# STUDIES OF POLYCYCLIC AROMATIC HYDROCARBONS IN URBAN ATMOSPHERES

by

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## SUMMARY

Polycyclic aromatic hydrocarbons (PAH) are known to exist in urban atmospheres and are suspected of carcinogenic potential.

The implementation of emission control regulations and changes in fuel usage over the last twenty-five years has affected air quality in general and PAH concentrations in particular. In addition, recent thermodynamic evidence suggests that previous determinations of PAH might be inaccurate. For these reasons, ambient concentrations of PAH have been investigated.

The methodology involved in determining PAH has been re-examined within the context of a routine monitoring programme. Quantitative recovery of PAH from collected aerosols with their separation from the aliphatic component has been accomplished using a dimethyl sulphoxide extraction system.

The concentrations of five representative PAH have been routinely determined at three environmentally dissimilar sites around Birmingham. The values found are less than 10 ng $m^{-3}$ and show a marked seasonal variation. Multiple regression analysis between concentration and various meteorological parameters has been used to compare monitored and predicted concentrations of PAH.

The internal residential concentrations of PAH appear to be essentially similar to external values. From the above data the background exposure of a Birmingham resident to benzo(a)pyrene was calculated and found to be approximately equivalent to the exposure of smoking one cigarette per day.

Size distribution analysis indicates that PAH are predominantly associated with submicron particulate and are consequently capable of penetrating to human lungs as far as the alveoli.

The recoveries of PAH from soot, when exposed to NOx, decrease with time at rates which correlate with molecular properties. Hence even in the absence of photolytic degradation a chemical route exists whereby the atmospheric PAH burden might be decreased.

KEY WORDS

Polycyclic aromatic hydrocarbons, atmospheric pollution, size distribution.

# ACKNOWLEDGMENTS

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# CHAPTER I

## GENERAL PROPERTIES OF POLYCYCLIC AROMATIC HYDROCARBONS OF ENVIRONMENTAL IMPORTANCE

### 1.1 Introduction

Civilisation, by its nature, creates pollution.

Since the Industrial Revolution, there has been a marked increase in the amount of waste products that must be dispersed to the soil, water and atmosphere of the planet. Many waste products are harmless, although unpleasant, but the example of Minomata, Seveso and Harrisburgh, Three Mile Island, have dramatically highlighted the dangers of some pollutants. However, some forms of pollution are less obvious as a source of risk. Low level, long term exposure to pollutants in the soil, water and air may be more lethal in terms of total number of deaths than short term exposure to high concentrations. One group of pollutants that has been demonstrated to occur in the atmosphere (and soil and water) are polycyclic aromatic hydrocarbons (PAH). The fact that many PAH are carcinogenic to animal and human tissue has lead to the determination of their concentrations in the environment.

The introduction of legal requirements, demanding reductions in the amount of wastes expelled, untreated, to the atmosphere and rivers has promoted an improvement in the urban environment. Certainly, chronic smogs that occurred during the winter months in London and which led to serious bronchial infections are now uncommon. In addition, changes in the usage of fuels for domestic and industrial sources will have caused changes in the pattern of atmospheric pollution. Over the last ten years, for example, Britain has changed from town gas to natural gas. The impact of these changes, coupled with the influence of increasing numbers of motor vehicles, which pervade the environment close to where man lives and works, need to be fully assessed.

Scientists in Britain, such as Commins, Stocks, Cooper, Lawther and Waller, have shown that PAH exist in the atmosphere in measurable concentrations. So far, studies in this country have been restricted to simply determining the concentrations of PAH. Little work on particle and PAH size distribution or possible synergistic effects of other pollutants has been performed. Attention was paid originally to developing methods of sampling and analysis but, recently, data produced by various authors has demonstrated that certain problems in the determination of ambient PAH concentrations have been overlooked or not fully understood. Even if the concentrations found by the early workers were not subject to errors inherent in the analysis, the changing patterns of pollution demand a fresh appraisal of the PAH in the urban environment.

This project was sponsored jointly by DOE/DHSS, the Transport and Road Research Laboratory and the EEC with the aims of reconsidering the methods of sampling and analysis, to determine the concentrations and size distributions of selected PAH at different sites and to assess their subsequent fate and hence the potential hazard that they pose.

To date, only the USSR has required an upper limit of PAH that should not be exceeded in the general urban atmosphere. Benzo[a]pyrene (BaP) is chosen as the standard and its concentration should be less than 1 ng $m^{-3}$ of air. Whether other European countries set similar limits in the near future is a moot point but relevant data must be available for any constructive policy to be formulated.

## 1.2 Structure and Nomenclature

The nomenclature used throughout this presentation is that adopted by the International Union of Pure and Applied Chemistry (IUPAC) and by Chemical Abstracts Service. The most important rules are the following:

1) The structure diagram is written to present the greatest possible number of rings in a horizontal row.

2) The molecule is orientated in such a way as to place the maximum number of rings in the imaginary upper right quadrant and the minimum in the lower left quadrant.

3) The carbon atoms are numbered in a clockwise direction starting with the carbon atom that is not part of another ring and is in the most anti-clockwise position of the uppermost ring farthest to the right; atoms common to two or more rings are not numbered.

4) The faces of the rings are now lettered in alphabetical order, 'a' being between carbon atoms 1 and 2 and continuing clockwise round the molecule; ring faces common to two rings are not lettered.

5) In naming a compound formed by the addition of a component, the numbers and letters are placed in square brackets immediately after

TABLE 1.1.

Some polycyclic aromatic hydrocarbons (PAH) known to exist in urban aerosols.

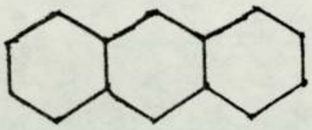
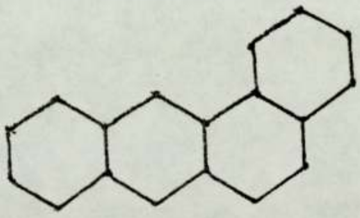
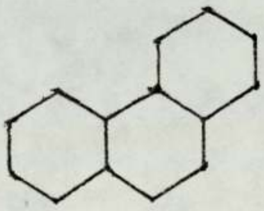
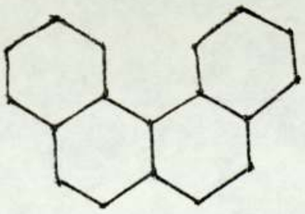
| Compound. | Structure. | Carcinogenicity. NAS (1972). |
|---|---|---|
| Anthracene. |  | - |
| Benz [a] anthracene. |  | + |
| Phenanthrene. |  | - |
| Benzo [c] phenanthrene. |  | +++ |

TABLE 1.1. contd.

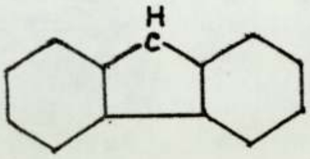
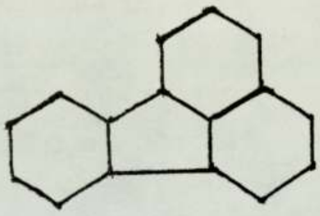
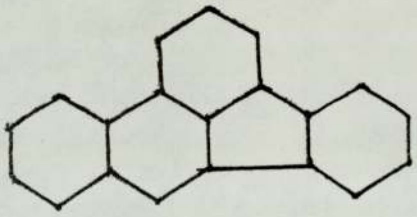
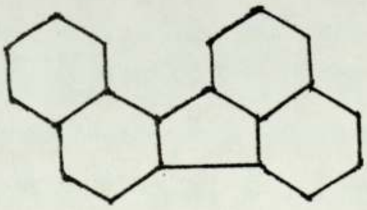
| | | |
|---|---|---|
| Fluorene. |  | - |
| Fluoranthene. |  | - |
| Benzo [b]<br>fluoranthene. |  | + + |
| Benzo [j]<br>fluoranthene. |  | + + |

TABLE 1.1. contd.

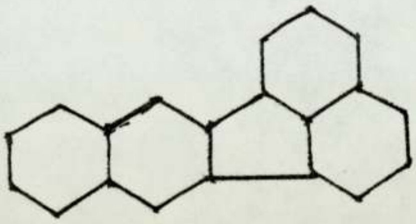
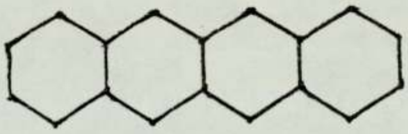
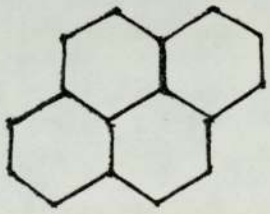
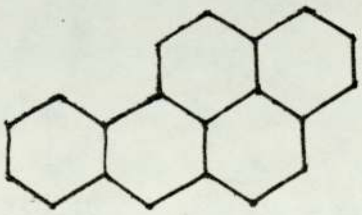
| | | |
|---|---|---|
| Benzo [k] fluoranthene. |  | - |
| Benz [b] anthracene. |  | - |
| Pyrene. |  | - |
| Benzo [a] pyrene. |  | + + + |

TABLE 1.1. contd.

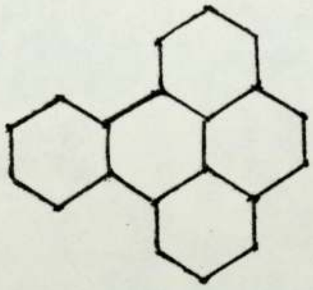
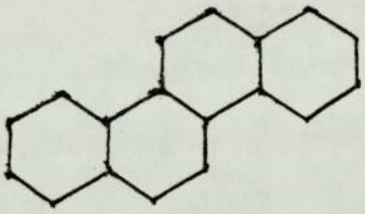
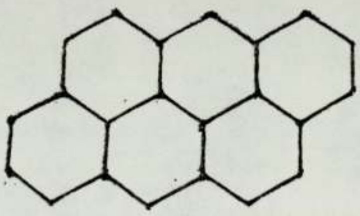
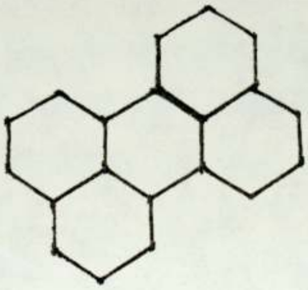
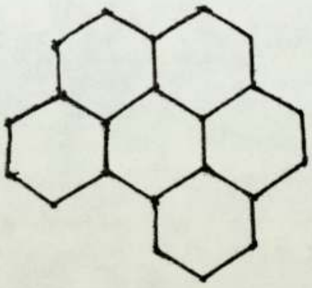
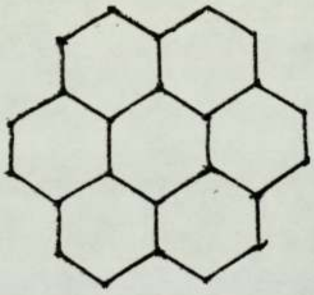
| | | |
|---|---|---|
| Benzo [e] pyrene. |  | - |
| Chrysene. |  | + |
| Anthanthrene |  | - |
| Perylene. |  | - |

TABLE 1.1 contd.

| | | |
|---|---|---|
| Benzo[g h i] perylene. |  | - |
| Coronene. |  | - |

the name of the added component, showing where a substituent group is attached or where a ring is fused to the face of the molecule. If a ring is fused to more than one face of the molecule, this is indicated by using the letters of the faces involved.

Most of the compounds shown in Table 1.1 are organic molecules identified in the urban atmosphere. The carcinogenicity of a compound is indicated by the use of the following code:

| | |
|---|---|
| - | not carcinogenic |
| ± | uncertain or weakly carcinogenic |
| + | carcinogenic |
| ++ +++ ++++ | more strongly carcinogenic |

## 1.3 Formation of PAH

PAH are products of incomplete combustion of organic fuels. Precursors to their formation include methane, other simple saturated and unsaturated hydrocarbons, peptides, lipids, terpenes, nicotine and leaf constituents. Production is generally favoured by an oxygen deficient flame, temperatures in the range 650°C - 950°C and fuels that are not easily oxidised.

Several theories of hydrocarbon pyrosynthesis have been proposed, involving such intermediates as ethylene and 1, 3- butadiene along with associated free radicals. Badger et al (1958) have developed a mechanism involving the dimerisation of a 1, 3- butadiene intermediate followed by cyclisation and dehydrogenation. The formation of PAH from aliphatic hydrocarbons at high temperatures was also examined and the authors were able to postulate a mechanistic scheme for the formulation of benzo[a]pyrene (BaP). The mechanism is shown in Figure 1.1.

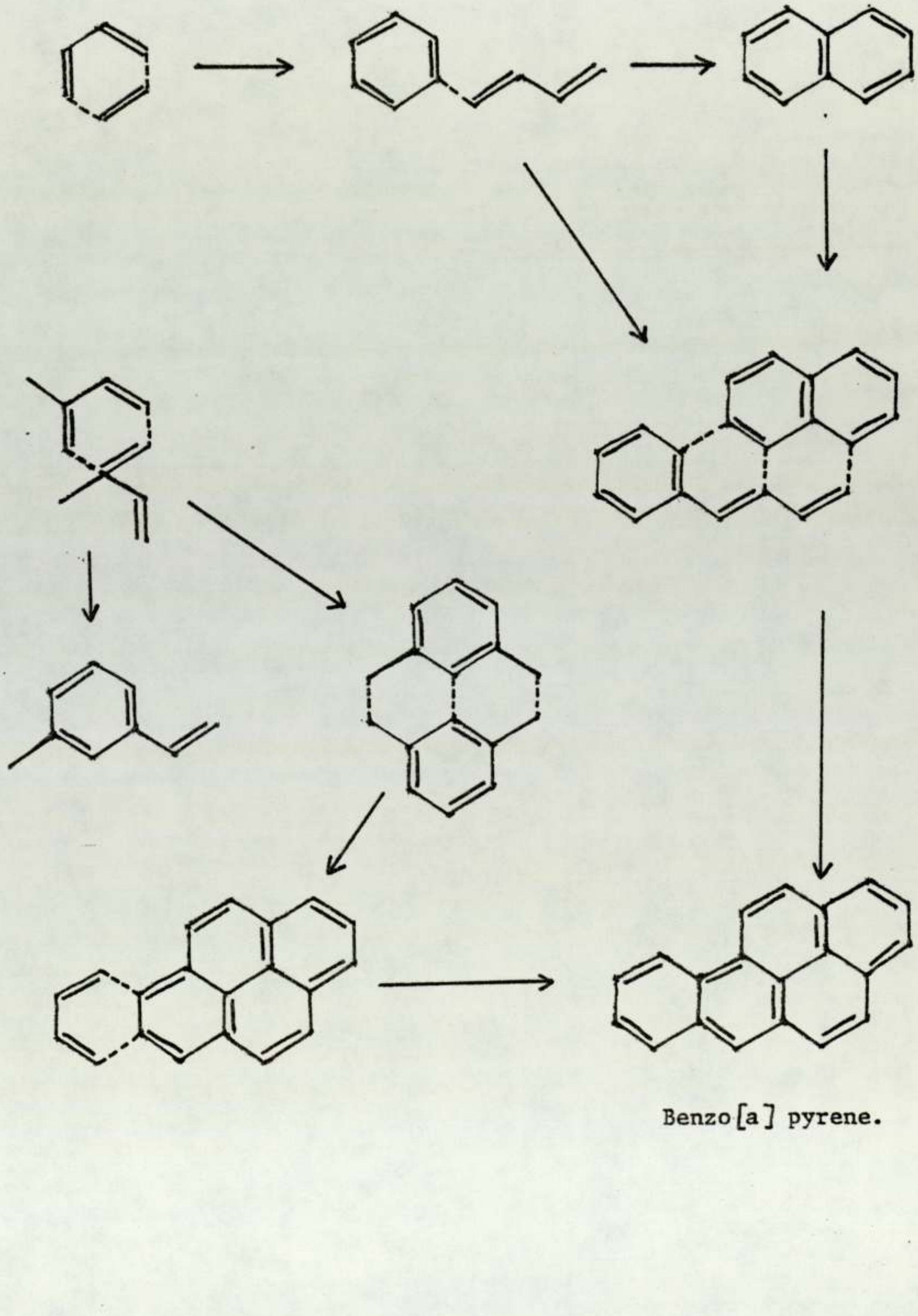
The idea that BaP is formed from simpler units by a stepwise synthesis is only the basic scheme; it is unlikely that any single PAH is produced exclusively by one mechanism. Moreover, the intermediates may be produced from fragments larger than ethene and complex hydrocarbons need not necessarily break down to give the next step of the synthesis; ring closure, for example, may be a possible preferred route. Compounds that contribute intermediate structures, such as tetralin, promote PAH formation.

It is known, for instance, that treating tetralin with aluminium chloride can lead to complex molecules containing three six membered rings joined by an aliphatic chain. Badger and Kimber (1960) have shown that cyclodehydrogenation of these molecules produces BaP and small amounts of perylene. Examination of the products of pyrolysis of styrene by Badger et al (1958) has shown that several PAH are produced. Phenanthrene, pyrene, anthracene, chrysene and BaP were identified and accounted for about 18% of the total percentage yield by weight. A radical mechanism is postulated with the most important radicals being $Ph^\bullet$, $^\bullet CH = CH_2$, $Ph - CH = \dot{C}H$, $Ph - \dot{C} = CH_2$ and $^\bullet C_6H_4 - CH = CH_2$

Other starting products have been demonstrated by Badger and his coworkers to be capable of forming PAH and the concept of radical formation of PAH at high temperatures is now generally accepted.

FIGURE 1.1.

Postulated schemes for the formation of BaP. Badger et al 1958.



Benzo[a] pyrene.

Table 1.2 shows some products of pyrolysis of various starting materials.

An early study by Lindsey (1960) on the pyrolysis of pure hydrocarbons has shown that the total yield of PAH varies with the temperature of pyrolysis. Later Ray and Long (1964) examined the aromatic hydrocarbons that are produced by diffusion flame burners and by diesel engines. The effects of rate of supply of air to fuel was also studied. They found that increasing the air to fuel ratio decreased the amount of soot, pentane soluble material and BaP produced. The addition of chain growth inhibitors into the system was investigated and was shown to cause a marked reduction in the amount of BaP produced.

Commins (1969) has shown that, as combustion becomes gradually less complete, the proportion of lower molecular weight PAH produced in the particulate matter increases and a corresponding decrease in the higher molecular weight PAH (coronene, anthanthrene, etc.) is observed. Commins was also able to show that the amount of PAH produced was related to the temperature of pyrolysis, the maximum being formed between 740°C and 800°C.

The combustion formation of PAH is closely associated with the production of soot. The mechanism of soot formation within flames involves reactions such as:

$$C_2 + C_2H_2 \rightarrow C_4H^{\bullet} + H^{\bullet}$$
$$C_4H^{\bullet} + C_2H_2 \rightarrow C_6H^{\bullet} \text{ etc.}$$

TABLE 1.2

## PRODUCTS OF PYROLYSIS OF VARIOUS MOLECULES AT ELEVATED TEMPERATURES

| STARTING MATERIAL | PYROLYTIC TEMPERATURE °C | % yields by weight of some important PAH products | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | PHENANTHRENE | ANTHRACENE | FLUORANTHENE | PYRENE | CHRYSENE | BENZO[a] PYRENE | BENZO [e] PYRENE |
| STYRENE (a) | 710 | 11.1 | 0.3 | - | 1.9 | 3.3 | - | 0.02 |
| 1 PHENYL (a) buta-1.3 diene | 700 | 13.3 | - | 3.7 | - | 1.3 | 0.89 | 0.12 |
| TETRALIN (a) | 700 | 0.15 | 0.29 | 0.04 | 0.01 | 3.43 | 2.6 | 0.17 |
| INDENE (a) | 700 | 0.38 | 0.20 | 0.27 | 0.10 | 31.7 | 4.6 | 0.002 |
| ETHYLENE (b) | 700 | 13.0 | - | 3.7 | 6.5 | 0.5 | 0.4 | 2.0 |
| TOLUENE (c) | 700 | 0.12 | 0.01 | Trace | Trace | 0.03 | 0.015 | 0.02 |

(a) Badger at al (1958)

(b) Badger, Lewis and Napier (1960)

(c) Badger and Spotswood (1960)

Fenimore and Jones (1969) have employed mass spectrometry to demonstrate the existence of $C_4H_2$ and higher polyacetylenes within premixed hydrocarbon flames prior to soot formation. As mentioned earlier, increasing the air to fuel ratio decreased the amount of soot and PAH formed. Chakraborty and Long (1967) have examined the formation of soot and PAH from ethylene and ethane diffusion flames. Under similar combustion conditions ethane produced 2.6 times more PAH than did the ethylene but the ethylene flame produced three and a half times as much soot.

### 1.3.1 Association of PAH and particulate

When PAH are formed it is likely that they are emitted as vapours from the zone of combustion and as they cool they condense onto existing particles or form very small particles themselves. It is possible that small particles in the atmosphere may act as nucleation centres for PAH aerosols when such vapours are supersaturated.

The PAH containing particulate matter is dispersed in air by turbulence and hence may be transported from the site of production by the effect of winds. The fate of PAH in the atmosphere is, therefore, closely related to the lifetime of the particulate on which it resides. Not only will the lifetime of the PAH in the atmosphere be related to the properties (e.g. size) of the particulate but, as will be discussed, the potential carcinogenic activity is also affected by adsorption. As noted in Section 1.5.5 the retention of PAH in the respiratory system is related to the size of the carrier particle.

In view of the inter-relationship of PAH and atmospheric particulate matter the physics of aerosols needs to be carefully studied.

### 1.3.2 Removal of aerosols particulates from the atmosphere

The ultimate fate of atmospheric particulate material is deposition on the earth's surface. Aerosol particles are deposited directly as a result of gravitational settling or incorporated in precipitation as a part of raindrops and snow. In the precipitation scavenging process two mechanisms are important; one - 'rainout' which involves the incorporation of aerosols into cloud droplets prior to the formation of raindrops within the cloud and, two - 'washout' which involves the scrubbing of particles from the atmosphere below clouds by raindrops when they fall from the clouds. Since both dry deposition and precipitation scavenging of aerosols are much more efficient processes when larger particles are involved, the agglomenation or coagulation of small Aitken particles into micro-sized particles is also an important factor in aerosol scavenging processes.

The 'rainout' process is dependent upon capture of particles smaller than 0.1 µm radius by cloud droplets. Particles less than 0.1 µm radius are called Aitken nuclei and are subject to Brownian diffusion. Dufour (1969) has calculated the half-life for nuclei of 0.01, 0.05 and 0.1 µm radius in the presence of 200 droplets $cm^{-3}$ of 10 µm radius as 35 min., 10.8 h and 32 h, respectively. These data show that the efficiency with which particles are incorporated into cloud droplets increased with decreasing particle size.

The efficiency of removing sub-micron particles by rain has been calculated by Junge (1963) in terms of a factor defined by -

$$x = \frac{E\,h\,\rho}{L\,H}$$

Where E is the rainout efficiency, h is the amount of rainfall, $\rho$ is the density of water, L is the liquid water content of the cloud, H is the depth of the atmosphere to the top of the aerosol layer and x is the fraction of the aerosol removed.

The rainout efficiency, E, can be estimated from the equation -

$$E = \frac{CL}{Co\,\rho}$$

Where C is the aerosol concentration of precipitation and Co is the aerosol concentration in air, $L/\rho$ may be taken as $10^{-6}$. It should be noted that E can vary between 0 and 1 only. Robinson and Robbins (1971) have calculated the value of E for sulphate, nitrate, copper and lead atmospheric aerosols as 0.48, 1.00, 0.29 and 0.51 respectively.

Assuming that aerosol concentration is uniform in the troposphere, Junge shows that where washout is negligible the amount of aerosol left in the air after t days may be expressed by -

$$1 - x = \exp\left(\frac{-EL\rho t}{LH}\right)$$

By substituting values of $h = 0.25$ cm day$^{-1}$ and $H = 12$ km Robinson and Robbins have calculated the time in days necessary to remove 25%, 50%, 90% and 99% of the atmospheric aerosol. These times are shown in Table 1.3.

Obviously, as E decreases the particle residence time increases and

FIGURE 1.2.

Calculated aerosol size distribution changes as a function of time without the influence of cloud droplet condensation. Junge and Abel (1965).

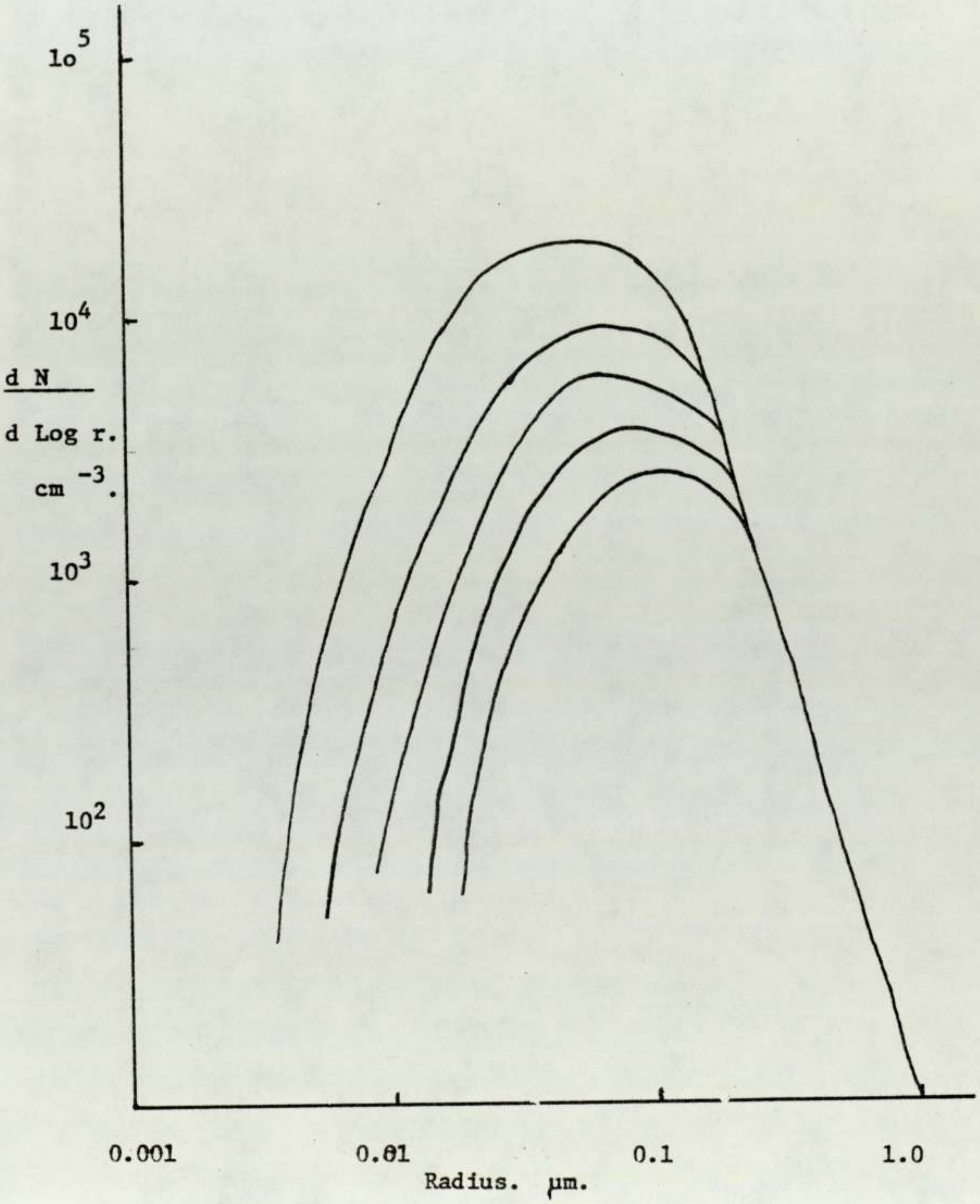


TABLE 1.3

Calculated times for the removal of given percentages of aerosols as a function of rainout efficiency E. Butler 1979.

| EFFICIENCY | TIME IN DAYS TO REMOVE | | | |
|---|---|---|---|---|
| E | 25% | 50% | 90% | 99% |
| 1.00 | 1.3 | 3.3 | 11 | 22 |
| 0.75 | 1.7 | 4.4 | 15 | 29 |
| 0.50 | 2.6 | 6.6 | 22 | 44 |
| 0.25 | 5.2 | 13 | 44 | 88 |
| 0.10 | 13 | 33 | 110 | 220 |

as seen from the table; even for values of E = 1.00 it will take eleven days for the removal of 90% of the aerosol. For E = 0.50 (approximately the value of lead) the 90% residence time is greater than three weeks. Over such time periods it is reasonable to conclude that aerosols may be transported over greater distances.

Aerosol coagulation is an important factor in the removal of the smallest particles. The coagulation process is a function of diffusion coefficients of the particles and of the total aerosol concentration, i.e. at higher pollution concentrations coagulation increases and consequently the removal rate also increases.

Coagulation control by diffusion coefficients of the particles involved is most important for particles in the smaller or Aitken size range. The relationship is shown in Figure 1.2 which shows the results of calculations made by Junge and Abel (1965) of the changes in aerosol size distribution as a result of coagulation processes occurring over a period of about five days.

The concentration of particles larger than 0.1 µm radius change very little, whereas the concentration of particles smaller than 0.1 µm become progressively less through the five day coagulation period. Particles less than 0.01 µm radius are shown to disappear almost completely in twelve hours. This coagulation process predicts on a mass basis an increase in the total mass of particulate material in the range 0.1 and 1.0 µm at the expense of the aerosol mass in the Aitken range.

Esman and Corn (1971) have calculated the residence time of atmospheric aerosols in the dry atmosphere. Using a membrane filter exposed in the horizontal plane and another for sampling the ground level concentration of the suspended particulate matter, ground level concentration and flux of the atmospheric aerosol were measured. With the assumption of a ceiling height of 2 km they were able to show that the mean residence time is related to particle size. For sub-micron particles, say 0.1 to 1 µm, in the absence of precipitation, the residence time was calculated in the range $10^2$ - $10^3$ h. Particles in the size range 1 - 10 µm have a shorter life - of the order of 10 - $10^2$ h. Clearly, based purely on the potential lifetime of particles, submicron aerosols might be transported greater distances than those greater than 1 µm.

## 1.4 Sources of PAH

As already mentioned PAH may be formed in any incomplete combustion of fuels containing carbon and hydrogen. Sources may be divided into two major sub-divisions:- natural and anthropogenic.

### 1.4.1 Natural Sources

In the urban atmosphere the contribution of PAH from natural sources will be small and difficult to estimate accurately. NAS (1972.b) have reported that open burning of vegetation such as forest fire and emissions from volcanos have produced a small background BaP concentration. The concentration of PAH in the upper layers of earth is in the range 100 - 1000 µg $kg^{-1}$ of soil. It has been suggested (Andelman and Suess (1974) and Suess (1976)) that biosynthetic activity

TABLE 1.4

EMISSIONS OF BaP FROM MOTOR SOURCES IN THE U.S.A. IN 1971
(NAS 1972 c)

| VEHICLE TYPE | BaP EMISSION $\mu g\ gal^{-1}$ | BaP EMISSION tonnes $year^{-1}$ |
|---|---|---|
| PETROL POWERED | | |
| Cars | 170 | 10 |
| Trucks | 500 | 12 |
| DIESEL POWERED | | |
| Trucks and Buses | 62 | 0.4 |
| TOTAL | | 22 |

of active tissues of plants and micro-organisms are possible sources of PAH in soils. Accurate estimation of the amount of PAH so formed would be almost impossible. However, PAH existing in plants will be retained and will not come into contact with human populations except possibly through the food chain.

### 1.4.2 Anthropogenic sources

The planet's natural background concentration of PAH has dramatically increased as a consequence of industrialisation. The man-made emission sources can broadly be sub-divided into transportational and stationary sources.

Because the motor-car operates close to where man lives and works it has received considerable attention as a source of pollution. The National Academy of Sciences (NAS 1972c) has estimated BaP emissions for several types of motor traffic as in Table 1.4.

The amount of BaP produced in exhaust gases per gallon of fuel consumed is related to the age of the vehicle. Generally, as the engine efficiency decreases (e.g. by engine wear) then emission of hydrocarbons increases. NAS (1972d) concludes that the introduction of emission control devices has resulted in about an 85% reduction in BaP emissions from pre-1965 levels. Bridbord et al (1976) have also reported a decrease in PAH tailpipe emissions. This work indicates that PAH emission factor for pre-1968 (uncontrolled) motor vehicles was 100 units, by 1975 the general emission factor for the whole of the United States was 4.4 units and for California where standards are more stringent the figure was 2.6. It is expected that statutory requirements implemented to further reduce carbon monoxide and hydrocarbon concentrations will also have the effect of decreasing PAH emissions still more.

Bergeman and Colucci (1968) have indicated that labelled BaP present in motor fuels can pass through the internal combustion engine without reaction. In addition, Candeli et al (1975) have demonstrated that the amount of PAH emitted from motor vehicles increases with increasing aromatic content of the fuel.

Other transportational related sources of PAH are aircraft and the degradation of car tyres.

The stationary sources of man-made PAH formation are responsible for the greater part of the anthropogenic emissions (probably about 90% in the U.S.A. (NAS 1972e)). Again NAS have summarised the available data and these are given in Table 1.5.

TABLE 1.5

Stationary Emissions of BaP in the USA in 1971 from NAS (1972e)

| Source of BaP | BaP Emission tonnes $year^{-1}$ |
|---|---|
| Heat and power generation | 500 |
| Refuse burning | 600 |
| Coke production | 200 |

Comparison of Tables 1.4 and 1.5 indicate the relatively small emissions from motor sources. However, it is important to note that emission from stationary sources is usually localised in contrast with that of mobile sources. This often results in high atmospheric PAH concentrations in the vicinity of major emitters.

More recent date, produced by Suess (1976) and shown in Table 1.6, indicates the size of the total BaP emissions worldwide. It must be remembered that BaP is only one member of total group of PAH, over twenty of which have been frequently determined in the urban atmosphere. Suess's data allows some estimation to be made of the percentage contribution which transportational sources make to the total excluding trains and aeroplanes, 45 x 100/5044%, i.e. less than 1% of total Ba P emissions to the atmosphere is derived from transport sources.

TABLE 1.6

Estimated BaP emissions to the atmosphere (Suess 1976)

| SOURCE | BaP EMISSION TONNES/YEAR<br>U.S.A. | WORLD-WIDE |
|---|---|---|
| **Heating and Power Generation** | | |
| Coal | 431 | 2376 |
| Oil | 2 | 5 |
| Gas | 2 | 3 |
| Wood | 40 | 220 |
| **Industrial Process** | | |
| Coke production | 192 | 1033 |
| Catalytic cracking | 6 | 12 |
| Refuse burning | 588 | 1350 |
| **Vehicles** | | |
| Trucks and buses | 12 | 29 |
| Cars | 10 | 16 |
| TOTALS | 1283 | 5044 |

### 1.4.3 Emission ratios

There have been several attempts to ralate the ratios of PAH produced to individual emission sources, notably Hangebrauck et al (1967), Sawicki et al (1965) and Falk et al (1960) Studies by Hangebrauck et al (1964) of PAH produced from coal-burning systems have shown that the ratio of pyrene to BaP was in all cases greater than unity, ranging from 1.5 to 23. Ratios of BaP to benzo [ghi] perylene were found to vary between 1.3 and 6.5 and ratios of BaP to coronene ranged from 1.0 to 3.0. Ratios of BaP to benzo [ghi] perylene of 0.1 and of BaP to coronene of 0.41 were found for gas burning systems. These values are lower than those associated with coal-fired sources and are similar to the lower ratios typically found in motor vehicle exhausts.

Smith and Gruber (1966) have examined the emission of PAH from bitumous coal fires under various stoking methods. Analysis of data produced by these workers reveals that the ratio of pyrene to BaP can vary from 1.5 to over 10 depending on the method of stoking employed. Similar wide ranges in ratios are apparent for coronene, BaP and fluoranthene.

Commins (1969) has devised an equation to estimate the amount of BeP produced by motor vehicles. One version of the equation may be written as -

$$kx + 0.25(1 - x) = y$$

Where y is the long term ratio of the concentration of coronene to BeP, x is the fraction of the total BeP present that is contributed by motor traffic and k is the ratio of coronene to BeP monitored during summer periods. The value of 0.25 is included to take into account the coal smoke coronene to BeP ratio of 0.25 to 1. Thus, by substituting the monitored values of y and k, the amount of BeP derived from traffic can be assessed.

In the mixed urban atmosphere, away from the immediate source of production, the ratios of PAH will be dependent upon many factors. The age and nature of the aerosol itself, the pertaining meteorological parameters, the presence of other urban pollutants, such as ozone and the rates of any photo-oxidative dimerisation and decomposition reactions will all affect the PAH ratios. These considerations emphasize that the practice of selecting one PAH (usually BaP) as a general indicator of PAH concentration is not recommended.

## 1.5 Carcinogenesis

### 1.5.1 Evidence of cancer production in man from occupational exposure to PAH

A committee of the World Health Organisation (WHO 1964) suggested that 85% of human cancers might be caused by environmental agents. It is, therefore, clearly desirable to eliminate the production and use of known carcinogens or, where this is not possible, to reduce to a minimum the amounts released.

One of the first reports of the production of cancer in man by PAH containing materials is that of Sir P. Pott in 1775 concerning cancer of the scrotum in chimney sweeps. Since then similar materials have been shown to have a close association with a high incidence of skin cancer after prolonged and direct exposure. Cancer of the skin in workers in the coal, tar and pitch industry was first described by Butlin (1892) and in 1907 the Workman's Compensation Act recognised officially that cutaneous epitheliomas could be caused by commercial pitch, tar and tarry products, including creosote oils. Occupational cancers due to contact with mineral oils and their fractionation and distillation products have been noted. (Henry 1947).

The health hazard posed by exposure of workers to atmospheres containing elevated PAH concentrations has been examined. The investigation by Doll and his co-workers was based on mortality of workers in the British gas industry. In their first paper, Doll et al (1965) describe a study of a selected population of employees of the industry. (At the time of the study the term "gas" refers to coal gas and not natural gas from the North Sea). The population was followed for the eight year period from September 1953 to August 1961 and included only those with at least five years employment and who were 40 - 65 years old at the beginning of the observation period. Workers were divided into three broad categories of exposure: heavy, intermediate ( e.g. maintenance workers) and minimal exposure (meter readers, etc.) Relative to the group without significant exposure the heavily exposed workers had a 69% higher incidence of lung cancer and, unexpectedly, a 126% higher death rate from bronchitis. Smoking habits were believed not to differ from those of the general population. In the second paper (Doll et al 1972) the same employees were followed for another four years up to August 1965, and data for 1957 to 1965 were also presented for 4,687 more men (1,176 in the category at greatest risk) from four other Gas Boards, not included in the original survey. For workers with heavy exposure mortality rates from lung cancer, bladder cancer and cancer of the skin were significantly higher than national rates. With respect to lung cancer, work as a "topman" (i.e. above the retort and hence the greatest PAH exposure) was found to be particularly hazardous. For workers with minimal exposure it was concluded that the data "did not provide any substantial evidence ..... of any specific occupational hazard." For the four additional Gas Boards the results were in broad agreement with respect to lung and bladder cancer risk.

Doll et al's study was epidemiological and did not include any environmental measurements, but Lawther et al (1965) give concentrations of BaP and other PAH in gas work retort houses and go some way towards putting in context Doll et al's epidemiological findings. Details of Lawther's measurements are shown in Table 1.7.

Lawther et al found that in certain areas the average BaP concentration was 3 $\mu g\ m^{-3}$ over long periods, this being over 100 times the average annual concentration for the City of London, away from traffic, up to 1965. It must be remembered, however, that cancer takes many years to manifest itself, and that Lawther et al's measurements were made near the end of the period covered by Doll's study, when conditions may have changed. However, above the retorts, the concentration of BaP was greater than 200 $\mu g\ m^{-3}$ which might explain Doll et al's finding that the "topman's" work appears to be particularly dangerous.

TABLE 1.7

Mean Concentration of Suspended Matter and PAH in Air of Gas Works (after Lawther et al 1965) Related to Standardised Lung Cancer Mortality Rate

| EXPOSURE GROUP | STANDARDISED MORTALITY RATE | SUSPENDED MATTER gm $^{-3}$ | AMBIENT EXPOSURE OF BaP ngm$^{-3}$ | DAILY INTAKE OF BaP(ng) | STANDARDISED DAILY BaP INTAKE(b) |
|---|---|---|---|---|---|
| Rural | 0.5 | - | - | - | - |
| Urban | 1.00 | - | 30$^{c}$ | 450<br>(e) | 1 |
| Intermediate | 1.69 | 1000 | 4800 | - | - |
| | | 925 | 1400 | | |
| | | 1100 | 2700 | 15300(a) | 34 |
| Heavy | 5.00(d) | 374100 | 216000 | 1080000(a) | 2400 |
| Above retorts | | | | | |

a) assumes 8 hour working day, 16 hour non-working and daily intake of 15 m$^3$ of air.

b) assumes all BaP retained

c) approximate London concentration of BaP at the time of Lawther's work.

d) Lloyd (1971)

e) assume 24 hours exposure total daily intake of 15 m$^3$ of air.

Similar results to those reported by Doll were found in the United States of America. Lloyd (1971).

NAS (1972f) have reviewed several important, epidemiologic studies regarding the BaP content of the atmosphere and have developed as a working hypothesis that there is a casual relationship between air pollution and lung cancer. They conclude that an increment of 1 $\mu g\ m^{-3}$ of BaP in the atmosphere will correspond to an increase in the lung cancer mortality rate of 5%. As can be seen from Fig. 1.3 England, Wales and Scotland suffer the highest rate of male deaths (per $10^5$ deaths) from lung cancer in Western Europe and so a 5% reduction here would produce the largest saving in terms of numbers.

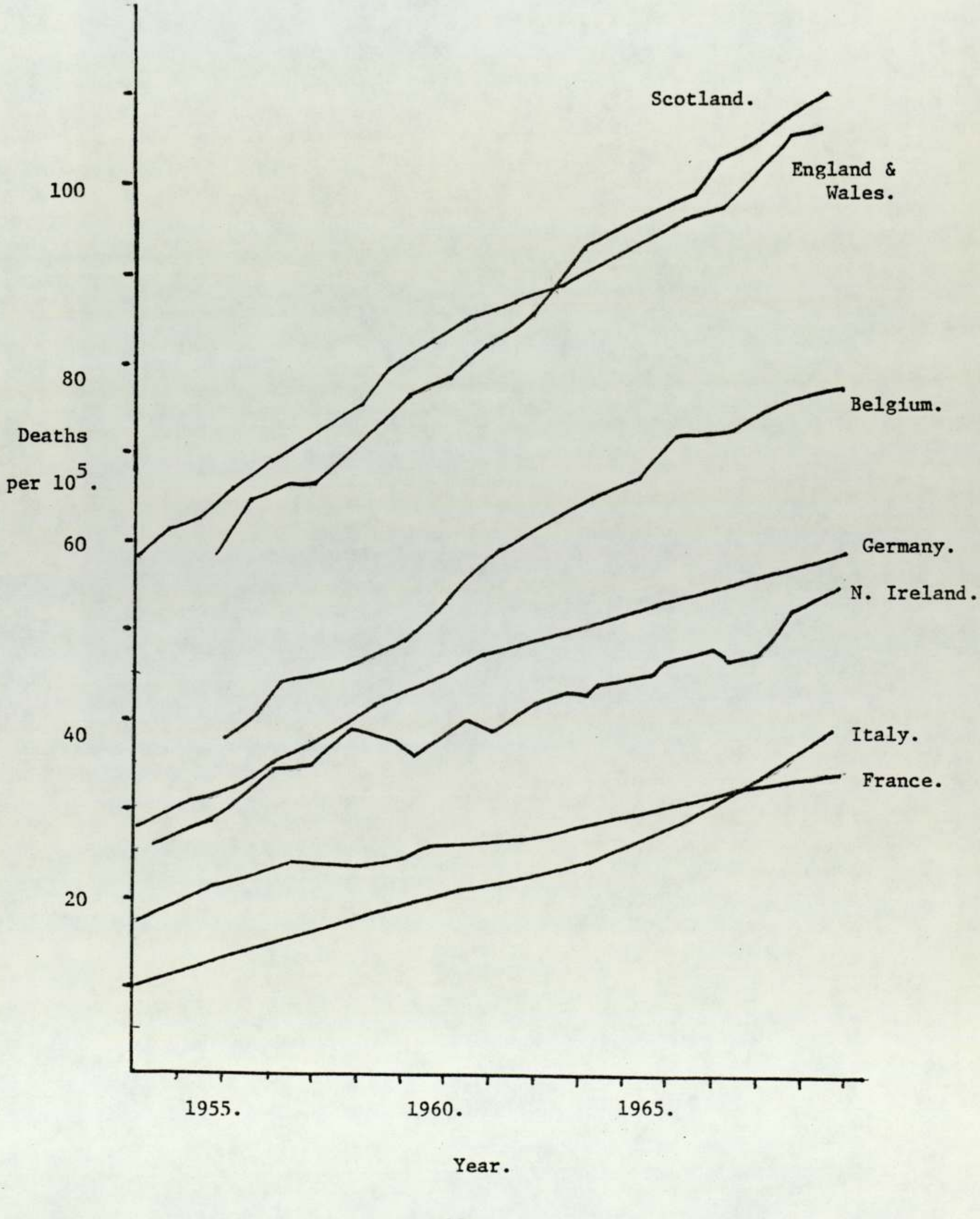
The fact that British-born immigrants to New Zealand, South Africa and Australia (see for example Dean 1964) have a higher incidence of lung cancer mortality than the indigenous population has prompted the suggestion that exposure to environmental factors prior to emigration could be responsible.

In addition, Stocks and Campbell (1955) have demonstrated that lung cancer mortality rates increase with increasing population density and that the difference between urban and rural rates cannot be attributed to smoking habits alone.

The data indicate that elevated PAH concentrations, increased degree of urbanisation and environmental factors peculiar to Britain can lead to increased lung cancer mortality. It is, therefore, essential

FIGURE 1.3.

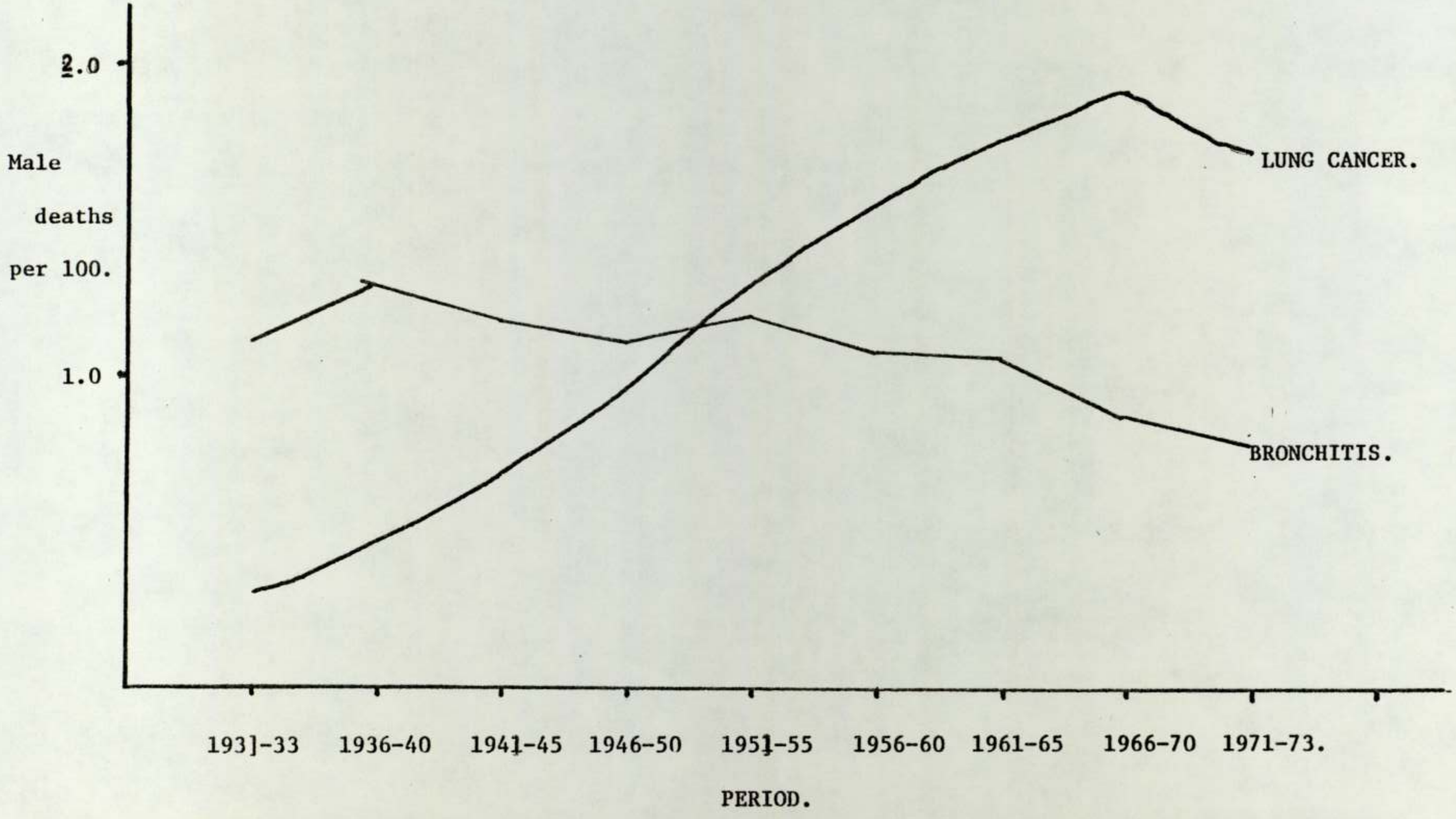
Comparison of the number of male deaths from lung cancer in Western European countries. Butler (1976).



to determine the ambient air concentrations of PAH and other pollutants to assess the potential impact on urban dwellers. This, of course, will vary from time to time, hopefully occasionally from the implementation of more efficient anti-pollution regulations. For example, since the Clean Air Act 1956 there has been a dramatic decrease in the concentrations of smoke and $SO_2$ as measured by the National Air Pollution Survey. Similarly, concentrations of PAH are now generally less than one tenth of their 1950's values. Examination of recent medical statistics Clarke (1977) reveals that these decreases have been mirrored by a decrease in male deaths from bronchitis. Figure 1.4 shows that from 1931 to 1955 male deaths in England and Wales from bronchitis varied from 1.1 per 100 deaths to 1.3 per 100 deaths; the mean value for this period being about 1.2 per 100 deaths. Since 1955 the standardised number of deaths fell steadily and by 1971 - 1973 the figure had fallen to approximately 66% of its 1955 value.

Figure 1.4 also shows the relative changes in the number of males deaths due to lung cancer. This plot does not display a steady decrease from 1955 onwards. The continuing upward trend reaches a maximum for 1966 - 70 after which a slight decrease is noted. It is possible that this decrease might also be attributed to the implementation of the Clean Air Act. Whereas bronchitis deaths would fairly rapidly respond to changes in air pollutant concentrations, lung cancer may have a more extended period between exposure and death. If this is so, then a greater decrease in lung cancer deaths might be anticipated.

FIGURE 1.4. Male deaths from bronchitis and lung cancer per 100 deaths ( Clarke 1977.)



However, economic factors may conspire to alter these trends. For example, in the last two years the national economic climate and confusion caused by government circulars on Rate Support Grants have resulted in the slowing down of the process of drafting and implementing smoke control programmes. On the wider economic front, the staggering increase in the cost of oil from oil producing and exporting countries (OPEC) combined with greater Government support for the National Coal Board, is beginning to lead to a change from the use of oil back to coal.

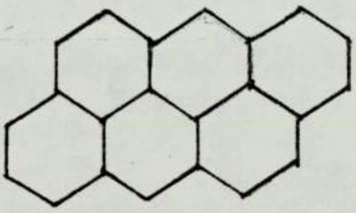
If the improvement in the general quality of the air is to be maintained, then economic, social and political changes must be monitored as carefully as the atmosphere itself. To a certain extent the determination of criteria for our national air pollution standards has passed from Central Government and rests with the relevant Council of the E.E.C. If E.E.C. standards are adopted in the form of directives, it will then be incumbent upon the member nations of the Community to enact legislation to enforce them.

### 1.5.2 Mechanism of PAH as carcinogens

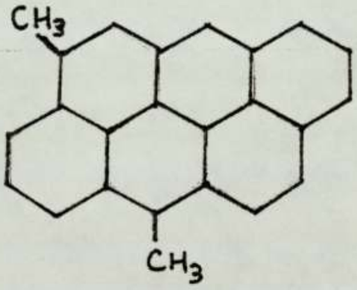
Benzo [a] pyrene was the first carcinogenic constituent of coal tar to be identified, Cook (1943) and Kennaway (1955). Subsequently, other carcinogenic substances have been shown to be present (e.g. benzo [c] phenanthrene) with potency equal to that of BaP when tested by subcutaneous injection on animal skin. PAH, their derivatives and analogues form an important sub-group of chemical compounds found to be carcinogenic. The carcinogenicity of some of the more common PAH are indicated in Table 1.1.

PAH have several features that distinguish them from many of the more recently discovered carcinogens. They act at the site of application, the effective dose is minute, of the order of micrograms, and they have been found to induce tumours in almost every tissue and animal species on which they have been tested. Clar (1962).

Substituting groups into the ring system can often lead to increased carcinogenisis, for example anthanthrene (I) is inactive, but its dimethylate derivative (II) is a potent carcinogen.



I.

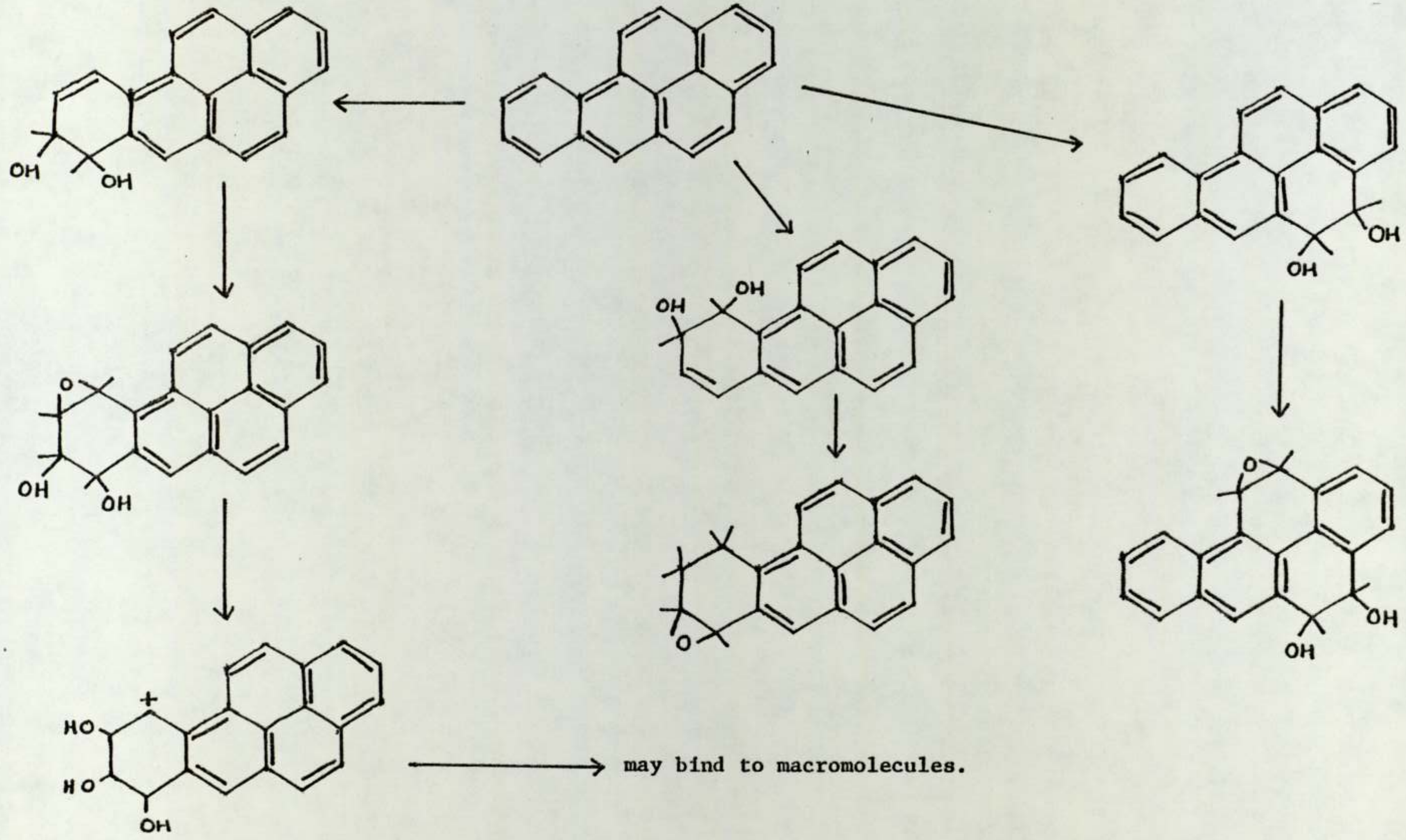


II.

Among PAH a degree of molecular complexity and chemical reactivity is required for carcinogenic action (Badger (1948)). Earlier workers, especially in France, sought to correlate potency with the molecular and electronic structure of the compound and the theoretical concept that the important position of PAH is at the phenanthrene double bond (or K region) was developed. Arcos and Argus (1968), Coulson(1953) tabulated over 40 hydrocarbons, or N- analogues, of varying degrees of carcinogenic activity arranged in order of total charge ($\pi$ electron density) at the K region. The data, whilst showing an approximate relationship, indicates also some serious discrepancies between the regular rise in the figure given for the charge, and on the other hand the order of potency which, so far from increasing regularly, exhibits a number of maxima and minima. These fluctuations do not support any firm generalisation based on a direct correlation between charge and carcinogenic potency. Zajdela and Buu-Hoi (1951) have examined the relationship between potency and total charge at the k - region of acridine derivatives. Here too serious limitations are apparent, for example the 2, 3 10- trimethyl derivative of 5,6 - Benzacridine is graded +++ for potency, its total charge being given as 2.016, yet the 1, 4, 10 - analogue which has almost the same value, 2.015, is graded as a single +. Limitations such as these have meant that the idea of finding an accurate correlation between electronic charge at a single bond and carcinogenic activity has fallen into disfavour.

It is now appreciated that every chemical carcinogen binds covalently with DNA, RNA, and protein of the target tissue. NAS (1972g). However, although BaP and other PAH cause cancer at the site of application they cannot themselves bond covalently; it has been proposed that they must be metabolically converted into chemically reactive molecules. The metabolism of both carcinogenic and non-carcinogenic hydrocarbons has been examined in detail by Boyland and Sims (1964) and recently reviewed by Boyland (1978). The first step in the process was the formation of epoxides or arene oxides. Some examples of the epoxidation of BaP are given in Figure 1.5.

FIGURE 1.5. Some diol-epoxides derived from BaP . Boyland (1978).



Such oxides formed by the enzymatic addition of oxygen to a double bond are reactive alkylating compounds. Most of the active intermediate metabolites are inactivated by detoxifying reactions, such as rearrangement to give phenols and reactions with water to give diols. Boyland (1978). If PAH must be metabolically activated in order to induce cancers, surveys ofhuman tissues for their ability to carry out this reaction should be of practical importance in assessing the mechanism of PAH carcinogenesis in humans. For example, Cohen and Moore (1978) have recently shown that different portions of the respiratory tract metabolise BaP to different extents.

The arene oxides produced by metabolism can react with macromolecules including proteins and DNA. Boyland (1978) has found that the carcinogenic hydrocarbon 1,2,5,6 - dibenzanthrene, reacts with nucleic acid more than do non-carcinogenic hydrocarbons, but that both active and inactive compounds react with protein, the reaction of the carcinogenic ones being more rapid with DNA. Boyland ascribes the preferential reaction of carcinogenic hydrocarbons (which are planar molecules) with DNA as being due to their physical affinity; the similarity in shape between the hydrocarbon and specific sites in the DNA molecule can lead to relatively easy interaction within the DNA helix.

An alternative viewpoint postulated by Cavalieri et al (1978) supposes that one electron oxidation to radical actions is the critical activation step leading to carcinogenesis for many PAH. The postulated intermediates for non-substituted hydro carbons with relatively high ionisation potentials are again arene oxides.

Although it is now recognised that metabolic activation of the parent hydro-carbon is required for the induction of cancers other factors are also important; as previously stated steric factors may govern reactivity. Finally the species, age, sex, nutritional and hormonal state and the phase of the mitotic activity of a particular cell may also be important in determining the effect of carcinogens on living tissues.

### 1.5.3 Synergistic aspects of PAH carcinogenesis

Bioassays on mouse skin, subcutaneous mouse tissue (Hueper at al (1962)) and in new born mice (Epstein et al (1966)) have shown that particulate matter of city air can be carcinogenic to experimental animals. Hueper, using fractionation studies of urban pollutants, suggests that PAH may play an important role in the overall carcinogenicity and tumour-initiating activity of urban pollutants in experimental animals.

Exposure of mice by inhalation of road sweepings, chimney soot and air dust have produced pulmonary adenomes. Kotin and Falk (1960) have demonstrated that mice exposed to simulated auto smog show an increased incidence of tumours and pulmonary tumours.

Synergism has also been noted between $Fe_2 O_3$ and BaP to produce a carcinogenic system. NAS (1972h) Intratrachial instillations of the $Fe_2O_3$/BaP into hamsters have produced tumours with an incidence greater than for instillations of BaP alone. It was noted that this system caused cancer incidence of up to 76%. This increased incidence is thought to be related to physical factors prolonging the residence time of the carcinogens at the target site. It has been postulated that the carcinogenic effect is made possible by the adherence of the hydrocarbon to the surface of the particle, from which it is slowly released into the tissue, thereby achieving a more prolonged and constant action. The elimination of BaP from the lungs appears to be related to the size of the carrier particle, the elimination progressing more slowly from smaller particles.

Laskin et al (1975) have performed experiments which are perhaps the most relevant to air pollution inhalation studies. Rats and hamsters have been exposed to a combination of sulphur dioxide and BaP aerosols. Animals were exposed to 10 ppm of $SO_2$ for 6 hours per day, 5 days a week, plus a combination of 10 $mgm^{-3}$ of BaP and 3.5 ppm of $SO_2$ for 1 hour per day, 5 days a week. Malignancies of the lung were induced in rats. Increased squamous cell tumours of the lung were noted for those animals receiving the BaP/$SO_2$ mixture for 1 hour per day plus the 6 hour exposure to 10 ppm of $SO_2$ above those receiving the BaP/$SO_2$ mixture without the 10 ppm $SO_2$. Confirmation that a BaP/$SO_2$ system is more carcinogenic to the lung of the rat than either $SO_2$ or BaP singly is shown in Table 1.8.

Laskin has also carried out carcinogen - irritant inhalation studies on rats with BaP and nitrogen dioxide. At a concentration of 25 ppm of $NO_2$ evidence of major mucosal changes in various sections of the respiratory system were observed.

These data indicate the complexity in assessing the potential hazard

TABLE 1.8

Carcinogen-Irritant Inhalation Studies with Rats(Laskin et al(1975))

| TYPE OF EXPOSURE (5 days week$^{-1}$) | NO. OF ANIMALS | CANCER INCIDENCE % |
|---|---|---|
| AIR | 15 | 0 |
| 10 ppm $SO_2$ 6 hr day$^{-1}$ | 15 | 0 |
| 10 mgm$^{-3}$ BaP 1 hr day$^{-1}$ | 30 | ? |
| 10 ppm $SO_2$ 6 hr day$^{-1}$<br>+<br>10 mgm$^{-3}$ BaP 1 hr day$^{-1}$ | 30 | 6.7 |
| 10 mgm$^{-3}$ BaP )<br>+ ) 1 hr day$^{-1}$<br>4 ppm $SO_2$ ) | 45 | 8.9 |
| 10 ppm $SO_2$ 6 hr day$^{-1}$ )<br>+ )<br>10 mgm$^{-3}$ BaP) )<br>) 1 hr day $^{-1}$)1<br>4 ppm $SO_2$ ) ) | 46 | 19.6 |

of atmospheric pollutants. Synergistic effects in the urban environment are likely to occur and it may be that long term exposure to low level carcinogen/irritant is a more serious danger than relatively higher doses of carcinogens alone.

### 1.5.4 The human situation

The difficulty in defining cause - dose relationships of PAH (and indeed, other carcinogens) and lung cancer arise from the long latent period - possibly as long as 30 years - and that its peak incidence occurs after the age of 50. The long interval between initial exposure to the cancer-inducing agent and the appearance of detectible disease makes aetiologic analysis difficult, e.g. changes in occupation, place of residence, social habits (smoking), nutrition and socio-economic status may all alter within a 30 year period. In addition the nature and amounts of environmental contaminents are likely to change.

A supposedly carcinogenic compound found to correlate with a higher incidence of lung cancer in a specific human population can lead to the following inferences:

1) The substance is not a lung specific carcinogenic agent and another substance(or substances) is in fact the responsible agent.

2) The substance is carcinogenic for the lung but only if -

   a) its effect is added to that of another carcinogenic substance

   b) it accompanies other substances that possess an initiating effect

   c) a carrier species or some other favourable conditions operate so as to keep the suspect compound in contact with the target cells

d) there is some conbination of the above.

Despite the difficulties some epidermiologic studies strongly support the proposition that urban air pollution is related to an increased lung cancer death rate.

Curwen et al (1954) examined the mortality due to cancer of the lung and larynx in county boroughs of London and the urban districts and rural areas of different parts of England and Wales. These workers concluded that standardised mortality ratios increased with increasing population density and increasing degree of urbanisation. Results from districts designated as rural but containing different population concentrations showed a similar relationship.

### 1.5.5 Distribution, elution and excretion of carcinogens

Exposure to PAH - laden soot in contaminated air results in its respiration and deposition in human lung. This is well demonstrated from post mortems of urban residents whose lungs invariably contain soot particles. Falk, Kotin and Markul (1958). The depth of penetration and degree of retention is governed by the particle size of the aerosol.

The major sub-divisions within the respiratory system differ markedly in structure, size, function and response to deposited particles. They also have different mechanisms and rates of particle elimination. Determination, therefore, of an effective tissue dose from an inhaled aerosol depends on 1) regional deposition, 2) retention times at the deposition site and along the deposition pathways, and 3) the physical and chemical properties of the particles and adsorbed compounds.

The deposition efficiency in each region depends on the aerodynamic properties of the particles, the anatomy of the airways and the geometry of flow through them.

Particle size is generally the most important parameter in determining regional deposition. A complicating factor for water-soluble particles is the change in size which may take place in the humid atmospheres of the lung causing significant changes in deposition pattern. Additionally, the geometry of the air-way system varies from person to person and this too affects deposition; in cases of abnormal deposition virtual blockage of the airway can lead to serious respiratory disease. Lippmann and Altschuler (1975) have demonstrated that deposition may be affected by the presence of other species in the atmosphere, e.g. decreased particulate deposition within the alveoli may be attained by exposure to 12 ppm of $SO_2$. This may, in part, help to explain the work of Laskin et al (1975) reported earlier, whereby a BaP/$SO_2$ system was found to be more carcinogenic to the lung of the rat than either $SO_2$ or BaP alone.

Consideration of the above points indicates that accurate prediction of particulate deposition is difficult. However, at sites of concentrated deposition, the epithelial cells receive higher than average doses of carcinogens and it might be expected that tumours would occur here predominantly. This is confirmed by Schlesinger and Lippmann (1972) who reported that the average distribution of particle deposition within the lobar bronchi was remarkably similar to the distribution of primary bronchial cancers.

One of the earliest studies of tissue distribution and excretion of PAH was performed by Peacock (1936). He injected colloidal suspensions of BaP and dibenzo [a, h] anthracene into rabbits and chickens and found that fluorescent material was rapidly cleared from the blood and excreted into the bile.

Heidelberger et al (1951) examined the rate of clearance of labelled PAH after subcutaneous injection of mice and found that the relative carcinogenicity at low doses was directly proportional to the duration of retention.

Falk, Koten and Markul (1958) studied the disappearance of carcinogens from soot in human lungs. All lung specimens were obtained from males aged between 60 and 90 and who, at the time of death, displayed no neoplastic disease. Extraction of tissue from eleven lungs showed the presence of pyrene but not BaP; checks showed that the absence of BaP was not caused by the analytical methods employed. Thus, the possibility that its absence reflected a specific pattern of rapid metabolic degradation, which had followed BaP elution from the soot, was cited. The amount of soot localised in the lung varies according to several host factors, such as site of residence, occupation, age and associated pulmonary disease. The last factor is particularly significant as interference with normal respiratory activity may mean that soot deposition and localisation are abnormally facilitated.

In addition to the deposition of soot within the body, the elution of carcinogens from the carrier particles is critical in the estimation of potential hazard. Creasia et al (1976) have considered the elution of BaP from carrier particles in the respiratory track of mice. They were aware that increased retention of BaP did not necessarily result in increased carcinogenicity and, therefore, they examined the elution of BaP from carrier particles of two size ranges 15-30 μm and 0.5-1.0 μm. The method used allowed simultaneous measurement of the lung clearance rate of the carrier particles and the BaP 0.5-1.0 μm BaP crystals without carbon was cleared rapidly, 50% of the initial dose was eliminated in 1.5 hours and more than 95% within 24.0 hours. Elimination of BaP coated on 0.5-1.0 μm particles was slower, 50% clearance in 36 hours and after 4 days more than 10% of the original dose remained. The pulmonary clearance of the carbon particles was even slower, 50% in 7 days.

In comparison BaP adsorbed on 15-30 μm particles was eliminated from the lung at a much slower rate; 50% elimination in about 4.5 days. This rate of clearance was similar to the rate at which the carbon particles were themselves eliminated from the lung. Thus little of the BaP was dissociated from the larger particles during the time of their retention in the animal lung. The very rapid clearance of BaP crystals (50% in 1 - 2 hours) explains their relatively low carcinogenetic activity. In addition an investigation by Pylev (1967) has indicated the significance of particle surface area in lung retentivity. This worker adsorbed different amounts of BaP on soots of various size ranges, with specific surface areas of 10 - 250 $m^2g^{-1}$. He exposed rats to these soots and evaluated particle retention after dissection of lung tissue. Pylev was able to show that the amount of BaP left in the rat's lungs differed markedly depending on the specific surface area of the particles. The higher the specific surface area, then the more difficult was the elution of the PAH. Whilst not agreeing completely with the work of Creasia et al (1976) who conclude that particle size is the dominent feature of the rate of clearance, Pylev's work does indicate the complex interaction and possible potency of PAH/particulate systems. These works do, however, indicate that it is not only a consideration of ambient concentrations of PAH that is important in determining the potential hazard, but the size and nature of the carrier particle also needs to be taken into account.

### 1.5.6 PAH in tobacco smoke

PAH are produced during the combustion processes involved in smoking; consequently smokers are exposed to elevated concentrations and will be potentially at greater risk than non-smokers.

An excellent review by Hoffman, Wynder et al (1978) summarises current knowledge of PAH/tobacco carcinogenesis. They have demonstrated by chemical - analytical studies and bioassays that PAH contribute significantly to the carcinogenicity of tobacco smoke by acting as tumour initiators and as co-carcinogens. It was noted that a marked reduction of PAH in the smoke is paralleled by a significant reduction in the tumorigenicity.

During the last two decades, new methods and techniques have led to a meaningful reduction of PAH in smoke, several commercial cigarettes have incorporated these modifications and it is possible that future epidemiological data will reveal a reduction in the number of smokers developing cancer of the larynx and lung.

Society's present attitude to smoking suggests that despite adverse publicity, a high percentage of men and women will continue to smoke. (It is perhaps interesting to note that the number of cigarettes smoked per capita in the U.S.A. has decreased progressively since the early sixties). Therefore, product modification so as to reduce the PAH burden from cigarettes might be a major advance in the field of preventative medicine.

Some PAH tumor initiating and co-carcinogenic agents present in the particulate phase of tobacco smoke are shown in Table 1.9.

TABLE 1.9

Some Tumour Initiating and Co-carcinogenic Agents in the Particulate Phase of Tobacco Smoke.(Hoffman and Wynder (1978)).

| COMPOUND | CARCINOGENICITY | ng/CIGARETTE |
|---|---|---|
| Tumour-Initiators | | |
| Benzo[a]pyrene | +++ | 10 - 50 |
| Dibenz[a,h]anthracene | ++ | 40 |
| Benzo[b]fluoranthene | ++ | 30 |
| Benzo[j]fluoranthene | ++ | 60 |
| Benzo[c]phenanthrene | +++ | present |
| Benz[a]anthracene | + | 40 - 70 |
| Chrysene | + ? | 40 - 60 |
| Benzo[e]pyrene | + ? | 5 - 40 |
| Co-carcinogens | | |
| Pyrene | - | 50 - 200 |
| Methylpyrene | ? | 50 - 300 |
| Fluoranthene | - | 100 - 260 |
| Benzo[ghi]perylene | - | 60 |
| Benzo[e]pyrene | + | 30 |

# CHAPTER 2

## EXPERIMENTAL TECHNIQUES

### 2.0 Introduction

Several methods of PAH analysis have been cited in the literature, notably Waller (1952), Wedgewood and Cooper (1953) and Cooper(1954). The basic steps involved in all these methods are:-

1) collection of particulate aerosols on a filter media,

2) extraction of the PAH into some suitable solvent,

3) separation and identification of the individual PAH,

and

4) determination of their concentration with respect to a unit volume of air or to a unit mass of particulate sampled.

However, recent thermodynamic studies have indicated that many methods previously accepted as being accurate might be subject to errors causing the concentrations of PAH recorded to be low. In view of this the methodology involved in determining a selection of several PAH has been re-examined and improvements made wherever possible.

### 2.1 Collection

### 2.1.1 Sampling principles

The first stage in measuring the concentrations of PAH in the atmoshere is to collect them on a suitable media. It has been assumed in the past that PAH were almost totally adsorbed onto the surface of the particles in the atmosphere and that capturing the PAH simply meant capturing the particulate.

Recently, however, Murray, Pupp et al (1974) have determined the equilibrium vapour concentrations (EVC's) of several PAH from thermodynamic data. They have concluded that measurements of PAH concentrations, made by particulate sampling, should be considered uncertain by an amount equal to the EVC of a PAH unless reduction of the EVC by adsorption of the PAH could be demonstrated.

Particulate concentrations in UK cities are generally less than 100 $\mu g\ m^{-3}$ of air and so high volume pumps are essential to collect sufficient aerosol for PAH analysis in a relatively short time. The efficiency of the collection media itself should be high and have the additional property of low resistance to air flow.

### 2.1.2 Sampling equipment

For routine determination of airborne particulate a Staplex (type S - H - 800) 'Hi-Vol' sampler operating at 0.566 $m^3\ min^{-1}$ was employed. The pump was fitted with a 'wide top' rectangular filter holder 25.4 x 20.3 $cm^2$. The flowrate was monitored using a rotameter which was calibrated at regular intervals or when the brushes of the pump required replacement. The rate was maintained using a variable voltage transformer. At the flow-rate selected 2500 - 4000 $m^3$ of air were sampled in 3 - 6 days. This provided enough particulate matter for a chemical determination of PAH to be performed. Naturally, the length of the sampling period is affected by the concentration of particulate in the atmosphere. It was found that 6 days was about the maximum period before a serious drop in the flow-rate was observed.

### 2.1.3 Collection media

To capture the particulate in the air some type of filter system must be employed. John and Reischl (1978) have examined the efficiencies of several filters using a condensation nuclei counter placed behind the filter to detect any particles that escape capture. The efficiencies of various types of filters examined by these workers are given in Table 2.1.

The use of Nucleopore and Whatman 41 filters to efficiently capture atmospheric aerosols is clearly not recommended. In this project Spectrograde Type A ($25.4 \times 20.3$ cm$^2$) Glass Fibre Filtration Media (Gelman Instrument Company, Michigan U.S.A.) have been used. As can be seen from Table 2.1, these filters have an efficiency greater than 99.9% for particles larger than 0.01 μm. In use they have a low pressure drop across their surface, hence high flow-rates may be employed keeping sampling periods relatively short. Also a large mass of particulate (~ 1.5g) can be collected before the filter pores become blocked and the flow-rate begins to drop.

### 2.1.4 Problems of sample collection

It has been suspected for some time that the volatility of some PAH might prevent complete collection on filters. In addition loss after collection, especially during any periods of heating, might occur. Determinations of such losses have been made (Commins and Lawther - (1958)); Commins (1962); Rondia (1965) and Grimmer and Hildebrandt (1965) . Although some of the experiments were unsystematic, all indicated that loss of PAH could take place.

As already mentioned, Murray, Pupp et al (1974) have published thermo-

TABLE 2.1

Filtration efficiencies of several filters (after John and Reischl (1978) to capture particles greater than 0.01 µm in size.

| FILTER TYPE | FLOW RATE<br>min $^{-1}$ | MEAN FILTRATION<br>Efficiency % |
|---|---|---|
| NUCLEPORE | 14 | 72 |
| 0.8 µm PORE | 28 | 72 |
| | 85 | 89 |
| WHATMAN 41 | 28 | 64 |
| CELLULOSE | 85 | 83 |
| GELMAN GA-1 5 um PORE | 28 | 99.1 |
| CELLULOSE ACETATE | 85 | 99.0 |
| EPA GLASS FIBRE | 28 | 99.8 |
| | 71 | 99.8 |
| GELMAN A | 28 | 99.9 |
| GLASS FIBRE | 71 | 99.9 |

dynamic data on several PAH enabling the theoretical values of the equilibrium vapour concentration (EVC) to be calculated. The EVC is the theoretical upper limit of PAH loss and may be calculated from -

$$\log \mathrm{EVC} = \frac{-A}{T} - \log T + C$$

Where A and C are constants and T in the absolute temperature. The values of A and C for several PAH are given in Table 2.2.

During sampling, in the absence of adsorption, an amount (in $\mu g\ 10^{-3}\ m^{-3}$) equal to the EVC will escape collection on the filter. In addition, air passing through a filter containing these substances will carry away amounts equal to or less than the EVC because of sublimation from that filter. The EVC's give the upper limits for losses of PAH and the actual vapour concentrations will be lower because of kinetic or adsorption phenomena.

The kinetic effect will have an influence mainly on the rate of loss from material already collected on a filter. For a slow flow rate, the air will become saturated with pollutant and the rate of loss per unit of air will equal the EVC. For faster flows, the rate of loss will be governed by the rate of sublimation. The rate of sublimation is proportional to the EVC and the exposed area so that at higher flow-rates the rate of loss per unit of air will be less than the EVC.

Losses due to high volatility may also take place during analysis, especially when, after extraction, solutions are heated to dryness.

TABLE 2.2

Values of A and C for some PAH, Murray, Pupp et al (1974).

| PAH | A (K) | C Unitless |
|---|---|---|
| PYRENE | 4840 | 23.586 |
| BENZ [a] ANTHRACENE | 5926 | 25.489 |
| BENZO [a] PYRENE<br>BENZO [e] PYRENE | 6182 | 25.089 |
| BENZO [h] FLUORANTHENE | 6792 | 26.373 |
| BENZO [ghi] PYRENE | 6674 | 25.046 |
| CORONENE | 7100 | 24.674 |

TABLE 2.3

Recovery of pyrene from untreated filters and from filter impregnated with 1 mg $cm^{-2}$ of glyceryl tripalmitate.(GTP).

| | RECOVERY OF PYRENE($ngm^{-3}$) | | NO GTP% |
|---|---|---|---|
| DATE | NO GTP FILTER | GTP FILTER | GTP |
| 2-6/7/77 | 0.20 | 0.47 | 43 |
| 01-7/9/77 | 0.16 | 0.28 | 57 |
| 14-18/10/77 | 0.17 | 0.40 | 42 |
| 18-21/10/77 | 1.23 | 1.70 | 72 |
| 28/10 - 2/11/77 | 0.30 | 0.36 | 83 |
| | | MEAN | 59% |

Elevating the temperature in the absence of an adsorbing substrate renders the measurements of all but the most involatile PAH inaccurate. Heating to dryness has been used in the past as an analytical step in PAH determination but consideration of equation 1 shows that this technique should be avoided.

Brockhaus (1974) has demonstrated an increased collection effiency of the volatile PAH, pyrene using filters coated with glycerine tricaproate at a loading of 3 mg $cm^{-2}$. Because of the high cost of glycerine tricaproate it was not possible to use it on a routine monitoring programme. After private communications with Brockhaus glyceryl tripalmitate (GTP) was employed. A loading of about 1 mg $cm^{-2}$ was adopted as standard enabling a reasonable amount of particulate to be collected before a serious drop in the flow-rate occurred.

In order to examine any benefit of impregnating the filters with GTP a series of tandem experiments were performed. Two pumps were operated at the same site, for the same time and at the same flow-rate. One of the pumps was fitted with an impregnated filter, whilst on the other a normal filter was used. Analysis procedure of back filter was identical and the recoveries of pyrene were noted. The results are shown in Table 2.3.

In all cases the recovery of pyrene was greater from the impregnated filter. There is also an indication that as the dates of sampling approach the winter months then the difference between the two values decreases. This is probably due to the increased sampling of colder air which in turn will cause less pyrene to be desorbed from the particulate. The role of the GTP is unclear but it may be that it is acting as an extra substrate onto which unadsorbed or desorbed PAH may be captured and held. Similarly during operation, particulate matter builds up on the filter so that partially used filters will be more efficient than unused ones.

In summary then, the loss of PAH, especially the more volatile ones, can occur during sampling and collection. The loss may be reduced when adsorption onto particulate is demonstrated. Losses due to sublimation are reduced when high flow-rates are employed. In the normal monitoring programme high flow-rates and sampling periods longer than 48 hours have been adopted. Treating the filters with GTP has been shown to improve the recovery of PAH.

It is generally considered that PAH are generated as vapours and are subsequently adsorbed. Since the attainment of adsorption equilibrium is much slower than simple condensation, initially the vapour concentration of PAH will equal the EVC. As adsorption increases the vapour concentration will be reduced significantly below the EVC. Consequently, it is highly probable that PAH determination by direct particulate sampling in flue gases and auto exhausts will be inaccurate by an amount equal to the EVC. However, during sampling of ambient air the adsorption equilibrium is likely to have been attained and the EVC will be considerably reduced.

Recently, high molecular weight polymers which efficiently capture

PAH from the vapour phase have become commercially available. Tenax (2, 6 di - phenyl paraphenylene oxide) is one such polymer. It has been used by Canteels and Von Cauwenberge (1978) to determine the amount of PAH in the vapour phase or leeched from the filter during sampling. These workers determined the ratio of pyrene on the particulate to the amount in the vapour phase as being 0.49, i.e. more than twice as much pyrene exists in the vapour phase or is desorbed during sampling than is retained by particulate. The corresponding ratios for BaA, chrysene, BaP and BeP were determined as 3.15, 3.13, 7.47 and 7.47. Methyl-pyrene was only detected on the particulate.

Miguel and Friedlander (1978) have attempted to detect PAH in the vapour phase in the atmosphere of Pasadena. Using a system of cold traps, the first consisting of a water - ice - salt mixture and the second of dry ice - acetone, the American workers concluded that no measurable amount of either coronene or BaP existed in the vapour phase.

It is apparent that further work is required to determine the extent of vapour phase PAH concentrations. Now that polymers such as Tenax are available in this country, it should be possible to determine what factors (e.g. temperature, rate of sampling) affect the ratio of vapour phase to particulate-associated PAH. Even disregarding any benefits obtained by using impregnated filters, both Canteels and Van Cauwenberge and Miguel and Friedlander indicate that greater than 87% of atmospheric benzo [a] pyrene may be determined by particulate sampling.

## 2.2 Extraction procedures

### 2.2.1 Choice of solvent

Once sufficient particulate has been captured on the filter, the next step is to obtain the PAH, in as pure a form as possible, in a suitable solvent.

Several methods recommend the use of cyclohexane as the extracting solvent, the separation of aliphatics and aromatics being accomplished by partitioning with a second solvent such as nitromethane. The aromatic material is preferentially soluble in nitromethane and is recovered by shaking the cyclohexane solution with excess nitromethane. Once the aromatics are dissolved in nitromethane the volume is reduced to dryness by heating under a stream of nitrogen and the resulting brown residue is dissolved in 1 - 2 $cm^3$ of cyclohexane which is then transferred to an alumina column. The work of Murray, Pupp et al (1974), discussed in the previous section, indicated that this method was subject to potentially large errors. Consequently, the nitromethane system was re-examined on the understanding that separation of aromatic/aliphatic mixtures was a requirement of a satisfactory extraction scheme. The major components of such a scheme are -

1) quantitative extraction of PAH from the filter,

2) separation of the aromatics from mixtures of aliphatics and aromatics in solution, and

3) the preparation of these aromatics into a form suitable for analysis without, where possible, the use of heat.

### 2.2.2 PAH Recovery from aromatic/aliphatic mixtures using Nitromethane

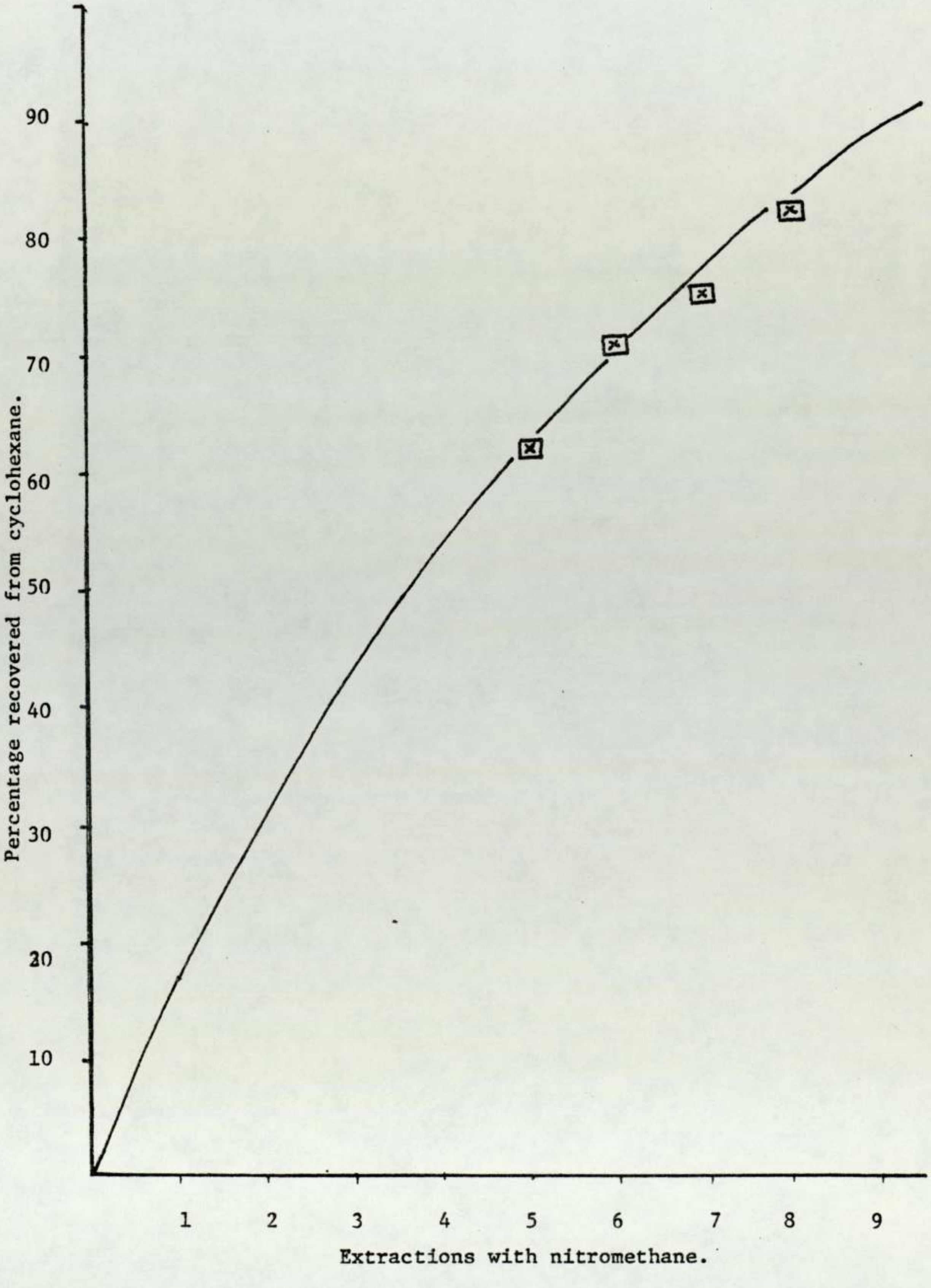
Generally, aromatic compounds are more soluble in nitromethane than are aliphatics; because of this nitromethane may be used to selectively separate aromatics from aromatic/aliphatic mixtures. To examine the efficiency of such a recovery procedure, a sample of pyrene in cyclohexane solution was shaken with small volumes of nitromethane. The concentration of the pyrene was 50 $\mu g\ cm^{-3}$ and the amount of nitromethane used was about 5 $cm^3$. After each extraction, the nitromethane was separated off. The amount of pyrene remaining in the cyclohexane was determined using UV analysis and another aliquot of nitromethane was added to the pyrene solution. After several such extractions the recovery of the PAH was plotted as a function of the number of extractions.

Figure 2.1 shows a typical plot of the recovery of pyrene from cyclohexane solution. It is evident that after eight extractions the amount of pyrene recovered is only about 84% of the original. Each extraction is time consuming and although it is admitted that more pyrene could be recovered with more extraction the time expended would be too great for the operation to be included in a routine monitoring system.

There are other problems involved in using nitromethane. For instance, it is not possible to use it as the solvent during UV analysis of many PAH. Sawicki et al (1964). To overcome this the usual method is to reduce the nitromethane to dryness, either at reduced pressure or under a stream of nitrogen. The resulting brown residue is then

FIGURE 2.1

Percentage recovery of pyrene from cyclohexane solutions after a given number of extractions with nitromethane.



dissolved in a small volume of cyclohexane or n - pentane, which may then be analysed or if separation is required, transferred to a suitable alumina column. In view of the work of Murray, Pupp et al (1976) this method was not considered valid.

To avoid the evaporation of nitromethane and the consequent loss of PAH an examination of their 'back-extraction' into n - pentane and n - hexane was undertaken. Known concentrations of pyrene in nitromethane were extracted with either n - pentane or n - hexane and the recovery of the PAH was followed spectroscopically. The mean percentage recovery of pyrene using n - pentane is shown in Figure 2.2.

The recovery obtained using n - hexane was essentially similar to that of n - pentane but as the boiling point of pentane (36°C) is lower than the hexane (68°C) solutions of the former may be more easily concentrated at room temperatures.

The results obtained in this section are illustrated diagramatically in Figure 2.3. It clearly shows that the recovery of PAH from aromatic/aliphatic systems cannot be accomplished either quantitatively or efficiently using nitromethane as the separating solvent. As a result of this work another solvent was sought which would preferentially dissolve PAH in the presence of aliphatic compounds.

### 2.2.3 Recovery of PAH from aromatic/aliphatic mixtures using dimethyl sulphoxide (DMSO)

Haenni (1962) indicated that dimethyl sulphoxide (DMSO) might be used to quantitatively recover aromatics from mixtures of aromatic

FIGURE 2.2.

Percentage recovery of pyrene from nitromethane solution using n-pentane.

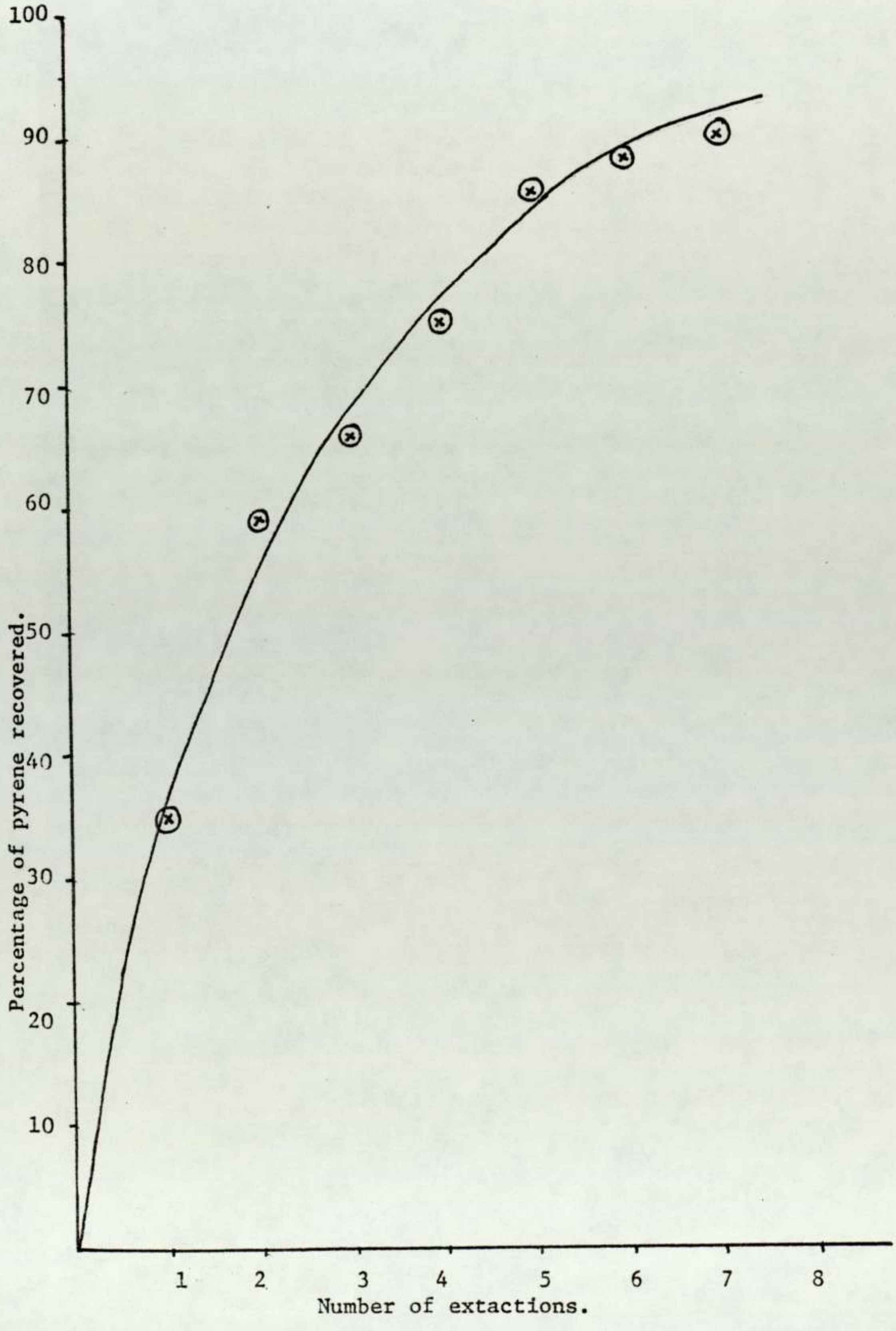
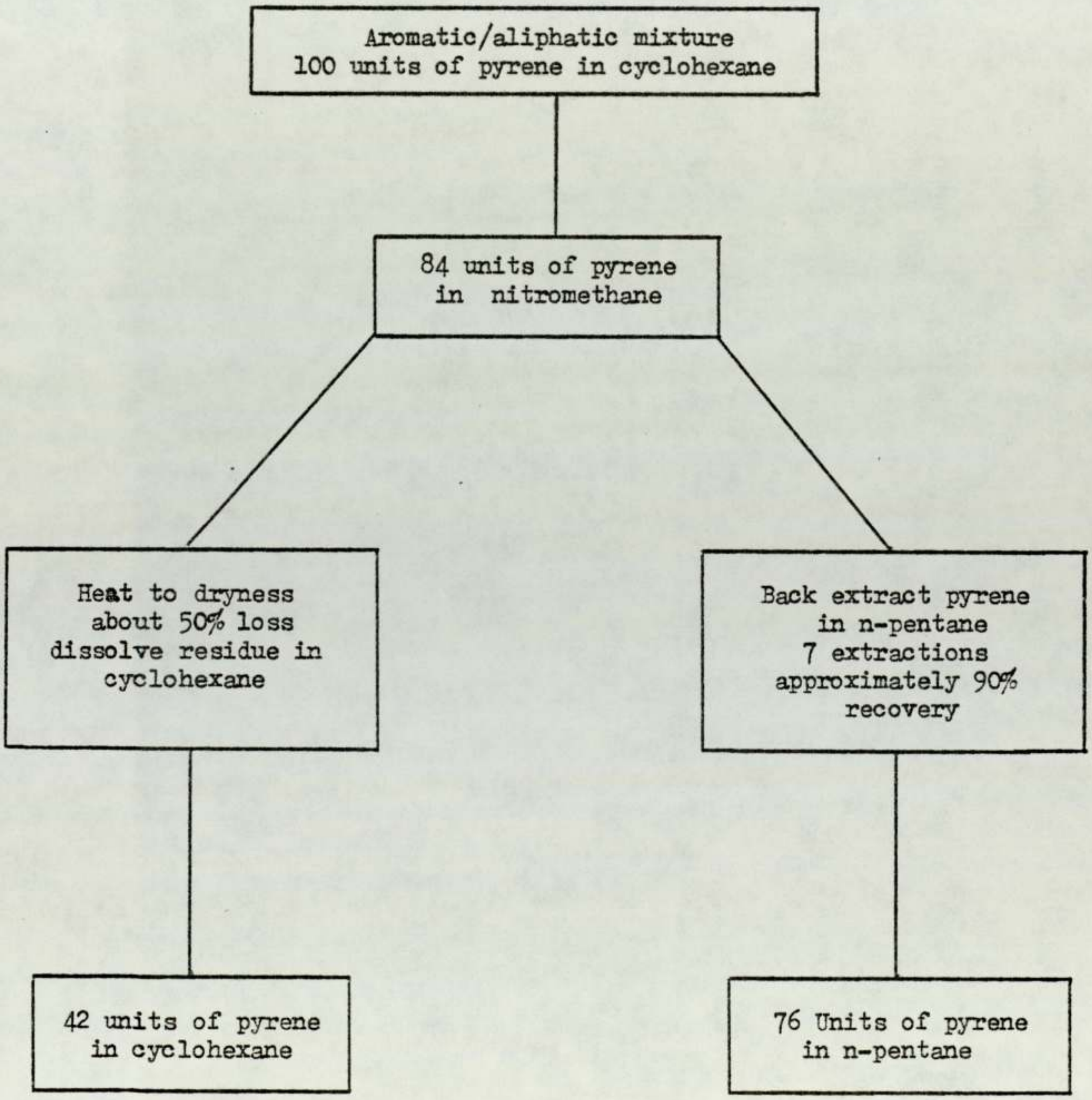


FIGURE 2.3

Recovery of pyrene from cyclohexane using a nitromethane system



and aliphatic materials. In one set of experiments the recoveries of various aromatics from n-hexane using several different solvents was examined. The extracting solvents used were DMSO, N, N dimethyl formamide, acetonitrile and nitromethane. Haenni was able to show that DMSO and N, N dimethyl formamide were more efficient than acetonitrile or nitromethane at removing BaP and dibenzo [a] anthracene from the n-hexane. Table 2.4. In addition, the work demonstrated that DMSO had the extra advantage of removing less non aromatic material than the other solvents.

In an attempt to confirm the findings of Haenni, the recovery of pyrene from cyclohexane solution using DMSO was examined. As with the nitromethane recovery procedure the amount of PAH remaining in solution after each extraction was determined by UV spectrophotometry. Table 2.5 lists the mean recovery of pyrene after each extraction with DMSO and Figure 2.4 shows the comparative recoveries of DMSO and nitromethane.

The recovery of the pyrene from DMSO solution is very easily accomplished. DMSO, unlike nitromethane, is completely miscible with water; the addition of an equal volume of water tends to 'throw' the aromatics out of solution and they may be efficiently back extracted into n - pentane. See Table 2.6.

It was found that a single extraction with n - pentane recovered 95% of the pyrene from DMSO/water. In order to standardise the method four extractions with n - pentane were adopted. From Table 2.4 it is apparent that this corresponds to a calculated recovery greater

TABLE 2.4

Recovery of PAH from n - hexane using various solvents. Haenni(1962)

PERCENTAGE OF PAH EXTRACTED

| PAH | SOLVENT | EXTRACTIONS 1 | 2 | 3 | TOTAL |
|---|---|---|---|---|---|
| | DMSO | | | | |
| ANTHRACENE | | 7.9 | 15.5 | 4 | 98 |
| BENZO [a] PYRENE | | 90.5 | 8 | 1 | 99 |
| CHRYSENE | | 90 | 8 | 1.5 | 99 |
| DIBENZO [a,h] ANTHRACENE | | 95 | 4.5 | 0.5 | 100 |
| | N,N DIMETHYL FORMAMIDE | | | | |
| BENZO [a] PYRENE | | 92 | 8 | 1 | 101 |
| DIBENZO [a,h] ANTHRACENE | | 95 | 5.5 | 0.5 | 101 |
| | ACETONITRILE | | | | |
| BENZO [a] PYRENE | | 60 | 23.5 | 9.5 | 92 |
| DIBENZO [a,h] ANTHRACENE | | 68 | 22 | 6 | 96 |
| | NITROMETHANE | | | | |
| BENZO [a] PYRENE | | 63 | 22 | 8.5 | 93.5 |
| DIBENZO [a,h] ANTHRACENE | | 68 | 22 | 7.5 | 97.5 |

TABLE 2.5

Comparison of the recovery of pyrene from cyclohexane using DMSO or nitromethane extractions.

| NUMBER OF EXTRACTION | EXTRACTING SOLVENT | |
|---|---|---|
| | DMSO | NITROMETHANE |
| 1 | 43 | - |
| 2 | 70 | - |
| 3 | 85 | - |
| 4 | 93 | - |
| 5 | 96 | 62 |
| 6 | 98 | 71 |
| 7 | - | 75 |
| 8 | - | 84 |

FIGURE 24.

Comparison of the recovery of pyrene from cyclohexane solutions using DMSO and nitromethane.

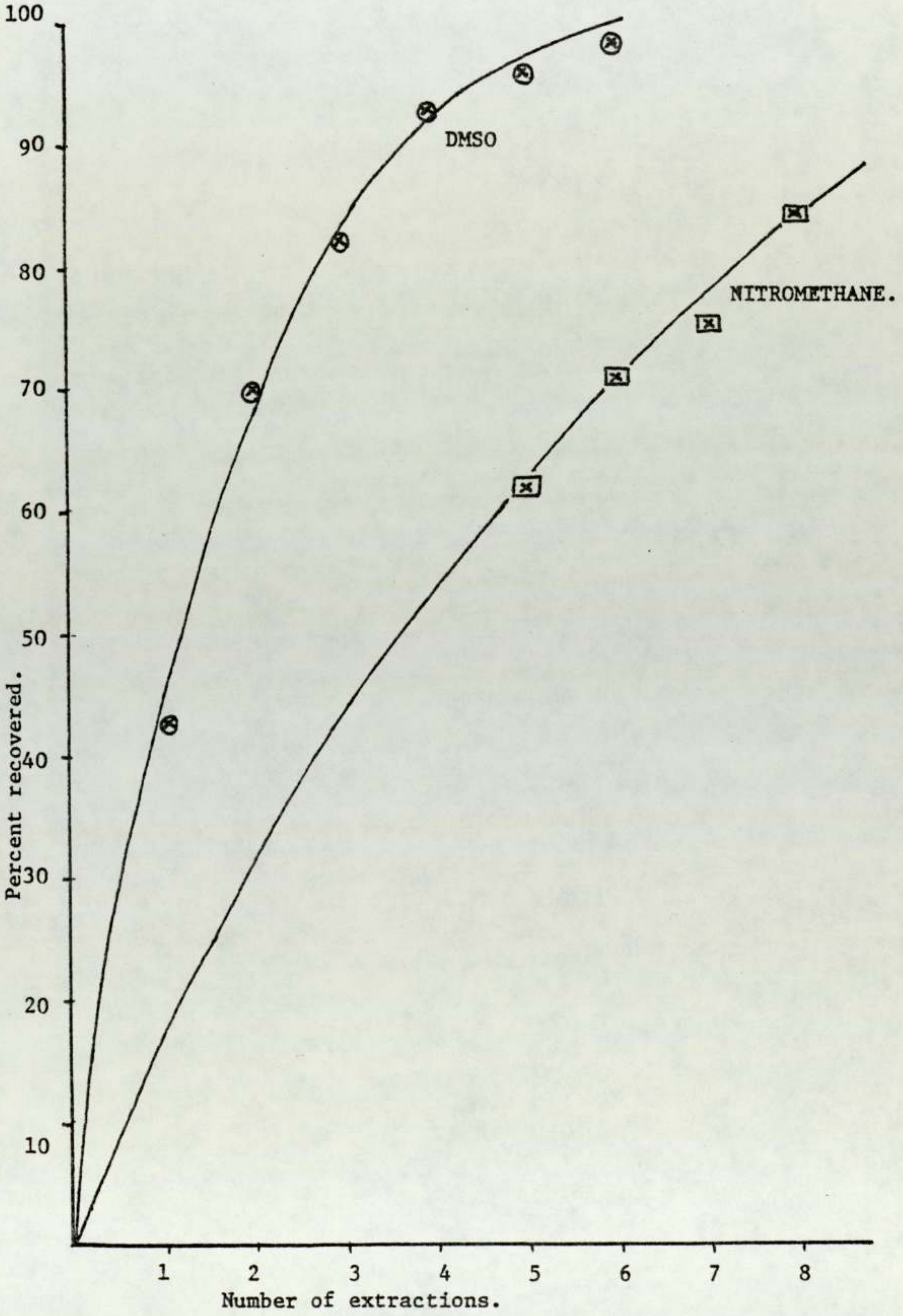


TABLE 2.6

Recovery of pyrene from DMSO/water using n-pentane extractions.

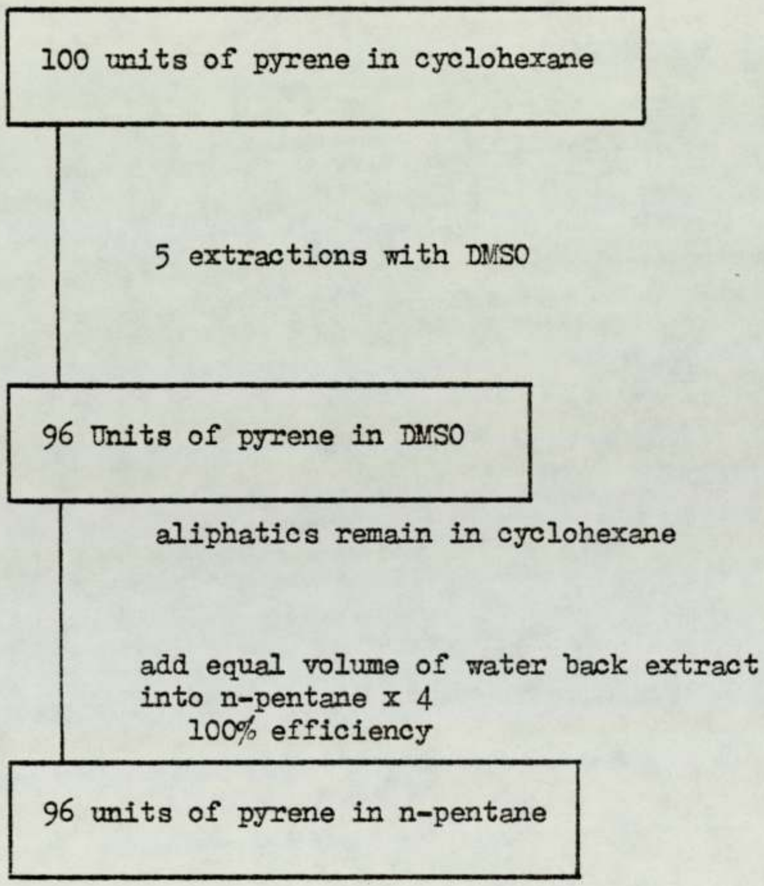
| NUMBER OF EXTRACTIONS | PYRENE RECOVERED<br>EXPERIMENT<br>1 | <br><br>2 | CALCULATED RECOVERY BASED ON 95% EFFICIENCY |
|---|---|---|---|
| 0 | 0 | 0 | 0 |
| 1 | 95 | 95 | 95 |
| 2 | 100 | 100 | 99.75 |
| 3 | 100 | 100 | 99.99 |
| 4 | 100 | 100 | 99.9995 |

than 99.999%.

A diagrammatic representation of the DMSO recovery system is shown in Figure 2.5.

FIGURE 2.5

Schematic Recovery of pyrene from cyclohexane using a DMSO system.



It is evident that loss of pyrene results from an insufficient number of extractions with DMSO. Further extractions could reduce the 4% loss but the method is time consuming and unsuitable for long term monitoring programmes. The most direct method of overcoming this problem was to use DMSO as the extracting solvent.

### 2.24 Comparison of Solvents

Many solvents have been recommended for removing PAH from the particulate and filter media. The most common are cyclohexane, Wedgwood and Cooper (1958), Markman et al (1967), Commins (1976) and Cantuti et al (1964); benzene, Gordon and Bryan (1974) and Miguel and Friedlander (1978); acetone, Cleary (1962) and Cooper (1954); and methylene chloride, Sawicki (1960). Carbon tetrachloride has been used by Goldberg et al (1973) because of its I.R. transparency and carbon disulphide by Grob and Grob (1971) because of its very low flame ionisation response in a gas chromatograph detector.

Although cyclohexane has been widely recommended, Gordon (1974) has examined the extraction of airborne particulate matter collected on large multi-pleated fibre-glass filters using 17 different solvents in an attempt to relate relative solvent extraction efficiencies to already known solvent properties. The solvent properties considered were dielectric constants, solvent polarity, $E_T$ and solvent strength, $E^o$.

Table 2.7 shows these parameters together with the dry extracted weight ( in µg per $cm^{-2}$ of filter) for some of the solvents.

Gordon concludes that solvents with $E^o$ values of 0.3 or larger seem to be adequate for recovery of PAH. The $E^o$ of cyclohexane is given as 0.04 and, therefore, its use as an extracting solvent must be open to question.

TABLE 2.7

Solvent properties and extract yield ( $\mu g\ cm^{-2}$) of some common solvents used in the extraction of PAH. (Gordon (1974)).

| SOLVENT | DIELECTRIC CONSTANT | SOLVENT POLARITY $E_T$ | SOLVENT STRENGTH $E_o$ | EXTRACT YIELD( $\mu g\ cm^{-2}$) |
|---|---|---|---|---|
| n-Hexane | 1.88 | 30.9 | 0.01 | 187 |
| Cyclohexane | 2.02 | 31.2 | 0.04 | 163 |
| Carbon Tetrachloride | 2.35 | 32.5 | 0.18 | 228 |
| Toluene | 2.38 | 33.9 | 0.29 | 264 |
| Benzene | 2.27 | 34.5 | 0.32 | 263 |
| Acetone | 20.70 | 42.2 | 0.56 | 630 |
| Nitromethane | 39.40 | 46.3 | 0.64 | 520 |
| Ethanol | 24.30 | 51.9 | 0.88 | 616 |
| Methanol | 32.63 | 55.5 | 0.95 | 717 |

Grosjean (1975) has also examined various solvents used to extract organics from atmospheric particulate and has produced a list of extraction efficiencies (EF's). The EF of a particular solvent is related to benzene (EF = 100 standard) by

$$EF_i = \frac{\text{total extracted material, i}}{\text{total extracted material, benzene}} \times 100$$

Some extraction efficiencies of solvents determined by various workers are given in Table 2.8.

Grosjean concludes that benzene is more efficient than cyclohexane in extracting organics from atmospheric particulate. This, taken in conjunction with the previously mentioned work of Gordon and Murray, Pupp et al, indicates that at the concentrations of PAH reported using cyclohexane as the extracting solvent, followed by reduction to dryness at elevated temperatures are certainly inaccurate for the more volatile PAH.

At this stage the use of DMSO had proved so superior to the nitromethane separation that its possible use as the actual extracting solvent was mooted. Grosjean had reported the extraction efficiency of DMSO as 364 (Table 2.8) compared to benzene with a value of 100 so there was some practical evidence supporting its use. In an attempt to test the efficiency of DMSO as the extracting solvent, PAH were successively extracted from airborne particulate collected on glass fibre filters and from laboratory prepared soots. The exposed filters were placed in a glass container and covered with approximately 50 $cm^3$ of DMSO. The container was placed in a thermostated water bath, set at 100°C for a period of 12 hours. After this period the DMSO was allowed to cool and decanted off. A second volume of DMSO was added to the filter and the extraction process was repeated. The amount of pyrene, BaP and coronene in each sample was determined by the usual methods and the recovery of the second extract was compared to recovery of the first. The results are shown in Table 2.9.

From these results it was concluded that DMSO could be satisfactorily employed as the extracting solvent. Due to the restriction of time it was not possible to optimise the extracting conditions, the 12 hours heating in a 100°C water bath being adopted as standard throughout.

## 2.25. The Chosen Method

The developments described in the previous sections were incorporated into a standardised procedure which is displayed diagrammatically in Figure 2.6.

Once the PAH had been obtained from the aqueous DMSO using n-pentane, it proved more practicable to separate them on an alumina column using cyclohexane as the eluting solvent. The boiling point of n-pentane is only 36°C and so the combined volume from the four extractions could easily be reduced using a small air-fan, hence the need to heat the sample with the consequent dangers outlined in Section 2.1.4 was

TABLE 2.8

Relative extraction efficiencies (EF) of solvents determined by various workers.

| SOLVENT | EF GROSJEAN(1975) | EF GORDON(1974) | EF STANLEY(1967) |
|---|---|---|---|
| n-pentane | 71 | - | 66 |
| n-hexane | 78 | 71 | - |
| carbon tetrachloride | 81 | 87 | - |
| cyclohexane | 84 | 64 | - |
| benzene | 100 | 100 | 73, 75, 82 |
| chloroform | 118 | - | 112, 107 |
| dichloromethane | 126 | 107 | 105, 106 |
| acetone | 250 | 239 | 197, 194, 141 |
| DMSO | 364 | - | - |
| water | 407 | - | - |

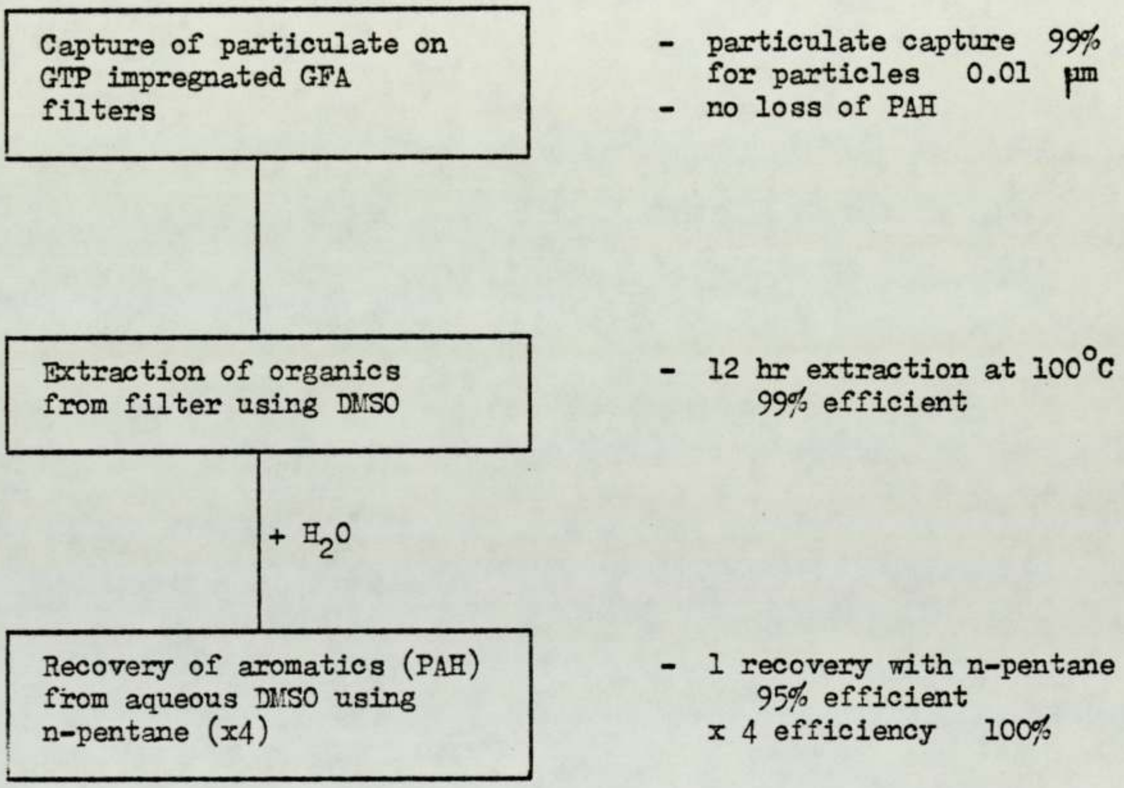
TABLE 2.9

Recovery of PAH from glass fibre filters and from soot using a second extraction with DMSO.

| SOURCE | PAH RECOVERED AS A% OF FIRST EXTRACT | | |
|---|---|---|---|
| | PYRENE | BaP | CORONENE |
| glass fibre filter | no trace | no trace | no trace |
| | no trace | no trace | no trace |
| Soot | 1 | 1 | - |
| | no trace | 1 | no trace |

FIGURE 2.6

Diagram showing the stages adopted for a standardised programme for the analysis of PAH in the urban atmosphere.



avoided. The temperature of the n-pentane during this period was determined as -4°C. The advantage of this low temperature reduction over reduction at even room temperature (say 20°C) using some other solvent may be estimated by the comparison of the EVC's at - 4°C at 20°C using the data given in Table 22. The EVC of pyrene, in the unadsorbed state, is 1458 and 39844 $\mu g\ 10^{-3} m^{-3}$ at temperature of 269K (-4°C) and 293K (20°C) respectively. In addition there is no need to evaporate to complete dryness as the small amount of n-pentane remaining has no effect on the PAH separation. When the volume of n-pentane is only about 1 $cm^3$ a similar volume of distilled cyclohexane is added and the solution is quantitatively transferred to the alumina column for separation.

## 2.3 Separation, Analysis and Measurement of PAH

### 2.3.1 Choice of Methods

Recently several new and improved methods have been employed to determine the concentrations of PAH in the ng $m^{-3}$ range. Janini et al (1975), for example, have demonstrated that gas-liquid chromatography in the nematic region of N, $N^1$ - bis ( p - methoxybenzylidene) - $\alpha$ -, $\alpha^1$ - bi - p - toluidine could produce base line separation of geometric PAH isomers; Van Vaeck and Van Cauwenberghe (1978) used an advanced programmed multiple - ion - detector mass spectrometer in conjunction with a gas chromatographic system to separate and measure atmospheric PAH. Whilst these methods of analysis point the way to monitoring of the future, restrictions of both finance and time required that methods of separation, analysis and measurement should be those presently accepted in the literature.

Within the limits stated the method of detection employed was ultraviolet (UV) spectrophotemetry. This method requires that PAH mixtures should be separated into individual components so that errors caused by interference are reduced. Separation of the PAH was performed using specially activated alumina columns.

### 2.3.2 UV analysis of PAH

PAH in cyclohexane display intense, characteristic $\pi \rightarrow \pi^*$ transition absorbance peaks in the 450 - 250 nm range. The absorbance trace of each PAH show several peaks which may be used as a "fingerprint" to determine its prescence.

Samples of PAH, obtained from commercial and other sources, were made into standard solutions using distilled cyclohexane as the solvent. The UV absorbance of these solutions were examined using a PYE-UNICAM SP-800 DOUBLE BEAM SPECTROPHOTOMETER. For each PAH, the absorbance of a given peak was measured using the base-line technique of Cooper, (1954), at a variety of concentrations. Hence a series of calibrations curves were produced. Table 2.10 shows the concentrations of PAH which will produce an absorbance of 0.01 units on the spectrophotometer. With a knowledge of the volume of solution the amount of PAH may be readily determined.

The response of the instrument was checked periodically during operation using standard filters and solutions to ensure accuracy and consistency.

In a real sample (even after separation) the PAH is examined, not in

TABLE 2.10

Concentration of PAH ( $\mu g\ cm^{-3}$) required to give an adsorption of 0.01 units on the SP800 spectrophotometer.

| PAH | CONCENTRATION(C) $\mu g\ cm^{-3}$ | ABSORPTION PEAK MEASURED (nm) | OTHER CONFIRMATORY ABSORPTION PEAKS (nm) |
|---|---|---|---|
| Pyrene | 0.039 | 335 | 319, 306, 273 |
| Chrysene | 0.233 | 320 | 268, 257, 250 |
| Benzo [ a ] pyrene | 0.104 | 384 | 364, 297, 347 |
| Benzo [ e ] pyrene | 0.100 | 331 | 317, 289, 278, 258 |
| Coronene | 0.057 | 339 | 324, 345, 302 |

isolation but as a mixture of components. The presence of each PAH in the mixture was determined by comparing the UV trace with standard plots and also with plots of PAH mixtures, e.g. Cleary (1962), Monkman et al (1967) and Thomas and Moore (1968)

### 2.3.3 Separation of PAH mixtures

Several workers have used alumina columns to separate mixtures of PAH prior to identification and measurement by UV spectrophotometry, examples are Cooper (1954), Monkman et al (1967), Cleary (1962), Gordon and Bryan (1974) and Commins (1976). Cleary used columns 58.5 cm in length with a water content of 13- 13.5%. The eluent was collected in 25 $cm^3$ fractions and nearly 2000 $cm^3$ of solvent were required to complete the separation. It was considered that although this system did provide discrete separation of the sample, it would be unsuitable for use in a routine monitoring programme. Consequently, the activity of the alumina was investigated.

Activated alumina (UGl Laporte Industries, Ltd.) was heated in an oven at 240°C for four hours. After cooling in a desiccator several 50 g samples of the alumina were placed in stoppered flasks and covered with distilled cyclohexane. The activity of the white slurry produced could be changed by the addition of water. The water was added slowly from a microburette and the slurry was well shaken after each addition to ensure even dispersion of the water. Addition was continued until the alumina had a 6 percent water content. The slurry was transferred to a pyrex glass tube 1 cm.in diameter to make up the 15 cm. long alumina column. Generally, elution of PAH from such a column was complete after the collection of between 30 and 35 fractions, each

$3.6\ cm^3$ in volume.

Sawicki et al (1972) have noted that not all the PAH placed on the column is recovered. In order to determine these retention losses mixtures of standard solutions of PAH were eluted through columns of the adopted length and activity (i.e. 15 cm. and 6% water content) and the amount of each PAH retained was noted. The mean recoveries of several PAH are given in Table 2.11.

This series of experiments confirms the work of Sawicki et al (1972). The amount of PAH lost is both measurable and fairly constant. The mean recoveries were used to apply a correction factor to the amount of PAH determined in the routine monitoring programme.

### 2.3.4 Measurement of PAH concentration

After collection the PAH content of each fraction was determined using the SP 800 spectrophotometer. The concentration, C, of an individual PAH was determined from -

$$C(\ \mu g's) = \frac{V \times A \times Ca}{k}$$

Where V is the total volume of sample in which the PAH was found ($cm^3$) A is the total height of absorbance measured at the calibration peak, (units of absorbance), Ca is the concentration of PAH required to give an absorbance peak of 0.01 units and k is a constant to correct for column loss.

This value was then expressed either in terms of the total volume of

TABLE 2.11

Recoveries of PAH from 15 cm. alumina columns. (6% water content) expressed as a percentage of the amount placed on the column.

| PAH | PYRENE | CHRYSENE | B(a)P, B(e)P | CORONENE |
|---|---|---|---|---|
| % Recovered | 92 | 82 | 91 | 94 |
| | 84 | 82 | 95 | 95 |
| | 93 | 82 | 89 | 94 |
| | 89 | 80 | 91 | 92 |
| | 87 | 85 | 92 | 94 |
| | 89 | 86 | 91 | 95 |
| | 89 | 86 | 93 | 96 |
| Mean | 89 | 83 | 92 | 94 |
| n | 7 | 7 | 7 | 7 |
| SD | 2.8 | 2.2 | 1.8 | 1.2 |

TABLE 2.12

Comparison of PAH recovery from two identically exposed glass fibre filters and from two soot samples (mg $kg^{-1}$).

| PAH | FILTER RECOVERY (mg $kg^{-1}$) | | | SOOT RECOVERY (mg $kg^{-1}$) | | |
|---|---|---|---|---|---|---|
| | F1 | F2 | $\frac{F2}{F1}$ % | S1 | S2 | $\frac{S2}{S1}$ % |
| Pyrene | 65.8 | 51.8 | 78 | 6165 | 4969 | 81 |
| Chrysene | 157.3 | 149.8 | 95 | - | - | - |
| Benzo [ a ] pyrene | 91.6 | 79.4 | 82 | - | - | - |
| Benzo [ e ] pyrene | 97.9 | 92.0 | 93 | 611 | 563 | 92 |
| Coronene | 8.7 | - | - | 654 | 609 | 93 |

air sampled, giving a result in ngm$^{-3}$ or in terms of the total mass of particulate collected, giving a result in mg kg$^{-1}$.

### 2.3.5 Reproducibility of analytic method

To establish the degree of uncertainty involved in the final estimation of PAH, a pair of filters were exposed simultaneously, under identical conditions and at the same site. The recovery of PAH from each filter (F1 and F2) was determined. In addition, a sample of laboratory produced soot was divided into two portions (S1 and S2) and the pyrene, BeP and coronene contents measured. The results are summarised in Table 2.12.

The mean percentage difference in the recoveries of PAH from the two pairs of samples is 11%. In view of the possibility of slight variation in flow-rates between the two pumps, the possible heterogenity of the soot and the complex nature of the analytical scheme, this result was taken as acceptable.

## 2.4 Conclusions

This chapter has indicated some of the problems involved in determining PAH in the urban atmosphere. Where possible these problems have been resolved and a routine analytical scheme,outlined in Figure 2.7, adopted. The main findings may be summarised as follows:

1) Use of high grade glass fibre filters has allowed 99.9% efficient capture of particles greater than 0.01 μm in diameter.

2) Doubts that PAH in the vapour phase or those 'leeched' from the filter during sampling could not be determined by particulate capture have been examined. As a precaution against such losses the filters have been treated with glyceryl tripalmitate. The recoveryoof pyrene from untreated filters is only about 60% of the recovery from treated ones.

3) The method of extracting PAH from the filter has been examined. A comparison of PAH recovery using various solvents and an inspection of the available literature has resulted in dimethyl sulphoxide (DMSO) being chosen as the extracting solvent. Not only has quantitative recovery of PAH been demonstrated but its use is beneficial in separating aromatic/aliphatic mixtures.

4) A clean, efficient and reproducible recovery of PAH from aromatic/aliphatic mixtures has been accomplished. The method of heating solvents to dryness, with possible consequent loss of PAH, has been avoided. The superiority of this method over nitromethane-heating to dryness and nitromethane - n - pentane back extraction methods has been investigated and established.

5) The recovery of PAH from aqueous DMSO using n - pentane has been examined. The volume of the n - pentane used may be easily reduced using a small air fan. During this operation the temperature of

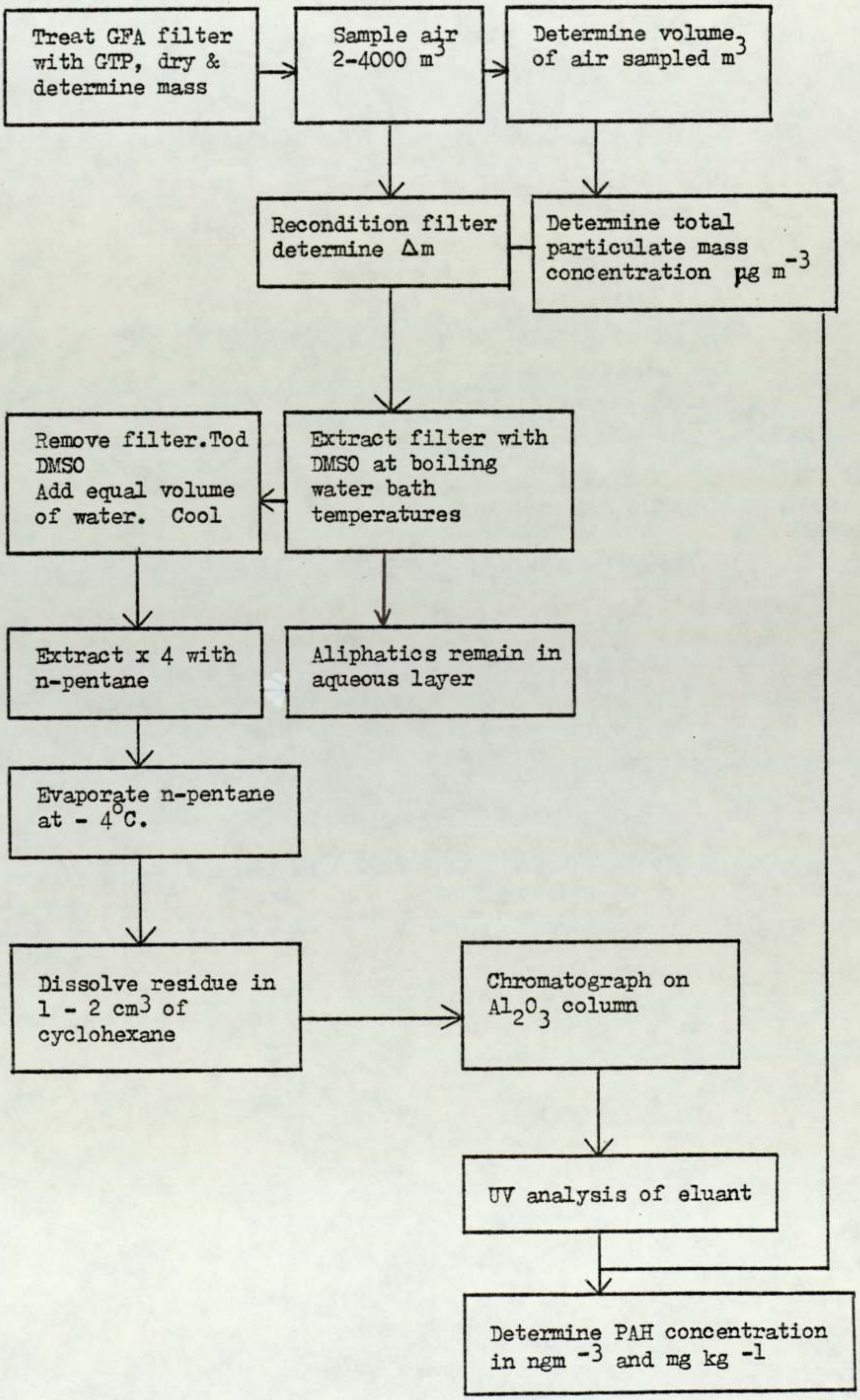
the n - pentane is only $-4^{\circ}C$, and so potential loss caused by elevated equilibrium vapour concentrations has been reduced.

6) Separation of PAH mixtures has been accomplished using specially activated alumina columns. By carefully adjusting the water content and thereby the activity of the alumina the column length has been standardised at 15 cm., suitable for a routine monitoring programme.

7) The method outlined in Figure 2.7 enabled several PAH to be determined in the atmosphere of a large European city at relatively low cost and on a routine basis.

FIGURE 2.7

Analytical scheme for determining the PAH content of the atmosphere



# CHAPTER 3

## ROUTINE MONITORING OF PAH

### 3.1 Monitoring sites

### 3.1.1 Factors affecting site selection

In any project where measurements are to be made out of the controlled environment of the laboratory, great care must be exercised to ensure that they are both meaningful and representative. Site selection requires consideration of the factors which might influence pollutant concentrations, i.e. topography, nature and distribution of sources in the region of the site.

For the study of potential health effects, the site selection must ensure that the sample collections are truly representative of the air that is actually breathed by the exposed population groups. For example, concentrations of pollutants vary with height of the sampling point above ground level and so it was decided from the outset that all samples would be taken at a height of between two and three metres. This height approximates to the height of an average adult.

It is evident that the intake of air pollutants by man will be dependent upon where he spends his time. To assess the exposure to PAH in air, long-term average concentrations are considered to be of prime importance, whereas short-term fluctuations may have little meaning. Because PAH in the urban environment are derived from a variety of sources, it is difficult to determine overall exposures except on the basis of mean concentrations of individual carcinogens over long periods.

On a more practical level the sampling site must be large enough to hold the equipment, it must have electrical power and be unoffensive to the people in the neighbourhood, safe from outside interference and yet be easily accessible to allow rapid monitoring of flow-rates and general maintenance.

### 3.1.2 The Selected Sites

Eventually three sites were selected in and around Birmingham to forefill the above requirements. They were chosen because they had environmentally different surroundings and it was hoped that this would provide the maximum amount of information.

The first site designated S-C, was at the complex motorway interchange at Gravelly Hill. It was expected that this site would reveal any influence on urban atmospheric PAH concentration arising from motor traffic. It has been shown for coronene at least, Gordon and Bryan(1974), that correlation between monitored concentration and traffic density is good.

The second, designated C-C, was on the campus of the University of Aston, which is located in the centre of Birmingham within 1 km of the main shopping area, but not in close proximity to traffic.

The third, designated S-U, was at Sutton Coldfield - a sub-urban residential area about 15 km due north of the city centre.

Furthermore, the University campus and Sutton Coldfield are two sites used for the National Survey for smoke and $SO_2$.

## 3.2 Results

The concentration of total particulate matter (TPM $\mu g\ m^{-3}$) and of PAH ($ng\ m^{-3}$ and $mg\ kg^{-1}$) are given in the following tables together with the date of sampling, the mean windspeed (WSP $ms^{-1}$) and temperature (TMP $^{o}C$).

The PAH determined on a routine basis are only a selection of those generally observed after chromotography and spectrophometric identification. Table 3.1 gives a complete list of those PAH definitely identified during the sampling programme. All have been reported by other workers.

TABLE 3.1

PAH determined as being present in the urban atmosphere around Birmingham.

Fluorene

Phenanthrene

Fluoranthene

Pyrene

Methyl-pyrenes

Benz [a] anthracene

Chrysene

Benzo [a] pyrene

Benzo [e] pyrene

Perylene

Dibenz anthracenes

Benzo [ghi]perylene

Anthanthrene

Coronene

### 3.2.1 PAH and particulate concentrations monitored at Salford Circus site (S-C)

The monitoring equipment was located in an electricity sub-station close to Salford Circus, part of the Gravelly Hill Midlands motorway interchange (Fig. 3.1). The collection head was two metres above ground level. Sampling commenced in November 1976 and finished in January 1979.

Table 3.2a gives PAH concentrations expressed in terms of the volume of air sampled ($ngm^{-3}$) and Table 3.2b in terms of the mass of particulate collected. ($mg\ kg^{-1}$).

The maximum observed and calculated mean values for the site are given in Table 3.3.

The correlation coefficients between pairs of PAH and between PAH and particulate concentrations are given in Table 3.4.

A summary of the multiple regression analysis relating pollutant concentrations to windspeed and temperature are reported in Table 3.5.

Figure 3.1

Schematic map of Salford Circus site -
Gravelly Hill Midlands Motorway Interchange.

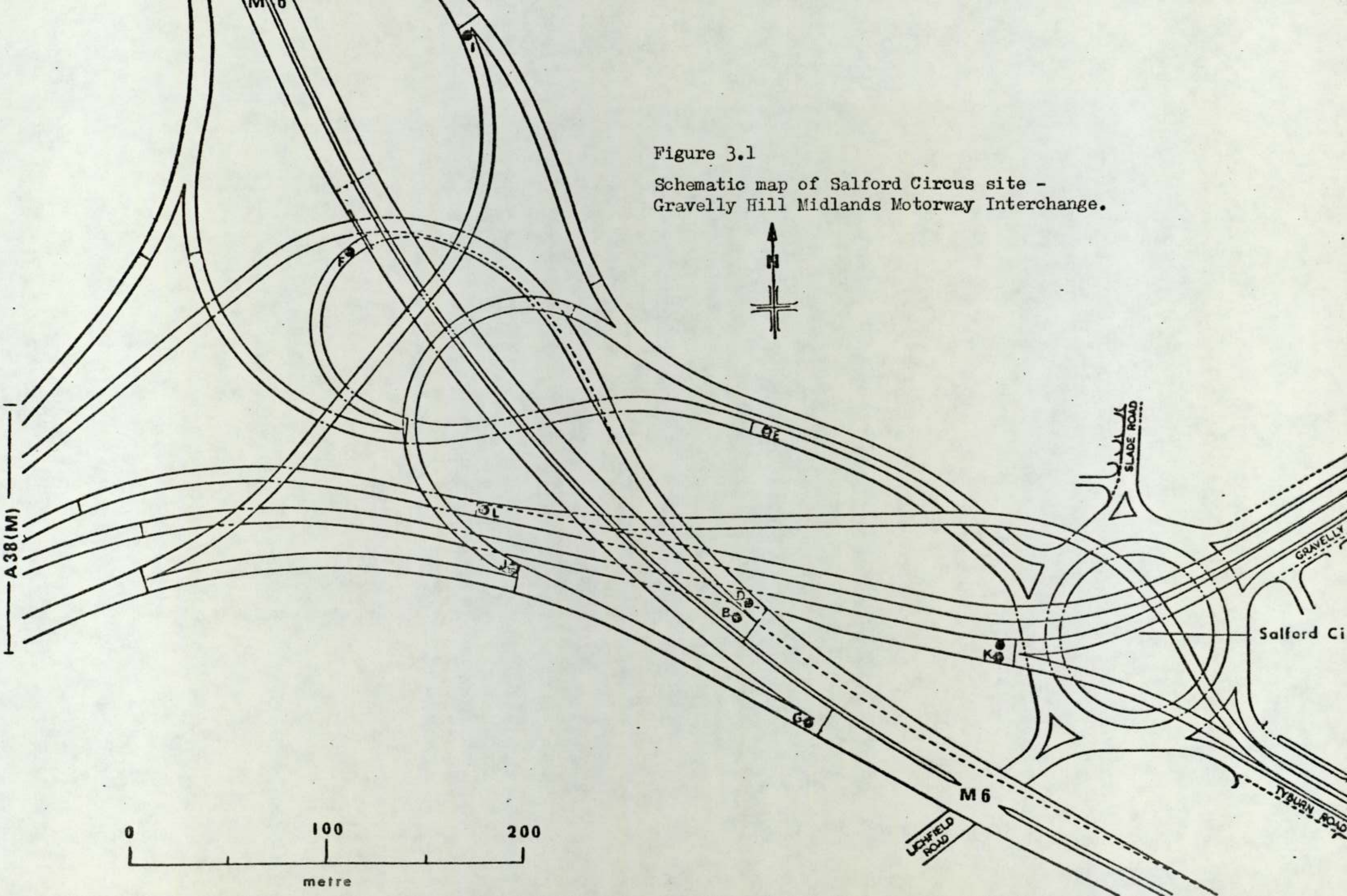


TABLE 3.2a

Concentrations of total TPM ( $\mu gm^{-3}$) and PAH ($ngm^{-3}$) monitored at Salford Circus (S-C).

| DATE | WIND SPEED $ms^{-1}$ | TEMPERATURE °C | TPM $\mu gm^{-3}$ | PYRENE | CHRYSENE | BaP | BeP | CORONENE |
|---|---|---|---|---|---|---|---|---|
| | | | | ngm -3 | | | | |
| 13-19/11/76 | 2.09 | 5.89 | 50 | 1.78 | | 4.65 | 2.57 | 1.21 |
| 06-09/12/76 | 5.11 | 4.22 | 62 | - | | 2.18 | 1.29 | 0.58 |
| 06-10/01/77 | 3.75 | 3.60 | 49 | 1.69 | | 4.87 | 1.51 | 1.10 |
| 26-31/01/77 | 3.82 | 1.75 | - | 0.85 | | 1.61 | - | 0.77 |
| 28/02-03/03/77 | 4.94 | 8.17 | 111 | 1.70 | | 6.48 | 2.57 | 5.24 |
| 29/03-03/04/77 | 5.92 | 4.98 | 55 | 1.13 | | 2.02 | 1.11 | 1.63 |
| 12-17/05/77 | 4.06 | 7.11 | 39 | 0.84 | | - | 1.64 | 0.98 |
| 15-17/06/77 | 5.11 | 11.07 | 40 | 1.24 | | 0.61 | 0.46 | 0.34 |
| 14-18/07/77 | 3.58 | 15.33 | 43 | 0.55 | | 0.92 | 0.72 | 0.39 |
| 20-26/09/77 | 3.39 | 11.84 | 62 | 0.76 | | 2.69 | 1.84 | 0.99 |
| 05-10/10/77 | 4.08 | 11.08 | 57 | 0.64 | | 1.74 | 1.34 | - |
| 14-18/10/77 | 2.10 | 10.59 | 127 | 0.40 | | 2.02 | 1.00 | 0.65 |
| 22-28/11/77 | 4.87 | 3.42 | 66 | 3.47 | | 3.32 | 3.49 | - |
| 07-12/12/77 | 5.36 | 7.63 | 54 | 0.85 | | 2.20 | 1.81 | 1.25 |
| 10-15/01/78 | 3.94 | 0.29 | 68 | 2.74 | 5.09 | 5.52 | 2.76 | 1.25 |
| 03-08/02/78 | 3.95 | 3.37 | 71 | 2.01 | 4.68 | 2.91 | 2.65 | 2.16 |
| 15-22/03/78 | 6.49 | 4.75 | 41 | 1.30 | 2.33 | 1.46 | 1.68 | 0.68 |
| 09-16/04/78 | 4.45 | 2.92 | 44 | 1.42 | 4.57 | 2.22 | 1.83 | 1.04 |
| 23-31/05/78 | 2.85 | 14.18 | 62 | 0.92 | 2.24 | 1.04 | 1.14 | 0.71 |
| 12-21/06/78 | 3.31 | 12.20 | 42 | 0.35 | 0.41 | 0.67 | 0.86 | 0.53 |
| 25-31/07/73 | 4.32 | 17.15 | 41 | 0.21 | 0.20 | 0.71 | 0.73 | 0.53 |
| 07-12/08/78 | 3.69 | 14.16 | 55 | 0.32 | 0.42 | 0.76 | 0.64 | 0.57 |
| 18-25/09/78 | 4.02 | 14.22 | 45 | 0.20 | 0.27 | 0.58 | 0.38 | 0.29 |
| 17-23/10/78 | 3.26 | 9.52 | 45 | 0.45 | 2.06 | 3.83 | 1.95 | 1.11 |
| 13-21/11/78 | 7.64 | 10.36 | 54 | 0.56 | 1.76 | 1.89 | 1.63 | 1.02 |
| 07-15/12/78 | 5.41 | 8.15 | 38 | 0.80 | 1.42 | 2.45 | 2.54 | 1.82 |
| 10-15/01/79 | 3.47 | -0.38 | 81 | 3.96 | 4.36 | 5.10 | 4.80 | 1.01 |

TABLE 3.2b

PAH concentrations (mg kg$^{-1}$)

| DATE | PYRENE | CHRYSENE | BaP | BeP | CORONENE |
|---|---|---|---|---|---|
| 13-19/11/76 | 34.78 | - | 93.91 | 51.84 | 24.50 |
| 06-09/12/76 | - | - | 35.22 | 20.74 | 9.32 |
| 06-10/01/77 | 34.63 | - | 99.78 | 31.10 | 19.24 |
| 26-31/01/77 | - | - | - | - | - |
| 28/02-03/03/77 | 15.32 | - | 58.48 | 23.16 | 47.24 |
| 29/03-03/04/77 | 21.05 | - | 37.83 | 20.74 | 30.37 |
| 12-17/05/77 | 21.27 | - | - | 41.47 | 24.87 |
| 15-17/06/77 | 30.89 | - | 15.15 | 11.41 | 8.42 |
| 14-18/07/77 | 12.79 | - | 21.43 | 16.79 | 9.07 |
| 20-26/09/77 | 12.37 | - | 43.67 | 29.90 | 16.13 |
| 05-10/10/77 | 11.32 | - | 30.92 | 24.54 | - |
| 14-18/10/77 | 3.15 | - | 15.89 | 7.87 | 5.11 |
| 22-28/11/77 | 52.23 | - | 49.90 | 52.92 | - |
| 07-12/12/77 | 15.78 | - | 40.71 | 33.54 | 23.06 |
| 10-15/01/78 | 40.40 | 75.08 | 81.36 | 40.68 | 18.44 |
| 03/08/02/78 | 28.13 | 65.49 | 40.69 | 37.11 | 30.23 |
| 15/22/03/78 | 31.91 | 57.09 | 35.79 | 41.20 | 16.70 |
| 09-16/04/78 | 32.55 | 105.02 | 51.04 | 41.95 | 23.89 |
| 23-31/05/78 | 14.93 | 36.35 | 16.88 | 18.50 | 11.52 |
| 12-21/06/78 | 8.25 | 9.80 | 15.97 | 20.47 | 12.44 |
| 25-31/07/78 | 5.08 | 9.94 | 17.16 | 17.64 | 12.81 |
| 07-12/08/78 | 5.81 | 7.61 | 13.76 | 11.58 | 10.37 |
| 12-18/09/78 | 4.41 | 5.96 | 12.74 | 8.42 | 6.43 |
| 17-23/10/78 | 10.00 | 46.23 | 86.04 | 43.86 | 25.00 |
| 13-21/11/78 | 10.37 | 32.81 | 35.25 | 30.39 | 19.00 |
| 07-15/12/78 | 20.89 | 37.20 | 64.01 | 66.41 | 47.56 |
| 10-15/01/79 | 48.92 | 58.85 | 63.09 | 59.49 | 12.45 |

TABLE 3.3

Maximum and mean concentrations of TPM and PAH determined at Salford Circus

|  | MAXIMUM VALUE |  | MEAN CONCENTRATION & LIMITS* |  |
|---|---|---|---|---|
| TPM ( $\mu gm^{-3}$) | - | 12.7 | 57.77 ± 7.14 |  |
|  | $ngm^{-3}$ | mg $kg^{-1}$ | $ngm^{-3}$ | mg $kg^{-1}$ |
| Pyrene | 3.96 | 52.23 | 1.20 ± 0.32 | 21.09 ± 4.79 |
| Chrysene | 5.09 | 105.02 | 2.29 ± 0.89 | 41.73 ±14.66 |
| BaP | 6.48 | 99.78 | 2.48 ± 0.56 | 43.07 ± 8.96 |
| BeP | 4.80 | 66.41 | 1.73 ± 0.34 | 30.91 ± 5.35 |
| Coronene | 5.24 | 47.56 | 1.12 ± 0.34 | 19.34 ± 3.92 |

* limits expressed at the 90% confidence level

TABLE 3.4

Correlation coefficients (R) between pairs of PAH and TPM at Salford Circus (S-C).

| | TPM | PYRENE | CHRYSENE | BaP | BeP | CORONENE |
|---|---|---|---|---|---|---|
| Particulate | 1 | 0.794 | 0.648 | 0.613 | 0.655 | 0.321 |
| Pyrene | | 1 | 0.837 | 0.810 | 0.903 | 0.405 |
| Chrysene | | | 1 | 0.780 | 0.749 | 0.598 |
| BaP | | | | 1 | 0.866 | 0.543 |
| BeP | | | | | 1 | 0.598 |
| Coronene | | | | | | 1 |

TABLE 3.5

Summary of linear multiple regression analysis relating pollutant concentration with wind speed and temperature at Salford Circus (S-C)

(PAH ngm $^{-3}$ Particulate μgm $^{-3}$)

| | REGRESSION EQUATION | R | $\bar{x}$ | n |
|---|---|---|---|---|
| Pyrene | 3.05 - 0.95 Wsp - 0.17 TMP | 0.822 | 1.21 | 25 |
| Chrysene | 5.62 - 0.202 Wsp - 0.286 TMP | 0.916 | 2.29 | 13 |
| BaP | 5.49 - 0.293 Wsp - 0.218 TMP | 0.654 | 2.48 | 26 |
| BeP | 3.52 - 0.109 Wsp - 0.159 TMP | 0.744 | 1.73 | 26 |
| Coronene | 1.04 + 0.107 Wsp - 0.048 TMP | 0.284 | 1.12 | 24 |
| TPM | 101.4 - 7.153 Wsp - 1.382 TMP | 0.460 | 60 | 27 |

R = correlation coefficient

Wsp = windspeed (ms$^{-1}$)

TMP = temperature ($^{o}$C)

$\bar{x}$ = average value ngm$^{-3}$ for PAH and μgm$^{-3}$ for total particulate matter

n = number of results

### 3.2.2 PAH and particulate concentrations monitored around a city centre site (C-C)

The monitoring equipment was located in a store room on the Campus of the University of Aston in Birmingham. It was selected to represent general pollution concentrations close to the centre of a large city. The site was about 1 km from the main shopping centre in Birmingham. The instrument was positioned approximately 3 m above ground level overlooking a large grassed area. Sampling commenced in November 1976 and was terminated in January, 1979.

The results of the monitoring at this site are given in the following tables.

TABLE 3.6a

Concentrations of total TPM ( $\mu gm^{-3}$) and PAH ($ngm^{-3}$) monitored at the city centre, University of Aston (C - C).

| DATE | WIND SPEED $ms^{-1}$ | TEMPERATURE °C | TPM $\mu gm^{-3}$ | PYRENE | CHRYSENE | BaP | BeP | CORONENE |
|---|---|---|---|---|---|---|---|---|
| | | | | $ngm^{-3}$ | | | | |
| 24-30/11/76 | 5.41 | 7.11 | - | 3.31 | | 2.41 | 1.88 | 0.79 |
| 17-20/12/76 | 3.45 | 11.25 | 67 | 3.25 | | 5.30 | 2.34 | |
| 12-17/01/77 | 4.86 | 0.21 | 67 | 1.15 | | 4.29 | 1.38 | 0.62 |
| 08-11/02/77 | 5.58 | 6.87 | 76 | 4.44 | | 7.75 | 5.65 | 3.91 |
| 14-18/03/77 | 6.50 | 7.23 | 79 | 0.51 | | 1.64 | 1.24 | 1.10 |
| 18-25/03/77 | 4.31 | 5.75 | 70 | 0.23 | | 3.17 | 1.30 | 0.77 |
| 03-09/05/77 | 4.67 | 7.97 | 43 | 0.72 | | 1.63 | 0.80 | 0.71 |
| 20-26/05/77 | 5.95 | 12.22 | 68 | 0.63 | | 1.70 | 1.14 | 0.30 |
| 01-07/09/77 | 2.31 | 4.06 | 40 | 0.28 | | 0.33 | 0.35 | 0.37 |
| 18-21/10/77 | 3.12 | 13.39 | 113 | 1.70 | | 5.17 | 3.53 | 3.12 |
| 28/10-02/11/77 | 5.73 | 10.62 | 39 | 0.36 | | 1.70 | 0.84 | 0.56 |
| 10-15/01/78 | 3.96 | 0.29 | 46 | - | 2.71 | 2.32 | 1.12 | 0.63 |
| 03-09/02/78 | 3.62 | 3.17 | 65 | 2.18 | 5.24 | 2.64 | 3.08 | 1.23 |
| 16-23/03/78 | 6.87 | 5.03 | 21 | 0.75 | 0.91 | 0.89 | 1.21 | 0.40 |
| 09-16/04/78 | 4.45 | 2.92 | 25 | 0.64 | 1.06 | 0.79 | 0.69 | 0.28 |
| 23-31/05/78 | 2.85 | 14.18 | 69 | 0.71 | 0.31 | trace | 0.24 | 0.21 |
| 05-12/06/78 | 5.03 | 13.06 | 40 | 0.24 | trace | 0.24 | 0.34 | 0.32 |
| 13-21/07/78 | 4.35 | 15.18 | 53 | 0.13 | trace | 0.26 | 0.37 | 0.26 |
| 02-11/08/78 | 4.23 | 14.53 | 62 | 0.27 | trace | 0.35 | 0.28 | 0.36 |
| 18-25/09/78 | 3.44 | 13.34 | 63 | 0.34 | 0.23 | 0.82 | 0.42 | 0.41 |
| 18-23/10/78 | 3.07 | 10.19 | 67 | 0.59 | 1.64 | 1.15 | 1.66 | 1.11 |
| 16-24/11/78 | 7.22 | 10.73 | 36 | 0.40 | 0.92 | 1.13 | 1.63 | 0.79 |
| 7-15/12/78 | 5.41 | 8.15 | 37 | 0.68 | 1.54 | 1.35 | 1.54 | 0.76 |
| 11-15/1/79 | 3.47 | -0.38 | 114 | 6.67 | 7.28 | 6.87 | 4.71 | 1.50 |

TABLE 3.6b

PAH concentrations (mg $kg^{-1}$) at the city centre site (C-C)

| DATE | PYRENE | CHRYSENE | BaP | BeP | CORONENE |
|---|---|---|---|---|---|
| 24-30/11/76 | - | - | - | - | - |
| 17-20/12/76 | 48.56 | - | 79.16 | 34.99 | 1.50 |
| 12-17/01/77 | 17.24 | - | 64.02 | 20.66 | 9.29 |
| 08-11/02/77 | 58.16 | - | 85.27 | 74.01 | 51.20 |
| 14-18/03/77 | 6.38 | - | 20.58 | 15.55 | 13.76 |
| 18-25/03/77 | 3.31 | - | 44.98 | 16.09 | 11.02 |
| 03-09/05/77 | 16.55 | - | 37.74 | 18.51 | 16.38 |
| 20-26/05/77 | 9.26 | - | 24.79 | 16.74 | 4.37 |
| 01-07/09/77 | 7.13 | - | 8.41 | 8.92 | 9.43 |
| 18-21/11/77 | 15.03 | - | 45.71 | 31.21 | 27.59 |
| 28/10-02/11/77 | 8.88 | - | 41.91 | 20.71 | 13.80 |
| 10-15/01/78 | - | 58.76 | 50.29 | 24.28 | 13.66 |
| 03-09/02/78 | 33.52 | 80.56 | 40.59 | 47.33 | 18.91 |
| 16-23/03/78 | 34.97 | 42.47 | 41.64 | 56.71 | 18.70 |
| 09-16/04/78 | 25.64 | 42.55 | 31.64 | 27.68 | 11.24 |
| 23-31/05/78 | 10.29 | 4.47 | 1.82 | 3.49 | 3.05 |
| 05-12/06/78 | 5.93 | 4.46 | 5.21 | 8.51 | 8.00 |
| 13-21/07/78 | 2.46 | 3.00 | 4.93 | 7.00 | 4.93 |
| 02-11/08/78 | 4.47 | 2.34 | 5.64 | 4.53 | 5.82 |
| 18-25/09/78 | 5.41 | 3.67 | 12.97 | 6.71 | 6.54 |
| 18-23/10/78 | 8.91 | 24.68 | 17.24 | 24.87 | 16.67 |
| 16-24/11/78 | 11.26 | 26.04 | 31.83 | 45.92 | 22.29 |
| 07-15/12/78 | 18.58 | 42.01 | 36.81 | 41.98 | 20.72 |
| 11-15/01/79 | 58.22 | 63.73 | 59.85 | 41.26 | 13.10 |

TABLE 3.7

Maximum and calculated mean concentrations of TPM and PAH at C-C

| | MAXIMUM VALUE | | MEAN CONCENTRATION ± LIMITS* | |
|---|---|---|---|---|
| TPM ( $\mu gm^{-3}$) | 113 | | 57.57 ± 7.88 | |
| PAH | $ngm^{-3}$ | $mg\ kg^{-1}$ | $ngm^{-3}$ | $mg\ kg^{-1}$ |
| Pyrene | 4.44 | 58.16 | 1.09 ± 0.45 | 18.64 ± 6.34 |
| Chrysene | 5.24 | 80.56 | 1.63 ± 1.04 | 30.68 ± 13.08 |
| BaP | 7.75 | 85.27 | 2.18 ± 0.74 | 34.48 ± 8.39 |
| BeP | 5.64 | 74.01 | 1.43 ± 0.47 | 25.99 ± 6.56 |
| Coronene | 3.91 | 51.20 | 0.87 ± 0.35 | 14.00 ± 3.74 |

* limits expressed at the 90% confidence level

TABLE 3.8

Correlation coefficients calculated for pairs of PAH and TPM at C-C

| | TPM | PYRENE | CHRYSENE | BaP | BeP | CORONENE |
|---|---|---|---|---|---|---|
| TPM | 1 | 0.310 | 0.427 | 0.493 | 0.380 | 0.683 |
| Pyrene | | 1 | 0.974 | 0.944 | 0.850 | 0.599 |
| Chrysene | | | 1 | 0.978 | 0.918 | 0.747 |
| BaP | | | | 1 | 0.935 | 0.785 |
| BeP | | | | | 1 | 0.876 |
| Coronene | | | | | | 1 |

TABLE 3.9

Summary of multiple regression analysis at C-C for PAH and TPM

| | REGRESSION EQUATION | R | $\bar{x}$ | n |
|---|---|---|---|---|
| TPM<br>$\mu g\ m^{-3}$ | 69.2 - 2.929 Wsp - 0.342 TMP | 0.206 | 53 | 24 |
| Pyrene<br>ng $m^{-3}$ | 2.34 - 0.086 Wsp - 0.92 TMP | 0.322 | 1.05 | 22 |
| Chrysene<br>ng $m^{-3}$ | 4.53 - 0.296 Wsp - 0.213 TMP | 0.693 | 1.63 | 8 |
| BaP<br>ng $m^{-3}$ | 4.13 - 0.156 Wsp - 0.144 TMP | 0.339 | 2.10 | 22 |
| BeP<br>ng $m^{-3}$ | 1.97 + 0.028 Wsp - 0.076 TMP | 0.293 | 1.39 | 23 |
| Coronene<br>ng $m^{-3}$ | 1.10 - 0.009 Wsp - 0.024 TMP | 0.125 | 0.84 | 22 |

R = correlation coefficient

$\bar{x}$ = average concentration(PAH ngm $^{-3}$, particulate $\mu g\ m^{-3}$)

n = number of results

TMP = temperature $^{o}C$

Wsp = windspeed $ms^{-1}$

### 3.2.3 PAH and TPM concentrations monitored at a suburban site(S-U)

The third site was selected to represent a sub-urban environment. Monitoring was performed at a property in Hollyfield Drive, Sutton Coldfield, a residential area approximately 15 km. due north of the city-centre. The instrument sample head was located 1 m above ground. Sampling commenced during November 1976 and was terminated in January 1979.

The results of the monitoring programme for this site are given in the following tables.

TABLE 3.10a

Concentrations of TPM ( $\mu gm^{-3}$) and PAH ($ngm^{-3}$) Monitored at Sutton Coldfield. (S-U)

| DATE | WIND SPEED $ms^{-1}$ | TEMPERATURE °C | TPM $\mu gm^{-3}$ | PYRENE | CHRYSENE | BaP | BeP | CORONENE |
|---|---|---|---|---|---|---|---|---|
| | | | | $ngm^{-3}$ | | | | |
| 08-14/11/76 | 2.31 | 2.62 | - | 2.44 | | 6.03 | 3.03 | 1.33 |
| 13-16/12/76 | 1.75 | 2.17 | 57 | 8.55 | | 9.30 | 3.22 | 2.08 |
| 18-23/01/77 | 4.27 | 4.47 | 84 | 2.40 | | 1.56 | 2.06 | 0.31 |
| 15-20/02/77 | 5.21 | 5.10 | - | 1.43 | | 3.21 | 1.13 | 0.91 |
| 16-23/03/77 | 4.85 | 6.31 | 50 | 1.17 | | 1.53 | 1.39 | 0.34 |
| 18-21/04/77 | 4.31 | 7.73 | 74 | 0.60 | | 1.43 | 1.08 | trace |
| 03-09/05/77 | 4.67 | 7.97 | 22 | 1.05 | | 3.78 | 1.02 | 0.50 |
| 02-06/06/77 | 2.76 | 18.48 | 40 | 0.47 | | trace | 0.46 | 0.34 |
| 21-28/07/77 | 5.60 | 14.84 | 20 | 0.21 | | 0.27 | 0.32 | 0.10 |
| 20-25/09/77 | 3.48 | 11.49 | 37 | 0.82 | | 2.65 | 1.82 | 0.51 |
| 07-11/10/77 | 3.83 | 9.70 | 55 | 0.59 | | 2.61 | 1.51 | 1.04 |
| 22-26/11/77 | 7.11 | 4.38 | 68 | 2.06 | | 1.87 | 1.98 | trace |
| 07-12/12/77 | 5.36 | 7.63 | 44 | 1.14 | | 2.79 | 2.17 | 1.55 |
| 10-15/01/78 | 3.95 | 0.29 | 46 | 3.03 | 3.79 | 2.65 | 1.17 | 0.66 |
| 25-30/01/78 | 4.70 | 3.18 | 44 | 2.71 | 6.41 | 2.83 | 2.65 | 0.89 |
| 07-11/02/78 | 3.29 | -1.77 | 61 | 5.75 | 5.74 | 3.37 | 4.17 | 1.00 |
| 16-22/03/78 | 6.56 | 4.83 | 31 | 0.52 | 2.39 | 1.15 | 1.78 | 0.25 |
| 09-16/04/78 | 4.45 | 2.92 | 30 | 0.87 | 1.76 | 0.86 | 0.90 | 0.25 |
| 23/05-02/06/78 | 2.67 | 14.52 | 62 | 0.38 | 0.63 | 0.26 | 0.60 | 0.26 |
| 05-12/06/78 | 5.03 | 13.06 | 57 | 0.30 | 0.27 | trace | 0.21 | 0.19 |
| 18-31/07/78 | 4.87 | 15.90 | 44 | 0.21 | 0.22 | 0.40 | 0.17 | 0.14 |
| 02-10/08/78 | 4.02 | 14.22 | 60 | 0.31 | 0.39 | 0.45 | 0.31 | 0.22 |
| 18-25/09/78 | 3.44 | 13.34 | 59 | 0.25 | 0.53 | 1.08 | 0.52 | 0.29 |
| 18-24/10/78 | 6.03 | 9.50 | 51 | 0.61 | 2.04 | 1.33 | 0.96 | 0.71 |
| 14-21/11/78 | 7.60 | 10.49 | 46 | 0.83 | 0.89 | 0.86 | 1.04 | 0.43 |
| 7-15/12/78 | 5.41 | 8.15 | 36 | 0.61 | 1.58 | 0.82 | 0.96 | 0.43 |
| 11-15/01/79 | 3.47 | -0.38 | 96 | 5.64 | 3.54 | 4.45 | 4.03 | 1.72 |

TABLE 3.10b

PAH concentrations (mg kg$^{-1}$) at S-U

| SAMPLE | PYRENE | CHRYSENE | BaP | BeP | CORONENE |
|---|---|---|---|---|---|
| 08-14/11/76 | - | - | - | - | - |
| 13-16/12/76 | 150.24 | - | 157.57 | 56.54 | 38.58 |
| 18-23/01/77 | 28.64 | - | 18.56 | 24.62 | 3.74 |
| 15-20/02/77 | - | - | - | - | - |
| 16-23/03/77 | 23.31 | - | 30.63 | 27.77 | 6.81 |
| 18-21/04/77 | 8.05 | - | 19.26 | 14.58 | 2.73 |
| 03-09/05/77 | 48.40 | - | 174.13 | 46.66 | 23.01 |
| 02-06/07/77 | 11.83 | - | - | 11.58 | 8.56 |
| 21-28/07/77 | 10.50 | - | 13.48 | 15.98 | 5.00 |
| 20-25/09/77 | 32.07 | - | 71.52 | 48.99 | 13.73 |
| 07-11/10/77 | 10.77 | - | 47.65 | 27.57 | 19.00 |
| 22-26/11/77 | 30.46 | - | 27.75 | 29.35 | - |
| 07-12/12/77 | 25.98 | - | 63.44 | 49.49 | 35.26 |
| 10-15/01/78 | 65.88 | 82.24 | 57.47 | 25.29 | 14.24 |
| 25-30/01/78 | 61.03 | 144.28 | 63.62 | 59.58 | 19.92 |
| 07-11/02/78 | 94.81 | 94.64 | 46.23 | 68.74 | 16.53 |
| 16-22/03/78 | 16.47 | 76.44 | 36.82 | 57.18 | 8.17 |
| 09-16/04/78 | 28.83 | 58.82 | 28.79 | 29.99 | 8.15 |
| 23/05/-02/06/78 | 6.09 | 10.18 | 4.15 | 9.57 | 4.23 |
| 05-12/06/78 | 5.34 | 4.83 | 2.63 | 3.79 | 3.31 |
| 18-31/07/78 | 4.73 | 4.99 | 9.16 | 3.91 | 3.08 |
| 02-10/08/78 | 5.14 | 6.50 | 7.42 | 5.10 | 3.74 |
| 18-25/09/78 | 4.24 | 8.94 | 18.22 | 8.76 | 4.90 |
| 18-24/10/78 | 12.08 | 40.25 | 26.25 | 18.93 | 14.06 |
| 14-21/11/78 | 18.10 | 19.25 | 18.67 | 22.45 | 9.42 |
| 07-15/12/78 | 16.76 | 43.42 | 22.61 | 26.47 | 11.90 |
| 11-15/01/79 | 58.94 | 36.97 | 46.57 | 42.15 | 17.96 |

## TABLE 3.11

Maximum and mean concentrations of TPM ( $\mu gm^{-3}$) and PAH ($ngm^{-3}$ and $mg\ kg^{-1}$) recorded at S-U

| | MAXIMUM VALUE | | MEAN CONCENTRATION ± LIMITS* | |
|---|---|---|---|---|
| TPM ( $\mu gm^{-3}$) | 96 | | 50.96 ± 6.15 | |
| PAH | $ngm^{-3}$ | $mg\ kg^{-1}$ | $ngm^{-3}$ | $mg\ kg^{-1}$ |
| Pyrene | 8.55 | 150.24 | 1.66 ± 0.62 | 31.15 ± 11.59 |
| Chrysene | 6.41 | 144.28 | 2.12 ± 0.95 | 45.13 ± 19.73 |
| BaP | 9.30 | 174.13 | 2.22 ± 0.68 | 42.19 ± 14.98 |
| BeP | 4.17 | 56.54 | 1.51 ± 0.37 | 29.40 ± 6.56 |
| Coronene | 2.08 | 38.58 | 0.64 ± 0.18 | 12.34 ± 3.38 |

* limits expressed at the 90% confidence level

TABLE 3.12

Regression coefficients between PAH and TPM monitored at S-U.

| | TPM | PYRENE | CHRYSENE | BaP | BeP | CORONENE |
|---|---|---|---|---|---|---|
| TPM | 1 | 0.105 | -0.126 | 0.000 | -0.013 | 0.128 |
| Pyrene | | 1 | 0.829 | 0.833 | 0.848 | 0.836 |
| Chrysene | | | 1 | 0.935 | 0.849 | 0.890 |
| BaP | | | | 1 | 0.866 | 0.893 |
| BeP | | | | | 1 | 0.822 |
| Coronene | | | | | | 1 |

TABLE 3.13

Summary of linear multiple regression analysis equations (UASTATS XDS3) between concentration of pollutant and mean temperature and windspeed at S-U. (PAH in ng $m^{-3}$, TPM in µg $m^{-3}$)

| | REGRESSION EQUATION | n | R | $\bar{x}$ |
|---|---|---|---|---|
| TPM | 64.1 - 2.142 Wsp - 0.466 TMP | 24 | 0.262 | 49 |
| Pyrene | 5.82 - 0.505 Wsp - 0.251 TMP | 23 | 0.776 | 1.65 |
| Chrysene | 5.26 - 0.146 Wsp - 0.296 TMP | 12 | 0.858 | 2.09 |
| BaP | 6.76 - 0.652 Wsp - 0.206 TMP | 23 | 0.721 | 2.27 |
| BeP | 3.32 - 0.150 Wsp - 0.149 TMP | 23 | 0.792 | 1.52 |
| Coronene | 1.52 - 0.122 Wsp - 0.048 TMP | 23 | 0.613 | 0.62 |

n = number of results

R = correlation coefficient

$\bar{x}$ = average value (PAH ng $m^{-3}$, particulate µgm $^{-3}$)

TMP = temperature °C

Wsp = windspeed $ms^{-1}$

### 3.2.4 Relative PAH concentrations indoors and outdoors at a sub-urban location

It has been established that indoor concentrations of airborne lead approach those existing out-of-doors, especially at night; Butler and Macmurdo (1974). The principle reason for this arises from the fact that lead emissions from motor vehicles are predominantly in the sub-micron particle-size range, Lee et al (1971). Such particles may survive in the atmosphere in suspended form until either growth, through coagulation, causes gravitational loss or impaction and capture results in their removal from the atmosphere. Gillette (1972). Consequently, sub-micron particles may relatively easily enter the home.

Evidence presented in the next chapter and also from Pierce and Katz (1975) indicates that PAH are primarily associated with sub-micron particles. To determine the extent to which urban and sub-urban populations are exposed to PAH it is essential to know the concentration in the home where a person might be expected to spend 50% of his time.

A detached residential house situated away from main roads has been employed. None of the occupants smoked cigarettes, cigars or pipes. The house is located in the Sutton Coldfield area approximately 11 km due north of the city centre. When originally constructed in 1935 open-hearth fireplaces were fitted, but these had not been used for the last fifteen years. Instead, gas fired central heating has been installed with supplementary heating from electric fires. None of these heating systems was in operation during PAH measurement.

Aerosol particulate was collected using GF/A filters mounted on A STAPLEX 'HI-VOL' pump under conditions similar to those employed for external monitoring. The pump was located in the dining room and the filter 1 m above the floor. The door leading to the hall was left open, as were the doors from the hall to the kitchen and lounge. Thus, air could freely circulate through all the downstairs rooms as well as the staircase and the upstairs landing. Metal-framed windows and doors leading outside were kept shut.

The mean results of the indoor concentrations of PAH and particulate are given in Table 3.14 together with the results of corresponding outdoor samples.

TABLE 3.14

Comparison of external and internal concentrations of TPM and PAH at sub-urban sites. Mean results with limits expressed at the 90% confidence level

| | OUTSIDE | INSIDE |
|---|---|---|
| TPM ( $\mu g\ m^{-3}$) | 47.5 ± 13.2 | 56.0 ± 41.3 |
| | $ng\ m^{-3}$ | $ng\ m^{-3}$ |
| Pyrene | 2.62 ± 1.42 | 1.32 ± 1.41 |
| Chrysene | 4.56 ± 2.19 | 3.98 ± 3.31 |
| BaP | 2.88 ± 0.54 | 2.10 ± 1.88 |
| BeP | 2.19 ± 0.95 | 2.28 ± 2.16 |
| Coronene | 0.92 ± 0.38 | 0.43 ± 0.24 |
| | $mg\ kg^{-1}$ | $mg\ kg^{-1}$ |
| Pyrene | 54.3 ± 21.1 | 25.0 ± 27.2 |
| Chrysene | 91.2 ± 30.7 | 72.6 ± 63.7 |
| BaP | 72.0 ± 42.7 | 41.0 ± 37.4 |
| BeP | 46.5 ± 14.1 | 40.8 ± 43.1 |
| Coronene | 21.8 ± 7.7 | 7.3 ± 1.5 |

TABLE 3.15

Relative percentage concentrations of PAH inside and outside at sub-urban sites

| PAH | $\frac{\text{CONCENTRATION INSIDE(ng m}^{-3})\%}{\text{CONCENTRATION OUTSIDE(ngm}^{-3})}$ | $\frac{\text{CONCENTRATION INSIDE(mg kg}^{-1})\%}{\text{CONCENTRATION OUTSIDE(mg kg}^{-1})}$ |
|---|---|---|
| Pyrene | 50.38 | 45.99 |
| Chrysene | 88.44 | 79.55 |
| BaP | 72.94 | 56.94 |
| BeP | 104.10 | 86.19 |
| Coronene | 46.74 | 33.58 |
| Mean | 72.5% | 60.45% |

## 3.3. Discussion

The most obvious feature of PAH pollutant concentrations at all of the three external sites is that they are in the ng $m^{-3}$ range and are generally less than 10 ng $m^{-3}$. The overall mean concentrations are, of course, much lower and do not exceed 2.5 ng $m^{-3}$ for any measured PAH. In addition, the concentrations at all the sites display marked seasonal variation with maximum values being recorded during the winter months.

Examination of concentrations recently determined by other workers (Table 3.16) reveals that there is broad agreement in values determined at a variety of urban sites. All indicate the same general level of PAH concentration.

There is evidence to suggest that these current concentrations may

TABLE 3.16

Comparison of Concentrations of PAH determined by other workers, (ng $m^{-3}$) with the mean Birmingham values.

| PAH | BIRMINGHAM | SYDNEY (a) | ROME (b) | LONDON (c) | LOS ANGELES(d) | NORWAY (e) |
|---|---|---|---|---|---|---|
| Pyrene | 1.3 | 2.6 | 5.8 | - | 2.0 | 3.3 |
| Chrysene | 2.0 | 3.4 | 10.2 | - | 2.6 | - |
| BaP | 2.3 | 3.5 | - | 5.0 | 1.1 | 2.1 |
| BeP | 1.6 | 3.2 | 2.3 | 5.0 | 3.0 | 2.6 |
| Coronene | 0.9 | 2.7 | - | 3.0 | 6.4 | 0.18 |

a) Cleary (1962), b) Zoccolillo et al (1972), c) Commins and Hampton (1976), Gordon and Bryan (1973), Lunde and Bjorseth (1977).

represent a significant improvement in air quality experienced over the last twenty-five years. For example Commins and Hampton (1976) reported PAH concentrations for a site at St. Bartholomew's Hospital in London during 1972 - 1973 together with the corresponding concentrations for 1962 - 1963. The 1962 - 1963 figures were 26, 16 and 4 ng $m^{-3}$, in 1972 - 1973 the concentrations were reported as 5, 5 and 3 ng $m^{-3}$ for BaP, BeP and coronene respectively.

It is probable that these marked decreases in PAH concentrations are due to the implementation of the various Clean Air Acts. Evidently, the dramatic five-fold decrease in BaP concentrations has not been mirrored by a similar decrease in coronene values. The reason for this is that coronene is generally associated with motor vehicular pollution which has increased since 1962 - 63. The overall decrease in BaP concentrations is certainly due to reduced emissions from domestic and industrial sources.

Using a previously published procedure (Commins (1969))Commins and Hampton were able to calculate the increased effect of motor traffic on urban air pollution. They found that in 1962 - 1963 the percentage of benzpyrenes, in a busy London street, attributable to vehicular source was 50% but by 1972-73 the corresponding value was almost 100%.

Applying the method of Commins (1969), mentioned in Section 1.4.3, it is possible to estimate the percentage of benzo [e] pyrene at each Birmingham site derived from motor traffic:-

$$xk + (1 - x)\ 0.25 = y$$

For S-C, C-C and S-U the values of y were determined as being 0.642, 0.608 and 0.434 respectively. The corresponding coronene to BeP summer ratios (k) were calculated from all results measured during the period April to September as 0.709, 0.696 and 0.433. Hence, the percentage of BeP at S-C, C-C and S-U attributable to vehicular pollution is 85%, 80% and approximately 100%. For comparison, the calculations were repeated with the summer ratios being determined from data collected in June, July and August. The estimated amounts of BeP on this basis were 86%, 51% and 104%. Commins also reported that as the ratio BaP to BeP in coal smoke was similar to the ratio in motor-generated smoke, the percentage of both benzpyrenes produced by motor traffic should be essentially the same.

Whilst it is acknowledged that the method is not capable of exactly quantifying the percentage of BeP, it does at least indicate that the majority of benzpyrene pollution at each of the sites is vehicular in origin.

Evidence for the seasonal variation in PAH concentrations may be obtained by inspection of Figures 3.2 and 3.3 where maximum values are shown during the winter periods. The mean winter (December, January and February) concentration of pyrene derived from all sites is approximately seven times the summer (June, July and August) mean. For BaP the corresponding value was also seven and for coronene the figure was about four times. Several authors have reported similar winter maxima (e.g. Van Vaeck and Van Cauwenberghe (1978)). The possible causes of such a trend are -

FIGURE 3.2. Variation in chrysene concentrations with month of the year at S-C.

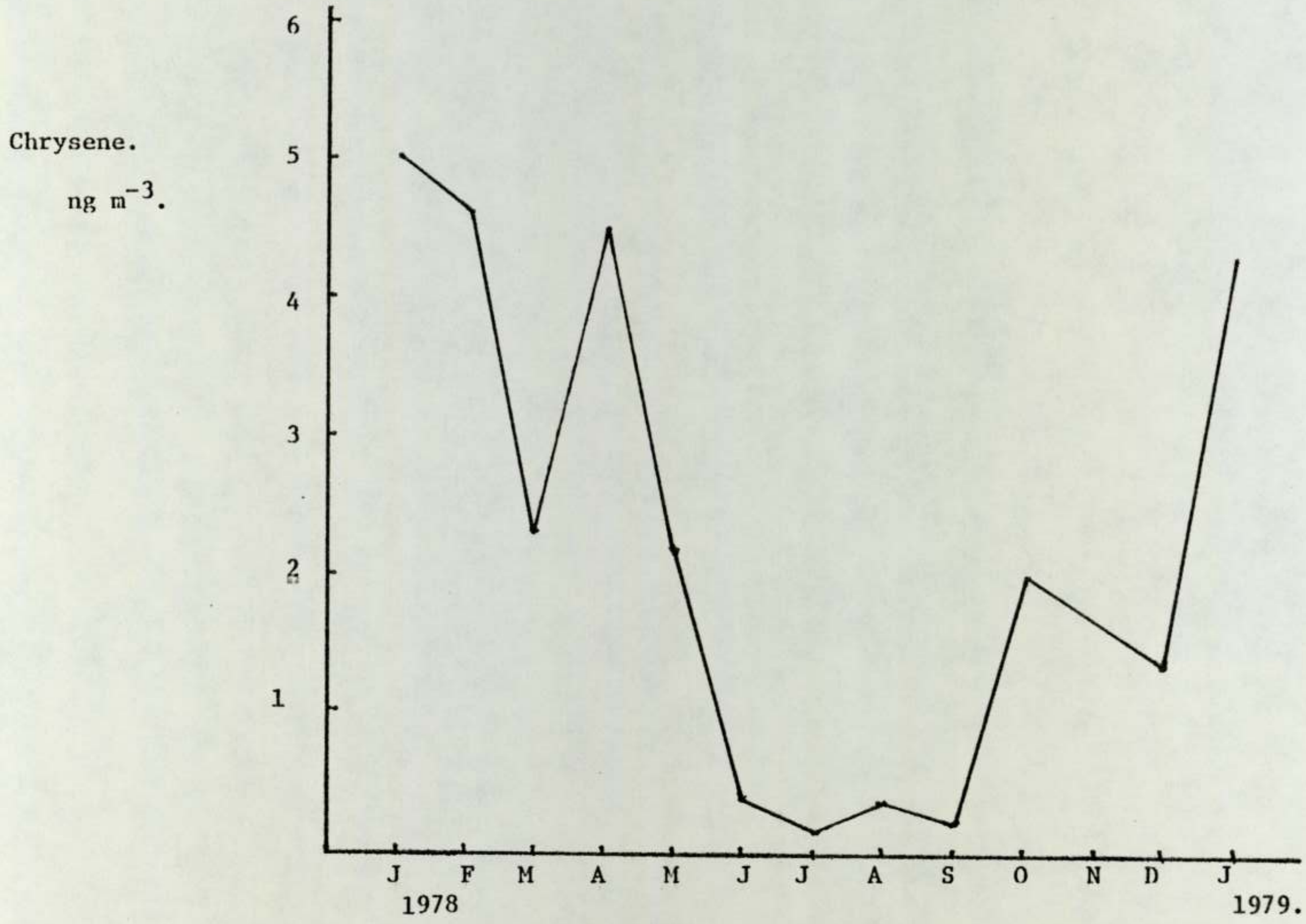
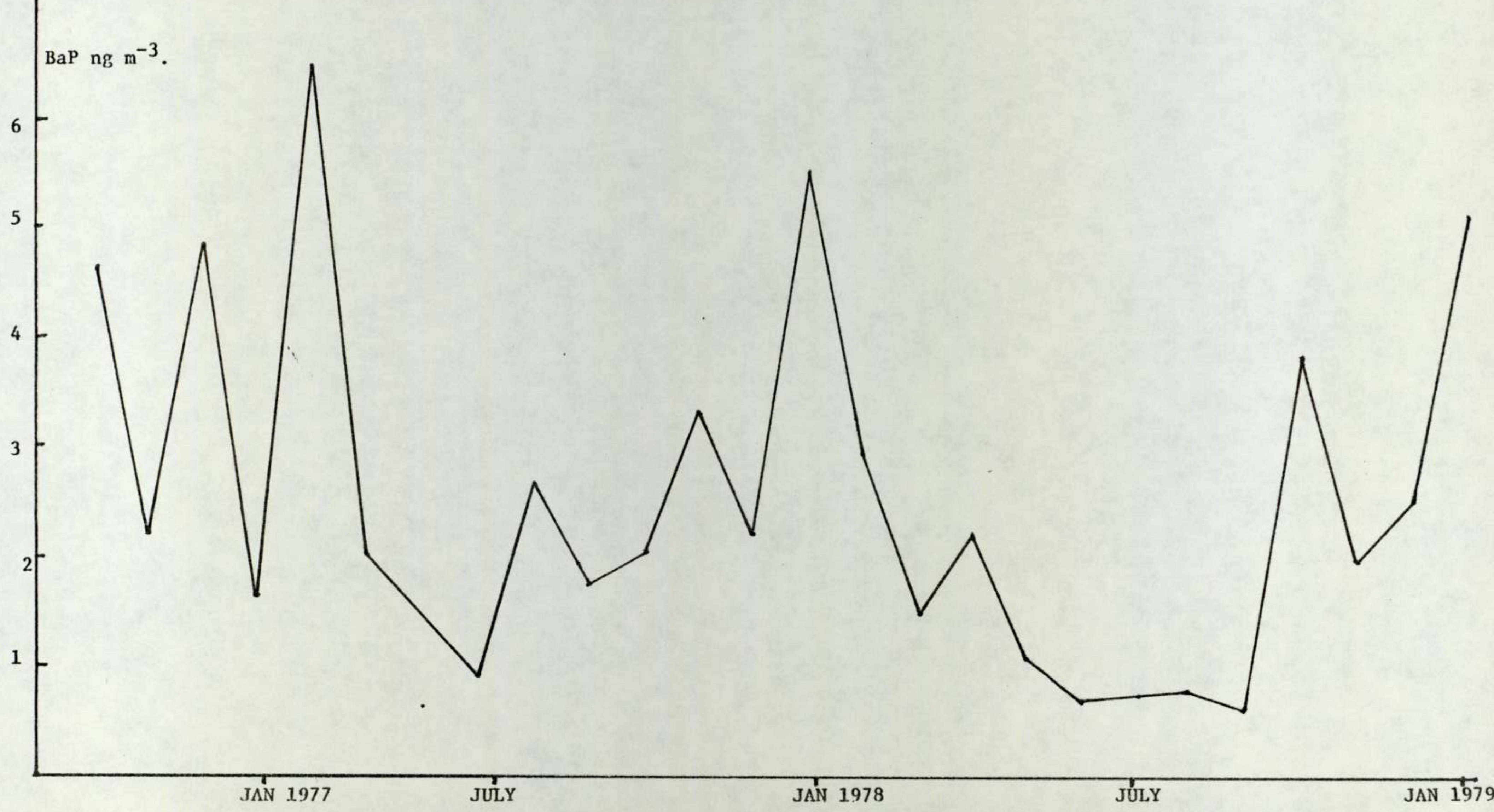


FIGURE 3.3 Seasonal variation in BaP concentrations (ng $m^{-3}$) at S-C.



1) increased input to atmosphere from emission sources, i.e. increased usage of fuel during the cold winter months,

2) decreased loss of PAH due to photolytic degradation or by sampling of warm air, and

3) decreased dispersion of PAH due to the increased frequency of periods of temperature inversions.

The relationship between monitored concentrations of pairs of PAH and between individual PAH and particulate at each of the sites was examined using simple linear regression analysis. The correlation coefficients (R) are given in Table 3.4, 3.8 and 3.12 for S-C, C-C and S-U respectively.

At S-C good correlation was found between pairs of PAH, the highest value being R = 0.903 for pyrene and BeP. The lowest value was R = 0.405 for pyrene and coronene. Generally the correlations between PAH and particulate were not as good as those between pairs of PAH. However, it appears that statistical correlation between particulate and PAH other than coronene does exist. The reason for the apparently anomolously low correlation between particulate and coronene is not known.

At C-C the simple linear regression analysis indicates good correlation between all pairs of PAH. The highest R value (0.978) is observed for chrysene and BaP and the lowest is 0.599 between pyrene and coronene. The values of the correlation coefficients between PAH and particulate are generally lower than the corresponding values of

S-C. With the exception of coronene/particulate (R = 0.683) all values are below R = 0.5.

At S-U there is good correlation between all pairs of PAH with all R values > 0.82. In contrast there is no correlation between the monitored concentrations of particulate and any of the PAH. All values are less than 0.13.

In Chapter 4 it will be shown that PAH is primarily associated with sub-micron material; however, the total particulate matter (TPM) contains a range of particle sizes, the relative contribution of each dictating to some extent the behaviour of the total aerosol. Consequently, where the determined correlation between PAH and particulate is good, for example at S-C, the sub-micron (or PAH - associated size range) is dominent; conversely where the correlation poor (e.g. at S-U) the particulate larger than 1 μm, such as wind-blown soils and dust and material from the surfaces of buildings, etc. will be the dominent part of the aerosol.

The two most important meteorological parameters which affect PAH or other pollutant monitored concentrations are windspeed and temperature. These two parameters may be considered as dispersion factors in the transportation of airborne pollutants in the lateral and vertical planes respectively. Multiple linear regression analysis between these parameters and the corresponding particulate and PAH concentrations monitored at each site was performed using a standard statistical package (UASTAT x DS3). The analyses produced equations which could be used to 'predict' pollutant concentrations at each site in terms of a constant plus a function of the windspeed plus a function of the temperature. The multiple linear correlation coefficients were also determined and were a measure of the extent of agreement between actual and predicted concentrations.

The results of the multiple linear regression analyses are given in Tables 3.5, 3.9 and 3.13 for S-C, C-C and S-U respectively. They indicate that at S-C and S-U (with the exception of coronene at S-C) there is fairly good correlation between the monitored and predicted concentrations, all $\bar{R}$ values being greater than 0.6. At C-C it appears that there is no significant correlation between monitored and predicted concentrations of PAH.

The low correlation obtained at C-C may be due to some artifact of the site itself. The local 'background' concentrations of PAH, denoted by the constants of the regression equations, may be influenced by near-by, unidentified, irregular emission sources. Additionally the presence of buildings, the proximity of a complex matrix of roads around the site or irregular wind-canyon effects may act to negate the influence of the dispersion characteristics of the regression equations.

The predicted concentrations of pyrene ($ngm^{-3}$) at S-C are calculated in Table 3.17 from the equation:-

$$\text{Pyrene } (ngm^{-3}) = 3.05 - 0.095 \text{ Wsp} - 0.17 \text{ TMP}$$

Where Wsp is the windspeed ($ms^{-1}$) and TMP is the temperature. ($^\circ$ C)

TABLE 3.17

Comparison of actual and predicted pyrene concentrations at S-C calculated from: Pyrene(ngm$^{-3}$) = 3.05 - 0.095 Wsp - 0.17 TMP.

| SAMPLE NUMBER | WIND SPEED (Wsp) (ms$^{-1}$) | 0.095 x WIND SPEED | TEMPERATURE (TMP) °C | 0.17 x TMP | ACTUAL PYRENE (ngm$^{-3}$) | PREDICTED PYRENE (ngm$^{-3}$) |
|---|---|---|---|---|---|---|
| 1 | 2.09 | 0.20 | 5.89 | 1.00 | 1.78 | 1.85 |
| 2 | 5.11 | 0.49 | 4.22 | 0.72 | - | 1.84 |
| 3 | 3.75 | 0.36 | 3.60 | 0.61 | 1.69 | 2.08 |
| 4 | 3.82 | 0.36 | 1.75 | 0.30 | 0.85 | 1.46 |
| 5 | 4.94 | 0.47 | 8.17 | 1.39 | 1.70 | 1.19 |
| 6 | 5.92 | 0.56 | 4.98 | 0.85 | 1.13 | 1.64 |
| 7 | 4.06 | 0.39 | 7.11 | 1.21 | 0.84 | 1.46 |
| 8 | 5.11 | 0.49 | 11.07 | 1.88 | 1.24 | 0.68 |
| 9 | 3.58 | 0.34 | 15.33 | 2.61 | 0.55 | 0.10 |
| 10 | 3.39 | 0.32 | 11.84 | 2.01 | 0.76 | 0.72 |
| 11 | 4.08 | 0.39 | 11.08 | 1.88 | 0.64 | 0.78 |
| 12 | 2.10 | 0.20 | 10.59 | 1.80 | 0.40 | 1.05 |
| 13 | 4.87 | 0.46 | 3.42 | 0.58 | 3.47 | 2.01 |
| 14 | 5.36 | 0.51 | 7.63 | 1.30 | 0.85 | 1.24 |
| 15 | 3.94 | 0.37 | 0.29 | 0.05 | 2.74 | 2.63 |
| 16 | 3.95 | 0.38 | 3.37 | 0.57 | 2.01 | 2.10 |
| 17 | 6.49 | 0.62 | 4.75 | 0.81 | 1.30 | 1.63 |
| 18 | 4.45 | 0.42 | 2.92 | 0.50 | 1.42 | 2.13 |
| 19 | 2.85 | 0.27 | 14.18 | 2.41 | 0.92 | 0.37 |
| 20 | 3.31 | 0.31 | 12.20 | 2.07 | 0.35 | 0.66 |
| 21 | 4.32 | 0.41 | 17.15 | 2.92 | 0.21 | 0 |
| 22 | 3.69 | 0.35 | 14.16 | 2.41 | 0.32 | 0.29 |
| 23 | 4.02 | 0.38 | 14.22 | 2.42 | 0.20 | 0.24 |
| 24 | 3.26 | 0.30 | 9.52 | 1.62 | 0.45 | 1.12 |
| 25 | 7.64 | 0.73 | 10.36 | 1.76 | 0.56 | 0.56 |
| 26 | 5.41 | 0.51 | 8.15 | 1.39 | 0.80 | 1.15 |
| 27 | 3.47 | 0.33 | -0.38 | -0.06 | 3.96 | 2.78 |
|  |  | Means and Limits |  |  | 1.20 ± 0.32 | 1.25 ± 0.30 |

The mean predicted value and mean actual value for pyrene are also given. A plot of the variation in actual and predicted concentrations with time are given in Figure 3.4. Similar plots for BaP and BeP at the S-C site are given in Figure 3.5 and Figure 3.6 respectively. The graphs indicate that reasonably good correlation between actual and predicted concentrations of PAH may be achieved using a constant plus two easily determined measurements, viz. windspeed and temperature.

It must be remembered, however, that equations of this form cannot be used to predict maximum concentration of PAH by setting temperature and windspeed equal to 0. These parameters are a measure of the vertical and horizontal dispersion of the pollutant, when equal to zero, or no dispersion, background concentrations of PAH would build up to unpredictable levels at the site of emission.

In Section 3.2.4 the relative PAH concentrations indoors and outdoors at a sub-urban site were reported. The principal finding of the results in that section was that indoor concentrations of PAH are of the same order of magnitude as the corresponding external values. The mean concentration of PAH indoors was approximately 70% of that outside. As no fires were in use or none of the occupants of the house were smokers, it appears that ingress of PAH from external sources must be responsible for the internal concentration. PAH are generally associated with sub-micron particulate (Chapter 4) and so ingress may be relatively simple.

Stocks et al (1961) found that internal concentrations of PAH of up

FIGURE 3.4. Comparison of monitored and 'predicted' pyrene concentrations at S-C.

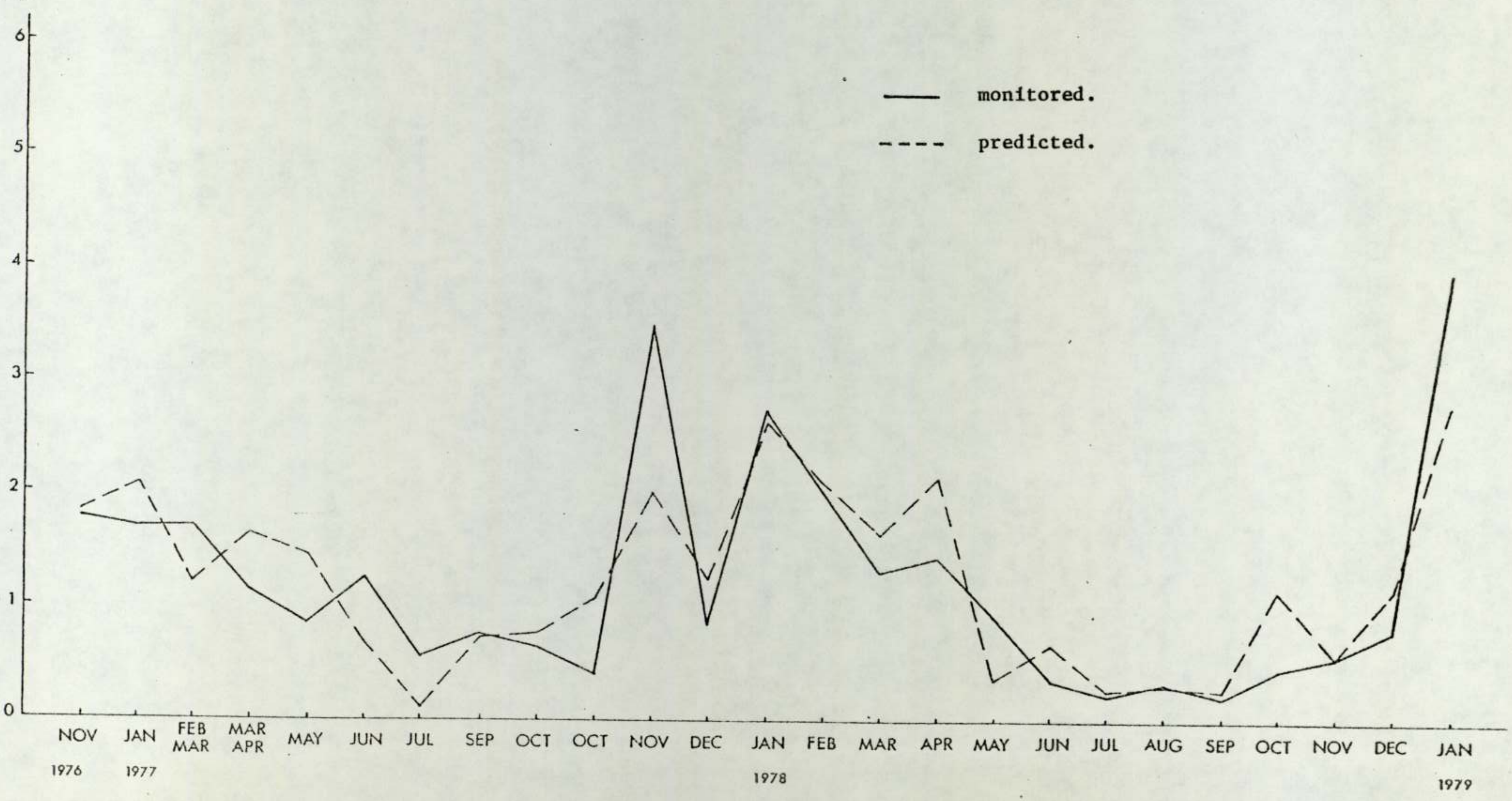


FIGURE 3.5. Comparison of monitored and 'predicted' concentrations of BaP at S-C.

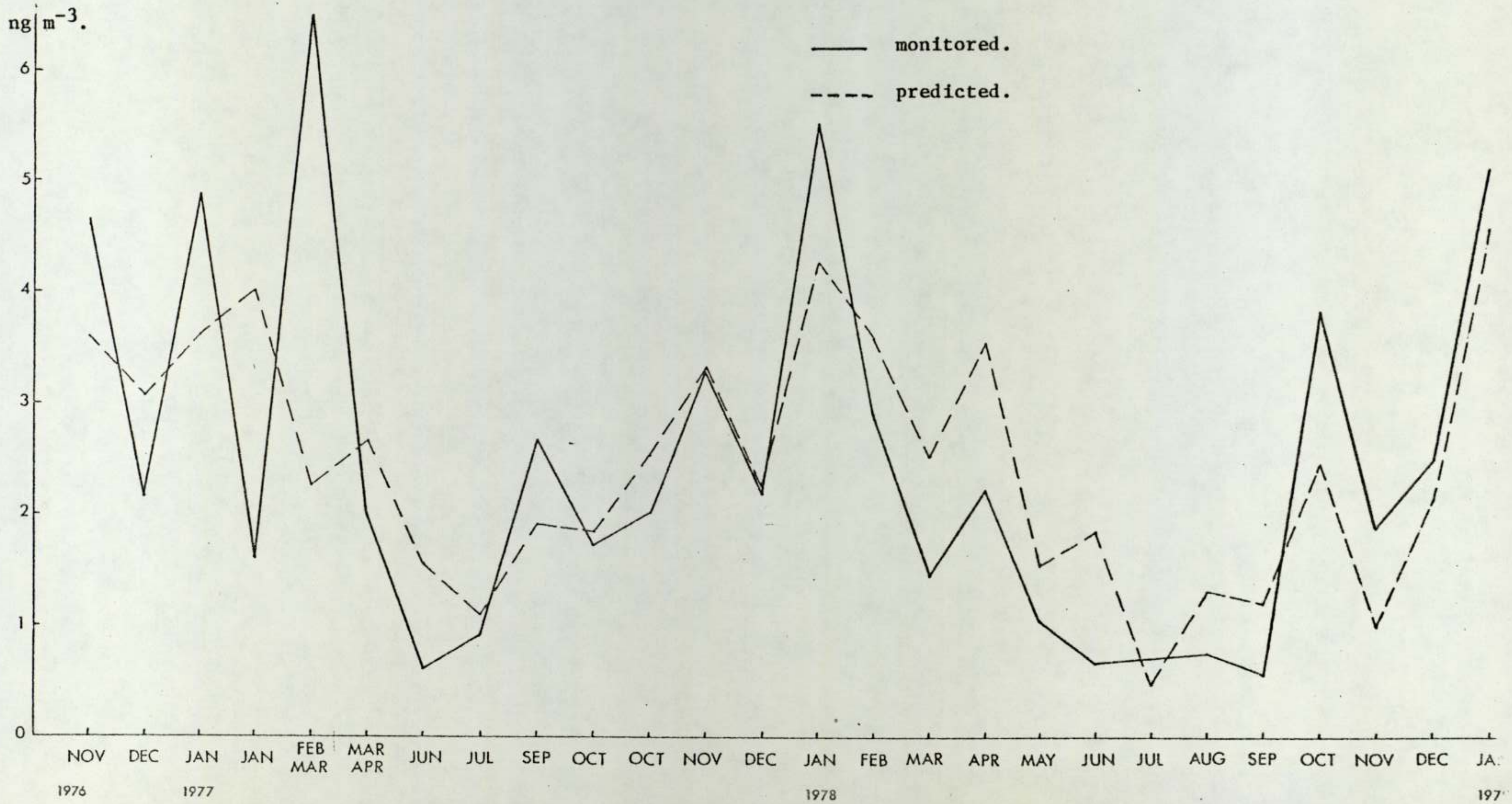
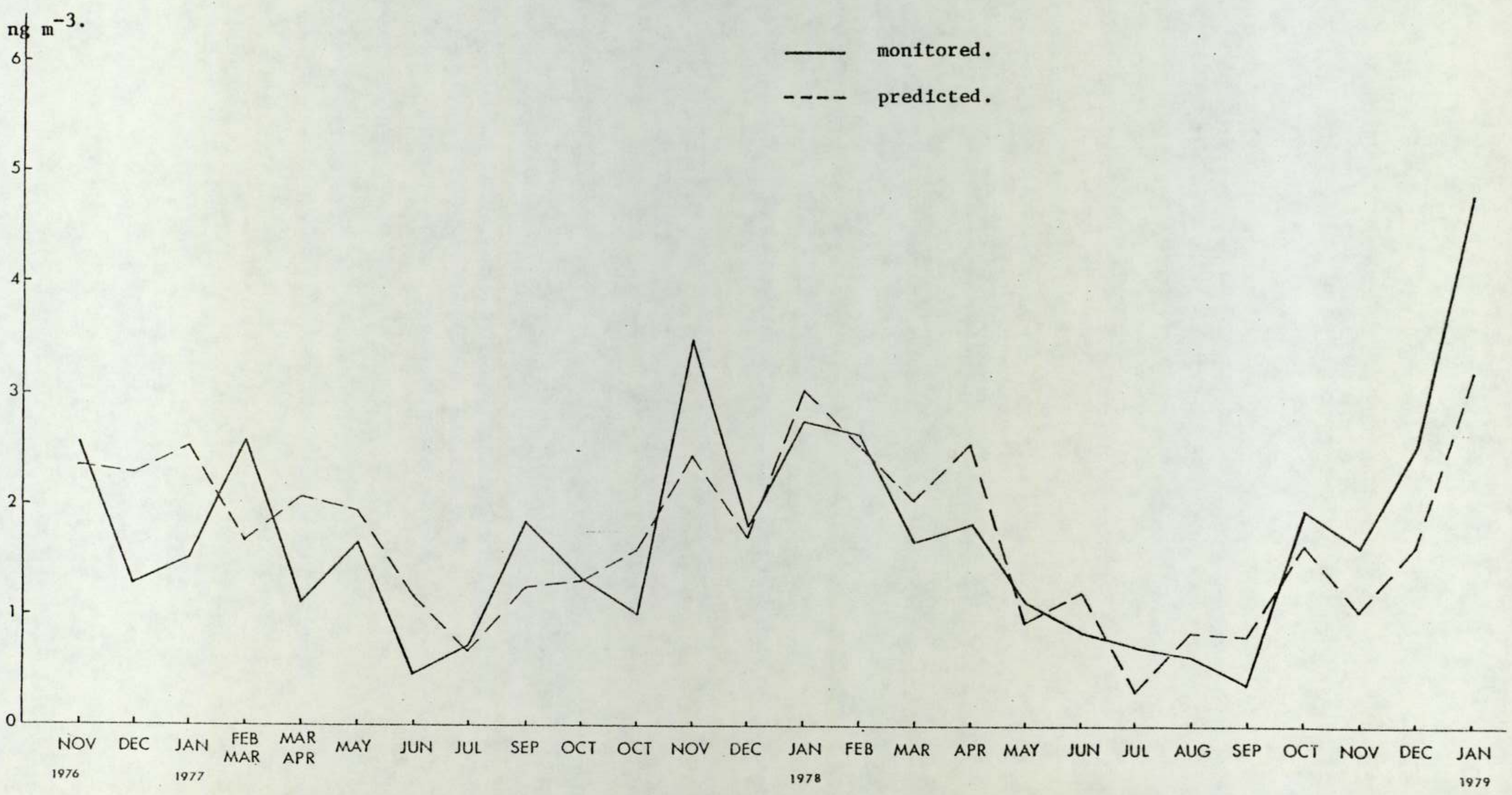


FIGURE 3.6. Comparison of monitored and 'predicted' concentrations of BeP at S-C.



to 75% of external concentrations existed in offices in northern England.

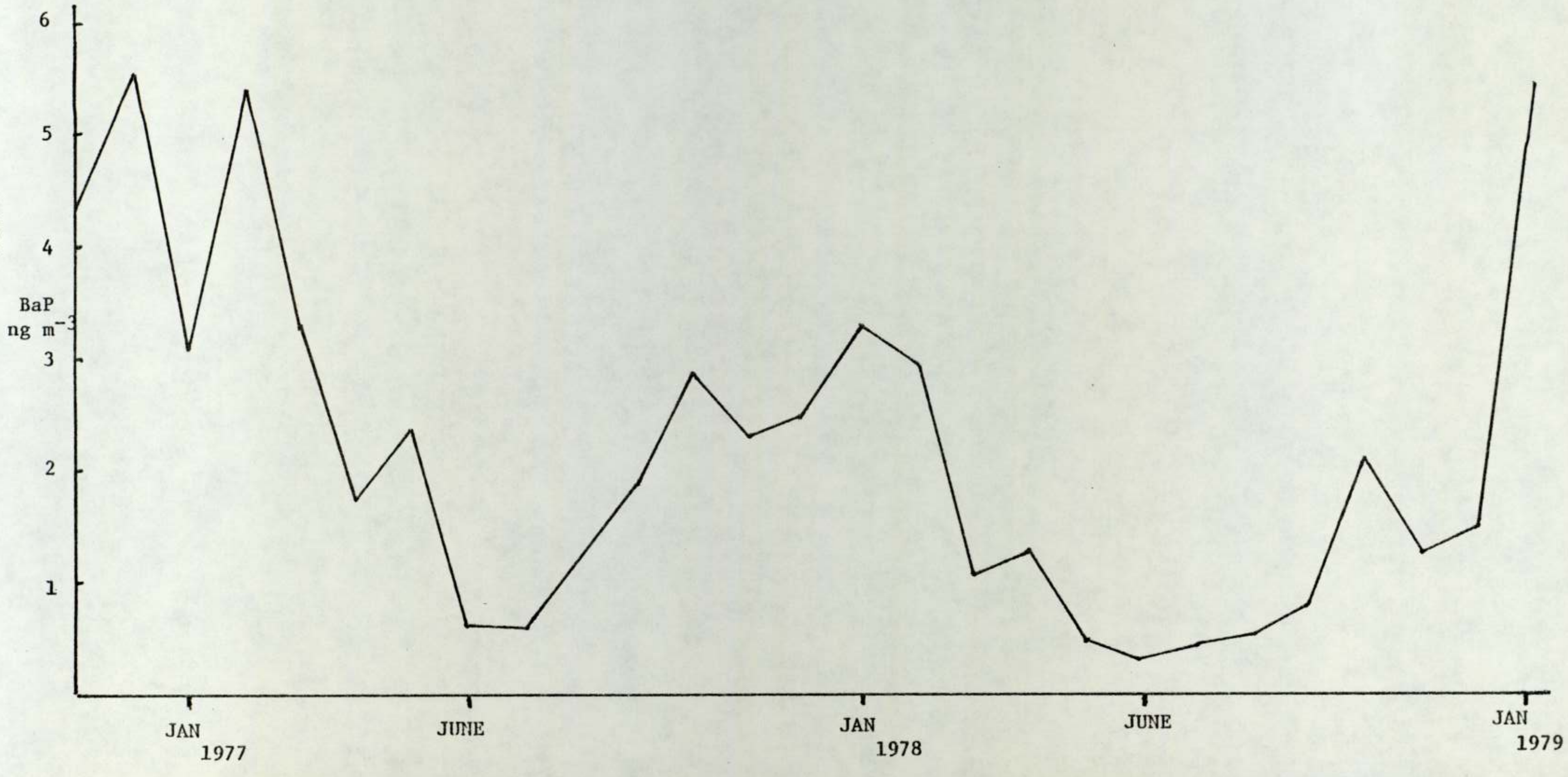
No details of heat sources or smokers were quoted and it is known that internal concentrations of PAH may be significantly affected by tobacco smoke. In a survey of the beer-halls of Prague, Galuskinová (1964) reported BaP concentrations thirty times those of external values. This was attributed to the presence of tobacco smoke. It is possible that residents in houses where other residents smoke, may experience concentrations of PAH in excess of those found outside in the typical urban environment.

In order to estimate the background airborne concentration of PAH in Birmingham the results from the three sites have been combined. Figure 3.7 shows the monthly mean concentrations of BaP (ngm$^{-3}$) derived from all sites. The average of all the monthly mean values is 2.25 ngm$^{-3}$ and assuming that the internal concentrations are similar to the external ones, as indicated in 3.2.4, it is reasonable to use this figure as the mean BaP exposure concentration for a Birmingham resident. Consequently, a person breathing at a rate of 15 m$^3$ of air per day will inspire 15 x 2.25 ng of BaP. Information given in Chapter 4 will indicate the PAH are primarily associated with sub-micron particulate - approximately 90% of BaP being associated with aerosol less than 3 $\mu$m in diameter. Such particles are capable of penetrating deep into the human respiratory system. Hence a background exposure to the lung of -

$$15 \times 2.25 \times \frac{90}{100} \approx 30 \text{ ng of BaP per day}$$

is to be expected.

FIGURE 3.7 Monthly mean concentrations of BaP (ng $m^{-3}$) compiled from all sites.



For comparative purposes this value may be expressed in terms of the BaP content of a cigarette. According to information summarised by Wynder and Hoffmann (1964) one cigarette will deliver about 39 ng of BaP to the body by means of mainstream smoke, i.e. smoke drawn through the cigarette, when smoked at a rate of one puff of two seconds duration every minute. Cigarette smoke held in the lungs for 5 and 30 seconds will result in retention of 82 and 97% respectively. Assuming about 85% retention as average, approximately 33 ng of BaP will be captured by the lung. Hence, it is apparent that breathing the atmosphere of Birmingham for one day results in a BaP intake roughly equivalent to smoking one cigarette.

Earlier in this section, the decrease in reported concentrations of PAH over the last twenty five years was noted. Waller (1952), for example, recorded January concentrations of BaP at County Hall, London in excess of 140 $ngm^{-3}$ and summer concentrations of 12 $ngm^{-3}$. Based on these figures what would be the daily cigarette equivalent intake?

If a mean annual concentration of 60 $ngm^{-3}$ is assumed from Waller's paper together with a size distribution of say 50% of BaP associated with particulate less than 3 µm in diameter, the

daily intake of BaP of a man breathing 15 $m^3$ of air per day will be $15 \times 60 \times \frac{50}{100}$ ng BaP

$$= 450 \text{ ng BaP.}$$

This is equivalent to approximately 14 cigarettes a day.

Epidemiological studies which have related smoking to increased standardised lung cancer mortality would indicate that the apparent decrease of inhaled 'cigarette equivalents' should be reflected by a decrease in standardised mortality rates. In addition, recent trends in the habit of smokers (viz. decrease in the number used and the increased use of filter cigarettes) may similarly lead to reduced mortality. Due to the time delay between exposure to PAH and the appearance of any disease it might be that the combined effect of lowering ambient PAH concentrations and the decrease in cigarette usage may not lead to a decrease in mortality rates for several years.

Bridbord et al (1976) have examined the influence of occupational exposure on BaP intake which they have also expressed in terms of 'cigarette pack equivalents'. These workers have reported that ambient BaP concentrations for 8 hours $day^{-1}$ exposure is equivalent to smoking 0.05 cigarette packs $day^{-1}$ (i.e. about 1 cigarette $day^{-1}$). The BaP in 'cigarette pack equivalents' per day for various exposures are given in Table 3.18. In Chapter 1 the increased occurrence of lung cancer amongst occupationally exposed workers (i.e. coke oven operatives) above that of the general population was discussed. The data in Table 3.18 indicates the relative hazard of the general atmosphere compared with occupational exposure. It is apparent that compared with groups of occupationally exposed workers, the general populations exposed to current concentrations receive only about one fortieth the daily intake of a restaurant employee or approximately $2.67 \times 10^{-5}$ the exposure of a coal tar pitch worker.

In addition to mean PAH concentrations, the potential hazard posed by these compounds is also determined by their exposure to lung tissue. As noted in Section 1.5.5 this is, in turn, determined by the size

TABLE 3.18

Intake of BaP in 'cigarette pack equivalents' per day.
Bridbord et al (1976)

| EXPOSURE | CIGARETTE EQUIVALENTS (PACKS/DAY) | BaP INTAKE ( ug/day) |
|---|---|---|
| Smoking one pack of cigarettes each day | 1 | 0.4 |
| Coke oven workers | | |
| - top side | 450 | 180 |
| - side and bench | 175 | 70 |
| Coal tar pitch worker | 1875 | 750 |
| Restaurant employee | 2 | 0.8 |
| Exposure to ambient BaP levels | 0.05 | 0.02 |

distribution of the particulate with which the PAH are associated. It is important, therefore, to examine the distribution of PAH in the urban aerosol.

# CHAPTER 4

# SIZE DISTRIBUTION OF URBAN ATMOSPHERIC POLLUTANTS

## 4.1 Introduction

Atmospheric aerosols consist of particles in a large range of sizes. The larger ones may be up to 100 μm in diameter (accounting for about 1% of the aerosol mass, Lundgen and Paulus (1975)), whilst the smallest may be less than 0.001 μm.

The size of the particle not only affects the residence time in the atmosphere but also the degree of penetration and retention within the human respiratory system; clearly any pollutants adsorbed onto the particles are similarly affected.

Due to the heterogeneous nature of dispersed aerosols, they exist in a variety of shapes and sizes, ranging from small compact spheres, loose irregular aggregates to long needle-like fibres. This makes the actual definition of particle size somewhat arbitary. One way of overcoming this problem is to define the particle in terms of an equivalent "aerodynamic diameter", i.e. the particle is ascribed a size equal to the diameter of an equivalent sphere of unit density which would behave in the same manner as the actual aerosol particle or, more specifically, the aerodynamic diameter of an irregular shaped particle is the diameter of a sphere of unit density with the same terminal settling velocity as the particle.

To measure accurately aerosol size distributions over the wide range of size known to exist, more than one instrument is required. The larger particle fraction - greater than 0.5 μm - may be observed with a variety of techniques, involving either indirect samplers (optical counters) or direct collection of particles(impactors, filters or centrifuges). For particles less than 0.5 μm, there are only a few methods of analysis. Among them are the Aitken nuclei counter, in which a small adiabatic expansion chamber allows nuclei to grow sufficiently in a supersaturated water vapour to be counted optically and the electrostatic analyser, which depends on the specificity of the relation between an equilibrium electric charge and particle size. The latter device appears to operate most satisfactorily at an equivalent diameter of 0.04 - 0.2 μm. (Husar et al (1970)).

To date only meagre data is available in the literature on the size distribution of aerosols in urban atmospheres and even less on the distribution of PAH with respect to particle size. To our knowledge the results contained in this chapter are the first to be published on the size distribution of PAH at urban locations in the U.K.

## 4.2 Relation of size distribution to regional deposition and biological potential

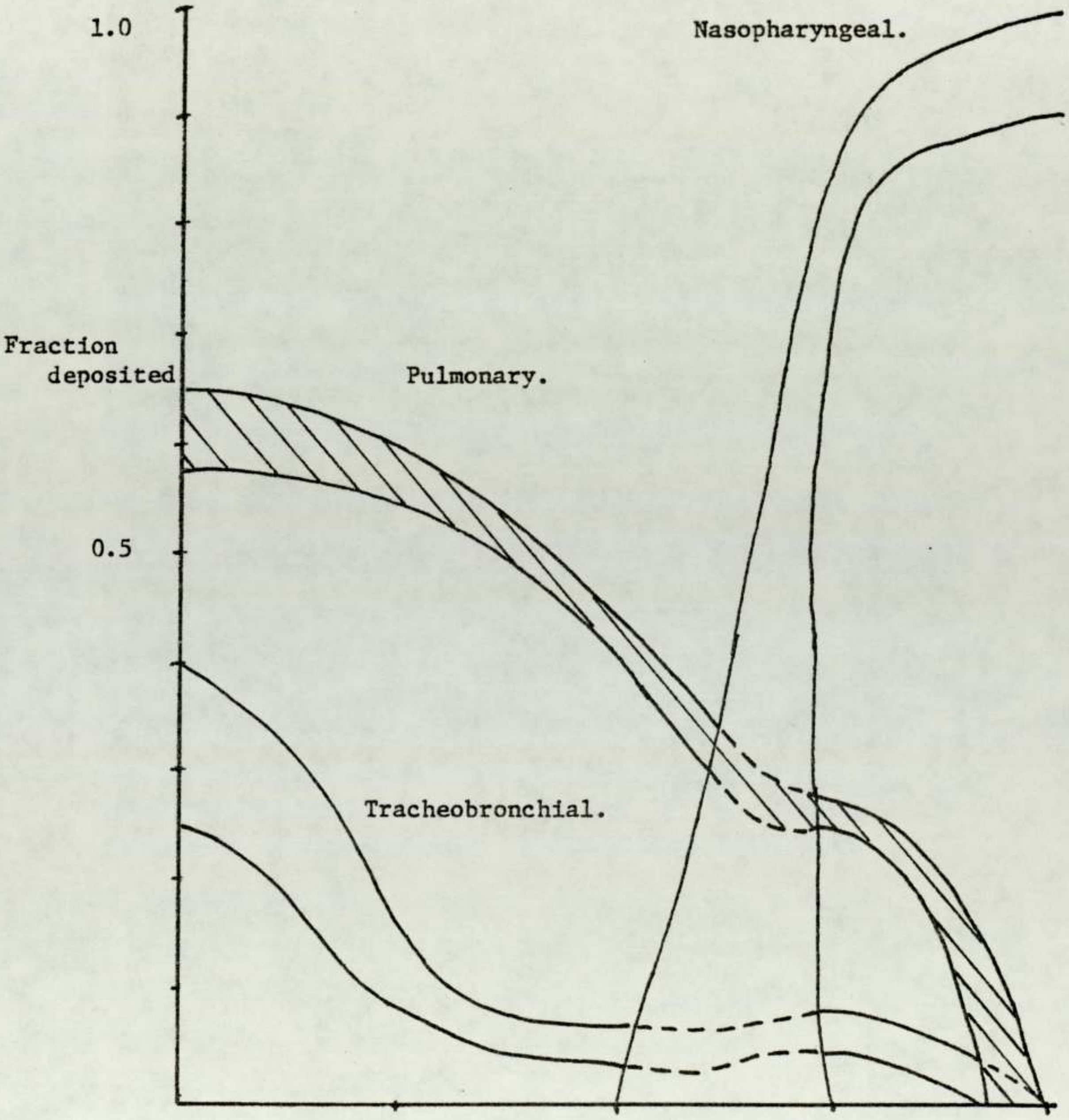
The size of particles entrained in the air breathed by man affects the degree of penetration, the pattern of deposition, the amount retained and the rate of desorption of the particles within the human respiratory system. Obviously, these factors in turn, determine the potential toxicity of an inhaled species. For example, Lloyd, Davies and Harding (1950) have noted that aerosols containing course manganese dioxide particles caused no adverse effects on man over a period of many years; in contrast aerosols containing similar concentrations of manganese dioxide, but with 80% of the particles below 2.0 µm in size, caused pneumonitis.

Natusch and Wallace (1974) have reviewed the available data concerning regional deposition as related to particle size. Figure 4.1 shows a simplified summary of their findings. Particles deposited in the two upper regions of the respiratory tract, i.e. the nasopharyngeal and the tracheobronchial areas, do not remain there long. Such particles are normally removed to the pharynx, often by ciliary action and swallowed in a matter of hours. Consequently, any extraction of possible toxic species will take place in the stomach, where the actual residence time is likely to be short; therefore, any potential danger posed by these particles is relatively small. On the other hand, deposition in these regions may become potentially more harmful if the toxic species are readily extractable or if the particles themselves act so as to paralyse ciliary action.

Pulmonary clearance is much slower. Morrow (1965) concludes that particles deposited in the pulmonary region may remain there for weeks or even years. Hence extraction of toxic species from the particles is probably more rapid than the rate of their clearance. In addition, extraction of comparatively insoluble toxic species is performed more efficiently in the pulmonary region than in either the tracheobronchial or nasopharyngeal regions. For example, barium sulphate retained in the lung is extracted into the blood-stream in a matter of days but ingested barium sulphate is not significantly absorbed. Natusch and

FIGURE 4.1.

Respiratory deposition efficiency as a function of the size of inhaled particles . Natusch and Wallace (1974).



Wallace (1974). This is probably due to the particle size as the rate of extraction per unit mass depends upon the surface to volume area of the particle. The efficiency of membrane transport characteristics are also likely to be influential.

In the urban atmosphere mixing of emissions, each with its own size distribution characteristics, will occur. The resulting total aerosol when averaged, tends to an approximate log normal distribution which may be described by -

$$\frac{dM}{d(\ln x)} = \frac{1}{\sqrt{2\pi}\ \ln \sigma g} \exp\left[ - \frac{(\ln x - \ln \mathrm{MMED})^2}{2 \ln^2 \sigma g} \right]$$

as noted by Smith and Jordan (1964); where x is the particle diameter $\sigma g$ is the geometric standard deviation of the size distribution and M and MMED are the mass and mass median equivalent diameter of the species respectively. Analysis of these size distribution parameters has enabled Natusch and Wallace (1974) to produce deposition profiles of several components of the urban aerosol. The integration of these profiles leads to a value for the percentage deposition within the three major regions of the respiratory system. Examples of size distribution characteristics together with calculated deposition percentages for iron, lead and benzo [a] pyrene are given in Table 4.1.

It is clear from the data presented in Table 4.1 that as the mass medianequivalent diameter decreases the degree of penetration to and percentage deposition within the pulmonary regions increases. For BaP almost 40% of the particles inhaled will be deposited and retained within the lower regions of the human respiratory system. This type

TABLE 4.1

Size distribution characteristics and percentage deposition of iron, lead and BaP, Natusch and Wallace (1974)

| AEROSOL COMPONENT | MMED ( μm) | σg. | % deposition in N | T | P |
|---|---|---|---|---|---|
| Iron | 2.7* | 2.9* | 48 | 7 | 22 |
| Lead | 0.56* | 4.1* | 17 | 6 | 32 |
| Benzo [a] pyrene | 0.15a | 3.0a | 5 | 7 | 39 |

MMED = mass median equivalent diameter

σg = geometric standard deviation

N = nasopharyngeal

T = tracheobronchial

P = pulmonary

* = data from Lee et al (1972)

a = estimated data

of deposition is potentially the most harmful because, as indicated earlier, retention here may be measured in terms of weeks or even years.

Where a species is associated with a carrier species it is important to determine the nature of the distribution. If, for example, zinc were uniformly distributed throughout all iron containing particles in an aerosol then its mass median equivalent diameter would be the same as that of the iron; the respiratory deposition percentages would also be identical. However, if the zinc were primarily associated with surface adsorption to the iron then Natusch and Wallace (1974) have calculated that the MMED of zinc would be 1 µm and consequently a marked difference in the percentage deposition figures would be noted. This effect would be evident for organic species which, after formation, rapidly cool and condense and adsorb to the surface of particles already in the atmosphere. In addition to regional deposition, the biologic potential of PAH laden particulate is also determined by the rate at which PAH is cleared from the respiratory system. (Section 1.5.5).

These date imply that PAH associated with sub-micron carrier particles will be potentially more harmful than PAH adsorbed onto particles greater than, say 5 - 10 microns in diameter.

## 4.3 Theory and interpretation of size distribution data

The relative number of each size of particulate in an aerosol is governed by probability functions which have been described by

Yan (1974) and Espenscheid et al (1964). Moreover, in the urban atmosphere mixing of particles from a wide variety of emission sources, each with its own characteristic distribution, produces considerable modification of the individual source distribution.

Particles with a distribution described by the equation of Smith and Jordan given in section 4.2 display a linear relationship for ECD vs probability when plotted on log-probability paper. Thus as an illustration let us assume that an aerosol has been collected into five discrete size fractions and that the mass of the aerosol collected in each fraction is as shown in the second column of Table 4.2. The third column is the cumulative weight which is derived from the second column by adding successively the individual weights of each stage together. These are then expressed as a cumulative percentage in column four and then as 100 - minus the cumulative weight percentage. The final column (ECD µm)are the size diameters of the individual particle groupings and are determined as a characteristic property of the collecting device. A plot of the last two columns, 100 - cumulative weight % vs the ECD ( µm) is shown in Figure 4.2 on log-probability paper. The calculated correlation co-efficient, R, is 0.965 indicating a good straight line fit and hence the application of the log-normal size distribution is valid within the particle size range quoted.

In addition to demonstrating the applicability of the log-normal distribution function further information on the size distribution may be obtained from the graph. The percentage of the aerosol by weight less than or equal to a given size may be read directly, i.e.

TABLE 4.2

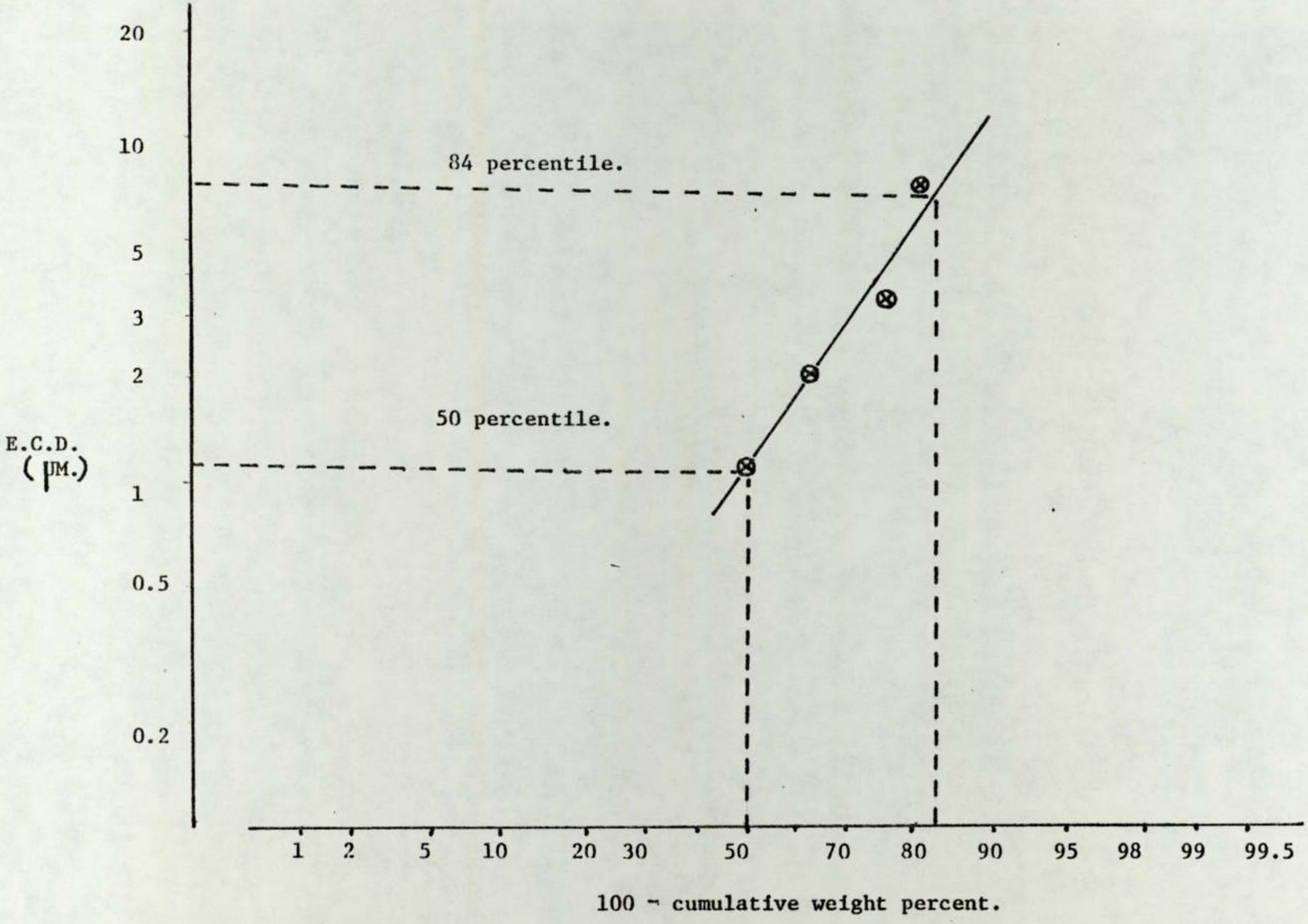
Analysis of aerosol data to indicate a log-normal size distribution

| FRACTION | NETT WEIGHT mg | CUMULATIVE WEIGHT mg | CUMULATIVE WEIGHT % | 100-CUMULATIVE WEIGHT % | ECD µm |
|---|---|---|---|---|---|
| 1 | 216.6 | 216.6 | 18.25 | 81.75 | 7 |
| 2 | 62.5 | 279.1 | 23.51 | 76.49 | 3.3 |
| 3 | 162.0 | 441.1 | 37.16 | 62.84 | 2.0 |
| 4 | 166.0 | 607.1 | 51.14 | 48.86 | 1.1 |
| 5 | 580.0 | 1187.1 | 100.00 | 0 | 0.01 |

ECD = effective cut-off diameter

FIGURE 4.2.

Analysis of size distribution characteristics calculated in Table 4.2.



the percentage less than 1, 2 or 3 µm in diameter are, in this example, 48, 62 and 69% respectively. The mass median equivalent diameter (MMED) can be read off on the particle diameter axis and corresponds to 50% value on the cumulative weight % axis. The geometric standard deviation, $\sigma g$, can readily be calculated from the equation:

$$\sigma g = \frac{84\% \text{ size}}{50\% \text{ size}} = \frac{50\% \text{ size}}{16\% \text{ size}}$$

In this case the 50% size (or MMED) is 1.15 µm and the 84% size is 6.7 µm and hence the geometric standard deviation is 5.8. This value is a measure of the slope of the plot. Other parameters which are occasionally quoted are the arithmetic mean diameter (d) and the particle size, Xm, about which will be clustered those particles with the greatest frequency of occurrence. They may easily be determined from the equations -

$$\ln d = \ln \text{MMED} + 1.1513 \ln^2 \sigma g$$

$$\text{and} \quad \ln Xm + \ln \text{MMED} - \ln^2 \sigma g$$

The log-probability plot just outlined is insensitive to the multi-modal characteristics that may exist in the urban aerosol. A second method of size distribution analysis has been recommended by Whitby et al (1972) and Lundgren et al (1975). This method, sometimes known as the Lundgren analysis, uses a plot of $\Delta$ mass/$\Delta$ log Dp (Ngm$^{-3}$) against log Dp, where Dp is the particle diameter in µm, and takes into account the size range of particles within each group. By using the weights given in Table 4.2 and subjecting them to the 'Lundgren' analysis the information given in Table 4.3 is obtained from which the

TABLE 4.3

Lungden analysis of data to reveal any tendency to multi-modal size characteristics.

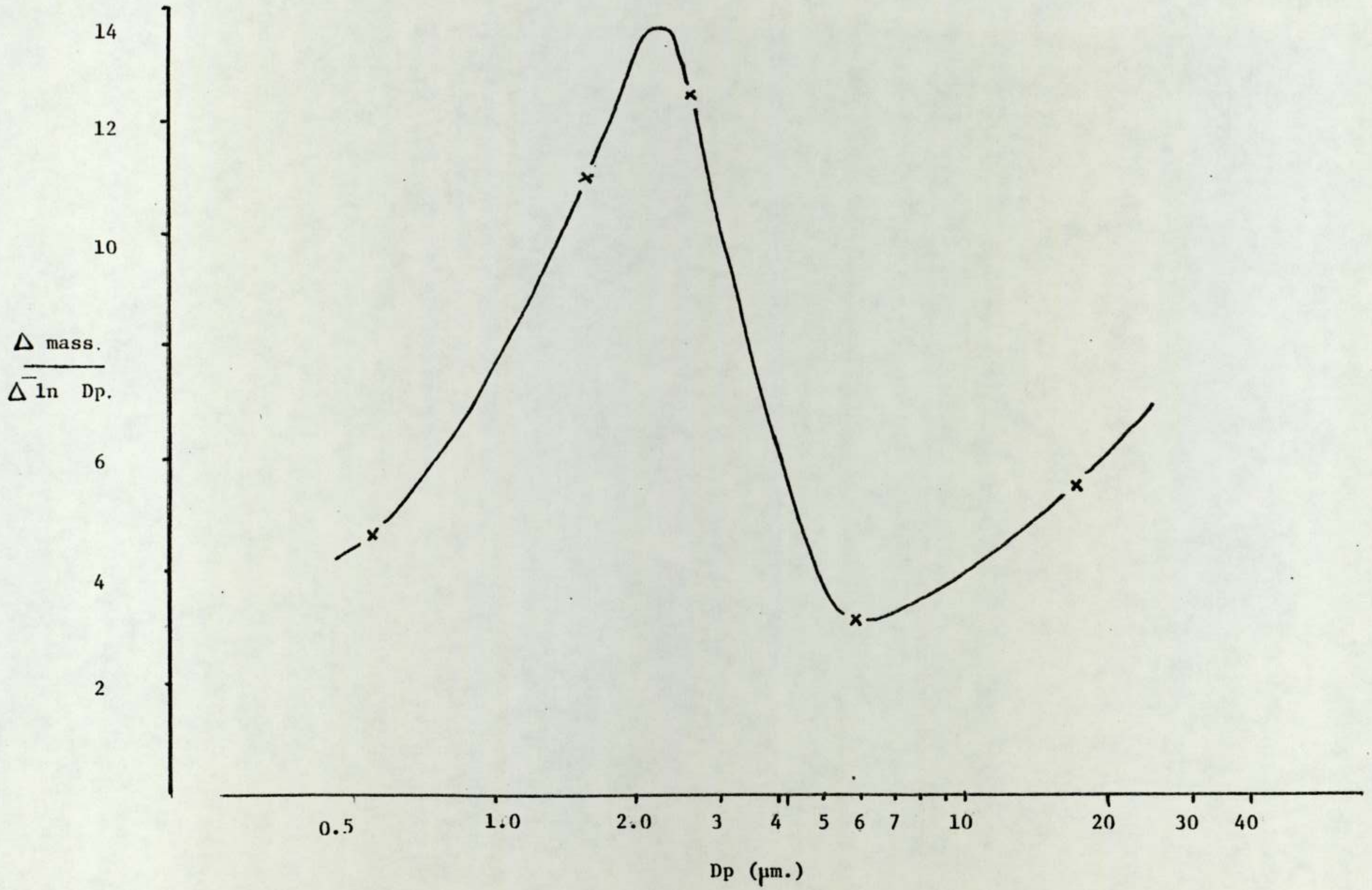
| STAGE | ECD μm | ln Dp | Nett wt g | Δ mass μg m-3 | Δ m/Δln Dp |
|---|---|---|---|---|---|
| 1 | 7(< 30) | 1.45 | 0.2166 | 8.32 | 5.74 |
| 2 | 3.3 | 0.75 | 0.0625 | 2.40 | 3.20 |
| 3 | 2.0 | 0.50 | 0.1620 | 6.22 | 12.40 |
| 4 | 1.1 | 0.60 | 0.1660 | 6.38 | 10.63 |
| 5 | 0.01 | 4.7 | 0.5800 | 22.27 | 4.74 |

$$\ln Dp_n = \ln ECD_{n-1} - \ln ECD_n$$

$$\text{Mass} = \frac{\text{nett wt}}{\text{air volume}}$$

| SIZE RANGE ( μm) | MID - POINT OF PARTICLE DIAMETER RANGE μm. | Δ mass/Δ lnDp |
|---|---|---|
| 30 - 7.0 | 18.50 | 5.74 |
| 7.0 - 3.3 | 5.15 | 3.20 |
| 3.3 - 2.0 | 2.65 | 12.40 |
| 2.0 - 1.1 | 1.55 | 10.63 |
| 1.1 - 0.01 | 0.56 | 4.74 |

Figure 4.3. Lundgren analysis of size distribution for data given in Table 4.3.



plot given in Figure 4.3 is produced. The graph indicates a distribution maximum at about 2.2 µm, but there is evidence that another maximum exists at a particle size in excess of 20 µm. The example used is based on only five discrete size intervals producing four data points for the log-normal analysis and five for the Lundgren analysis. In attempting to describe a non-linear multi-peak graph more than five data points are realistically required. A collection device that is able to separate the aerosol into eight or ten fractions is clearly necessary. The equipment available for size distribution analysis for this project was an Andersen 2000 cascade impactor. This sampler has five collection stages and is designed to simulate the human respiratory system. It is inadequate for investigating aerosol characteristics in detail over a wide range of particle sizes.

## 4.4 Theory of particle separation by cascade impaction

If particles of different size and mass are entrained in an air stream which is incident upon a flat surface those particles with sufficient momentum to escape the stream of air will not be reflected from the surface. Hence the incident and reflected streams of gas will have different compositions; the reflected stream being deficient of large particles compared to the incident stream. If the reflected stream is made to impinge on a second flat surface thus becoming an incident stream, and if, in addition, the velocity of the gas is increased, particles of a second smaller size range can be selectively removed.

The theory of such a process has been examined by Mercer (1964) and by Ranz and Wong (1952) who have considered the impaction of a round aerosol jet stream on a uniformly flat surface of infinite area. The efficiency of impaction, E, is given by -

$$E = \left[ \frac{S_2 - S_1}{S_2 \exp S_1 h - S_1 \operatorname{esp} S_2 h} \right]^2$$

$$\text{where} \quad h = \frac{1}{q} \tan^{-1} \left[ \frac{(1 - 4k)\, 8\, Kq}{(8K - 1) + (4\, Kq)^2} \right]$$

$$S1,\ 2 = (-1/4K) \pm \left[ (1/4K)^2 + 1/2K \right]^{\frac{1}{2}}$$

$$\text{and} \quad q = \left[ (1/K) - (1/4K)^2 \right]^{\frac{1}{2}}$$

When the size of the particles is large in comparison to the mean free path of the carrier gas then -

$$K = \frac{pvd^2}{18\eta D}$$

where $p$ = particle density (g $cm^{-3}$)

$v$ = velocity of the gas (cm $5^{-1}$)

$d$ = diameter of the aerosol particle (cm)

$D$ = diameter of gas jet stream (cm)

and $\eta$ = gas viscosity (poise)

Some calculated values for $K, q, h, S_1, S_2$ and E are given in Table 4.4. These data taken from Butler (1979) indicate how the efficiency changes with changing particle size if the values of p, v, $\eta$ and D remain constant. It is apparent that particles of 4.0 µm diameter are retained with the greatest efficiency.

TABLE 4.4

Calculated values for the efficiency E, for selected values of d( μm), when p = 1.0, v = 760 cm $s^{-1}$, $\eta$ = 180 x $10^{-6}$ poise and D = 0.158 cm. Butler (1979).

| d um | K | q | h | $S_1$ | $S_2$ | E |
|---|---|---|---|---|---|---|
| 2.40 | 0.085 | 1.77 | 0.85 | 0.87 | -6.73 | 0.29 |
| 2.45 | 0.089 | 1.83 | 0.77 | 0.87 | -6.49 | 0.34 |
| 2.50 | 0.093 | 1.87 | 0.70 | 0.86 | -6.26 | 0.38 |
| 2.75 | 0.112 | 1.99 | 0.48 | 0.84 | -5.30 | 0.58 |
| 3.0 | 0.133 | 2.00 | 0.35 | 0.82 | -4.57 | 0.74 |
| 3.5 | 0.181 | 1.90 | 0.16 | 0.78 | -3.53 | 0.94 |
| 4.0 | 0.235 | 1.76 | 0.03 | 0.74 | -2.85 | 1.00 |

In this example, the efficiency tends towards zero for particles that are below 2.4 μm in size.

The Andersen 2000, five stage cascade impactor used in this project was manufactured to ASTM D2009 requirements. The instrument shown in Figures 4.4.I and 4.4.II consists of a series of plates which have holes drilled through them to allow the passage of the aerosol. Each plate has smaller diameter holes than the preceding one and consequently the aerosol velocity is increased from one plate to the next. In theory each stage should collect particles of a certain size and none smaller; in fact this is not achieved and a diameter has been ascribed to each stage to represent the average size of particle sampled. This proscribed size or 'effective cut-off diameter', ECD, is specified by the manufacturer and is the size at which the collection efficiency is equal to 0.5 or 50%. The ECD's of each stage of the Andersen, in terms of spherical particles of unit density, are given in Table 4.5 and plots of the probability of collection against particle size ( μm) as derived from manufacturer's data and from Rihm (1972) are shown in Figure 4.5. The size of particle collected on the final 'back-up' stage of the impactor is a function of the collection efficiency of the filter. The filter has an efficiency of greater than 99% for particles down to 0.01 μm in diameter.

## 4.5 Possible errors of data derived from the Andersen

Cascade impactors have been criticised as being subject to three types of error:

1) That material loss of particulate can occur on the stages of the instrument.

FIGURE 4.4.1. ANDERSEN 2000 CASCADE IMPACTOR.

FIGURE 4.4.II. EXPLODED VIEW OF ANDERSEN 2000 CASCADE IMPACTOR.

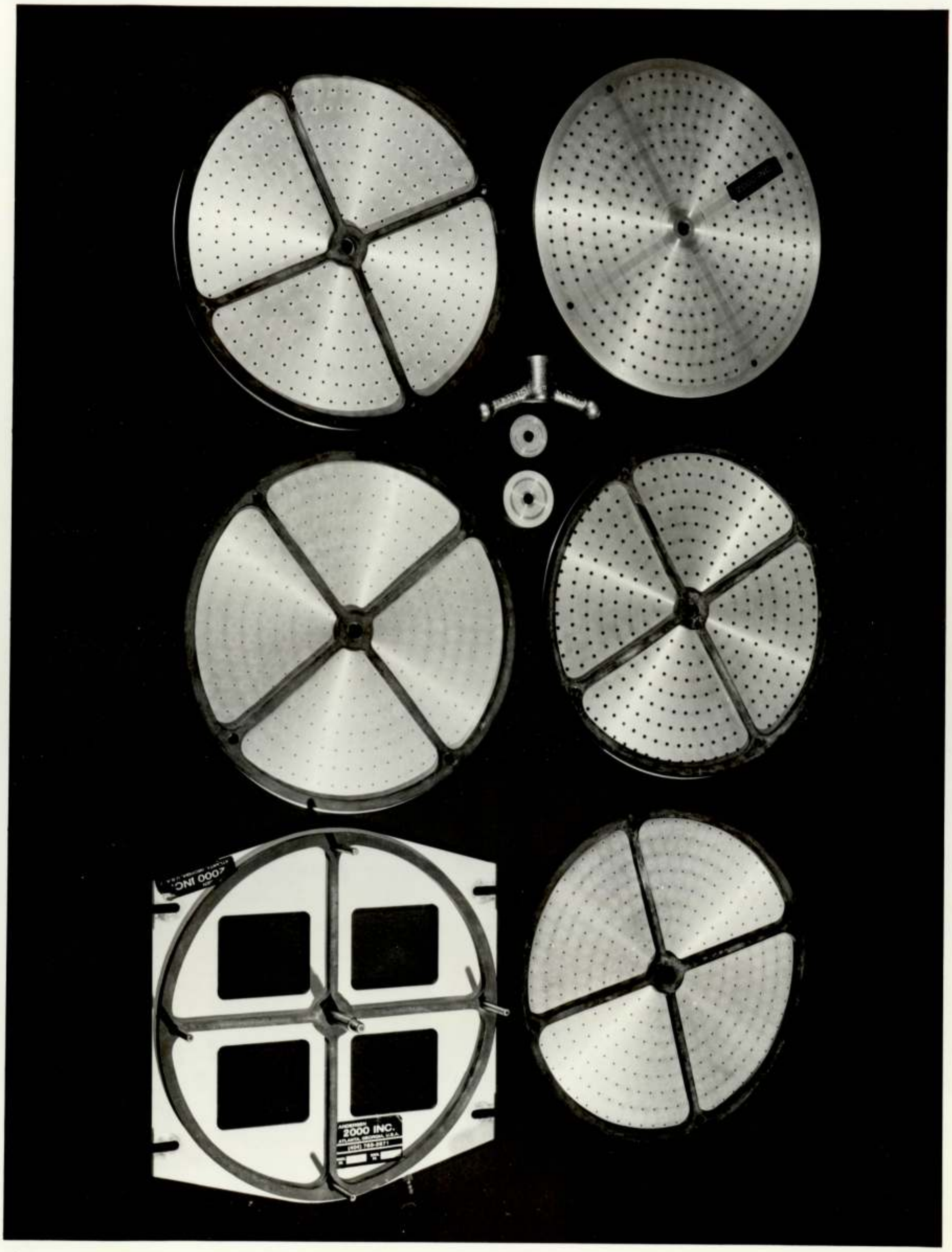
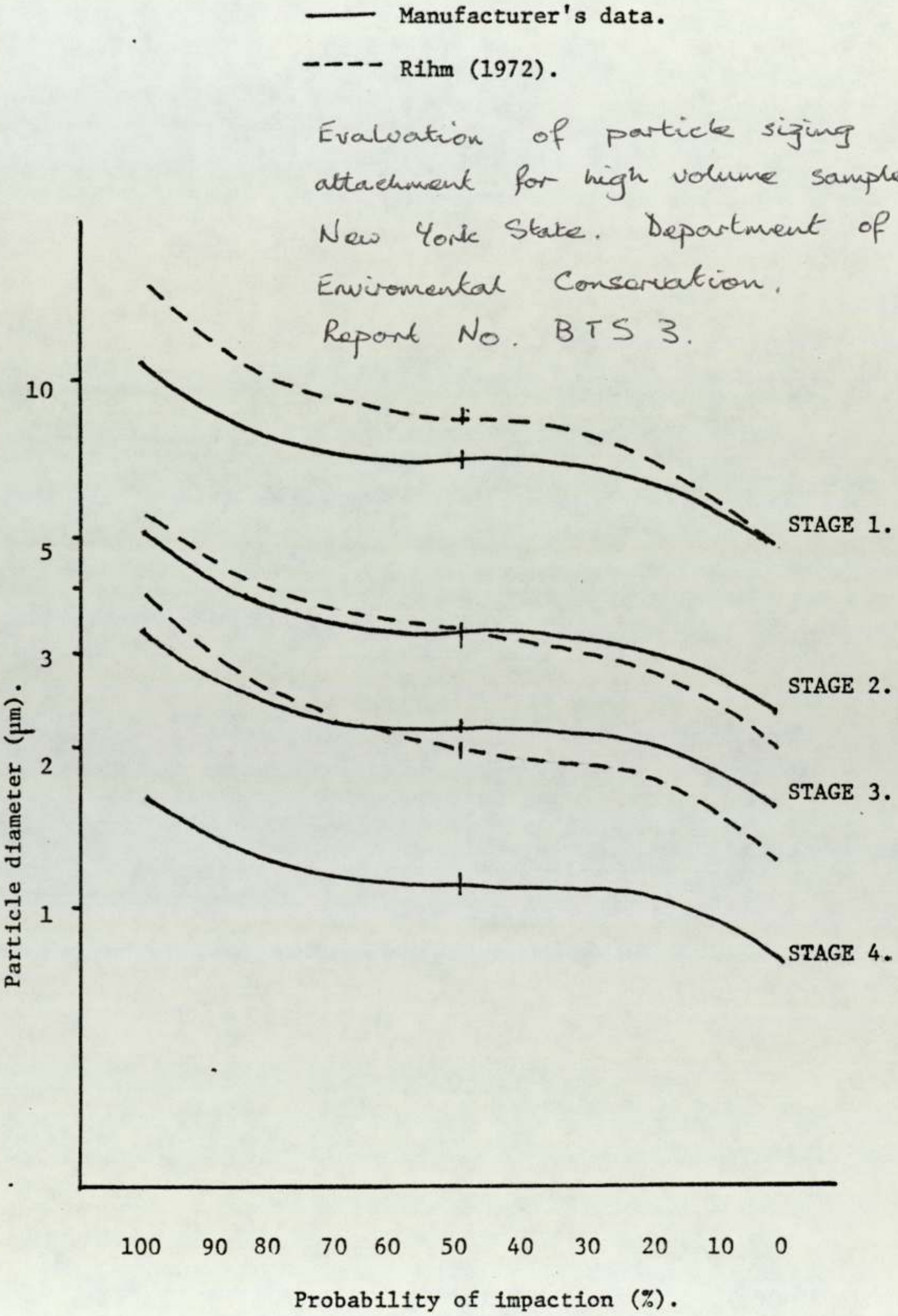


TABLE 4.5

Effective cut-off diameter (ECD) µm for each stage of the Andersen 2000

| Stage | ECD µm |
|---|---|
| 1 | 7.0 |
| 2 | 3.3 |
| 3 | 2.0 |
| 4 | 1.1 |
| 5 | 0.01 |

FIGURE 4.5 Probability of impaction vs. particle diameter (μm).



Evaluation of particle sizing attachment for high volume samplers New York State. Department of Environmental Conservation. Report No. BTS 3.

2) That particle 'bounce' causes inefficient capture on the collection plate, and

3) That re-entrainment of the particles into the air-stream could occur subsequent to impaction.

Several materials have been cited as being suitable for use as the collection surface. Aluminium foil has been used by Lee and Goranson (1972), polyethylene films by Gordon et al (1974), Teflon films and sticky tapes by Lundgren (1971), stainless steel plates by Lee and Patterson (1969) and plates covered with a thin layer of grease by Hu (1971). All suffer,to some extent, errors due to particle bounce but Hu reported that placing a glass-fibre filter on top of each collecting surface greatly reduced the effect and that in this way an Andersen cascade impactor might be operated without appreciable error. The effectiveness of glass-fibre filters in minimising bounce probably results from their porous, fibrous nature. If a particle is incident on a fibre and is not immediately captured it will be deflected and the probability is that it will impact and be captured on a neighbouring fibre.

Hu also noted that the use of glass-fibre filter has other advantages. Diffusional loss of the very fine particles did not occur and efficient capture and retention results in the problem of re-entrainment being reduced.

Wall losses are a function of particle size Hu (1971). It is difficult to measure the loss between each individual stage; the total loss, however, can be easily estimated. If the total particulate mass ( $\mu gm^{-3}$) is determined from both the Andersen and a Hi-Vol methods simultaneously then any difference in result may be due to loss of particulate on the walls of the Andersen. Results of such comparisons are given in Table 4.6.

These data indicate that total wall losses are generally small, less than 5% of the TPM determined from Hi-Vol results. This agrees with work of Lundgren (1967) who found that wall losses were small and increased with increasing particle size, i.e. 0.3% for 1 - 2 μm particles, 0.7% for 2 - 3 μm and 6.5% for 3 - 5.2 μm.

Burton et al (1973) has noted that the pH of the collection surface can affect the mass determined. When glass-fibre filters with a pH of 11.0 were used sulphate production, arising from the presence of sulphur dioxide, increased the mass determined. By using filters of pH 6.0 this source of error was eliminated.

By using an appropriate collection surface (i.e. a glass-fibre filter with a pH of 6.0) Andersen cascade impactors may be satisfactorily used to determine size distribution data of aerosols.

## 4.6 Operation of the Andersen Impactor

The Andersen sampler was sufficiently portable to be operated at the same sites as those used for the routine monitoring programme. Prior to each run the flow-rate of the Hi-Vol pump was re-calibrated and set to operate at a standard 0.566 $m^3 min^{-1}$, measured using the Dwyer oil manometer supplied with the instrument. The rate was maintained using a variable voltage transformer.

TABLE 4.6

Comparison of total particulate mass ( $\mu g\ m^{-3}$) determined from Andersen and Hi-Vol methods from various sources

Total Particulate Mass($\mu gm^{-3}$)

| Andersen $\mu g\ m^{-3}$ | Hi-Vol $\mu g\ m^{-3}$ | Number of samples | $\frac{\text{Andersen}}{\text{Hi-Vol}}$ % | Source |
|---|---|---|---|---|
| 90.6 | 96.4 | 10 | 94 | Burton et al (1973) |
| 82.14 | 84.56 | 82 | 97 | Rihm (1972) |
| - | - | 7 | 96 | Mainwaring & Harsha (1976) |
| 72.5 | 73.5 | 4 | 99 | Van Vaeck (1978) |
| 47.3 | 50.5 | 9 | 94 | Crossley |
| | | Mean | 96% | |

In order to obtain sufficient particulate on each stage to allow analysis for PAH the sampler was run continuously for periods of up to one month. This meant that on average 30,000 $m^3$ of air were sampled. With such large volumes of air it was found necessary to change the 'back-up' filter at regular intervals in order to ensure that the filter did not become so heavily loaded with particulate that the flow-rate was affected. After removal each back-up filter was returned to the laboratory and reconditioned to the same temperature and relative humidity as when they were weighed prior to operation. The filters were weighed to determine the mass of particulate collected and then stored in a sealed beaker containing DMSO in the dark. All the back-up filters were combined so that the PAH of the final stage could be determined. The PAH concentrations of stages one to four were individually determined. The results were expressed in terms both of the volume of air sampled and in terms of the mass of particulate collected.

## 4.7 Results of particle size analysis

This section records the results of particle size distribution characteristics recorded at the three sites used in the routine PAH monitoring programme. Information has been produced from log-probability plots of 100 cumulative weight % vs ECD described earlier. Table 4.7 lists the values of the MMED's, the $\sigma g$'s and percentage by weight of the aerosol, less than or equal to 1 and 3 μm in diameter. The importance of $\sigma g$ is that it provides an indication of the particle dispersion or range of particle sizes in an aerosol, Lee (1972); the larger the value of $\sigma g$ then the broader is the distribution.

TABLE 4.7

Particle size characteristics of total suspended particulate matter(TPM)determined at three sites in Birmingham.

| SITE | DATE | MMD (µm) | $\sigma_g$ | %age ≤ | |
|---|---|---|---|---|---|
| | | | | 1.0 µm | 3.0 µm |
| S-C | March - April 1977 | 1.1 | 6.8 | 48 | 70 |
| S-C | Nov - Dec 1977 | - | - | - | - |
| S-C | June - Aug 1978 | 1.2 | 14.2 | 47 | 62 |
| S-C | Jan - Feb 1979 | 0.8 | 5.5 | 55 | 78 |
| C-C | July - Aug 1977 | 1.3 | 5.8 | 44 | 69 |
| C-C | Feb - Mar 1978 | 0.7 | 12.1 | 56 | 72 |
| C-C | Oct - Nov 1978 | 1.0 | 8.0 | 51 | 71 |
| C-C | Nov - Jan 1978/79 | 1.3 | 5.4 | 43 | 69 |
| S-U | June 1977 | 1.1 | 12.7 | 48 | 64 |

Concentrations of total particulate matter (TPM) collected on each stage are shown in Figure 4.6. These plots show that concentrations are highest for stage 5 of the Andersen sampler (i.e. particles $\leq$ 1.1 μm), that the concentrations for stages 2, 3 and 4 are roughly equal and that the concentrations found on stage 1 (particles $>$7.0 μm) are generally greater than stages 2, 3 and 4 but less than stage 5. These figures do not take into account the size range of particles on each stage. In section 4.3 a mathematical analysis (Lundgren plot) was outlined in which size range was considered. The disadvantages of this type of interpretation were also noted for the instrument used in this work and for those reasons discussion of size distribution patterns is restricted to cumulative weight analysis.

The total weight of particulate, determined by summing the masses on all stages, has been normalised with respect to the total volume of air sampled. See Table 4.6. It appears that the concentration of particulate matter ( $\mu gm^{-3}$) determined by impactor-sampling is approximately equal to, but generally less than, the corresponding concentration determined by 'Hi-Vol' sampling.

It is possible to obtain detailed analysis of the physical composition and chemical nature of atmospheric samples collected on each of the stages of the impactor using techniques described by Butler et al (1976). Small, 1 cm diameter sections were cut from each stage and subjected to combined x-ray fluorescence and scanning electron microscopy (SEM). Figure 4.7 shows photographs obtained from the SEM for each stage together with a photograph of an unexposed filter. The exposed samples were taken from an Andersen experiment operated at S-C.

FIGURE 4.6.

Concentrations of particulate ($\mu g\ m^{-3}$) vs. stage number at various locations.

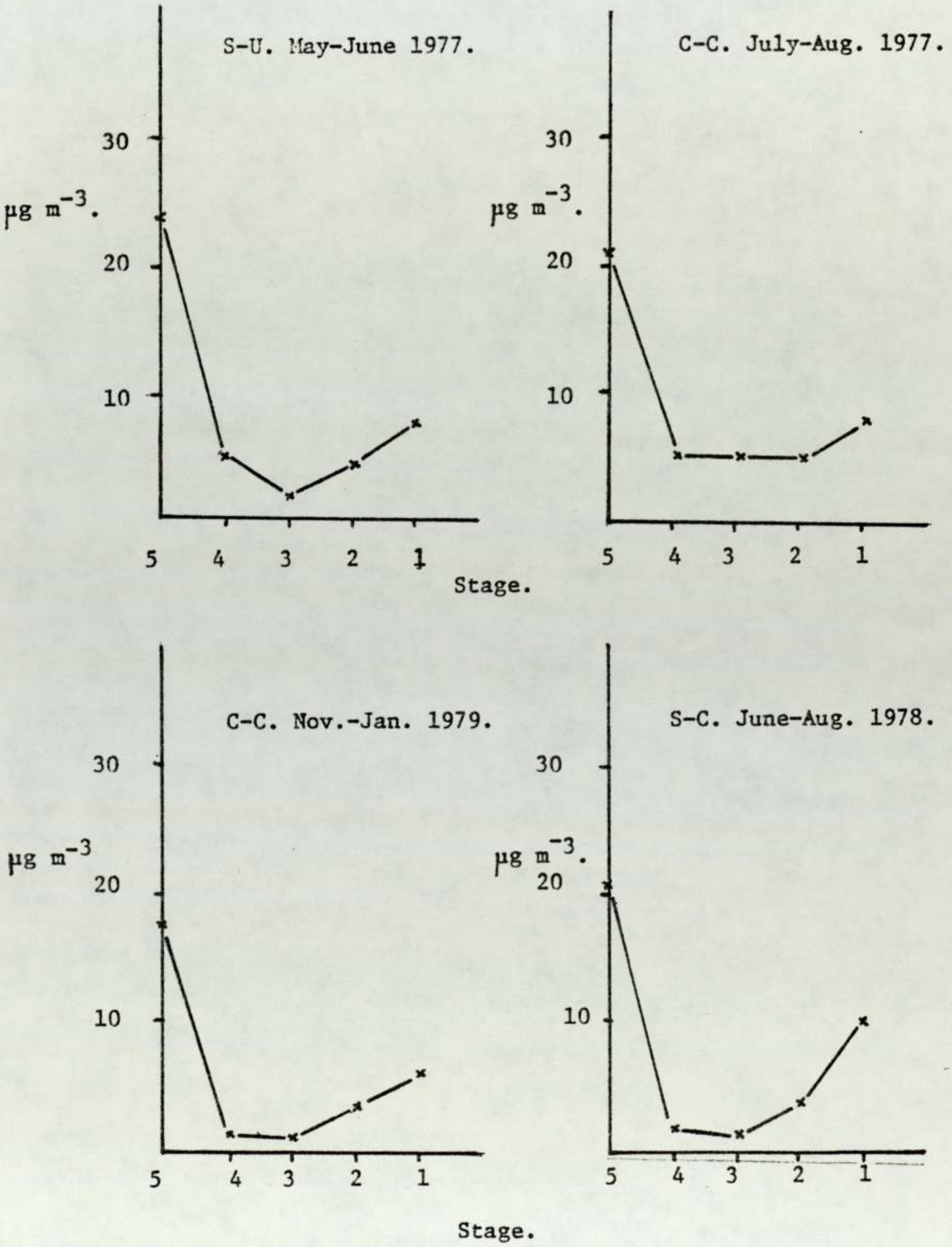
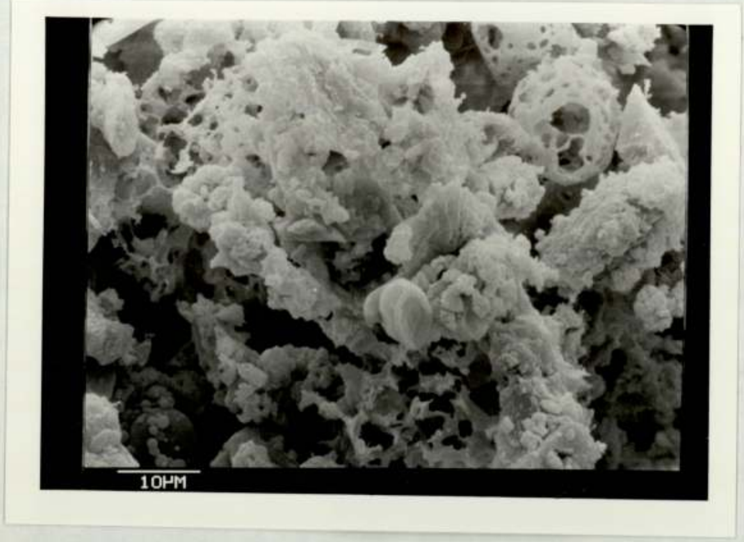


FIGURE 4.7

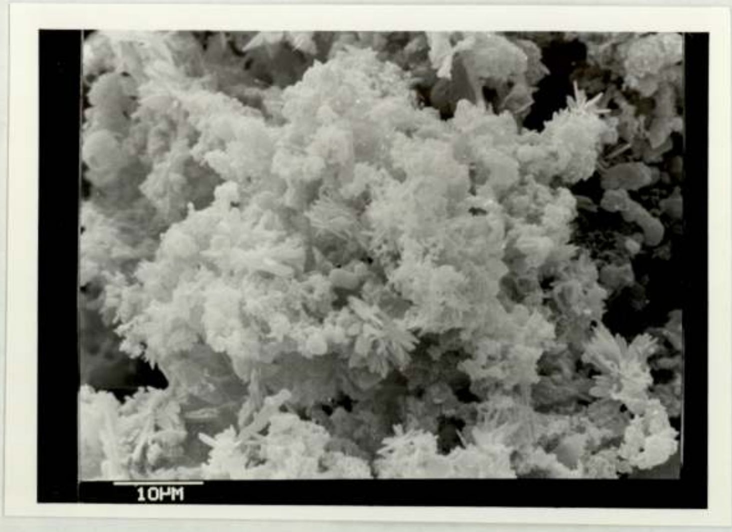
Scanning electronmicroscope photographs of the particulate collected on each stage of the Andersen at S-C



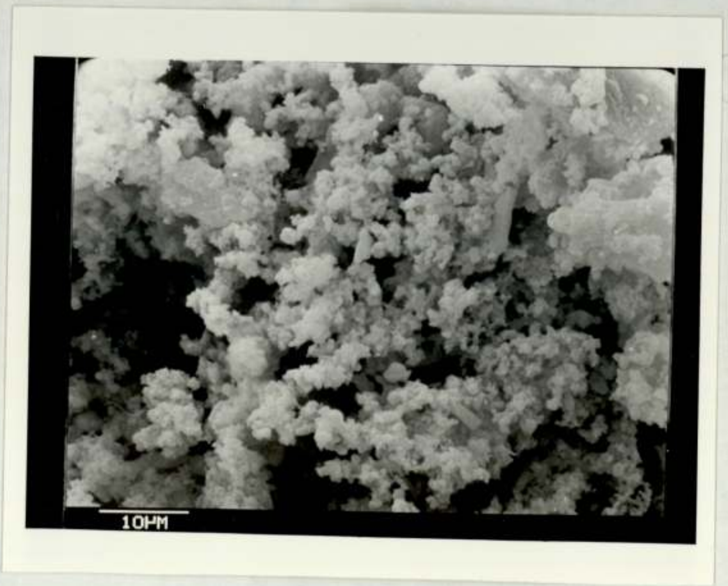
STAGE 1

STAGE 2

FIGURE 4.7 (contd).

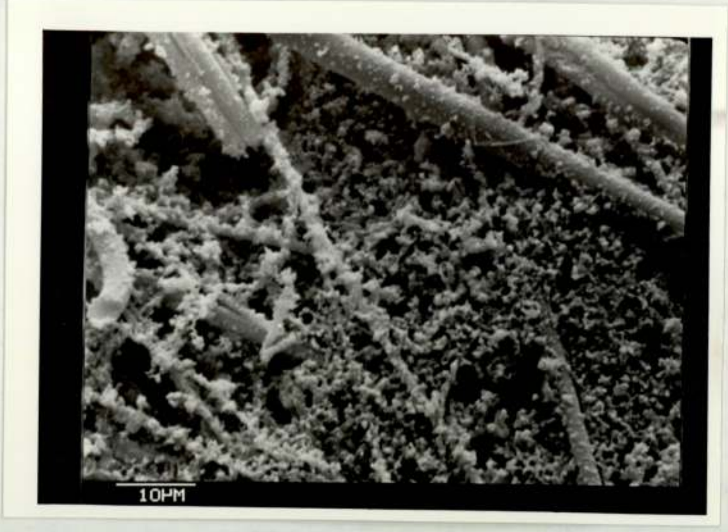


STAGE 3

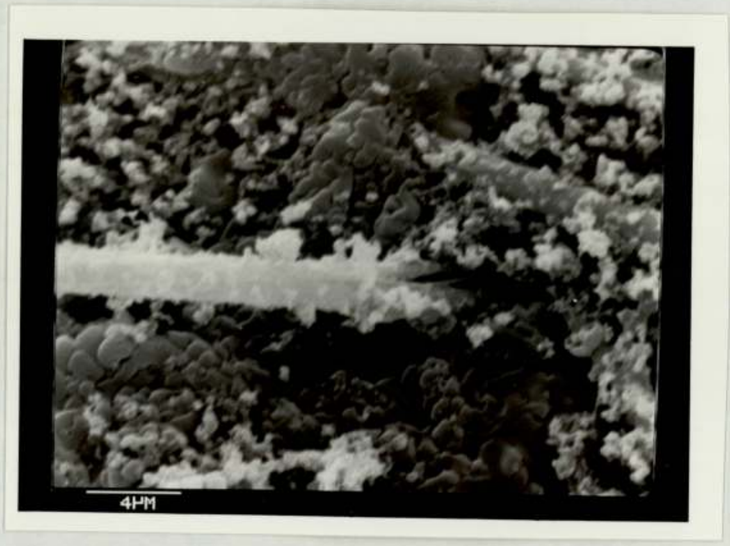


STAGE 4

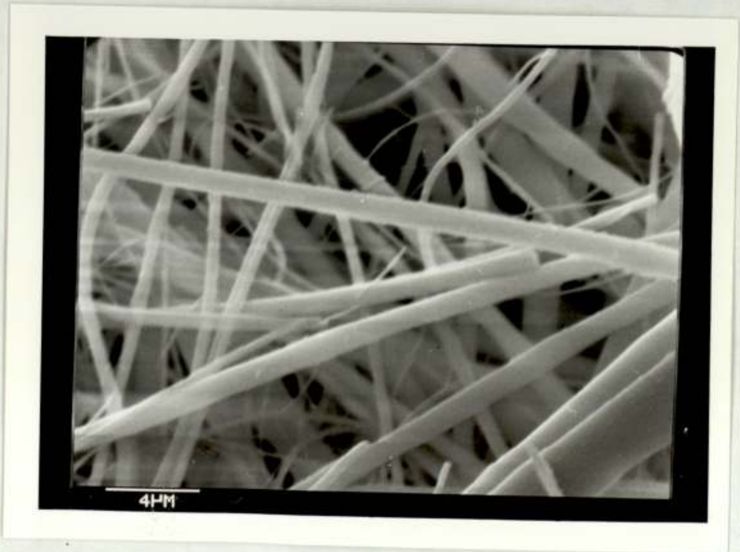
FIGURE 4.7 (contd)



STAGE 5



STAGE 5
higher
magnification



unexposed filter

It is not possible to directly compare size distribution obtained by optical inspection of the individual stages with that determined by cascade impaction. This is because MMED's are a measure of the equivalent diameter of spheres of unit density. Diameters obtained using the SEM are projected diameters of particle. However, the photographs do show that the particle size does decrease as the stage number increases.

### 4.7.1 Discussion of particle size distribution

Despite the fact that samples were taken from three environmentally different locations all the MMED's are similar and less than 1.5 µm. The mean value of all eight determinations is 1.06 ± 0.15 (limits expressed at the 90% confidence level). These results are in broad agreement with other recently published data on particulate size distributions (see Table 4.8). It appears that there is a growing body of information indicating that the MMED's of urban aerosols are approximately one micron in diameter. The value of 3.4 µm obtained by Mainwaring and Harsha (1975) in Melbourne is likely to have been affected by demolition work in the neighbourhood and the value of 1.79 µm at Ankara is explained by use of lignite coal in the area.

The generally accepted concept of atmospheric aerosols, as noted by Lee and Goranson (1976), attributes most of the larger, coarse particles of diameter 2.0 µm and above, to natural formation, i.e. by wind erosion and dust and soil re-entrainment. The smaller particles are considered to arise from anthropogenic sources, consisting mainly of secondary reaction products resulting from the conversion of gaseous products to aerosols. The MMED of particulate in Birmingham is

TABLE 4.8

Particulate characteristics determined at other urban locations compared to the mean Birmingham values

| SITE | MMED µm | $\sigma_g$ | n | Comments | Source |
|---|---|---|---|---|---|
| Antwerp | 1.15 | 5.5 | 4 | all winter samples | Cauteels and Cauwenberghe (1978) |
| Melbourne | 3.4 | 9.4 | 5 | - | Mainwaring and Harsha (1975) |
| Ankara | 1.79 | 5.20 | 10 | - | Lee & Smith(1972) |
| Chicago | 1.12 | 3.9 | 25 | - | Lee & Goranson(1972) |
| Denver | 1.06 | 7.2 | 12 | - | " |
| St. Louis | 1.46 | 5.0 | 24 | - | " |
| California | 0.76 | 8.18 | 10 | - | Lundgren (1970) |
| London | 0.43 | 8.04 | 7 | Feb. 1970 | Lee (1972) |
| London | 0.66 | 7.07 | 7 | May 1970 | " |
| Kew | 0.46 | 6.04 | 8 | Feb. 1970 | " |
| Kew | 0.43 | 6.12 | 9 | May 1970 | " |
| Eskdalemuir | 0.06 | 15.63 | 8 | Feb. 1970 | " |
| Eskdalemuir | 0.31 | 6.33 | 7 | May 1970 | " |
| Toronto (York) | 2.3 | 10.8 | 10 | Summer 1972 | Pierce & Katz(1975) |
| Toronto (York) | 2.4 | 6.2 | 15 | Winter 1972 | |
| Toronto (College) | 1.8 | 16.1 | 4 | Summer 1972 | |
| " | 3.4 | 13.5 | 5 | Winter 1972 | |
| Birmingham | 1.08 | 8.34 | 8 | 1977 - 1979 | |

approximately one micron in size and therefore indicates that the aerosol arises predominently and perhaps not unpredictably, from anthropogenic sources.

Mainwaring and Harsha (1975) have reported that standard geometric deviations in the range 5 to 14 are indicative of a broad range of particulate sizes; thus suggesting thorough mixing of the aerosol with no single dominating source. The range of standard geometric deviations recorded in Birmingham (5.4 - 14.2) lie within the values stated above and if Mainwaring and Harsha are correct it is apparent that the urban aerosol is generally well mixed throughout the city.

This helps to explain why the results of the TPM and PAH monitoring at the three sites are so similar. Firstly, it has been established that all the aerosols have MMED values of approximately 1 $\mu$m and are, therefore, predominently anthropogenic in nature. Secondly, Esman and Corn (1971) have calculated that the residence time of such particles, in the absence of precipitation, will be about 200 hours. Consequently, we are dealing with an aerosol which is relatively aged and homogenous in nature. The influence of individual sources are masked by general dispersion effects. The exception to this concept might be at C - C; in section 3.3 it was noted that the lack of correlation between pollutant concentrations and meteorological parameters might be explained if the site was being influenced by irregular emissions from one or more unidentified sources.

It is also necessary to consider the methodology involved in the programme. In order to collect sufficient particulate to perform chemical analysis of PAH a sampling period of about one month was required. Hence short term fluctuations of size distribution occurring within that period could not be determined. In terms of health standards long-term averages, together with information on seasonal and annual trends are more important than short-term fluctuations.

Seasonal trends in particle size distribution have been reported by Van Vaeck and Van Cauwenberge (1978) who found December MMED's were smaller than March or October values and by Pierce and Katz (1975) and Lee and Goranson (1976) who both reported increased winter MMED's. Lee and Goranson, working in the U.S.A., have attributed the increased winter MMED to the increased use of space heating, which gives rise to an increase in the number of larger particles and to the decreased photo-chemical activity, which in summer gives rise to many fine secondary particles.

With only eight results from three different sites it is not justifiable to make any claims about evidence either for or against seasonal changes in MMED, but, with the exception of the result obtained at C - C (November 1978 - January 1979) it appears winter MMED's were fractionally lower than summer values.

It is also not possible to interprete so few data to reveal any annual trends. In an extensive survey of urban particulate characteristics of U.S. cities, Lee and Goranson (1976) have noted an increase in annual average MMED's between 1970 and 1972. A decrease in the annual mean particulate concentration was also recorded. They suggest that a possible explanation of this observation may be the effectiveness of emission control measures progressively applied since 1970 toward motor vehicles.

## 4.8 Results of PAH size distribution analysis

Chemical analysis of the PAH content of each stage of the Andersen can provide concentrations expressed in terms of both volume of air sampled and the mass of particulate collected. For this reason it is possible to calculate two size distributions for PAH. The first would be produced from analysis of 100 - cumulative weight % (i.e. PAH expressed in $ngm^{-3}$) and the second from 100 - cumulative weight per weight % (i.e. PAH expressed in $mgkg^{-1}$). The difference arises from the fact that in the first case all the amounts of PAH are normalised with respect to the same figure (i.e. the total volume of air sampled);in the second the amount of PAH recovered on each stage is related to the amount of particulate on that individual stage. Virtually all data on PAH size distributions are quoted in terms of results calculated from concentrations expressed in $ng\ m^{-3}$; to maintain consistency this form of analysis will be used throughout.

The MMED's, $\sigma g$'s and percentage of PAH less than or equal to a given size refer to the particle with which the PAH is associated. For example, an MMED of 1.1 μm would indicate that 50% of PAH by weight is associated with particulate less than 1.1 μm in diameter. Size distribution characteristics of PAH are given in Table 4.9.

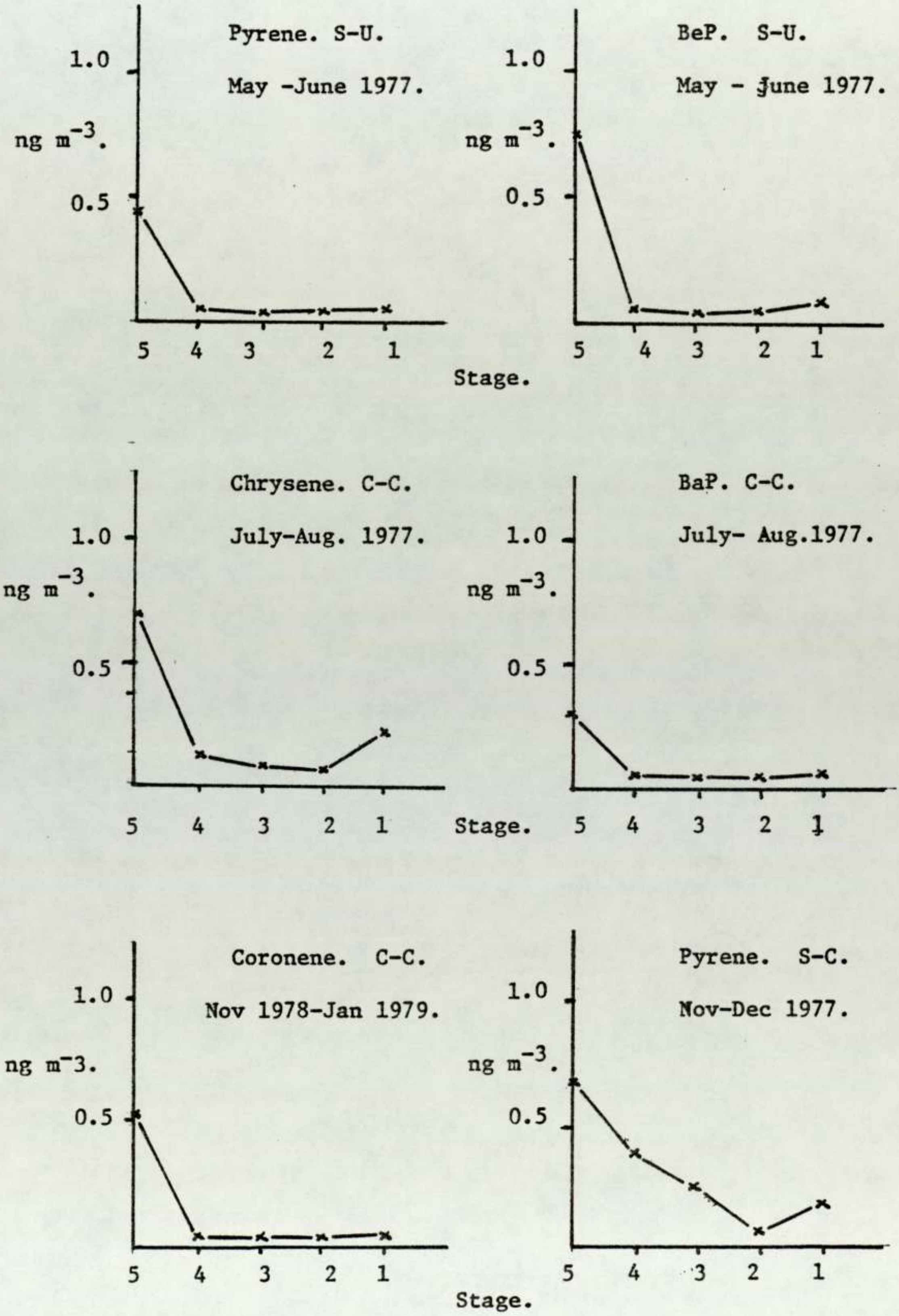
Typical plots of PAH concentration ($ngm^{-3}$) against stage number are

TABLE 4.9 SIZE DISTRIBUTION CHARACTERISTICS OF AIRBORNE PAH

| SITE/DATE | PYRENE |  |  |  | CHRYSENE |  |  |  | BaP |  |  |  | BeP |  |  |  | CORONENE |  |  |  |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
|  | MMED µm | $\sigma_g$ | %<1, <3 µm |  | MMED µm | $\sigma_g$ | %<1, <3 µm |  | MMED µm | $\sigma_g$ | %<1, <3 µm |  | MMED µm | $\sigma_g$ | %<1, <3 µm |  | MMED µm | $\sigma_g$ | %<1, <3 µm |  |
| MAR/APR 1977 S-C | 1.1 | 6.0 | 48 | 72 | 0.4 | 14.3 | 64 | 78 | 0.3 | 6.4 | 77 | 90 | 0.8 | 4.3 | 58 | 83 | 0.5 | 3.9 | 68 | 90 |
| NOV-DEC 1977 S-C | 1.1 | 3.4 | 46 | 79 | 1.3 | 1.6 | 32 | 97 | 1.4 | 2.7 | 38 | 78 | 1.4 | 2.0 | 32 | 87 | 2.0 | 2.1 | 16 | 70 |
| JUN-JUL-AUG 1978 S-C | 3.7 | 6.1 | 26 | 48 | 2.5 | 10.4 | 36 | 54 | 1.1 | 17.4 | 48 | 63 | 0.8 | 16.2 | 54 | 68 | 0.5 | - | 64 | 84 |
| JAN-FEB 1979 S-C | 0.7 | 2.7 | 64 | 93 | 0.6 | 2.5 | 68 | 95 | 0.5 | 2.9 | 73 | 95 | 0.5 | 2.8 | 75 | 96 | 0.4 | 3.6 | 75 | 94 |
| JUL-AUG 1977 C-C | 0.7 | 10.7 | 56 | 73 | 0.8 | 7.5 | 54 | 74 | 0.4 | 5.4 | 74 | 89 | - | - | - | - | 0.7 | 11.7 | 57 | 74 |
| FEB-MAR 1978 C-C | 0.9 | 3.2 | 56 | 90 | 0.7 | 3.5 | 63 | 88 | 0.4 | 2.5 | 82 | 98 | 0.6 | 3.3 | 70 | 90 | 0.8 | 2.1 | 56 | 72 |
| OCT-NOV 1978 C-C | 0.6 | 6.0 | 61 | 83 | 0.5 | 4.4 | 68 | 88 | 0.6 | 2.2 | 70 | 97 | 0.6 | 2.1 | 76 | 99 | 0.4 | 4.0 | 76 | 93 |
| NOV 1978 - JAN 1979 C-C | 0.7 | 2.6 | 62 | 95 | 1.0 | 2.4 | 50 | 89 | 1.0 | 1.8 | 54 | 98 | 0.9 | 1.7 | 60 | 99 | 0.5 | 3.2 | 72 | 94 |
| JUN 1977 S-U | 0.6 | 16.4 | 58 | 72 | 1.2 | 6.7 | 46 | 68 | 0.3 | 3.5 | 86 | 98 | 0.4 | 4.6 | 75 | 92 | 0.4 | 6.9 | 67 | 85 |
| AVERAGE | 1.12 |  |  |  | 1.00 |  |  |  | 0.67 |  |  |  | 0.75 |  |  |  | 0.69 |  |  |  |
| STANDARD DEVIATION | 0.93 |  |  |  | 0.60 |  |  |  | 0.38 |  |  |  | 0.29 |  |  |  | 0.48 |  |  |  |
| LIMITS ± | 0.61 |  |  |  | 0.39 |  |  |  | 0.25 |  |  |  | 0.21 |  |  |  | 0.32 |  |  |  |

FIGURE 4.8.

Concentration of PAH (ng $m^{-3}$) vs. stage number of the Andersen at various locations.



shown in Figure 4.8.

### 4.8.1 Discussion of PAH size distribution

To date only a limited number of studies have been reported relating the distribution of PAH with respect to particle size. Using a two-stage elutriator Demaio and Corn (1966) reported that in the atmosphere of Pittsburgh more than 75% by weight of selected PAH were associated with particles less than 5.0 μm in diameter. Using a four stage Casella cascade impactor backed up by a glass fibre filter, Kertesz-Saringer et al (1974) found that about half of the BaP in a polluted part of Budapest was associated with particles of radius 0.15 μm. Miguel and Friedlander (1978) using an eight stage low pressure impactor, reported 75% of BaP and 85% of coronene to be associated with particles less than 0.26 μm in diameter in the atmosphere of Pasadena. Using a six stage high volume cascade impactor, Van Vaeck and Van Cauwenberghe (1978) have found that between 95 and 98% of PAH are less than 3 μm during winter.

Three separate studies have been reported on the size distribution of PAH using high volume five stage Andersen cascade impactors. In the first, Albagli et al (1974) concluded that 85% of non-gaseous PAH in Ottowa are associated with particles less than 7 μm in diameter and that about 60% of the total is associated with particles less than 1.1 μm. In the second study, Starkey and Warpinski (1974) found that in central Green Bay, on average, only about 28% of BaP was associated with particles less than 1.1 μm in diameter. In the third study at several sites in Toronto, Pierce and Katz (1975) found that for all the test sites, 85 - 90% of the total PAH content was associated with particles less than 5 μm for the winter sampling period and 70 - 85% for the summer.

The data given in Table 4.9 shows that PAH in the atmosphere of a major U.K. city is primarily associated with particles less than one micron in diameter. As noted in Section 4.7.1 the relatively small size with which PAH are associated means that the residence time in the urban atmosphere will be considerable. The possibility therefore exists for individual particulate/PAH to become thoroughly mixed, leading to an homogenous urban aerosol. Thus, except where sampling is affected by a nearby emission source, the similarity of PAH concentrations found at three environmentally different sites is explained.

There is some evidence to suggest that the variability of MMED values at Salford Circus (S-C) is greater than at the University site (C-C). For example, at S-C the MMED for pyrene varies from 0.7 to 3.7 μm whilst at C-C the corresponding variation is 0.6 to 0.9 μm.

Seasonal trends in PAH size distributions have been discussed by Pierce and Katz (1975). The workers found that the MMED's of all PAH were lower in winter than in summer on data calculated from PAH distributions expressed in terms of μg PAH/g particulate. A comparison of the MMED's obtained at S-C during winter (January - February 1979) and summer (June - August 1978) is shown in Table 4.10. However, it would be unwise on the basis of this result to conclude that PAH generally increase in MMED values during the summer months. Van Vaecke et al have argued that increased emission of condensation aerosol generated by domestic space heating in winter causes the

TABLE 4.10

Comparison of winter and summer MMED values for PAH determined at S-C

| PAH | Summer<br>June-August 1978 | Winter<br>Jan-February 1979 |
|---|---|---|
| | µm | µm |
| Pyrene | 3.7 | 0.7 |
| Chrysene | 2.5 | 0.6 |
| BaP | 1.1 | 0.5 |
| BeP | 0.8 | 0.5 |
| Coronene | 0.5 | 0.4 |

change in size distribution. Further research will be required to determine whether the winter decrease holds generally and also if any annual trends in PAH size distribution can be observed.

Figure 4.8 shows that there is a marked change in PAH concentrations going from stage 4 (2.0 - 1.1 µm) to stage 5 (1.1 - 0.01 µm) and calculated MMED values for all PAH indicate that 50% by weight of PAH is associated with particles less than 1 µm in diameter.

Optical analysis of the aerosol deposited on each impaction filter (prior to PAH extraction) also revealed a distinction between particles on the fourth and fifth stages. It is noted that the degree of darkness increases with decreased particle size. Miguel and Freidlander (1978) using an eight stage impactor have also reported increased staining of filters at lower diameters. With the increasing resolving power, obtained by using extra stages, there workers found that maximum darkness was observed for particles in the range 0.075 - 0.12 µm.

More detailed optical analysis using the SEM also showed a difference between stages 1 to 4 and stage 5. Stages 1 to 4 contain rigid particles which can readily be distinguished from one another(see Figure 4.7). Stage 1 appears to comprise of large loose aggregates and some smaller 'harder' particles. Stage 2 again shows clearly defined individual particles, many with smooth surfaces. Stages 3 and 4 again contain fewer hard-type individual particles but appear to show some covering of carbon type aerosols. Moreover, on stage 5 there are few individual particles and the enlargement of stage 5 suggests that the globular carbon material has coalesced after impaction. Similar coalescence of small sized carbonaceous material has been reported. McCrone and Delly (1973).

This evidence clearly indicates that there is a general change in the nature of the aerosol less than 1.1 μm in diameter.

It has been suggested (Went, 1960) that atmospheric BaP and other PAH are adsorbed primarily on the surface of soot by hydrogen bonding. If it is assumed that the degree of darkness of the aerosol is a measure of the amount of soot present, as the evidence suggests, then these observations support Went's idea of PAH adsorption by soot. Lahaye and Prado (1974) have indicated that PAH are precursors of carbon (soot) particle formation, thereby representing a different mechanism for PAH - soot association. Whichever model accurately describes the PAH/soot relation it appears that in the urban atmosphere they are closely associated,with maximum concentration in the submicron range.

## 4.9 Results of elemental size distribution characteristics

It has been described earlier that physical and chemical information on atmospheric aerosols can be obtained using combined SEM and X-ray fluorescence techniques. This method described by Butler et al(1976) uses the electron beam of the SEM to generate fluorescence in the sample. The magnified image portrayed by the SEM allows chemical analysis by examination of the X-ray energy spectrum emitted by the image. Such a combined analysis technique was used to determine relative elemental concentrations on each stage of an Andersen sample collected at S - C.

X-ray fluorescence spectra of each stage was examined. The relative amounts of several components were determined with suitable corrections applied because of their presence, in low concentration, within the unexposed filters. Figure 4.9 shows a typical X-ray fluorescence spectrum obtained from the first stage of the Andersen. The concentration of each element was expressed in terms of arbitary units. The size distribution characteristics were obtained from graphical plots 100 - cumulative weight percent calculations (see Figure 4.10).

The estimated MMED's, geometric standard deviations and percentage by weight of each element less than or equal to 1 and 3 μm are given in Table 4.11.

### 4.9.1 Discussion of elemental size distributions

Generally the elements listed in Table 4.11 have greater MMED's than either particulate or PAH. This agrees with data published by Lee et al (1972) on the size distribution of metals in major U.S. cities and by Paciga and Jervis (1976) in Canada. (see Table 4.12) on the size distribution of some airborne metals.

In a recent study of urban aerosols of Nagoya in Japan,Kadowaki (1976) has reported a bimodal character with the two populations having MMED's of 0.4 - 0.6 μm and 3.0 - 5.0 μm. The larger particle size group consisted mainly of silicon, aluminium, iron, calcium, magnesium,

FIGURE 4.9.

X-ray fluorescence spectrum of sample obtained from Andersen experiment operated at S-C.

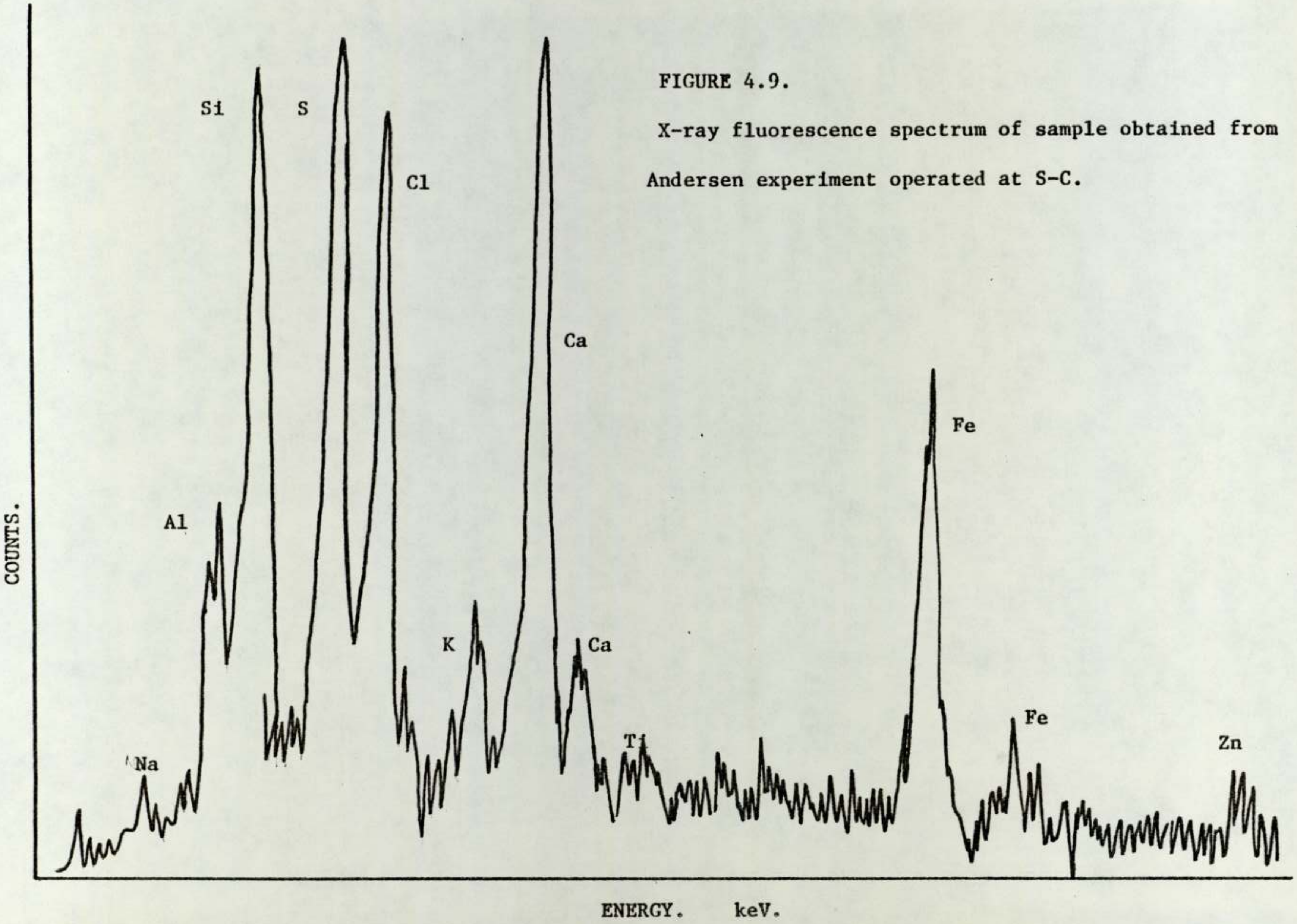


FIGURE 4.10. Elemental size distribution data obtained from Andersen results. S-C.

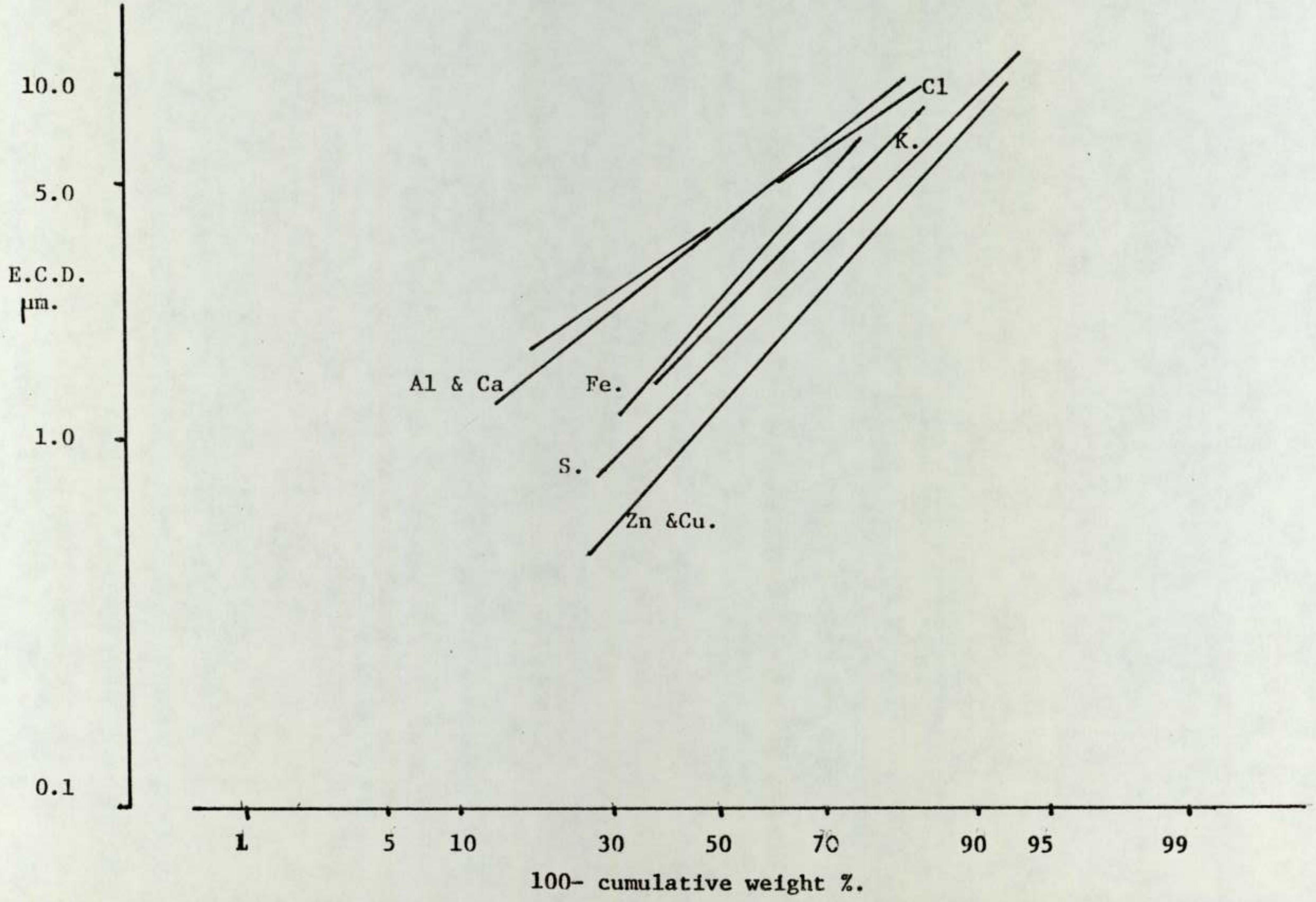


TABLE 4.11

MMED's, geometric standard deviations ($\sigma_g$) and the percentage of particulate containing the element which are less than 1 and 3 μm in diameter

| ELEMENT | MMED um | $\sigma_g$ | PERCENTAGE $\leq$ | |
|---|---|---|---|---|
| | | | 1.0 μm | 3.0 μm |
| Aluminium | 4.0 | 2.7 | 8 | 38 |
| Potassium | 2.5 | 3.4 | 22 | 56 |
| Calcium | 4.0 | 3.0 | 10 | 38 |
| Iron | 2.6 | 4.0 | 24 | 54 |
| Zinc | 1.3 | 4.3 | 42 | 72 |
| Sulphur | 1.8 | 3.5 | 30 | 65 |
| Chlorine | 4.0 | 2.4 | 5 | 36 |
| Titanium* | - | - | - | - |

* Titanium was found to be present only in stages 1, 2 and 3

sodium and chlorine. These distributions also agree with those found in the Birmingham aerosol.

It would appear that the elements listed in Table 4.12 are associated with particulate larger in size than are PAH. Consequently, the metals may not be readily available to catalyise PAH reactions and these elements are not small enough to penetrate deep into the human repiratory tract. The exception to this second point appears to be lead (MMED = 0.54 - 0.70 µm) which, therefore, represent a greater threat via inhalation.

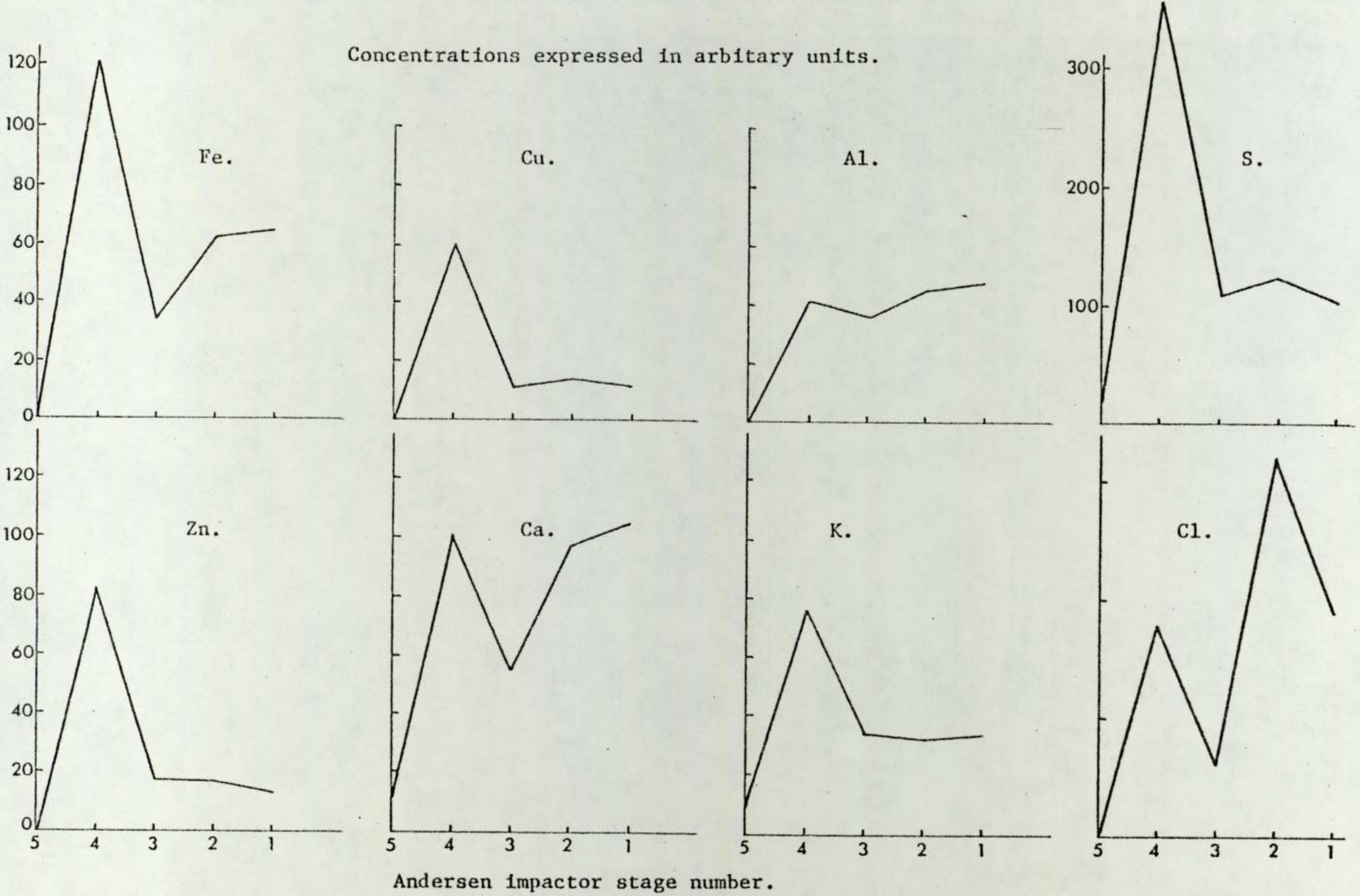
In addition to displaying increased MMED's, these elements also exhibit a marked difference in their concentration/stage number profiles. With PAH and particulate it was noted that maximum concentrations occurred on the final stage; for calcium and aluminium the maximum concentration was found on stage 1, for CL on stage 2 and for the rest on stage 4. The plots of elemental concentration vs stage number are shown in Figure 4.11.

## 4.10 Conclusion

Particulate aerosols of Birmingham have a mass median equivalent diameter of approximately 1 µm. It has also been shown that PAH are primarily associated with the sub-micron fraction of the aerosol. Several other named metals and elements which have been investigated are generally associated with particles greater than 2 µm in size.

Evidence is presented which indicates that the rate of elution of BaP from sub-micron aerosol is likely to be so rapid as to permit PAH to

FIGURE 4.11. Variation in elemental concentration with stage number.



Concentrations expressed in arbitary units.

TABLE 4.12

Metal size characteristics found in U.S. and Canadian cities, after Lee et al (1972) and Paciga and Jervis (1976). Taken from Butler 1979

| METAL | COUNTRY | ANNUAL MEAN CONCENTRATION µg m-3 | MMED µm | PERCENT ≤ 1.0 µm |
|---|---|---|---|---|
| Iron | U.S.A. | 1.02 | 2.73 | 17 |
| | Canada | 2.20 | 6.00 | 15 |
| Pb | U.S.A. | 1.92 | 0.54 | 68 |
| | Canada | 0.97 | 0.70 | 51 |
| Zn | U.S.A. | 0.55 | 1.25 | 40 |
| | Canada | 0.32 | 1.20 | 47 |
| Cu | U.S.A. | 0.18 | 1.33 | 35 |
| | Canada | 0.33 | 1.50 | 42 |
| Ni | U.S.A. | 0.06 | 1.33 | 39 |
| | Canada | 0.02 | 1.20 | 45 |
| Mn | U.S.A. | 0.05 | 1.97 | 25 |
| | Canada | 0.07 | 2.40 | 36 |

come into free contact with lung tissue. BaP/sub-micron particle systems have a greater carcinogenic effect than BaP/micron systems in experimental animals and, therefore, one may conclude that the PAH/carrier systems found in urban atmospheres fall in the particle size range that is potentially harmful to health.

# CHAPTER 5

# CHEMICAL REACTIVITY OF ATMOSPHERIC PAH

## 5.1 Introduction

It is important when considering the potential health hazard posed by atmospheric PAH to establish their lifetimes in the urban environment.

There are two separate influences which must be considered, one physical and the other chemical. Physical factors will include particle size, particle growth by coagulation and atmospheric scavenging processes such as dry deposition or precipitation. Chemical factors, on the other hand, will be governed by reaction initiated by sunlight and ozone or by interaction with other components that are present in atmospheric aerosols.

From the data presented in Chapter 4 and the work of Pierce and Katz (1975) there is clear evidence to indicate that PAH are primarily associated with the sub-micron fraction of the aerosol. Particles of such size are not only capable of penetrating deep into the respiratory system but are able to remain in the atmosphere for considerable periods of time. For instance, Esman and Corn (1971) have calculated that, in the absence of precipitation, the residence time of sub-micron particles will be $10^2$ - $10^3$ hours (4 - 40 days). The possibility exists, therefore, that these particles may be transported over long distances. Bjorseth et al (1979) have confirmed such long range transport of PAH laden aerosol. They have shown that airborne PAH concentrations in an air mass that had passed over the UK contained 2 - 3 ng $m^{-3}$ of BaP and 53 ng $m^{-3}$ of total PAH when monitored at Birkenes In Norway. These concentrations are similar to those experienced in urban atmospheres of Britain and suggests that long range transport has occurred without serious degradation of the PAH or dispersion of the aerosol.

## 5.2 Photochemical degradation of PAH

There is strong evidence to indicate that the lifetime of certain PAH may be affected by exposure to light. Thomas et al (1966) passed smoke, produced by the incomplete combustion of propane, into a 6" diameter pyrex tube. The tube, several meters in length, was surrounded by banks of fluorescent lamps. The PAH content of the smoke was determined at the entrance to and the exit from the reaction tube when the lights were on and off. From this work it was found that the half-lives of BaP was of the order of hours or days at the most. In a later paper Thomas et al (1968) concluded that 60% loss of BaP adsorbed onto soot would occur in 40 minutes if the soot was exposured to light of one quarter the intensity of mid-day, July sunlight.

The degradation of PAH has also been examined by Katz and Lane (1977). In addition to determining the effect of synthetic sunlight these workers examined the influence of ozone. PAH were spotted onto petri dishes and their rates of destruction monitored as a function of the following conditions:

1) artificial sunlight with no ozone
2) no sunlight, but ozone present in the range 0.19 - 2.28 ppm

and

3) artificial sunlight plus ozone.

During all the experiments the temperature of the reaction vessel was

TABLE 5.1

Measured halflives of PAH under various conditions. Katz and Lane, (1977).

| REACTION CONDITIONS | | HALF LIVES IN HOURS | | |
|---|---|---|---|---|
| Irradiation | Ozone (ppm) | Benzo [a] pyrene | Benzo [b] fluoranthene | Benzo [k] fluoranthene |
| - | 0.19 | 0.62 | 52.7 | 34.9 |
| - | 0.70 | 0.40 | 10.8 | 13.8 |
| - | 2.28 | 0.30 | 2.9 | 3.3 |
| ON | 0 | 5.3 | 8.7 | 14.1 |
| ON | 0.19 | 0.58 | 4.2 | 3.9 |
| ON | 0.70 | 0.20 | 3.6 | 3.1 |
| ON | 2.28 | 0.08 | 1.9 | 0.9 |

maintained at 35°C. The results obtained are shown in Table 5.1.

They indicate that sunlight can lead to 50% loss of PAH in less than one day, that the presence of an oxidising species, i.e. ozone, can also cause PAH degradation, that the rate of degradation caused by ozone alone is greater than that caused by sunlight, that the rate increases with increasing ozone concentration and that the rate of loss is greater under the influence of ozone and sunlight combined than under either separately.

Laboratory simulation, therefore, indicates that in the presence of ozone and sunlight PAH degradation takes place; such conditions will in the urban environment exist in summer but not during the winter months. In winter the only chemical route likely to cause a decrease in aerosol PAH content is interaction with other aerosol components. In polluted urban atmospheres the obvious canditates are the oxides of sulphur and nitrogen or their acid derivatives.

### 5.3 Exposure of PAH to laboratory air

Initial attempts to collect sufficient atmospheric aerosol to carry out experiments on PAH degradation proved to be impractical. It is known, however, that soot formation is always accompanied by production of PAH. Consequently, it was decided to generate soot/PAH from a flame in the laboratory using an ethene/air/oxygen/nitrogen gas mixture. The burner system employed is shown in Figure 5.1. Input of gases with typical compositions as shown in Table 5.2 resulted in soot/PAH production within the conical nexus. The operation of the burner system is described more fully by Page and Ates (1978).

FIGURE 5.1. Soot producing burner system.

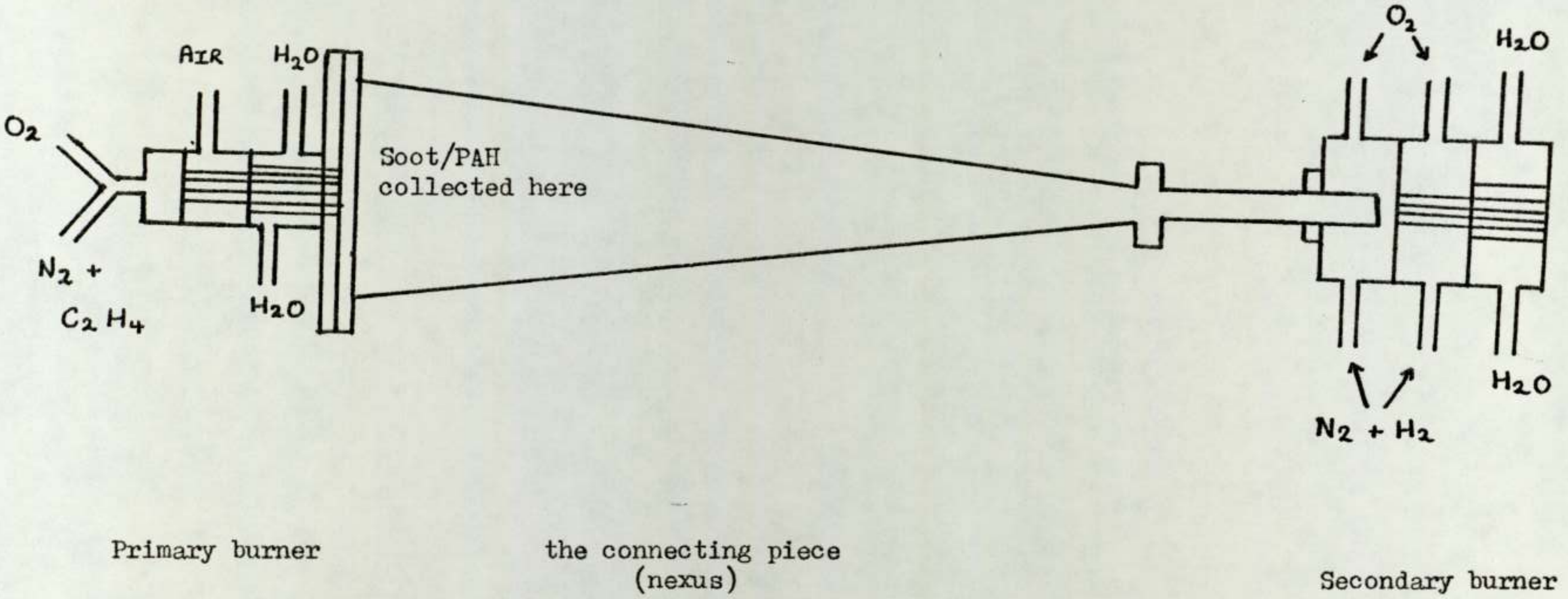


TABLE 5.2

Typical gas compositions fed to the primary burner to generate soot deposition within the nexus

| PRIMARY BURNER GAS FEED | 1 min$^{-1}$ | % vol. | % wt. |
|---|---|---|---|
| $O_2$ | 0.45 | 29 | 33 |
| $N_2$ | 0.30 | 40 | 38 |
| $C_2H_4$ | 0.61 | 31 | 29 |
| Air | 0.61 | - | - |

Samples of the soot/PAH mixture were collected, thoroughly mixed and placed in a beaker. The soot was protected from sunlight by surrounding the glass container with 'silver' foil but free exposure to laboratory air was allowed. From this sample small amounts of soot, between 0.02 and 0.04g, were removed periodically. The PAH content of these samples was analysed using the dimethyl sulphoxide/n-pentane method discussed in Chapter 2.

Table 5.3 shows the recoveries of various PAH after exposure to laboratory air for various periods of time.

Although the soot was well mixed before being placed in the glass beaker, sample inhomogeneity caused some variation in the concentration of individual PAH measured. To assist in the interpretation of the results the mean, standard deviation and limits expressed at the 90% confidence level were calculated. Table 5.4 shows the analysis of the results given in Table 5.3. The final column in Table 5.4 is the ratio of the limit to the mean expressed as a percentage and gives some indication of the degree of variability within the results.

These data indicate that even after more than 200 days of exposure to ambient air, but in the absence of direct sunlight, there has been no significant change in the concentrations of PAH recovered from soot. The figures in the last column indicate statistically that the limits of the mean are usually less than 15% of the calculated mean. Indeed the mean of the ten values in the final column is only 13.9%, i.e. at the confidence level quoted, 90 results out of every

TABLE 5.3

Concentrations of PAH (mg $kg^{-1}$) recovered from soot after exposure to laboratory air for different time periods

| | TIME IN DAYS | | | | | | |
|---|---|---|---|---|---|---|---|
| PAH | 3 | 14 | 20 | 34 | 52 | 143 | 231 |
| Phenanthrene | 63 | 52 | 62 | 130 | 79 | 58 | 52 |
| Fluoranthene | 2698 | 2440 | 2209 | 2461 | 2231 | - | 2819 |
| Pyrene | 5103 | 3790 | 4532 | 3773 | 5331 | 4681 | 5197 |
| Chrysene | 265 | 208 | 239 | 126 | 249 | - | 185 |
| Benz [ a ] anthracene | 781 | 380 | 590 | 1093 | 724 | 627 | 448 |
| Benzo [ a ] pyrene | 1581 | 1093 | 1230 | 1235 | 1365 | 1104 | 1206 |
| Benzo [ e ] pyrene | 952 | 716 | 834 | 808 | 886 | 667 | 749 |
| Anthanthrene | 1388 | 948 | 1037 | 1184 | 1093 | - | 1170 |
| Benzo [ ghi ] perylene | 2871 | 2850 | 2677 | 2336 | 2587 | - | 2827 |
| Coronene | 1108 | 717 | 516 | 850 | 634 | 345 | 701 |

TABLE 5.4

Mean Concentration of PAH recovered from soot after 231 days of exposure to laboratory air (mg kg$^{-1}$).

| PAH | MEAN CONCENTRATION LIMITS AT 90% (mg kg$^{-1}$) | STANDARD DEVIATION (s$_g$) | NO. OF READINGS | LIMITS% MEAN |
|---|---|---|---|---|
| Phenanthrene | 72 ± 18 | 26 | 8 | 25 |
| Fluoranthene | 2441 ± 222 | 310 | 7 | 9 |
| Pyrene | 4717 ± 439 | 625 | 8 | 9 |
| Chrysene | 212 ± 34 | 47 | 6 | 16 |
| Benz [a] anthracene | 671 ± 145 | 206 | 8 | 22 |
| Benzo [a] pyrene | 1272 ± 117 | 166 | 8 | 9 |
| Benzo [e] pyrene | 812 ± 93 | 141 | 8 | 11 |
| Anthanthrene | 1130 ± 99 | 129 | 7 | 9 |
| Benzo [ghi] perylene | 2681 ± 237 | 237 | 7 | 7 |
| Coronene | 688 ± 149 | 212 | 8 | 22 |

100 will be within 14% of the mean and this for a range of 10 PAH.

## 5.4 Exposure of PAH to air containing 5 ppm of sulphur dioxide ($SO_2$)

In order to examine the effect of oxides of sulphur on PAH lifetimes a slightly more complex arrangement was devised. Again soot/PAH was produced and collected from a multi-gas burner with similar gas ratios as shown in Table 5.2.

In this series of experiments the soot was exposed to air containing a known concentration of $SO_2$. This was achieved by drawing filtered air over a permeation tube containing $SO_2$ and then over the PAH/soot contained in a reaction vessel. (see Figure 5.2).

O'Keeffe and Ortman (1966) demonstrated that leakage of a gas contained within a Teflon tube occurs by permeation of the gas through the tube wall. The rate of gas loss into a dry atmosphere remains remarkably constant and may be measured by periodically determining the weight loss gravimetrically. The concentration (C) of the gas in parts per million in a flow of diluent gas $F_D$ (whose rate is given in ml $min^{-1}$) is given by -

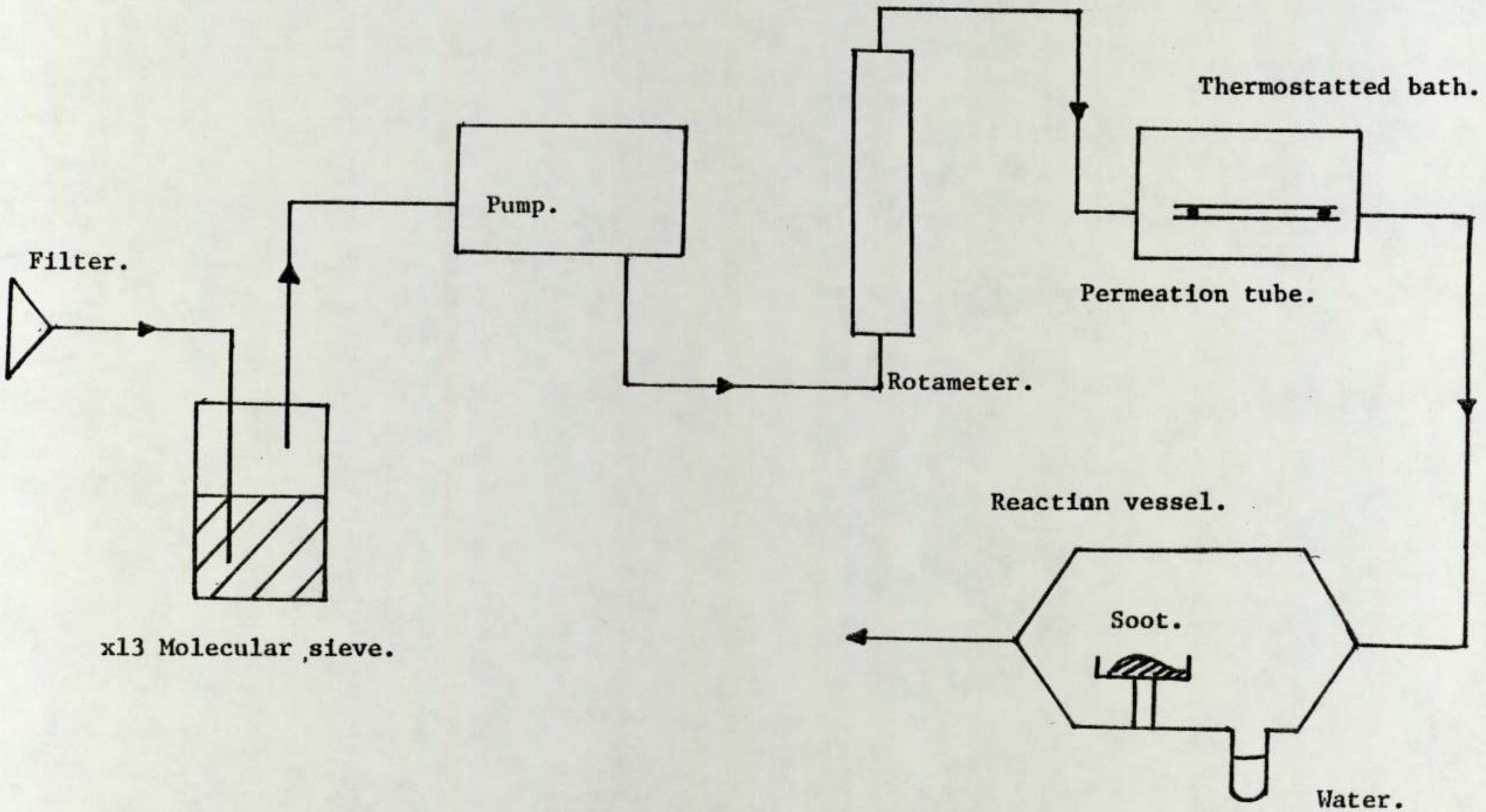
$$C = \frac{22.4 \times P_R \times T}{273 \times F_D \times M}$$

Where $P_R$ is the permeation rate of the gas (ng $cm^{-1}$ $min^{-1}$), T is the temperature and M is the molecular weight of the gas.

Using Teflon tubes containing $SO_2$ (BDH) and sealed with steel ball

FIGURE 5.2.

Scheme showing the arrangement used to expose PAH/ soot to a known concentration of $SO_2$.



bearings, air containing 5 ppm of $SO_2$ was allowed to pass over soot/PAH stored in a pyrex reaction chamber. The reaction chamber also contained a thimble of water because Novakov et al (1974) have shown that $SO_2$ can be converted into sulphuric acid in the presence of water vapour, air and soot. The soot acts as a catalyst and in attempting to simulate natural conditions as far as possible it was thought essential that any potential interation between sulphuric acid and PAH should be allowed.

Again samples of soot were withdrawn periodically from the reaction chamber and the concentrations of various PAH were determined. The results of these determinations are shown in Table 5.5 with the statistical analysis being given in Table 5.5.a

The concentration of 5 ppm of $SO_2$ used in this experiment corresponds to the Threshold Limit Value (TLV) and is certainly in excess of concentrations normally encounted in polluted atmospheres. During the London air pollution episodes of 1952, for instance, the highest daily concentration of $SO_2$ monitored was 1.46 ppm. Waller and Commins(1966). As with the soot sample exposed to laboratory air there is some variation in results and this is probably due to sample inhomogeneity. Nevertheless, it is clearly apparent that this concentration of $SO_2$ has failed to significantly alter PAH concentration over a period of nearly three months.

It can be seen that for Benzo [a] anthracene, BaP, BeP, anthanthrene and benzo [ghi] perylene, the variation (i.e. limit/mean%) has increased (the values for the other PAH are remarkably similar).

TABLE 5.5

Concentrations of PAH (mg $kg^{-1}$) recovered from soot after exposure to air containing 5 ppm $SO_2$ for different time periods.

| PAH | TIME IN DAYS | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | 0 | 12 | 19 | 27 | 49 | 66 | 87 | 99 |
| Phenanthrene | 168 | 167 | 87 | 112 | 93 | 64 | 182 | 108 |
| Fluoranthene | 4279 | 4069 | 4984 | 4310 | 4116 | 4009 | 5230 | 5241 |
| Pyrene | 7766 | 7172 | 7431 | 7725 | 8039 | 6084 | 8916 | 9217 |
| Chrysene | - | - | 529 | 514 | 478 | 311 | 430 | 366 |
| Benz [a] anthracene | 651 | 522 | 693 | 1126 | 2013 | - | 1664 | 1538 |
| Benzo [a] pyrene | 1105 | - | 1551 | 1372 | 1753 | 1204 | 776 | 959 |
| Benzo [e] pyrene | 883 | 1663 | 857 | 928 | 1144 | 658 | 553 | 963 |
| Anthanthrene | 1093 | 1701 | 1348 | 1064 | 1737 | 854 | 1151 | 726 |
| Benzo [ghi] perylene | 2896 | - | 3540 | 2617 | 4228 | 2342 | 2125 | 2601 |
| Coronene | 479 | 861 | 847 | 610 | 993 | 588 | 778 | 408 |

TABLE 5.5a

Statistical analysis of PAH recovery from soot after exposure to air containing 5 ppm of $SO_2$

| PAH | MEAN CONCENTRATION AND LIMIT* ($mg\ kg^{-1}$) | STANDARD DEVIATION ($s_g$) | NO. OF READINGS | LIMIT% MEAN |
|---|---|---|---|---|
| Phenanthrene | 123 ± 29 | 41 | 8 | 24 |
| Fluoranthene | 4530 ± 354 | 496 | 8 | 8 |
| Pyrene | 7794 ± 658 | 921 | 8 | 8 |
| Chrysene | 438 ± 71 | 79 | 6 | 16 |
| Benzo [a] anthracene | 1172 ± 424 | 536 | 7 | 36 |
| Benzo [a] pyrene | 1246 ± 249 | 314 | 7 | 20 |
| Benzo [e] pyrene | 956 ± 226 | 317 | 8 | 24 |
| Anthanthrene | 1209 ± 245 | 342 | 8 | 20 |
| Benzo [ghi] perylene | 2907 ± 540 | 682 | 7 | 19 |
| Coronene | 696 ± 137 | 196 | 8 | 20 |

* limits expressed at 90% confidence level

However, in general, the rate of any degradation is so slow that loss of even submicron aerosol from the atmosphere would be more rapid.

It is concluded that degradation of PAH by elevated concentrations of $SO_2$ is unlikely to play a significant role in the removal of PAH from the atmosphere.

## 5.5 Exposure of PAH to air containing 12 ppm of NOx

Another possible source of chemical attack of PAH in the atmosphere are the oxides of nitrogen. As in the previous section samples of soot/PAH were produced from the primary burner. These samples were mixed and placed in the reaction chamber of the apparatus shown in Figure 5.2. On this occasion the permeation tube contained oxides of nitrogen. Stoichiometric quantities of nitric oxide and air were mixed and allowed to condense at liquid nitrogen temperature to give a pale blue solid of dinitrogen trioxide:

$$2\,NO + \tfrac{1}{2}\,O2 \rightleftharpoons N2\,O_3$$

The solid was allowed to melt to give a deep blue liquid which was placed in a permeation tube. The tube itself was made of Teflon having an effective length of approximately 10 cm.and an internal diameter of 0.5 cm. Both ends of the tube were sealed using stainless steel ball-bearings.

The nitrogen oxide to nitrogen dioxide ratio derived from the $N_2\,O_3$ in the permeation tube will be richer in $NO_2$ than the ratio normally attained in air. Nevertheless, the use of $N_2\,O_3$ is very convenient experimentally and this advantage, at least for these prelimary experiments, outweighed the disadvantages.

Again the tube was weighed periodically in order to determine the rate of loss of the contents. In the previous section a relationship between the concentration of the pollutant gas (in ppm) and its molecular mass was indicated. In the case of $SO_2$ the molecular mass is known but in this experiment loss of gas from the tube will be in the form of several different oxides of nitrogen. To calculate a concentration, the molecular mass of $N_2O_3$ was ascribed to the chemical species designated NOx. The flowrate of diluant gas was then adjusted so that the concentration of NOx in the reaction chamber was 12 ppm.

Periodically, samples of soot/PAH exposed to the NOx were removed and analysed for PAH as before. These values of individual PAH in mg $kg^{-1}$ are shown in Table 5.6.

Table 5.6 shows that decreasing concentrations of PAH were recovered as exposure times increased. For several PAH the recovery after 39 days is only about 10% of the original recovery. Figure 5.3 shows the change in benz [a] anthracene concentration with respect to time. Similar trends are observed for other PAH.

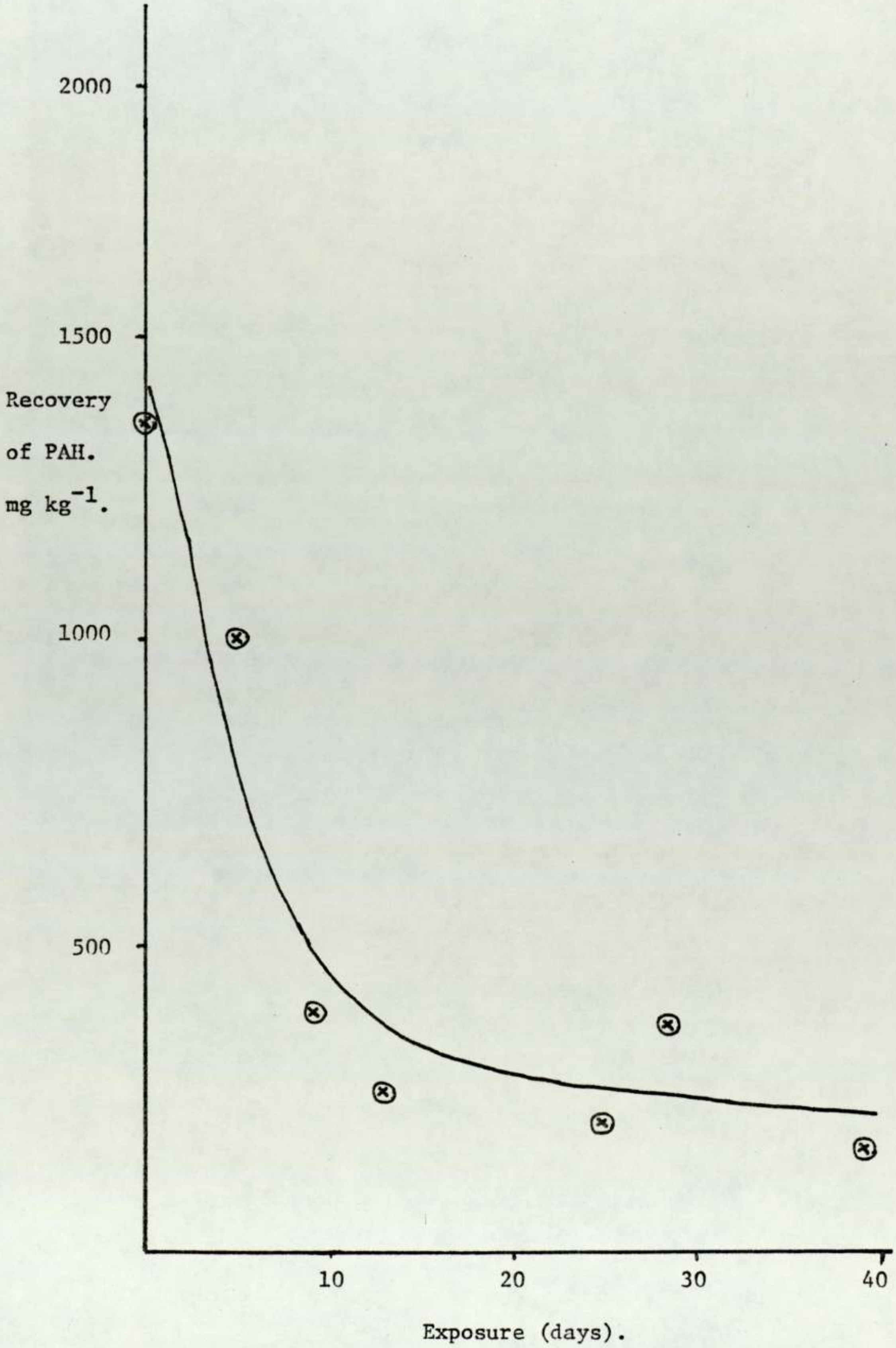
Butler et al (1975) have reported that concentrations of NOx in the urban atmosphere will only reach 1 ppm in close proximity to very dense traffic. (TLV for NO is 25 ppm and for $NO_2$ 5ppm.) The concentration of NOx used is, therefore, greater than the maximum values found in heavily polluted atmospheres but less than threshold limit

TABLE 5.6:

Concentrations of PAH (mg $kg^{-1}$) recovered from soot after exposure to air containing 12 ppm NOx for different time periods.

| | | | | DAYS. | | | |
|---|---|---|---|---|---|---|---|
| PAH | 0 | 5 | 8 | 13 | 25 | 29 | 39 |
| Phenanthrene | 244 | 186 | 195 | 165 | 136 | 122 | 70 |
| Fluoranthene | 7443 | 6162 | 5901 | 3959 | 3492 | 4789 | 2768 |
| Pyrene | 7743 | 7567 | 8072 | 4289 | 2288 | 3123 | 1103 |
| Chrysene | 433 | 320 | 291 | 195 | 268 | 251 | 244 |
| Benz [a] anthracene | 1355 | 994 | 382 | 250 | 207 | 365 | 157 |
| Benzo [a] pyrene | 1557 | 776 | 712 | 246 | 286 | 215 | 135 |
| Benzo [e] pyrene | 1108 | 694 | 880 | 344 | 437 | 607 | 356 |
| Anthanthrene | 1209 | 223 | 215 | 56 | 21 | 26 | 0 |
| Benzo [ghi] perylene | 2931 | 1956 | 1656 | 692 | 571 | 760 | 287 |
| Coronene | 586 | 627 | 646 | 204 | 314 | 402 | 204 |

FIGURE 5.3 Recovery of Benz (a) anthracene from soot after exposure to 12 ppm $NO_x$.



values. The results shown in Table 5.6 should be analogous to the behavious of PAH adsorbed onto soot in heavily polluted atmospheres.

Table 5.6 also indicates that the rate of decreasing recovery of PAH varies from compound to compound, i.e. some PAH react more rapidly than others. The implications of this observation are discussed in the next section.

## 5.6 Exposure of PAH to air containing 5 ppm of $SO_2$ and 10 ppm of NOx

In the real urban atmosphere $SO_2$ and $NO_x$ can usually be measured together. There is, therefore, the possibility that some synergistic influence might exist between them. To examine this a reaction scheme similar to that shown in Figure 5.2 was employed but on this occasion the thermostatted tank held two permeation tubes, one for $SO_2$ and one for $NO_x$. The weight loss of the tubes were determined from time to time and the concentrations of the pollutant gases were calculated. The flowrate of air over the permeation tubes was such that concentrations of 5 ppm and 10 ppm were attained for $SO_2$ and $NO_x$ respectively. As before samples of soot exposed to these pollutants were removed periodically and the PAH content determined. The results obtained are shown in Table 5.7

The results indicate that concentrations of PAH have, as in the previous section, been dramatically reduced. Again the rate of loss varies from PAH to PAH but the rate of loss for each individual PAH is very similar to that observed when the soot was exposed to air containing 12 ppm NOx. This fact would seem to indicate

TABLE 5.7

Concentrations of PAH (mg $kg^{-1}$) recovered from soot after exposure to air containing 5 ppm $SO_2$ and 10 ppm $NO_x$ for different time periods

|  | DAYS. |  |  |  |  |  |
|---|---|---|---|---|---|---|
| PAH | 0 | 5 | 12 | 21 | 29 | 51 |
| Phenanthrene | 257 | 213 | 226 | 254 | 193 | 148 |
| Fluoranthene | 5031 | 4397 | 4103 | 4845 | 3837 | 2498 |
| Pyrene | 9624 | 6153 | 4240 | 6772 | 997 | 957 |
| Chrysene | 573 | - | - | 475 | 344 | 203 |
| Benz [a] anthracene | 1562 | 851 | 674 | 493 | 310 | 246 |
| Benzo [a] pyrene | 3622 | 1073 | - | 294 | 384 | 74 |
| Benzo [e] pyrene | 1140 | 1207 | 916 | 625 | 545 | 195 |
| Anthanthrene | 1739 | 623 | 204 | 58 | 0 | 0 |
| Benzo [ghi] perylene | 4835 | 2535 | - | 616 | 175 | 156 |
| Coronene | 1054 | 837 | 873 | 293 | 430 | 149 |

that the $SO_2$ is still having no obvious effect on the life-time of the PAH. The similarity in rate of PAH loss when exposed to 12 ppm NOx and when exposed to 5 ppm $SO_2$ and 10 ppm NOx can be readily demonstrated by considering anthanthrene. If the results are normalised, i.e. by expressing the recovery at any given time as a percentage of the recovery at time $t = 0$ days, they may be more easily compared. The recoveries of anthanthrene (mg $kg^{-1}$) for both sets of exposure are given in Table 5.8 together with the normalised results and the combined percentage recoveries. A plot of the combined recovery (%) v time for anthanthrene and, for comparison, BeP is shown in Figure 5.4.

## 5.7 Discussion

The information given in the two previous sections indicates that NOx in air leads to decreasing recoveries of PAH adsorbed onto soot. Apparently, exposure to $SO_2$ does not produce a similar result and there is no obvious change in the rate of destruction when $SO_2$/NOx is used as compared with NOx alone.

Normalising and combining the results of $SO_2$/NOx and NOx exposure may be displayed graphically as in Figure 5.4. From these results the first order rate constant (k) and the half-life ($t\frac{1}{2}$) may be calculated from the equation

$$\ln \frac{Co}{C} = kt$$

Where Co is the concentration at t = o (i.e. 100%) and C is the concentration (percentage) at a time (t), the half-life will be when Co = 2C or

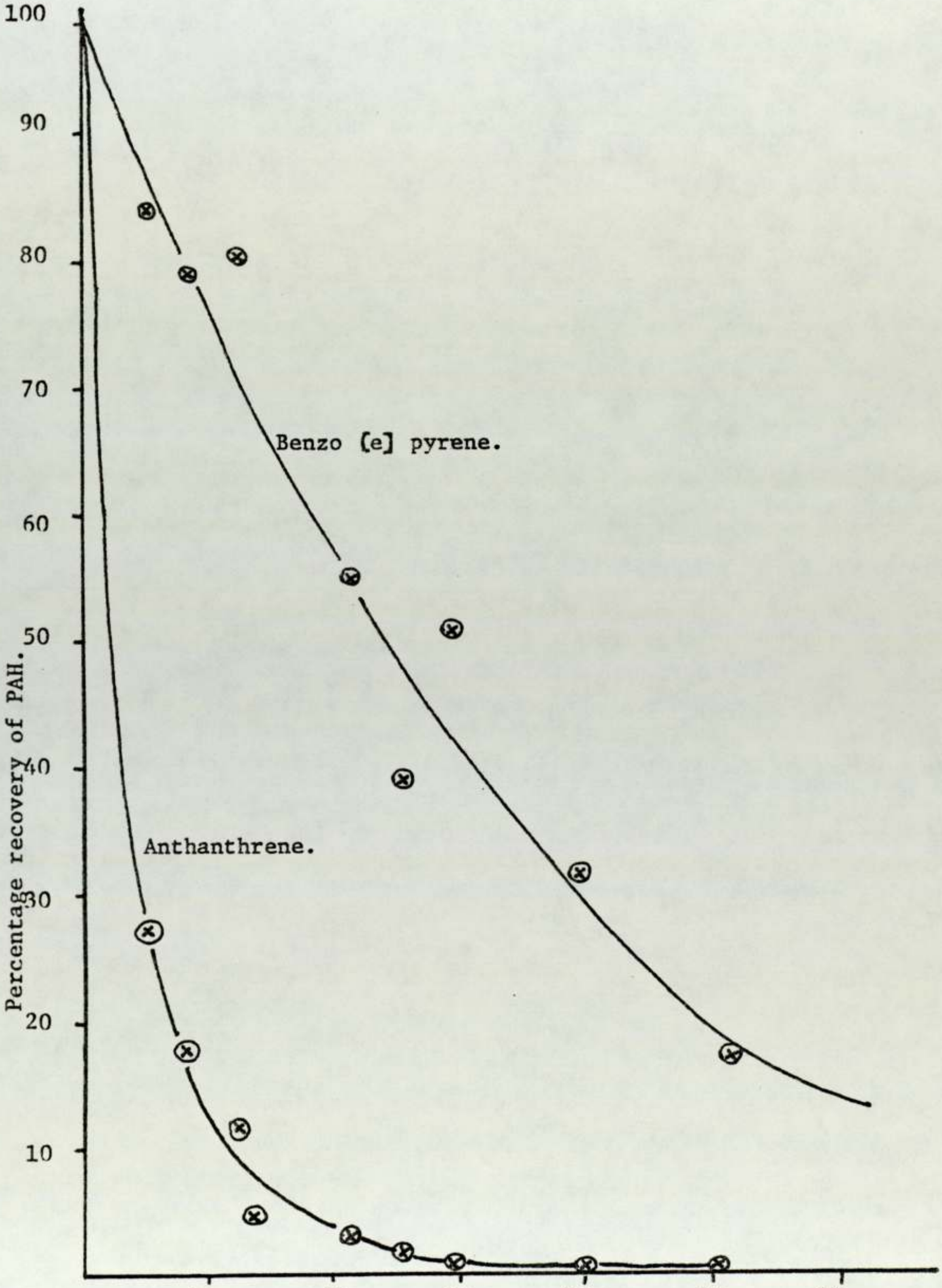
$$\frac{\ln 2}{k} = t\tfrac{1}{2}$$

TABLE 5.8

Recovery of anthanthrene from soot after exposure to $SO_2$/NOx and NOx.

| TIME OF EXPOSURE (DAYS) | RECOVERY AFTER EXPOSURE TO :- |  | NORMALISED RECOVERY % |  | COMBINED RECOVERY % |
|---|---|---|---|---|---|
|  | NOx | $SO_2$/NOx | NOx | $SO_2$/NOx |  |
| 0 | 1209 | 1739 | 100 | 100 | 100 |
| 5 | 223 | 623 | 18.4 | 35.8 | 27.1 |
| 8 | 215 | - | 17.1 | - | 17.8 |
| 12 | - | 204 | - | 11.7 | 11.7 |
| 13 | 56 | - | 4.6 | - | 4.6 |
| 21 | - | 58 | - | 3.3 | 3.3 |
| 25 | 21 | - | 1.7 | - | 1.7 |
| 29 | 26 | 0 | 2.2 | 0 | 1.1 |
| 39 | 0 | - | 0 | - | 0 |
| 51 | - | 0 | - | 0 | 0 |

FIGURE 5.4 Decrease in recovery of anthanthrene and benzo [e] pyrene with time following exposure to $NO_x$.



An example of such an interpretation is given in Table 5.9 where the mean rate constant and half-life of anthanthrene is calculated. The results of similar calculations for the other PAH are given in Table 5.10, arranged in order of increasing values of $t\frac{1}{2}$.

The results show that the half-lives of several PAH commonly found in the urban environment when exposed to relatively high concentrations of NOx are generally shorter than a month. Obviously the order is not related to the boiling points or molecular weights of the compounds; for instance the isomers BaP and BeP have half-lives of 6.9 and 23 days respectively. An explanation of the reported order may be derived from the work of Dewar. Dewar (1952), Dewar et al (1956 a) and Dewar et al (1956 b) have calculated the energy required to localise electronic groupings at specific sites within a molecule. This energy, called the localisation energy($\beta$), is a measure of the susceptibility of a site to electrophilic attack, that is to say the lower the value of $\beta$ at a site then the more readily will electrophilic substitution take place. Not only may the partial rate factors for the nitration of PAH be determined (Dewar (1956c)) but the relative positions of nitration may also be identified within a molecule. For example, the values of $\beta$ for the various sites within the BaP molecule are shown in Figure 5.5.

Electrophilic substitution can occur at any of the numbered sites but from the $\beta$ values it is apparent that site 6 is the preferred one. Indeed the total nitration products consist almost entirely of 6, 3 or 1 nitro benzo [a] pyrene. Table 5.11 lists the calculated half-lives together with the lowest localisation energies for each PAH

TABLE 5.9

Calculation of first order rate constant (k) and half-life of anthanthrene exposed to NOx

| TIME IN DAYS(t) | CONCENTRATION % C | $\frac{Co}{C}$ | $\ln \frac{Co}{C}$ | $\frac{1}{t} \ln \frac{Co}{C} = k$ |
|---|---|---|---|---|
| 0 | 100 | | | $day^{-1}$ |
| 5 | 27.1 | 3.69 | 1.31 | 0.2612 |
| 8 | 17.8 | 5.62 | 1.73 | 0.2158 |
| 12 | 11.7 | 8.55 | 2.15 | 0.1788 |
| 13 | 4.6 | 21.74 | 3.08 | 0.2368 |
| 21 | 3.3 | 30.30 | 3.41 | 0.1624 |
| 25 | 1.7 | 58.82 | 4.08 | 0.1630 |
| 29 | 1.1 | 90.91 | 4.51 | 0.1555 |
| | | | MEAN = | 0.190 |

Mean = 0.190 ± 0.025

Standard deviation = 0.030

$$\text{Half life (days)} = \frac{1}{k} \ln \frac{100}{50} = \frac{1}{0.190} \ln 2$$

$$= 3.65 \text{ days}$$

TABLE 5.10

Calculated first-order rate constants and half-lives of PAH exposed to air containing 12 ppm NOx and 5 ppm $SO_2$ or 10 ppm NOx

| PAH | MEAN RATE CONSTANT $day^{-1}$ | STANDARD DEVIATION | NUMBER OF DETERMINATION | HALF LIFE DAYS |
|---|---|---|---|---|
| Anthanthrene | 0.190 ± 0.025 | 0.030 | 7 | 3.7 |
| BaP | 0.101 ± 0.023 | 0.030 | 7 | 6.9 |
| Benzo [ghi] perylene | 0.082 ± 0.015 | 0.019 | 7 | 8.4 |
| Benz [a] anthracene | 0.064 ± 0.013 | 0.016 | 7 | 11 |
| Pyrene | 0.050 ± 0.006 | 0.008 | 7 | 14 |
| BeP | 0.030 ± 0.004 | 0.006 | 8 | 23 |
| Chrysene | 0.026 ± 0.012 | 0.017 | 8 | 27 |
| Fluoranthene | 0.026 ± 0.007 | 0.011 | 9 | 27 |
| Coronene | 0.024 ± 0.006 | 0.008 | 7 | 29 |
| Phenanthrene | 0.023 ± 0.009 | 0.011 | 7 | 30 |

FIGURE 5.5

Localisation energies ($\beta$) of sites within the benzo [a] pyrene molecule. Dewar (1952)

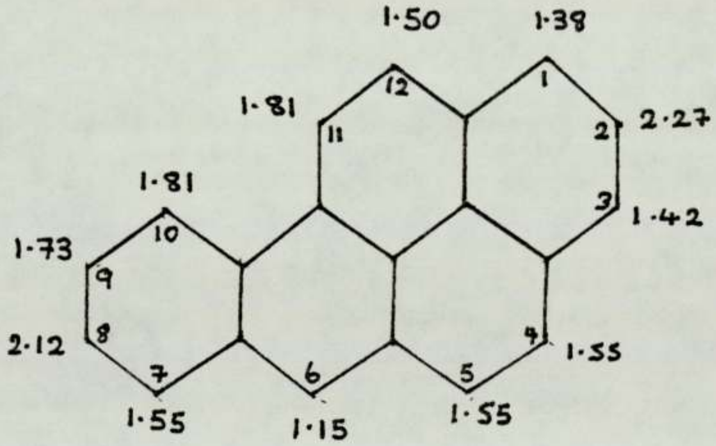


TABLE 5.11

Calculated half-lives of PAH exposed to NOx together with the lowest localisation energies within the ring system

| PAH | HALF-LIFE DAYS | LOCALISATION ENERGY ($\beta$) (ARBITARY UNITS) | SITE IN RING SYSTEM |
|---|---|---|---|
| Anthanthrene | 3.7 | 1.03 | 6 |
| Benzo [a] pyrene | 6.9 | 1.15 | 6 |
| Benzo [ghi] perylene | 8.4 | - | - |
| Benzo [a] anthracene | 11 | 1.35 | 7 |
| Pyrene | 14 | 1.51 | 1 |
| Benzo [e] pyrene | 23 | 1.63 | - |
| Chrysene | 27 | 1.67 | 2 |
| Fluoranthene | 27 | - | 3 |
| Coronene | 29 | 1.80 | 1 |
| Phenanthrene | 30 | 1.79 | 9 |

and the location of this site in the ring system.

Thus, the reactivity order found for PAH exposed to NOx/air atmospheres and the correlation with Dewar's work strongly indicate that a chemical route exists in the atmosphere, even in the absence of photolytic degradation, whereby PAH may be converted to a substituted nitro form.

In view of these findings it is pertinent to enquire into the carcinogenicity of these nitro derivatives. The survey carried out by the U.S. Department of Health, Education and Welfare (1970 - 1971) lists 6-nitro-benzo [a] pyrene, 7 nitro-benz [a] anthracene, nitropyrene and nitrochrysene as non carcinogenic.

Hence, it may be concluded that a chemical route exists whereby carcinogenic benzo [a] pyrene may be converted to the non-carcinogenic 6- nitroderivative and thus an aged aerosol in polluted air should not be as hazardous as a newly formed one.

# CONCLUSIONS.

The principal observations derived from the work described in this presentation may be summerised as:

1).PAH may be quantitatively extracted from atmospheric particulate using dimethyl sulphoxide.The described procedure has the advantage of efficiently separating the aromatic from the aliphatic content of the total extract.

2).PAH may be readily concentrated in small volumes of n-pentane by their back extraction from aqueous dimethyl sulphoxide.

3).Complex mixtures of PAH may be satisfactorily separated by elution on a 15cm. long alumina column of 6%water content.

4).Treating the glass fibre filters used to collect the particulate with a loading of 1mg $cm^{-2}$. of glyceryl tripalmitate leads to increased recovery of volatile PAH. For pyrene recovery from untreated filters is only 60% of that from treated filters.

5).The concentrations of five PAH have been routinely determined at three environmentally dissimilar sites around Birmingham. The results at the sites are generally less than 10ng $m^{-3}$ for all the PAH measured and each displays marked seasonal variation. Multiple regression analysis between concentration and various meteorological parameters has been used to compare monitored and predicted concentrations of PAH.

6).The concentrations found have been compared to those reported 20-30 years ago; they demonstrate a general decline in ambient PAH concentrations during that period.

7). PAH have been monitored within a residential property at concentrations similar to those experienced out of doors.

8).The current atmospheric BaP content has been calculated in terms of cigarette equivalents and compared to the value which might have been experienced 25 years ago. The data indicates that breathing the atmosphere of Birmingham is presently equivalent to smoking one cigarette per day whereas 25 years ago the figure might have been closer to 14 cigarettes per day.

9).Size distribution analysis has revealed that the urban aerosol of Birmingham has a mass mean equivalent diameter (MMED) of approximately 1μm,that PAH are generally associated with sub-micron particulate and that several metals found in the atmosphere have MMED's significantly greater than 1μm. There is obvious scope here for more work.For example, more data will be required to identify seasonal and annual trends .

10).Decreased recovery of PAH adsorbed onto soot was noted after the exposure of the soot to atmospheres containing $NO_x$. The rate of loss of the PAH was found to correlate with known electronic properties of the individual PAH molecule.The presence of $SO_2$ had no effect on the rates.Examination of the available literature indicates that the nitro-derivatives of PAH are generally non-carcinogenic.Thus it has been concluded that there may be a chemical route in polluted atmospheres whereby the' total carcinogenic burden might be reduced.

This particular series of experiments should be regarded only as the initial steps in this area of the work. Clearly more work will be required to see if these findings may be applied to real atmospheres. Detailed examination of the chemical species involved in the reactions will be required as will information on possible synergistic effects,the effects temperature and pressure and the concentrations required for the reaction to proceed. What the work does indicate is that the ratio between pairs of PAH in an urban atmosphere may be related more to the age of the aerosol than to the source of their formation.

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