyrene	0.62	1.19	2.11	0.34	-	0.76	1.19	2.93	1.62	1.06	0.57	0.82	1.10
Benz[a]anthracene	0.09	0.44	0.65	0.36	-	0.91	1.18	0.65	0.31	0.14	0.08	0.10	0.41
Chrysene	0.95	1.08	0.86	0.77	0.08	1.58	1.49	1.70	0.52	0.89	0.24	0.35	0.87
Benzo[b]fluoranthene	0.57	1.19	1.01	1.85	0.27	2.67	2.83	2.17	0.47	0.91	0.47	0.27	1.22
Benzo[k]fluoranthene	0.04	0.54	0.39	0.64	0.08	0.84	2.91	0.55	0.19	0.34	0.16	0.02	0.39
Benzo[a]pyrene	0.23	1.00	0.60	1.67	0.36	2.35	2.03	0.92	0.30	0.43	0.15	0.04	0.84
Benzo[ghi]perylene	0.58	2.50	1.02	2.36	0.56	3.84	3.59	2.68	0.84	1.66	0.68	0.37	1.72
Diben[a,h]anthracene	0.66	1.44	0.82	2.19	0.50	2.45	1.921	2.59	0.15	1.15	0.68	0.29	1.27
Indeno[1,2,3-cd]pyrene	0.56	2.00	1.18	2.20	0.55	2.73	2.26	1.82	0.45	0.75	0.35	0.18	1.25
Total PAHs (ng/m <sup>3</sup> )	5.04	12.90	10.52	13.46	2.39	20.24	19.39	17.33	5.71	8.03	3.76	2.87	10.2
Particulate Conc. (ug/m <sup>3</sup> )	122	102	144	107	46	88	90	92	63	149	121	127	104

Appendix 7.3 MONTHLY AVERAGE PAHs - PORT KEMBLA 1984

## APPENDIX 7.4

AMBIENT AIR - DETERMINATION OF POLYCYCLIC AROMATIC HYDROCARBONS (PAH)  
HIGH VOLUME SAMPLER COLLECTION (HIGH PERFORMANCE LIQUID  
CHROMATOGRAPHIC METHOD)CONTENTS

1. Scope
2. Application
3. Referenced documents
4. Principle
5. Reagents and materials
6. Apparatus
7. Sampling
8. Procedure
9. Calculations

1. SCOPE. This standard sets out a method for the determination of polycyclic aromatic hydrocarbons (PAH) in ambient air by high performance liquid chromatography (HPLC) after collection by filtration.

2. APPLICATION. This method is applicable to the determination of the following thirteen polycyclic aromatic hydrocarbons in ambient air:

Phenathrene, anthracene, fluoranthene, pyrene, benz[a]anthracene, chrysene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, benzo[ghi]perylene, dibenz[ah]anthracene, indeno [1,2,3-cd] pyrene, coronene.

The detection limit of the UV detector for each compound is listed in Table 5.

NOTE: Of the PAH species present in the air, these 13 are relatively abundant. They are involatile and are quantitatively collected by high volume filtration. This analysis procedure provides good HPLC separation of these compounds.

3. REFERENCED DOCUMENTS. The following standards are referred to in this standard:

- AS 2162 Code of Practice for use of Volumetric Glassware
- AS 2164 One-mark Volumetric Flasks
- AS 2166 One-mark Pipettes
- AS 2243 Safety in Laboratories - Part 2 - Chemical
- AS 2724 Ambient Air - Particulate Matter  
Part 3 - Determination of Total Suspended Particles  
(TSP) - High Volume Sampler Gravimetric Method

4. PRINCIPLE. Particulate matter in the atmosphere is collected in accordance with the procedure described in AS 2724.3. The PAH compounds associated with the particulate matter collected in the glass filter are extracted with cyclohexane by Soxhlet extraction. The extract is concentrated and purified by column chromatography. The polar fraction is then analysed by high performance liquid chromatography.

NOTE: Careful attention to detail is required in performing the analytical procedure. Some practice and experience are necessary before an analyst can be expected to conduct a successful analysis.

## 5. REAGENTS AND MATERIALS

5.1 General Requirements. Unless otherwise specified, all reagents shall be of analytical reagent grade and water shall be HPLC quality distilled in glass.

### 5.2 Solids

5.2.1 Sodium sulphate (anhydrous). Heat 50g of sodium sulphate ( $\text{Na}_2\text{SO}_4$ ) at  $400^\circ\text{C}$  for 4 hours in a shallow tray, allow to cool and store in a desiccator.

5.2.2 Silica gel (100-120 mesh). Before use, activate for at least 16 hours at  $130^\circ\text{C}$  in a foil-covered glass container.

### 5.3 Solvents.

5.3.1 Cyclohexane. Spectral grade.

5.3.2 Dichloromethane. HPLC grade.

5.3.3 Pentane. To be precleaned by passing through a silica gel column.

5.3.4 Acetonitrile. HPLC grade.

5.3.5 Acetone.

5.4 Calibration standards. The following reagents are required for instrument calibration.

5.4.1 Phenanthrene.

5.4.2 Anthracene.

5.4.3 Fluoranthene.

5.4.4 Pyrene.

5.4.5 Benz[a]anthracene\*

5.4.6 Chrysene\*

5.4.7 Benzo[b]fluoranthene\*

5.4.8 Benzo[k]fluoranthene\*

5.4.9 Benzo[a]pyrene\*

5.4.10 Benzo[ghi]perylene\*

5.4.11 Dibenz[ah]anthracene\*

5.4.12 Indeno(1,2,3-cd)pyrene\*

5.4.13 Coronene.



\* CAUTION: CARCINOGENS. These compounds have been reported to be carcinogenic. Consequently, extreme care shall be taken in handling laboratory equipment to avoid spilling solutions of PAH material on hands or other parts of the body. All operations using PAH compounds shall be carried out in a fume hood. Pipetting by mouth shall not be carried out. Laboratory practice for the handling of carcinogenic compounds shall be in accordance with AS 2243.2.

## 5.5 Standard solutions

5.5.1 Stock solutions (1000 ug PAH/mL). Using a series of thirteen 100mL ground glass stopper volumetric flasks, dissolve separately,  $0.100 \pm 0.001$  g of each calibration standard as listed in Table 10 in acetonitrile (5.3.4) and dilute to volume. Vigorous shaking may be required for complete dissolution. The stock solutions shall be stored in a refrigerator and checked frequently for signs of degradation or solvent evaporation, prior to preparing the working standard solution.

5.5.2 Intermediate mixed standard solution. Pipette aliquots of each stock solution (5.5.1) listed in Table 10 into a 250 mL ground glass stopper volumetric flask. Dilute to volume with acetonitrile (5.3.4). This solution shall be stored in the refrigerator when not in use.

5.5.3 Mixed working standard solution. Pipette 5.0 mL of intermediate mixed standard solution (5.5.2) into a 20mL volumetric flask and dilute to volume with acetonitrile (5.3.4). This solution shall be stored in the refrigerator when not in use and shall be checked frequently for signs of solvent evaporation.

NOTE: Commercially available stock solutions may be used as an alternative.

TABLE 10  
PREPARATION OF INTERMEDIATE MIXED STANDARD SOLUTION

Stock solution	Stock solution aliquot (mL)	Concentration (ug/mL)
Phenanthrene	5.0	20
Anthracene	5.0	20
Fluoranthene	10.0	40
Pyrene	10.0	40
Benz[a]anthracene	5.0	20
Chrysene solution	5.0	20
Benzo[b]fluoranthene	5.0	20
Benzo[k]fluoranthene	5.0	20
Benzo[a]pyrene	5.0	20
Benzo[ghi]perylene	10.0	40
Dibenz[ah]anthracene	10.0	40
Indeno[1,2,3-cd]pyrene	10.0	40
Coronene	40.0	160

## 6 APPARATUS

6.1 General. All glassware shall be washed with detergent solution, rinsed with tap water, then distilled water (not HPLC grade), then further rinsed with acetone (5.3.5) followed by cyclohexane (5.3.1) and dried before use. Grade A volumetric glassware complying with AS 2164 and AS 2166 shall be used. Use of volumetric glassware shall be in accordance with AS 2162.

6.2 Soxhlet extraction equipment. Consisting of:

6.2.1 Round bottom flask. 500mL capacity.

6.2.2 Soxhlet extractor. 60 mL capacity.

6.2.3 Extraction thimbles. 28 mm x 50 mm.

6.2.4 Condenser.

6.2.5 Heating mantle. Suitable for 500mL round bottom flask.

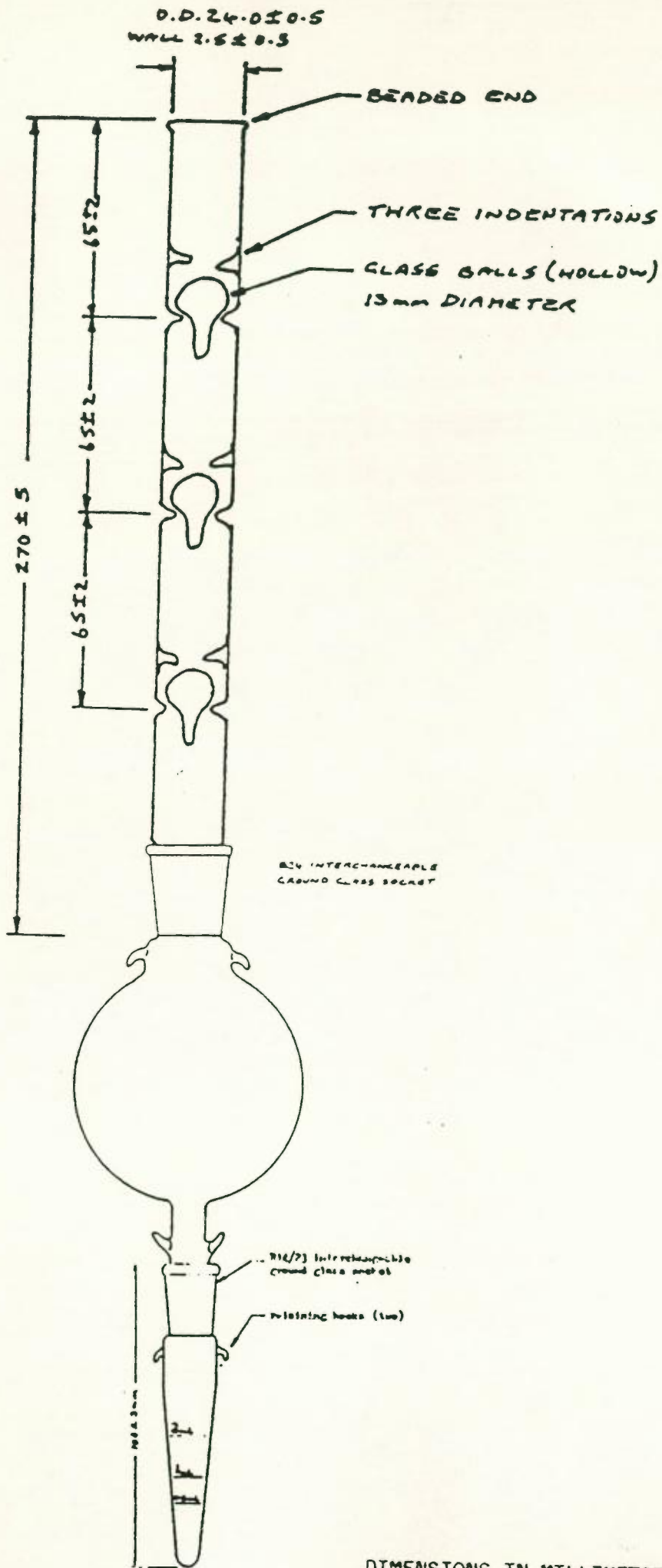
6.3 Boiling chips. Solvent extracted, approximately 10/40 mesh.

6.4 Kuderna-Danish (K-D) apparatus. (see Fig.14) Consisting of:

6.4.1 Evaporative Flask. 500 mL capacity. Attach to the concentrator tube with springs.

6.4.2 Concentrator tube. 10 mL graduated with a ground glass stopper to prevent evaporation of extract. The tube will be calibrated before use.

6.4.3 Snyder column. Three ball macro.



DIMENSIONS IN MILLIMETRES

Fig. 14. ASSEMBLED KUDERNA-DANISH APPARATUS

6.5 Water bath. With concentric ring covers and capable of temperature control to  $\pm 2^{\circ}\text{C}$ .

6.6 Chromatographic column. 250 mm x 10mm ID with coarse fritted disc at bottom. This shall be equipped with a ground glass joint at the top to accommodate a separating funnel as a solvent reservoir to prevent the column running dry.

6.7 HPLC instrument. An instrument with a constant flow solvent gradient pumping system, fitted with an HPLC column (6.7.1), constant column temperature control or column insulation and a UV detector (254 nm). The solvent program shall be set as follows:

- (a) Flow rate, 2.0 mL/min.
- (b) Set initial solvent mixture at 50 percent acetonitrile, (5.3.4), water mixture.
- (c) Program the solvent pump to deliver 90 percent acetonitrile, 10 percent water at 15 min after sample injection.
- (d) Hold the solvent concentration at 90 percent acetonitrile, 10 percent water for a further 15 min.

6.7.1 HPLC column. A PAH or equivalent column which will achieve the resolution of PAH compounds shown in Figure 6.

6.7.2 Recorder and integration system.

7 Sampling. The sample shall be collected in accordance with the procedure described in AS 2724.3, maintained in a dust proof, air-tight container and stored in the dark. If total suspended particulate analysis is not required, conditioning and weighing of the filter is not necessary.

## 8. PROCEDURE

8.1 Blank test. Carry out the procedure on the blank filter(s) obtained as described in Clause 6.1 of AS 2724.3.

8.2 Check test. In cases of dispute, one analysis of a certified reference material of PAH compounds (NBS-SRM-1647) shall be carried out under the conditions as the test sample.

NOTE: The certified reference material should contain the same components as the test sample.

8.3 Preparation of blank and test solution. The following procedure shall be applied equally to both the blank(s) and exposed filter(s) prepared in Clause 6.3 of AS 2724.3. The minimum number of blanks used shall be one per ten sample filters. For the determination, use the whole or a half or quarter that is representative of the whole of the exposed area of the filter. The filter shall be handled as little as possible. The cutting instrument shall be free from

contamination, clean sharp and shall cut cleanly to avoid dislodging material. The same procedure for taking the representative sample shall be used for each determination. The procedure shall be as follows:

- (a) Cut the selected filter into small pieces and insert into the extraction thimble (6.2.3).
- (b) Add 200 mL of cyclohexane (5.3.1) into the round bottom flask (6.2.1) add 30 to 40 clean boiling chips (6.3) to the flask.
- (c) Assemble the soxhlet extraction equipment (Clause 6.2) and extract the filter material for at least 16 h.

CAUTION: FLAMMABLE: All heating and evaporating procedures used for flammable solvents shall be carried out in a fume cupboard.

- (d) Cool the extract and transfer quantitatively into a 500 mL Kuderna-Danish flask (6.4.1).
- (e) Add 1 or 2 clean boiling chips (6.3) to the flask attach a three-ball Snyder column (6.4.3). Pre-wet the Snyder column by adding 1 mL of cyclohexane (5.3.1) to the top.
- (f) Place the K-D apparatus on a hot water bath (6.5) so that the concentrator tube is partially immersed in the hot water, and the entire lower rounded surface of the flask is bathed in water vapour. Adjust the vertical position of the apparatus and the water temperature to complete the concentration in 30 to 40 minutes (see CAUTION, Clause 8.3 (c)).

NOTE: At the proper rate of distillation, the balls of the column will activity chatter but the chambers will not flood.

- (g) When the volume of extract in the concentrator tube reaches 1 mL, remove the K-D apparatus and allow it to drain for at least 10 min while cooling.
- (h) Remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with 1 to 2 mL of cyclohexane (5.3.1).
- (i) Stopper the concentrator tube. The tube may be stored refrigerated if further processing cannot be performed immediately.

#### 8.4 Cleanup and separation

- (a) Prepare a slurry of 10 g activated silica gel (5.2.2) in dichloromethane (5.3.2) and place this in the chromatography column (6.6). Gently tap the column to settle the silica gel and elute the dichloromethane. Add 1 to 2 cm of anhydrous sodium sulphate (5.2.1) to the top of the silica gel.
- (b) Pre-elute the column with 40 mL of pentane (5.3.3) and discard the eluate. Just prior to exposure of the sodium sulphate layer to the air, transfer the cyclonexane sample (= 2mL) extract obtained in Clause 8.3 (i) onto the column using an additional 2 mL of cyclohexane (5.3.1) to complete the transfer.
- (c) Just prior to exposure of the sodium sulphate layer to the air, add 25 mL of pentane (5.3.3) and continue elution of the column. Discard the pentane eluate.
- (d) Elute the column at a rate of about 2 mL/min with 25 mL of a mixture of 40 percent dichloromethane 60 percent pentane and collect the eluate in a 500 mL K-D flask equipped with 10 mL concentrator tube (6.4.1 and 6.4.2).
- (e) Concentrate the collected fraction to dryness as described in Clause 8.3, steps (f) and (g). Use slow nitrogen stream if the extract in the concentrator tube is not fully dried.
- (f) Dissolve the residue with 0.5 mL of acetonitrile (5.3.4). Ensure that dissolution is complete and transfer quantitatively into a mini-vial. This is the test solution.

#### 8.5 Calibration

- (a) Inject 20 uL of working standard solution (5.5.3) into the HPLC and immediately activate the solvent program described in Clause 6.7, and the recorder integration system.

NOTE: Approximately 30 min is required to elute all of the compounds.

- (b) Identify the peaks obtained by comparing the retention times obtained with those obtained by injecting individual components of the mixture.
- (c) From the integration values obtained, calculate the response factor for each individual component of the standard solution.

#### 8.6 Determination

- (a) Inject 20 uL of test solution into the HPLC and immediately activate the solvent program described in Clause 6.7, and the recorder and integration system.

- (b) Identify the peaks obtained by comparison with the retention times of the calibration standards (see Clause 8.5).
- (c) Using the integrator values obtained and the response factors for each component obtained in Clause 8.5, step (c), calculate the mass of each component present in the test solution, in micrograms.
- (d) Repeat steps (a) to (c) for the blank filter solution.
- 9 CALCULATION. Calculate the concentration of individual PAH compounds from the formula.

$$\text{Concentration, (ng/m}^3\text{)} = \frac{(C_s - C_b) \times 1000}{V \times P}$$

where

$C_s$  = concentration of individual PAH in the exposed filter, in nanograms

$C_b$  = concentration of individual PAH in the blank filter, in nanograms

$V$  = air volume sampled corrected to 0°C and 101.3 KPa, in cubic metres

$P$  = the proportion of the filter paper used.