To My Parents

UNIVERSITY OF SOUTHAMPTON

POLYCYCLIC AROMATIC HYDROCARBONS IN SEASONAL SNOWCOVER

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ABSTRACT

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The chemical composition of snow can, under some circumstances, be used as a monitoring tool for the estimation of atmospheric contamination. Snowfall is often the most important hydological event in many parts of the world.

Polycyclic aromatic hydrocarbons are an important and wide-spread class of environmental contaminants. Many of them have been demonstrated to have toxic and/or carcinogenic properties. PAHs are prevalent in the atmosphere at trace-levels, and therefore can be expected to be incorporated in snowfall.

A sampling methodology and analytical protocol was devised to measure trace-level PAHs in snow. Samples of snow were collected from three contrasting locations: i) a remote, sub-arctic, mountain catchment in the Cairngorm Mountains of Scotland, ii) a remote boreal forest site in the Laurentian Mountains of Canada, and iii) urban and rural sites in Southern England. The samples were analysed by high performance liquid chromatography and gas chromatography with mass spectrometry detection for a maximum of 18 PAH compounds in both the dissolved and the particulate phases.

Total PAH concentrations found in aged snowpack in Scotland are high (max. 3500 ng l^{-1}). This is typical of the PAH content of snow in urban regions, and is consistant with results from previous studies of snow from the same location which show elevated concentrations of trace-metals, owing to the long-range transport of contaminants from source regions. Fresh snow had lower PAH values (c. 200 ng l^{-1}), more representative of snow from remote areas. A possible positive correlation between snow acidity and PAH content was observed, and there are indications that this may be a source specific relationship. Snow from an urban site in Southampton, U.K. had a very high PAH content (6800 ng l^{-1}). Dissolved phase PAHs in snow from Canada had low concentrations of PAHs (1.0 - 240 ng l^{-1}). Particulate phase PAH were not analysed.

Despite being of limited extent, the results of this study represent an important contribution to the current data available in the literature regarding trace-organic contaminants in snow.

POLYCYCLIC AROMATIC HYDROCARBONS IN SEASONAL SNOWCOVER

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CHAPTER 1: POLYCYCLIC AROMATIC HYDROCARBONS IN THE ENVIRONMENT

1.1 Introduction

Polycyclic aromatic hydrocarbons (PAHs) are compounds which contain carbon and hydrogen atoms only, and which have in common a molecular structure consisting of two or more fused six-membered or five- and six-membered carbon rings. They can exhibit varying degrees of alkylation. The compound with the lowest molecular weight is naphthalene ($C_{10}H_8$) which consists of two fused benzene rings. Theoretically the largest member of the group could extend to an infinite polymeric structure, based on the structure of graphite (Neff, 1979).

Confusion sometimes arises over the name for this group of compounds (Vo-Dinh, 1989). PAHs are often also commonly referred to as 'polynuclear aromatic hydrocarbons' and 'polyaromatic hydrocarbons', which are abbreviated as PNA and PAH respectively. A review of more recent literature shows that 'polycyclic aromatic hydrocarbons' is the most common term, and this is used in the current work.

Of additional note is the term 'polycyclic aromatic compounds' (PACs). This is used to describe all compounds that contain aromatic ring structures, including non-hydrocarbon compounds. For example, the term PACs not only includes the parent homocyclic and hydrocarbon-substituted PAHs (e.g. alkyl-PAHs) but also heterocyclic groups such as polycyclic aromatic nitrogen heterocycles (PANHs) and polycyclic aromatic sulphur heterocycles (PASHs). The compounds in these latter group contain one or more non-carbon atom(s) in the ring structures of the molecules. Other PACs include PAH molecules that have undergone extra-ring substitution by non-hydrocarbon groups to yield, for example, amino-PAHs, nitro-PAHs and cyano-PAHs.

As a group, PAHs include a large number of isomeric compounds. This confounds the accurate analysis of PAHs, as separation and positive identification of individual compounds is often difficult to achieve.

PAHs are ubiquitous environmental contaminants, resulting from natural and anthropogenic sources. Anthropogenic sources are by far the major source. The environmental presence of PAHs is of particular concern because certain PAH compounds are known or suspected to have carcinogenic, mutagenic and toxic properties. However, the true ecological impact of PAHs on the environment is largely unknown and difficult to define (Neff, 1979).

The Environmental Protection Agency (EPA) of the United States Government has classified PAHs among their 'priority pollutants' (EPA, 1982). The World Health Organisation (WHO) and the European Economic Community (EEC) have also issued directives with respect to permissible levels of PAHs in water for human consumption (WHO, 1971; EEC, 1980).

1.2 Physical and Chemical Properties of PAHs.

The physical and chemical properties of PAHs are mainly dictated by the presence of conjugated π-electrons. These are present as a result of the structure of benzene rings from which PAHs are primarily constructed. This type of arrangement results in PAHs being relatively chemically stable, and also accounts for their ability to fluoresce.

All PAHs fluoresce when exposed to ultra-violet (UV) and visible radiation. Absorption of photons causes the π-electrons to be excited to a higher energy state. The 'excess' energy subsequently released as light when the excited electrons return to their ground state, results in the emission of a photon at a lower energy than the one absorbed (Lee *et al.*, 1981; Grant and Meiris, 1981). The fluorescent light is emitted at wavelengths dependent on the molecular configuration of the compound in question. Weak phosphorescence is sometimes also observed (Lee *et al.*, 1981). The property of fluorescence can be exploited in the detection and determination of PAHs, as the spectrum obtained from a particular compound is often exclusively characteristic of that compound.

Hundreds of compounds occur within this group of hydrocarbons, yet PAHs can be classified into two groups based on their molecular topology. These two groups are known as kata-anellated and peri-condensed structures. In the former group, the tertiary carbon atoms are centres of two interlinked rings only, such as in anthracene (see Figure 1.1). In the latter group, some of the tertiary carbon atoms are centres of three interlinked rings, as in pyrene. Anellation can be linear, as in anthracene, or angular, as in phenanthrene. Some larger PAH compounds, such as dibenzo[a,h]perylene, can exhibit regions of peri-condensed structures with angular as well as linear anellated regions (Zander, 1983).

Further additions to the structural description of PAH molecules have arisen as a result of investigations into their carcinogenic properties. Thus there exists the concept of K- and L-regions within a molecule (Pullman and Pullman, 1955). According to this classification, a K-region is an area of high electron density and an L-region is one of low electron density (Figure 1.2). In addition, a PAH molecule is said to have a bay-region when it contains an angular structure (Figure 1.2) (Wood *et al.*, 1976 and 1979). The implications of these particular configurations is that the molecules with K- and bay-regions have proven to be those PAHs that are predominantly carcinogenic.

The exact structure of PAH compounds is highly significant because, in general, their physical and chemical properties depend on the size and the structure of the molecule (Zander, 1983). Appendix I illustrates the structures of the study PAHs.

As a group, the PAHs are the least volatile of all hydrocarbons, and with the exception of a few hydrogenated derivatives and some two ring compounds, they are all solids at room temperature. The boiling points of PAHs are distinctly higher than those of corresponding n-alkanes with the same carbon number. The lowest boiling points are in the region of 170°C, and increase with molecular

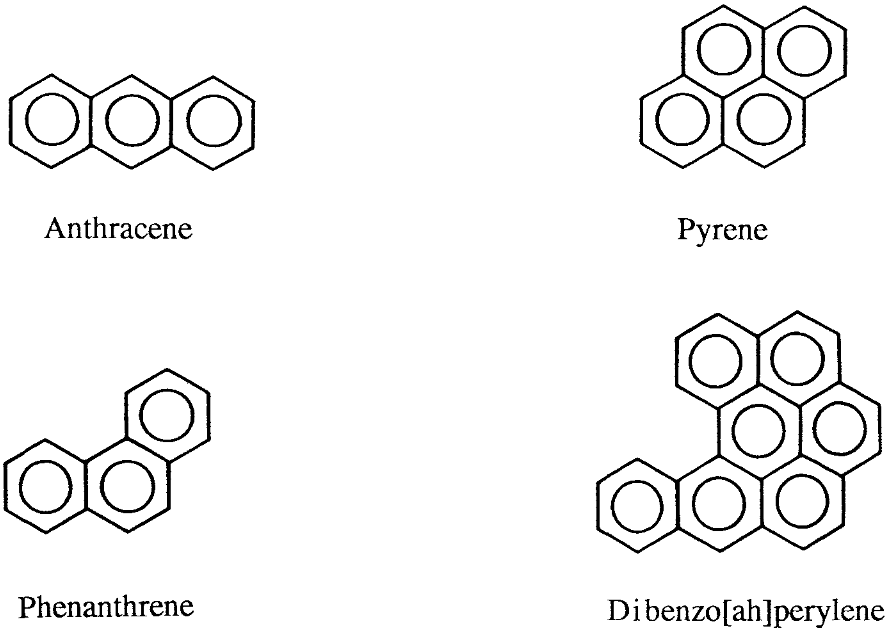


Figure 1.1 The molecular structures of four PAH compounds.

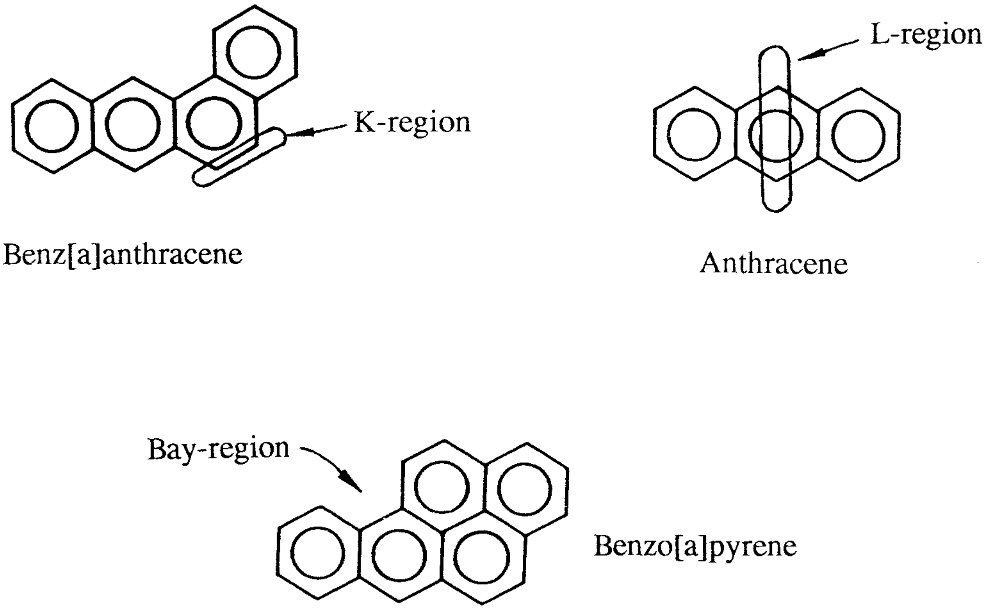


Figure 1.2 The positions of K-, L-, and bay-regions on PAH molecules.
(from Jerina *et al.*, 1978 and Wood *et al.*, 1980)

weight (Lee *et al.*, 1981). PAHs in the environment have a high degree of chemical inertness, but when they do undergo chemical reactions they tend to retain their conjugated ring structures (Lee *et al.*, 1981). The most important reactions to affect environmental PAHs are photochemical transformations and reactions with radical species, such as ozone.

PAHs are non-polar and lipophilic in nature, which combined with their relatively high molecular weights make them only sparingly soluble in water. Table 1.1 shows the aqueous solubilities of a number of PAHs.

Within the group a wide range of water solubilities can be found, from around 30 mg l^{-1} for naphthalene, to less than 0.5 μg l^{-1} for perylene (May *et al.*, 1978). In general, PAHs have higher aqueous solubilities than alkanes of similar molecular weight (McAuliffe, 1966).

Molecular configuration affects the solubility of PAHs to some degree (May *et al.*, 1978). Generally, linear configurations are less soluble than angular ones, and solubility tends to decrease with increasing alkylation. The solubility of PAHs has been predicted on this basis using 'Quantitative Activity Structure Relationship' (QASR) techniques with a variable degree of accuracy (Nirmalakhandan and Speece, 1989).

The solubility of PAHs in water is affected by the presence of particulate matter, the water temperature and the presence of other solutes (Harrison *et al.*, 1975; Futoma *et al.*, 1981).

Table 1.1 **Aqueous Solubilities of Selected PAH.**

Compound	m.w.	Ref. 1 (mg l^{-1})	Ref. 2 (mg l^{-1})	Ref. 3 (mg l^{-1})
Naphthalene	128.19	32.18	31.69	31.70
Acenaphthene	154.21	4.87	---	---
Fluorene	166.23	1.94	1.69	1.98
Phenanthrene	178.24	1.23	1.00	1.29
Fluoranthene	202.26	0.25	0.21	0.26
Pyrene	202.26	0.15	0.13	0.13
		(μg l^{-1})	(μg l^{-1})	(μg l^{-1})
Anthracene	178.24	---	45.00	73.00
Benzo[a]anthracene	228.30	11.99	9.40	14.00
Chrysene	228.30	---	1.80	2.00
Benzo[b]fluoranthene	252.32	1.49	---	---
Benzo[k]fluoranthene	252.32	0.80	---	---
Benzo[e]pyrene	252.32	4.82	---	---
Benzo[a]pyrene	252.32	3.99	---	3.80
Dibenz[ah]anthracene	278.36	0.51	---	---
Benzo[ghi]perylene	276.34	0.26	---	---

--- : not available

References: 1: Nirmalakhandan and Speece (1982)
2: May, *et al.* (1978)
3: Mackay and Shiu (1977)

The effect of suspended particulate matter on the solvent extraction of PAHs from unfiltered water was demonstrated experimentally by Acheson *et al.* (1976). It was found that increased suspended particulate matter reduced the efficiency of solvent extraction as the PAHs became absorbed on the solid phase.

All natural waters tend to be under-saturated with respect to dissolved PAHs because the majority of PAHs present are adsorbed onto particulate matter (Futoma *et al.*, 1981; Neff, 1981). In the aquatic environment, the distribution and transport of PAHs is controlled by their phase distribution: the majority of PAHs being associated with suspended particulate matter (Herrmann and Hübner, 1982; Herrmann and Thomas, 1984; Walters and Luthy, 1984; Van Zoest and Van Eck, 1990). Readman *et al.* (1982) found that the concentration of dissolved high molecular weight PAHs in an estuary system was inversely correlated with suspended particulate concentration and salinity, but that the low molecular weight PAHs (naphthalene, phenanthrene and anthracene) were uncorrelated, and their distribution was governed mainly by their high aqueous solubilities and vapour pressures.

May *et al.* (1978) demonstrated an increase in solubility of PAHs with increasing temperature. For example, the solubility of phenanthrene is increased by a factor of 3 over a temperature increase from 8.5°C to 29.9°C.

The occurence of mixtures of PAHs in aqueous solution can reduce the measured solubility of individual PAHs present. This is probably because of solute-solute interactions and/or the formation of solid solutions (Eganhouse and Calder, 1976). Organic compounds in water, such as detergents, solvents and humic and fulvic acids, can also affect the solubility of PAHs, as can the presence of organic colloid and micelle structures (Neff, 1981). Nonionic detergents are better solubilising agents of PAHs in water than ionic detergents (Lee *et al.*, 1981).

The ionic strength of water affects the solubility of PAHs, but to a lesser extent than temperature. May *et al.* (1978) demonstrated that a relationship exists between the ratio of the concentrations of PAHs in fresh water to saline water and the salinity of the water. As the salinity increases the solubility of the PAHs decreases. This is commonly known as a "salting out" effect (Neff, 1979). For example, in solutions of single PAHs in distilled water, the solubilities of naphthalene and phenanthrene at S‰ = 0 are 31.3 and 1.07 mg l^{-1} respectively, and at S‰ = 35 the solubilities are 22.0 and 0.71 mg l^{-1} (Eganhouse and Calder, 1976).

1.3 Biological Significance of PAHs.

1.3.1 PAHs and Animals.

The biological significance of PAHs had been suspected for some years before their effects were verified. One of the first reports of an environmental carcinogenic effect was made by Sir Percival Pott in 1775. He suspected that the high incidence of scrotal cancer in chimney sweeps was related to their exposure to soot and ash. Following this, reports were made of occurrences of cancer in workers from the coal tar and pitch industries. These findings were substantiated by experiments that induced sarcomas in animals exposed to such substances. In the 1930s the discovery and isolation of PAHs from coal tar, pitch and soot, and the finding that purified and synthesised PAHs could induce cancerous symptoms proved PAHs to be potential biological hazards (Zedeck, 1980).

Further research into the exact nature of the carcinogenic properties of PAHs followed, and the precise chemical process has been extensively researched. Reviews of this area of research may be found in Gelboin and Ts'o (1978) and Zedeck (1980).

Basically, PAHs require metabolic biotransformation of the parent molecule to enable the carcinogenic effect to occur. They are therefore referred to as indirect-carcinogens, as they are the main precursors of the compounds directly responsible for the carcinogenic activity. Activation of parent PAH molecules occurs as a result of enzymic transformations, primarily by the microsomal mixed-function oxidase (MMFO) system, which leads to a series of reactions resulting in a PAH-tetrahydro-epoxy species which is the ultimate carcinogen. The main sites of this process are the liver and kidneys (Zedeck, 1980).

The bioderivatives of PAHs include epoxides, quinones, dihydrodiol-, phenol- and dione-derivative species and glutathione conjugates of PAHs (Jones *et al.*, 1979). The principal ultimate carcinogenic metabolite of benzo[a]pyrene (BP) is believed to be BP-7,8-diol-9,10-epoxide (Wood *et al.*, 1979).

Initial research into this process by Pullman and Pullman (1955) led them to suggest that metabolisation of PAHs at the K-region (see previous Section) was responsible for the carcinogenic activity. However, it was later found that non-K-region metabolisation was also an important factor. Thus Wood *et al.* (1976) proposed their 'bay-region' theory. PAHs that possess a bay region can undergo metabolisation to a diol-epoxide derivative at this locality which is then highly reactive and able to bind to and react with DNA, causing a genetic disorder which can cause a mutagenic expression (Wood *et al.*, 1979). Figure 1.3 illustrates the representative type of reaction involved in the biotransformation of benzo[a]pyrene into a carcinogenic derivative.

The biological activity of PAH molecules is highly dependent on their individual shape and structure. Even differences between structural isomers can exist, as with benzo[a]pyrene, which is more carcinogenic than benzo[e]pyrene (Selkirk and MacLeod, 1979), and similarly with benzo[g]chrysene, which is more potent than benzo[c]chrysene (Lee *et al.*, 1981). Alkyl substitution also affects the bio-activity of PAHs, depending on the compound in question. Hoffmann *et al.* (1974) showed that of the six isomers of methylchrysene only 5-methylchrysene exhibited a strong carcinogenic effect, whereas 1-, 2-, 3-, 4- and 6-methylchrysene are inactive or weak carcinogens. They suggested that methylation of chrysene at the 5 position changes the electron distribution and/or conformation of the chrysene ring system to yield a potent pro-carcinogen. These facts highlight the need for a

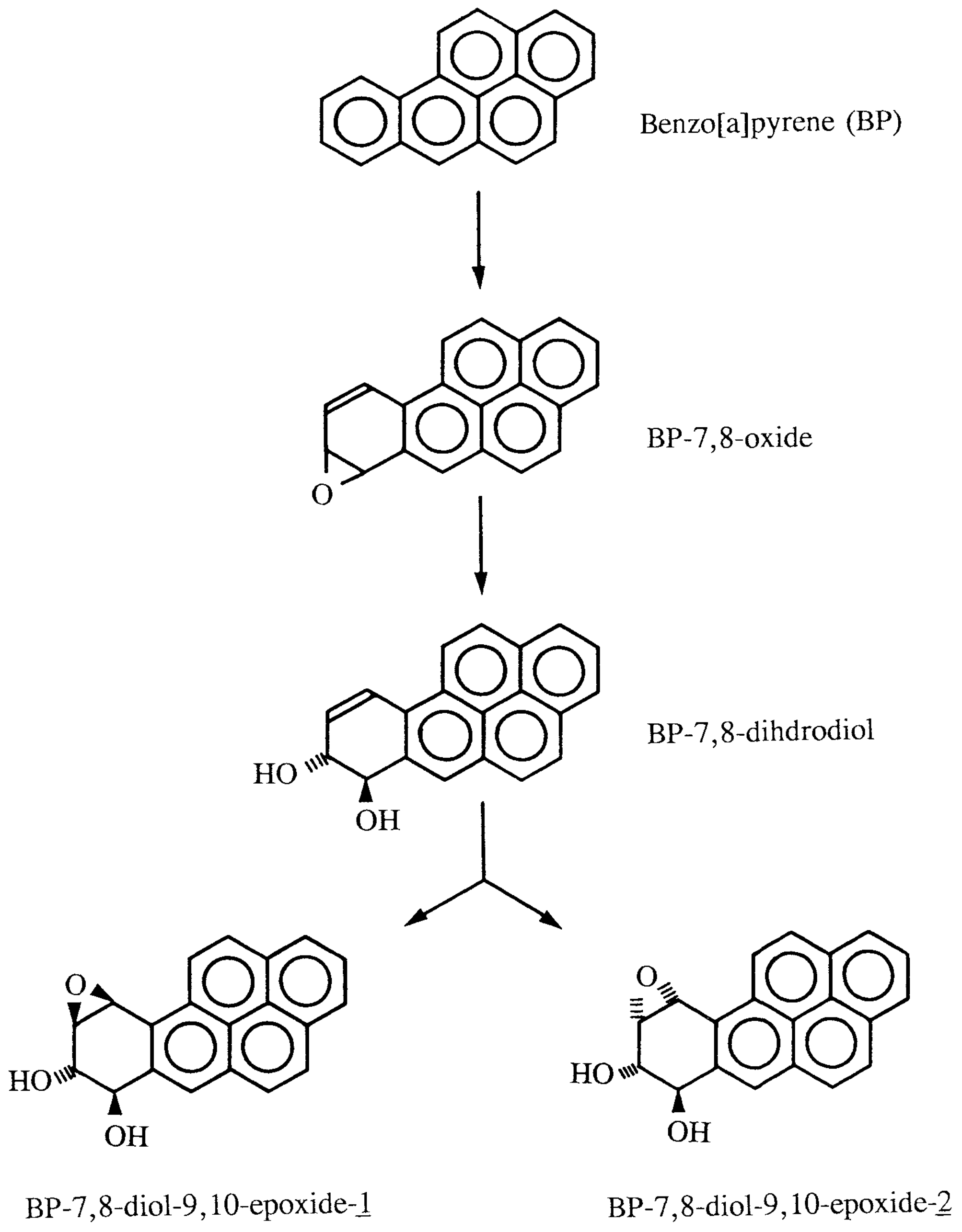


Figure 1.3 Representation of the metabolic transformation of benzo[a]pyrene to a carcenogenic diol-epoxide species.
(from Wood *et al.*, 1980)

satisfactory analytical technique capable of efficiently distinguishing PAH isomers and subtle structural differences.

Of further importance is the fact that PAHs can exhibit synergism in their carcinogenic effects. Hoffmann and Wynder (1963) found that the addition of certain non-carcinogenic PAHs to a carcinogenic PAH preparation increased the expected tumour incidence in test animals. This is notable, as PAHs in the environment are nearly always found in a mixture of PAH compounds.

In animals, PAHs are incorporated by being absorbed by the skin or following inhalation and ingestion. They then concentrate in the liver and kidneys from which they are eventually metabolised and excreted. Being lipophilic they also concentrate in lipid rich tissues, such as mammary and adrenal glands and fat reserves, where they remain for long periods of time. While PAH metabolism occurs in many species and organs there are marked differences between organs of a given species, between the same organs in different species and between male and female individuals (Zedeck, 1980).

1.3.2 PAHs and Plants.

PAHs have been detected in plants and plant products, and in some cases thought to be the products of plant biosynthesis (Borneff *et al.*, 1968; Hancock *et al.*, 1970). However, this area is still far from being clearly understood and some doubt exists as to the exact process and its significance. With respect to the biological effects of PAHs, far less work has been undertaken on the significance of PAHs to plant physiology and metabolism than on the significance to animals.

Graf and Diehl (1966) claimed that PAHs are synthesised during the germination and growth of rye, wheat and lentils. These findings were supported by Hancock *et al.* (1970), who provided evidence for the biosynthesis of benzo[a]pyrene in plant leaves. However, Grimmer and Duvel (1970) attribute the PAHs found in such studies to have originated from contamination by airborne particulate fallout during the analytical procedure.

PAHs can also be present in plant tissue as a result of translocation from soil and water and by deposition from the atmosphere (Hancock *et al.*, 1970). The relative importance of these two processes varies from species to species. Baum (1978) reports that benzo[a]pyrene is absorbed by barley roots and translocated to the shoots, whereas in kale and spinach, absorption of PAHs from the atmosphere onto the plant surfaces can be more significant.

The growth of certain algae can be enhanced by the presence of PAHs, and the degree of enhancement is correlated with the compound's carcinogenicity to animals, with the more carcinogenic compounds being better growth promoters (Graf and Nowak, 1966). A similar study showed that PAHs can stimulate growth, but also that they can inhibit growth or have no affect at all, dependent on the compound and species in question (Boney, 1974). It has further been shown that naphthalene inhibits growth and photosynthesis in algae (Kauss and Hutchinson, 1975; Vandermeulen and Ahern, 1976).

1.3.3 PAHs and Microorganisms

Investigations aimed at determining the presence of PAHs in bacteria and fungi have had the primary intention of proving or disproving the existence of biosynthesis and biodegradation.

As early as 1947, Sisler and ZoBell (1947) reported that benz[a]anthracene, dibenz[a,c]anthracene, naphthalene, anthracene and phenanthrene were oxidised by a mixed culture population of marine and soil bacteria.

It has subsequently been reported that microorganisms commonly present in sewage, sea water and soil are capable of utilising PAHs for growth and thus are capable of partially or fully degrading them (Wodzinski and Johnson, 1968; Catelani *et al.*, 1970; Gibson, 1977; Neff, 1979; Kerr and Capone, 1988).

Fungi are also capable of oxidative degradation of PAHs, though this has been less well studied. Fungi possess a cytochrome enzyme system similar to mammals (Cerniglia and Gibson, 1978) and it has been claimed that fungi are capable of degrading PAHs by much the same pathway as is characteristic of mammals (Ferris *et al.*, 1973). The importance of microbial degradation of PAHs by bacteria and fungi is not fully known, but is thought to be more prevalent in oxic than anoxic environments (Neff, 1979).

1.4 Formation of PAHs

PAHs can be formed by combustion processes, biological synthesis and by diagenetic processes. Combustion is the most important formation process for environmental PAHs.

PAHs are formed whenever organic matter is subjected to partial, inefficient combustion. During high temperature combustion processes, carbon and hydrogen radical species are generated which can recombine in a variety of ways, often resulting in the formation of PAH molecules (Badger, 1961).

Various hypotheses have been proposed for the formation of PAHs during pyrolysis. These mainly involve intermediate species such as acetylene, ethylene and 1,3-butadiene and their associated radicals. Most proposed mechanisms involve chain lengthening (polymerisation) reactions followed by cyclisation and dehydrogenation reactions (Crittenden and Long, 1976).

Once formed, relatively simple PAH compounds may undergo further reactions to yield more complex condensed ring structures (Smith, 1981).

The exact products in these reactions are highly dependent on fuel type and composition, and also on the temperature of combustion. PAHs are formed more abundantly in the temperature range of 650°C to 900°C (Crittenden and Long, 1976). Efficient, high temperature (>1000°C) combustion results in a low PAH yield as the majority of organic matter is converted more completely into carbon dioxide and water (Fazio and Howard, 1983).

The combustion temperature also affects the degree of alkyl substitution of the products, with lower temperatures producing relatively higher amounts of alkylated PAHs.

Fuel type is an important factor in the pyrolytic formation of PAHs. Intermediate structures, such as alkylated benzenes and PAHs themselves, when present in the fuel, enhance the yield of PAHs when the fuel is burned. So, fuels with a high molecular weight range of components, such as diesel, petrol and other fossil fuels, are capable of producing large amounts of PAHs (Schmeltz and Hoffmann, 1976).

One important aspect of the pyrolytic formation of PAHs is that this process has been implicated in the process of soot formation (Smith, 1981). Handa *et al.* (1980) have shown a linear relationship between the concentrations of PAHs and particulate matter in automobile exhaust gas.

Soot formation is also enhanced by the presence of alkylated PAH molecules in the fuel (Smith, 1981). Furthermore, Pasternak *et al.* (1982) found that when polyvinyl chloride (PVC) is burned it produces a high proportion of alkylated PAHs compared to non-chlorinated polyvinyls. This effect is attributed to the effect of the increased electron density owing to the presence of the chlorine atoms, and probably accounts for the reason why PVC produces more soot when burned than non-chlorinated polyvinyls.

As well as pyrolytic formation, PAHs are apparently formed by biosynthesis (see Section 1.2.2). They are also formed by the diagenesis in sediments of precursor compounds, such as naturally occurring plant terpenes and sterols. This occurs at low temperatures, under high pressures and over geological timescales in reducing environments (Hites *et al.*, 1980a; Wakeham *et al.*, 1979; Wakeham *et al.*, 1980;

Tan and Heit, 1981). Examples of PAHs naturally derived in this way are perylene, retene and certain alkylated chrysenes and picenes (Hites *et al.*, 1980b). Thus, fossil fuels such as coal and oil are relatively rich sources of PAHs (Wakeham *et al.*, 1980; Tripp *et al.*, 1981).

Some natural, rare minerals composed of PAHs have also been identified, such as pendletonite ($C_{24}H_{12}$), and idrialite and curtisite ($C_{22}H_{14}$) (Blumer, 1975).

1.5 The Occurence of PAHs in the Environment.

1.5.1 Introduction.

As outlined above, PAHs are produced by natural and industrial processes, but anthropogenic production is much greater than natural production (Suess, 1976; Edwards, 1983; Nikolaou *et al.*, 1984).

PAHs are generally present in the environment as complex mixtures containing alkylated and non-alkylated species. PAHs from different sources vary in the distribution of compounds, but can often show relatively uniform characteristics for one particular source (Hites *et al.*, 1980b).

The variation in the ratios of PAHs in a sample can give a certain degree of source indication. If the source is an oil or petroleum product, the PAH mixture present tends to have a low ratio of unsubstituted to substituted species. If the source is combustion, the mixture tends to be characterised by homologous series of PAHs, which decrease in abundance as the degree of substitution increases. If the source is the *in situ* aromatisation of naturally occurring precursors, the mixture tends to be less complex, and contains compounds which are structurally related to the precursor compounds (Hites *et al.*, 1980b).

For discrete geographically defined samples, the relative abundance of the PAHs present can sometimes indicate the probable source of the PAHs (Lee *et al.*, 1977). For example, retene (1-methyl-7-isopropylphenanthrene) can possibly be used as a source indicator for the combustion of coniferous wood (Ramdahl, 1983).

The ratios of certain PAHs in a sample can also indicate source. The fluoranthene-to-pyrene ratio of a particular sample can sometimes be applied to this end, as a ratio of 0.6 can indicate automobile and truck emissions (Hangebrauck *et al.*, 1967; Giger and Schaffner, 1978), a ratio of 1.0 for wood smoke and 1.4 for coal combustion emissions (Lee *et al.*, 1977). However, these emission values may not be applicable to environmental samples that contain PAHs from a number of sources and that have undergone some degree of degradation.

For example, Thomas (1986b) performed correlation analyses of PAH concentrations in snow cover. Benzo[ghi]perylene and fluoranthene were well correlated, but benzo[a]pyrene showed a distinct pattern that is thought to be related to different emission factors and a higher rate of photodecomposition.

It has been suggested that the ratio of PAHs to C12-to-C30 fatty acids can be used as an indicator of the predominance of anthropogenic or natural contribution to the organic content of precipitation (Kawamura and Kaplan, 1986). PAHs are typically anthropogenic in origin whereas the fatty acids are primarily biogenic.

Further indications of PAH sources can be gained from the sample content of certain trace metals. In this way, for example, a high correlation of PAH content to vanadium content might suggest that the common source is from an oil combustion process, whereas a high PAH to lead correlation suggests a vehicular petroleum combustion source (Valerio *et al.*, 1986).

However, the distribution of PAHs in a particular sample depends on the sum of its sources, and it must be stressed that such attempts to 'fingerprint' PAH samples to determine the source are likely to provide equivocal interpretation.

On a global scale, the qualitative PAH pattern is remarkably constant: the relative abundance of individual compounds does not change significantly (Laflamme and Hites, 1978). The total PAH abundance increases with proximity to human activity, further highlighting anthropogenic emissions as the major source of PAHs (Herrmann, 1978; Laflamme and Hites, 1978).

1.5.2 Natural Sources of PAHs.

The primary sources of naturally derived PAHs are forest and prairie fires (Hites *et al.*, 1980a) and volcanic activity (Ilnitsky *et al.*, 1977). These result in the direct injection of PAHs into the atmosphere and hydrosphere.

PAHs are produced on more localised scales by biosynthesis (see Section 1.3.3) and by geological synthesis (see Section 1.4). PAHs can also be introduced naturally to the environment by the weathering of PAH bearing rock, such as coal seams, and the natural seepage of oil.

This natural production of PAHs constitutes the natural or 'background' flux to the environment, and prior to wide-spread human production a natural balance was likely to have existed between production and degradation of PAHs (Furuta and Otsuki, 1983).

1.5.3 Anthropogenic Sources of PAHs.

The major sources of anthropogenic PAHs are combustion processes and in particular those that involve the combustion of fossil fuels. All major reviews of PAHs present data on the sources of PAHs and give values for estimated emissions and production. There appears to be a wide variation in the quoted values and the significance of particular sources (NAS, 1972; Siebert *et al.*, 1978; Guerin, 1978; Neff, 1979; Lee *et al.*, 1981).

The most predominant sources are heat-intensive industrial processes, such as heat-and power-generation. Table 1.2 illustrates some of the most important sources and emission values for benzo[a]pyrene. It can be seen that the annual global emission of this single compound could be high, more than 5000 metric tons. However, these are estimated values using crude data, and the figures are likely to be revised in view of changing global fuel usage.

Owing to the widespread production and emission of PAHs, they are found throughout the environment and have been detected in almost all phases of the environment (Simmleit and Herrmann, 1987). Concise reviews detailing the presence of PAHs in environmental samples include: Siebert *et al.*, (1978); Gelboin and Ts'o, (1978); Neff, (1979); Bjørseth, (1983); and Edwards, (1983).

PAHs chosen for analysis often vary from study to study and particular care should be taken when comparing 'total' PAH values, as this figure represents only the sum of the PAHs analysed for each study. For this reason, benzo[a]pyrene is sometimes used as a standard PAH against which different studies can be compared, as this compound can be used as an indicator of total PAH content (Herrmann, 1978; Siebert *et al.*, 1978; Lamparczyk *et al.*, 1988).

1.5.4 PAHs in the Atmosphere.

The atmosphere is an important reservoir and a major transportation medium for many pollutants. Many of the sources reported in Sections 1.5.2 and 1.5.3 result in the direct injection of PAHs into the atmosphere. Combustion processes are the major source of atmospheric PAHs.

PAHs introduced into the atmosphere by combustion sources are either emitted in the vapour phase when they are released at high temperatures or they are associated with fine particulate matter. As the mixture of gases cools down, higher molecular weight PAHs in the vapour phase condense, usually on to particles or form particles in the process (Andren and Strand, 1981). Those with relatively low molecular weights tend to remain in the vapour phase. PAH present

Table 1.2 **Anthropogenic Emissions of Benzo[a]pyrene.**
(from Lee *et al.*, 1981)

Source of B[a]P	Global Emission ($T.a^{-1}$)
Heat and Power Generation	
coal	2,736
wood	220
oil	5
gas	3
Industrial Processes	
coke production	1,033
catalytic cracking	12
Refuse and Open Burning	
commercial/industrial incineration	69
other incineration	33
coal refuse fires	680
forest and agricultural fires	420
other fires	148
Vehicles	
trucks and buses	29
automobiles	16
TOTAL	**5,404**

in the atmosphere in both phases in the atmosphere are present in the ng m^{-3} range (Nikolaou *et al.*, 1984).

The exact partitioning of PAHs between the two phases is difficult to quantify, as it varies with air temperature, the concentration and character of total suspended particulates and on the saturation vapour pressure (P_o) of the compound in question (Yamasaki *et al.*, 1982; Bidleman, 1988). Values of P_o calculated for some PAHs are shown in Table 1.3. Compounds with P_o values $> 1.3 \times 10^{-2}$ kPa should exist almost entirely in the vapour phase, whereas those with values $< 1.3 \times 10^{-6}$ kPa should exist almost completely in the particulate phase (Eisenreich *et al.*, 1981). However, it is critical to note that calculated P_o data for the same compound exhibit a large variation, dependent on the experimental method used. For example, for anthracene, P_o values of 8.43×10^{-7} and 3.17×10^{-5} kPa have been determined using different techniques (Lane, 1988). The significance of the P_o values for PAHs with respect to atmospheric vapour-particulate phase partitioning is illustrated in Figure 1.4.

PAHs may be adsorbed at active sites on particulate matter or embedded in the particle matrix, and thus be non-exchangeable and hence are not in equilibrium with the vapour phase (Bidleman, 1988). This would lead to a sampling or analytical artefact that may introduce an element of error into the calculation of vapour-particulate phase distributions.

Particles in the atmosphere can be classified into a number of groups, depending on their size and origin (Bidleman, 1988). Large, coarse particles of diameters (D) > 2.0 to 2.5 μm are produced mainly by mechanical means (eg. weathering, sea spray, pollen release). The smallest particles, in the range of D < 0.08 μm,

Table 1.3 **Saturation Vapour Pressures (P_o) of Selected PAHs and Predicted Vapour-Particulate Phase Partitioning in the Atmosphere.**

(from Andren and Strand, 1981)

COMPOUND	P_o (atm.)	m.w.	% Particulate	
			Urban	Rural
Naphthalene	1.2×10^{-4}	128	0	0
Acenaphthene	3.5×10^{-6}	154	0-5	0-5
Phenanthrene	9.8×10^{-7}	178	5-20	0-5
Pyrene	8.9×10^{-9}	202	5-30	0-10
B[a]anthracene	1.1×10^{-10}	228	75-95	60-90
B[a]pyrene	8.3×10^{-12}	252	100	100
B[e]pyrene	8.3×10^{-12}	252	100	100
B[k]fluoranthene	1.6×10^{-12}	252	100	100
B[ghi]perylene	1.6×10^{-13}	276	100	100

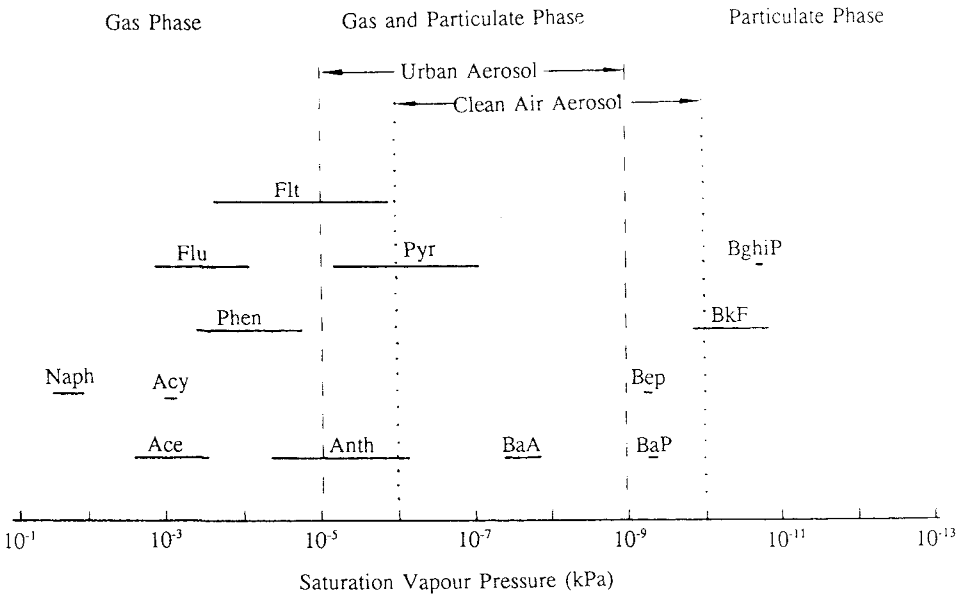


Figure 1.4 **Ranges of saturation vapour pressures (P_0) reported in literature, and predicted vapour-particulate phase partitioning behaviour for urban and clean-air aerosol.**

Abbreviations: Ace (acenaphthene); Acy (acenaphthylene); Anth (anthracene); BaA (benz[a]anthracene); BaP (benzo[a]pyrene); BeP (benzo[e]pyrene); BghiP (benzo[ghi]perylene); BkF (benzo[k]fluoranthene); Flt (fluoranthene); Flu (fluorene); Naph (naphthalene); Phen (phenanthrene); Pyr (pyrene).
(from Lane, 1988)

are produced by gas-to-particle conversion and are referred to as Aitken nuclei. Particles between these two groups (ie. $0.08 < D < 2.0$ μm) are called accumulation-mode particles. These are also produced by gas-to-particle conversion and by the coagulation of Aitken nuclei.

Atmospheric particles have a bimodal distribution, one mode occurring at $D < 1.0$ μm and the other at $D > 10$ μm (Bjørseth and Olufsen, 1983). Most particulate phase PAHs are associated with particles in the range of $0.2 < D < 2.4$ μm (Van Vaeck and Van Cauwenberghe, 1985).

The particle size distribution and the associated PAH distribution are of particular concern as the size range of respirable airborne particles is $D < 5.0$ μm (Nikolaou *et al.* 1984). It can be seen that particles containing PAHs can therefore be deposited in the alveoli of the lungs, and thus potentially contribute to the incidence of lung cancer (Simpson, 1990).

The particulate loading of the atmosphere varies spatially and temporally. The organic fraction of atmospheric particles is also highly variable. These factors make it difficult to assess or quantify accurately the PAH content of the atmosphere.

In a study of the particulate matter in the atmosphere above Lake Michigan, USA, the total particulate matter ranged between 9.5 and 151.0 μg m^{-3} over a period of a few months. The total organic carbon content of these particles ranged from 7.5 to 54%, and of this, approximately 0.1% was PAH, the concentration being in the range of 0.1 to 4.2 ng m^{-3} (Andren and Strand, 1981). Vapour phase PAHs were not quantified.

Baker and Eisenreich (1990) measured a concentration range of 2.5 to 6.3 ng m^{-3} for 13 PAHs in the atmosphere above Lake Superior. The partition between the aerosol-adsorbed and vapour phase ranged from 0-0.4% adsorbed for fluorene to 77-100% for indeno[1,2,3-cd]pyrene. They further suggest that the concentration range found is representative of continental background levels.

Higher concentrations of PAHs are found in and near urban locations, with lower concentrations in rural and remote areas (Gordon and Bryan, 1973; Herrmann, 1978; Kawamura and Kaplan, 1986). Levels in rural and remote areas often exceed expected levels because of the long-range transport of PAHs (De Wiest, 1978; Bjørseth *et al.*, 1979).

Because of their relative environmental stability PAHs can be used as a conservative tracer of atmospheric transportation and deposition (McVeety and Hites, 1988). The potential for long-range transport of PAHs in the atmosphere has been well studied (De Wiest, 1978; Bjørseth *et al.*, 1979; Bjørseth and Olufsen, 1983; Pacyna and Oehme, 1988; Brorström-Lundén and Lövblad, 1991). Small particles released at a height of 20 m above sea level into a wind of 5 m s^{-1} can be carried for at least 1500 km (Bjørseth and Olufsen, 1983). This process accounts for the contamination by PAHs of remote areas, such as the Arctic (Pacyna and Oehme, 1988), and also for the the global distribution of PAHs in ocean sediments (Hites *et al.*, 1980a).

Long-range transport of PAHs in the atmosphere is widespread but variable, being affected by meteorological conditions (De Wiest, 1978; Bjørseth *et al.*, 1979; Thomas, 1986), orographic effects (Schrimpff, 1980) and the PAH source (Leuenberger *et al.*, 1988).

In urban areas, PAHs show a pattern of concentration with time and area that correlates with road traffic density (Gordon, 1976). The concentration of PAHs in the atmosphere also appears to change seasonally, with increased concentrations observed in winter months owing to an increase in space heating (Gordon and Bryan, 1973; Czuczwa *et al.*, 1988). However, it is argued that this apparent increase is in fact a result of a shift in the phase partitioning ratio caused by a decrease in temperature that causes more PAH to partition into the particulate phase, thus introducing a sampling aretefact (Lane, 1988). Conversely, an increase in temperature causes a shift that favours the entry of PAHs into the vapour phase. This explains the occurence of five-ring PAHs in the vapour phase during periods of high air temperature (Yamasaki *et al.*, 1982).

Natural sources, such as bush fires, can cause temporary but significant increases in airborne PAHs that affect urban areas (Freeman and Cattell, 1990).

Physical and chemical processes act to remove PAHs from the atmosphere. Physical processes include fallout by gravitational settling of particles (dry deposition), and removal by inclusion in precipitation (wet deposition). Suess (1976) estimated that in the absence of rain and snow, atmospheric particles with $D < 1.0\ \mu m$ will remain suspended in the lower atmosphere for 4 to 6 weeks, and those of sizes $1.0 < D < 10.0\ \mu m$ remain in suspension for a few days.

The presence of PAHs in snow, rain and fog has been reported by a number of studies. This is given further consideration in Section 1.6.

In addition to wash-out, PAHs in the atmosphere are also susceptible to losses owing to a variety of chemical processes (Greenberg, 1989). These include photo-oxidation (Bjørseth and Olufsen, 1983), reactions with ozone (Lane and Katz, 1977), OH radicals, NO_x and N_2O_5 (Atkinson *et al.*, 1987; Pitts, 1987; Zielinska *et al.*, 1989) and also with SO_x species (Bjørseth and Olufsen, 1983). The chemical reactivity and fate of atmospheric PAHs has been reviewed by Nikolaou *et al.* (1984) and Lane (1988).

The chemical transformations of PAHs are of significance because some products, such as nitroarenes, are often direct and potent mutagens (Pitts *et al.*, 1979; Nikolaou *et al.*, 1984; Pitts, 1987). However, the extent of such reactions may be lessened by the fact that PAHs adsorbed on to certain particles, such as coal fly ash, can be resistant to photochemical degradation (Korfmacher *et al.*, 1980). Investigations have shown that this process is highly dependent on the particular substrate to which the PAHs are adsorbed (Behymer and Hites, 1988). Darker substrates stabilise the PAHs, and thus reduce the extent of photolytic degradation. There is still some debate as to the importance and extent of atmospheric modification of PAHs (Behymer and Hites, 1988).

1.5.5 PAHs in Water Systems.

The concentration of PAHs in natural waters varies widely and is dependent on such factors as the proximity to pollutant sources, catchment and drainage area characteristics and the source of the water. As noted earlier, all natural waters tend to be under-saturated with respect to dissolved PAHs (Futoma *et al.*, 1981; Neff, 1981).

PAHs have been analysed in: ground water (Simmleit and Herrmann, 1987; Babelek and Grochmalicka-Mikołajczyk, 1990); urban runoff (Bomboi and Hernández, 1991); river water (Herrmann, 1981; Smith *et al.*, 1991); lake water (McVeety and Hites, 1988); sea water (Lamparczyck *et al.*, 1988; Valls *et al.*, 1989); tap water (Kveseth *et al.*, 1982) and industrial waste-water (Walters and Luthy, 1984). Table 1.4 shows the range in values for PAH concentrations in the aqueous environment. Harrison *et al.* (1975) and Borneff and Kunte (1983) have published reviews of PAHs in water.

In a review of PAHs in river water, Borneff and Kunte (1983) report values of PAHs determined for a number of rivers. The concentrations vary widely, both from river to river and within the same river. The concentration of benzo[a]pyrene was shown to vary from less than 1.0 ng l^{-1} in the Rivers Danube (Hungary) and Moskwa (USSR), up to a maximum of 12 μg l^{-1} in the River Plyussa (USSR). This high concentration is attributed to industrial effluent entering the river. Similar high levels caused by effluent are reported by Samoilovich and Redkin (1968).

Table 1.4 **Concentrations of PAHs in Water Samples.**

Ref	Sample Type	No. PAHs*	Conc. Range
1	Ground water	6	52-444 ng l^{-1}
2	Urban runoff	16	15.1-35.5 μg l^{-1}
3	River water	7	78-907 ng l^{-1}
4	Lake water	15	0-0.7 ng l^{-1}
5	Baltic Sea water	11	10-180 μg l^{-1}
6	Coastal Med. Sea	4	3.8 ng l^{-1}
7	Tap water, Scand.	42	2-187 ng l^{-1}
8	Ind. waste water	11	1.9-2.0 mg l^{-1}

* = number of compounds analysed

References: 1: Babelek and Grochmalicka-Mikołajczyk (1990)
2: Bomboi and Hernández (1991)
3: Smith *et al.* (1991)
4: McVeety and Hites (1988)
5: Lamparczyk *et al.* (1988)
6: Valls *et al.* (1989)
7: Kveseth *et al.* (1982)
8: Walters and Luthy (1984)

Most investigations of PAHs in lacustrine systems have been directed at the fluxes of PAHs to lacustrine sediments, and across the air/water interface.

One study of PAHs in a lake system (McVeety and Hites, 1988) measured the concentration of PAHs in a small lake on an island in northern Lake Superior, USA. Water was sampled at depths of 3, 8 and 25 m. The surface water concentrations were significantly greater than the deeper concentrations. This is because the predominant source of PAHs is deposition by precipitation, and, to a lesser extent, there are more efficient removal processes for PAHs in the sediment/water boundary region.

In another study of lake water, Borneff (1975) found that the surface waters of Lake Zurich contained a higher average concentration of PAHs than did water from a depth of 30 metres. The concentration increased noticeably in the spring, and this effect was attributed to the input of water to the lake from Alpine snowmelt which was presumed to contain high concentrations of PAHs. Snowmelt has also been thought to be the cause of seasonal increase in the flux of PAHs in surface water runoff to coastal waters and sediments in Sweden (Broman *et al.*, 1988).

The sampling method and season needs to be carefully considered in studies of fresh water chemistry, to avoid systematic variations. The PAH concentration of the body of water can vary with seasonal events, such as flooding and snowmelt (Borneff and Kunte, 1983) and also with seasonal variations in deposition and remobilisation by volatilisation (Baker and Eisenreich, 1990).

It is also important to distinguish between the PAH load in the particulate and dissolved phases of a water body. Rivers typically contain a suspended solid load of up to 100 mg l^{-1} (Harrison *et al.*, 1975). Owing to their hydrophobic tendencies, PAHs tend to associate with the particulate fraction in the water. Lewis (1975) showed that the ratio of the concentration of PAHs in the particulate phase to that in the dissolved phase ranged from 1.9 to 50.5 for the River Trent and from 0.6 to 7.9 for the River Severn. Such considerations are important when river water is utilised as a source of water for huwn consumption.

As with investigations into lacustrine systems, most research of PAHs in the marine environment has been directed towards studies of sedimentary processes. This is owing to the fact that PAHs are present in the water column at very low concentrations, and also that the transport and fate of PAHs in the marine environment are largely governed by the dynamics of particulate matter (Herrmann and Hübner, 1982; Van Zoest and Van Eck, 1990). An exception to this are the low molecular weight PAHs naphthalene, phenanthrene and anthracene. The behaviour of these three compounds in an estuary was found to be governed more by volatilisation (Readman *et al.*, 1982).

PAHs have been measured in seawater by Lamparczyk *et al.* (1988), but it is not clear if the samples were filtered prior to extraction. Valls *et al.* (1989) determined the concentrations of phenanthrene, fluoranthene, pyrene and chrysene in the dissolved and particulate phases in water from the Western Mediterranean Sea. The values obtained were low: 0.7, 1.6, 0.2, 0.14 and 0.03, 0.1, 0.05, 0.06 ng l^{-1}, respectively.

Ehrhardt and Knap (1989) attempted to detect PAHs in open-ocean water from the Atlantic in the vicinity of Bermuda. Only naphthalene was detected, and this was not quantified.

1.5.6 PAHs in Soils and Sediments.

Soils and recent sediments contain complex mixtures of PAHs. Earlier hypotheses for their source and mode of formation suggested that they existed as a result of low temperature reactions within the soil or by biosynthesis by soil micro-organisms (Blumer, 1961). However, it is now widely accepted that the PAHs are present predominantly as a result of the long range transport of PAHs formed by pyrolysis (Blumer and Youngblood, 1975; Laflamme and Hites, 1978).

Even though biosynthesis of PAHs in soils can occur, it makes no significant contribution on a large scale and cannot account for the complex and relatively similar range of compounds found in geographically separate soils (Blumer and Youngblood, 1975).

Hites *et al.* (1980a) analysed 50 samples of sediments and soils from around the world, with representative samples from remote areas and those affected by human activity. The results showed that sites closer to human activity had a higher PAH load than the remote sites. Overall, a range of five orders of magnitude in concentration was found. In most cases, PAHs were present in complex mixtures of alkylated and non-alkylated species. The relative abundance of these species suggests that combustion is a common source. The lowest amounts found in remote areas are thought to represent the natural background flux of PAHs produced by natural pyrolytic processes. The decrease in the concentration of PAH in sediments with distance from urbanised areas exhibits a logarithmic profile (Pruell and Quinn, 1985; Broman *et al.*, 1988).

The average flux of individual PAHs to remote sediments and those close to urban areas in the U.S. in 1980 were estimated to be 0.8 and 35 ng $cm^{-2} a^{-1}$, respectively (Gschwend and Hites, 1981). The PAH input to the remote sediments can be attributed to atmospheric input only, whereas the flux to the latter sediments is probably dominated by urban runoff.

Non-pyrolytic sources of PAHs in soils and sediments can be important on a very localised scale. Such sources can be oil spills or seepage from natural deposits, and localised biosynthesis (Hites *et al.*, 1980a). In some cases perylene has been found to be present in sediments at unexpectedly higher concentrations than other PAHs (Wakeham *et al.*, 1980; Tan and Heit, 1981). It is thought that the source of perylene in such cases is diagenetic formation in the sediments.

Another source of PAHs in sediments are coal particles (Tripp *et al.*, 1981). Coal particles can form a significant fraction of sediments in coastal areas where coal has been mined or transported (Allen, 1987), and these have the potential to release pollutants, including PAHs, into the sediment and overlying water (Barrick *et al.*, 1984; Merril and Wade, 1985).

Some studies have investigated the historical flux of PAHs to sediments (Hites *et al.*, 1980b; Gschwend and Hites, 1981; Heit *et al.*, 1988; Smith and Levy, 1990). In a study of an anoxic river sediment from Rhode Island, USA, Hites *et al.* (1980b) identified two types of PAH groups: those from anthropogenic combustion sources (mainly pyrene and chrysene) and those from natural chemical aromatisation sources (mainly perylene and retene). The sediment was dated using ^{210}Pb and it was found that the PAH content of the sediment increased greatly between 1900 and 1950, after which the level drops. The initial rise correlates well with the widespread use of fossil fuels, mainly coal, that started at the turn of the century. The subsequent slight drop is attributed to the change in fuel use habit in North America in the 1950s when oil was beginning to be used more than coal.

Heit *et al.* (1988) also determined the change in the input of PAHs to sediments with time. From their analysis of sediments from a lake in New York state, USA, they concluded that the flux in the period of the 1850s was at least an order of magnitude less than in the period of maximum input in the period 1940 to 1955. The decline after 1955 was also proposed to result from the change in fuel use in the area.

Similar studies of lake sediments also conclude that anthropogenic activities began introducing significant amounts of PAHs into the environment at about the beginning of the twentieth century (Gschwend and Hites, 1981; Cranwell and Koul, 1989). Smith and Levy (1990) found that fjord sediments downstream from large aluminium smelting works showed that there was a gradual increase in the PAH flux in the early part of the century, followed by a rapid increase in the 1940s owing to major increases in aluminium production. The PAH distribution also showed that before 1964 the principal input was from atmospheric deposition, but this became secondary to direct discharges after this date.

1.6 PAHs in Snow.

1.6.1 Introduction.

The chemical composition of precipitation can, under some circumstances, be used as an indication of the extent of contamination of the atmosphere and can thus be used as a monitoring tool for the atmosphere (Lazrus *et al.*, 1970; Schrimpff *et al.*, 1979).

PAHs are a prevalent atmospheric contaminant, and can therefore be expected to be incorporated in precipitation. Their presence has been detected in rain, snow and fog (Lunde *et al.*, 1977; Kawamura and Kaplan, 1983; Ligocki *et al.*, 1985a; van Noort and Wondergem, 1985; Herrmann, 1987; Czuczwa *et al.*, 1988; Leuenberger *et al.*, 1988; Capel *et al.*, 1991) and typical values determined for rain and fog, and for snow, are presented in Tables 1.5 and 1.8, respectively.

1.6.2 Pollution of Snow.

Snow plays a significant part in the world's hydrological and meteorological cycles, particularly in alpine, sub-polar and polar regions. It forms a vital source of irrigation water for agricultural and natural vegetation (Steppuhn, 1981) and is also a significant source of water for domestic use (McKay, 1981). At midwinter, snow covers approximately 40 % of land in the northern hemisphere (Davies, 1989). An awareness of the chemical composition of snow as a measure of its water quality is therefore desirable, if not essential.

Pollution of snow has been evident for at least 100 years. In 1881, a fall of grey snow was observed in Norway (Overrein *et al.*, 1981) and in 1884 a fall of blackened snow was observed near Preston, Lancashire (Brimblecombe *et al.*, 1986). More recently, the potential of snow to act as a sink for environmental

Table 1.5 **The Concentration Range of Benzo[a]pyrene and Total PAH Reported in Rain and Fog (ng l^{-1}).**

Ref.	Type	B[a]P	TPAH*	N	Location
1	Rain	--	1700	9	Urban F.R.G.
2	Rain	--	100⁺	16	Urban U.S.A.
3	Rain	2.8	47	14	Urban U.S.A.
4	Rain	390⁺	4700⁺	7	Urban N.L.
5	Rain	--	17-261	7	Urban U.S.A.
5	Rain	--	27-80	7	Rural U.S.A.
6	Rain	5-66	35-112	3	Urban & Rural F.R.G.
7	Fog	0.03	0.78	2	Remote New Zealand
8	Fog	700	7120	20	Urban Switzerland
9	Fog	1200	28200	21	Urban Switzerland

* = sum of mean values of N PAHs
N = number of PAHs in study
⁺ = maximum value reported

References:
1: Georgii and Schmitt, (1983)
2: Kawamura and Kaplan, (1983)
3: Ligocki *et al.*, (1985)
4: van Noort and Wondergem, (1985)
5: Kawamura and Kaplan, (1986)
6: Thomas, (1986a)
7: Herrmann, (1987)
8: Leuenberger *et al.*, (1988)
9: Capel *et al.*, (1991)

contaminants has been well investigated (e.g. Thomas, 1986; Tranter *et al.*, 1986, 1987; Davies *et al.*, 1988, 1992; Leuenberger *et al.*, 1988).

One major aspect of snow chemistry that has been of interest is the phenomenon known as the 'acid flush'. This term is used to describe the rapid increase in acidity of watercourses fed by snow meltwaters during the thaw (Henriksen *et al.*, 1984). In temperate regions, where snow is a significant source of precipitation, the annual production of snowmelt is commonly the major hydrologic event. It is often a seasonal event, occurring in the spring, and has important environmental implications as it may coincide with the spawning of game fish. Such events have been shown to coincide with fish kills in Scandinavia, Britain and North America (Leivestad and Muniz, 1976; Overrein *et al.*, 1981; Wigington *et al.*, 1990).

Up to 80% of the total inorganic solute load of a snow pack can be released within the first 20% of meltwater (Cadle *et al.*, 1984). There is also evidence that preferential elution of the solutes within snow occurs, whereby certain ionic species are removed more quickly than others (Tranter *et al.*, 1986).

Less is known about the behaviour of hydrophobic organic compounds, such as PAHs, in snow. In a study of snowmelt, PAHs exhibited a 60 to 70 % loss with the first 40 % of meltwater, followed by a relative accumulation (Simmleit *et al.*, 1986). The accumulation phase is attributed to the consolidation of the snowpack with increased melting, thus reducing the permeability of the snowpack to particles with which such compounds are associated. This was also observed by Schöndorf and Herrmann (1987), who found that approximately 90 % of the fluoranthene, benzo[a]pyrene and benzo[ghi]perylene content of snow was eluted with the last 20 % of meltwater.

The release of PAHs from snow cover by melting has been indicated in studies of the PAH concentration in lake water (Borneff, 1975) and the concentration in, and fluxes to, estuarine sediment (Broman *et al.*, 1988).

A small number of investigations have been concerned with both trace organic and inorganic snow chemistry. A study of the behaviour of trace organic pollutants during snowmelt showed that they exhibited the same behaviour as ionic species: they were also predominantly released with the first 40 % of meltwater (see above) (Simmleit *et al.*, 1986).

Schrimpff *et al.* (1979) report that some trace metals (Zn, Cd and Cu) and PAHs had a similar regional pattern of distribution in snow in NE-Bavaria, which was related to orography, urbanisation and industrialisation. But the distribution of Pb and pesticides differed from that of PAHs, owing to the influence of automotive emissions and glass and ceramic production for Pb, and diffuse agricultural and forestry sources for pesticides.

Thomas (1986b) undertook correlation analysis of PAH and metal concentrations in snow cover. However, no high correlation coefficients were produced, though those for BghiP with Zn and Cd were significant at the 1 % level. The differences between PAH and metal distribution were attributed to the following factors: a) variations in the proximity of emission sources to sampling sites; b) PAH tend to be associated with smaller particles that have significantly longer atmospheric residence times; c) PAHs are subjected to some degree of photodecomposition in the upper layers of snow.

In contrast to research into inorganic snow chemistry, there has been very little research aimed at determining the occurence, concentration or processes affecting trace organic compounds in snow (see review by Gregor, 1991). A number of reviews addressing acidic snow deposition and inorganic snow chemistry have been published (IAHS, 1986; Jones and Orville-Thomas, 1987; Davies *et al.*, 1991; Wigington *et al.*, 1991).

PAHs have been found in snow samples at various geographical locations, but there have been relatively few such studies, and those that have been undertaken are often subjectively and objectively diverse. The range of PAH compounds investigated varies from study to study. Table 1.6 shows that over 24 different PAH compounds have been studied in snow samples. The most commonly detected compounds ($F > 4$) are phenanthrene, fluoranthene, pyrene, benzo[a]pyrene and benzo[ghi]perylene. These are all registered as priority pollutants by the US EPA (EPA, 1982). Because of the discontinuity of study compounds, direct comparisons between studies are not always possible. However, it is evident that PAHs are an important class of organic contaminants in snow.

1.6.3 The Inclusion of PAHs in Snow.

There are three major ways in which PAHs can become incorporated within snow. These are inclusion during the formation of individual ice crystals, scavenging by falling snow flakes (wet deposition) and deposition on to fallen snow (dry deposition). These processes relate to particulate and to vapour phase PAHs, and are given further consideration below. The subject of the process of snow formation and the effects on snow chemistry has recently been reviewed by Barrie (1991)

PAHs and other hydrophobic compounds in the atmosphere are mainly associated with aerosols, adsorbed on particles smaller than 10 μm. The majority of PAHs are present in the size range of 0.2 to 2.4 μm (Van Vaeck and Van Cauwenberghe, 1985). Particles in the size range of 0.1 - 1 μm can act as ice nuclei within clouds under suitable conditions (Schemenauer *et al.*, 1981). Particles containing PAHs can thus initiate the production of ice crystals, and in doing so, cause PAHs to become incorporated in snow (Simmleit *et al.*, 1986).

After initial formation, ice crystals can grow within the cloud by the processes of riming, clumping and scavenging of droplets, vapour and particles. These ice crystals then aggregate to form snow flakes. As snow flakes fall through the air, they can further scavenge particles and gases, and so increase their PAH loading. When this process occurs within the cloud it is referred to as 'in-cloud

Table 1.6 **PAHs detected in snow.**

Compound	Reference No.									F
	1	2	3	4	5	6	7	8	9	
Naphthalene	-	-	-	-	*	-	*	-	-	2
Σ M-naphthln	-	-	-	-	*	-	*	-	-	2
Biphenyl	-	-	-	-	-	-	*	-	-	1
Fluorene	-	-	*	-	-	-	-	*	-	2
Phenanthrene	*	-	*	-	*	-	*	*	*	6
Anthracene	*	-	*	-	-	-	-	-	*	3
Σ M-phenthrn	*	-	-	-	-	-	-	*	-	2
Fluoranthene	*	*	*	*	*	*	-	*	*	8
Pyrene	n	-	*	-	*	-	*	*	*	5
M-flrnthn	p	-	-	-	-	-	-	-	-	1
Benzo[a]flrn	n	-	-	-	-	-	-	*	-	1
Benzo[k]flrn	n	-	-	-	-	-	-	*	-	1
Σ M-pyrene	n	-	-	-	-	-	-	-	-	0
B[ghi]flrnthn	n	-	-	-	-	-	-	-	-	0
B[a]anthracn	*	-	-	-	-	-	-	*	*	3
M-B[a]anthrcn	*	-	-	-	-	-	-	-	-	1
Chrysene	n	-	*	-	-	-	-	*	*	3
B[b+j+k]flrnt	*	-	-	-	-	-	-	*	-	2
Benzo[e]pyrn	*	-	-	-	-	-	-	*	*	3
Benzo[a]pyrn	*	*	-	*	-	*	*	*	*	7
Perylene	p	-	-	-	-	-	-	-	-	1
I[123cd]pyrn	-	-	-	-	-	-	-	*	*	2
B[ghi]pryln	n	*	*	*	-	*	-	p	*	6
Coronene	-	-	*	-	-	-	-	-	-	1

(continued overleaf)

Table 1.6 **(continued)**

Key:

F = frequency of occurances
* = detected in snow
p = detected in particulate phase only
n = not detected
- = not analysed/reported
B = Benzo
M = Methyl
I = Indeno
Σ = sum of isomeric group

References:

1: Lunde *et al.*, (1977)
2: Schrimpff *et al.*, (1979)
3: Georgii and Schmitt, (1983)
4: Simmleit *et al.*, (1986)
5: Kawamura and Kaplan, (1986)
6: Thomas, (1986b)
7: Czuczwa *et al.*, (1988)
8: Leuenberger *et al.*, (1988)
9: McVeety and Hites, (1988)

scavenging' or 'wash-out'. When it occurs below the cloud base it is referred to as 'below-cloud scavenging' or 'rain-out', regardless of the type of precipitation (Forland and Gjessing, 1975; Schemenauer *et al.*,1981; Barrie, 1991).

The dendritic structure of the majority of individual snow flakes results in both a high surface area and a high surface roughness which combine to make below-cloud scavenging of aerosols by falling snow an efficient removal mechanism (Georgii and Schmitt, 1983; Barrie, 1991). It is thought that this mechanism is a combination of inertial impaction on individual crystals and a filtering effect as air moves through the mesh structure of snow flakes (Mitra *et al.*, 1990; Barrie, 1991). The efficiency of scavenging of aerosol by ice crystals has been demonstrated to be dependent on aerosol concentration (McVeety and Hites, 1988), particle size distribution (Mitra *et al.*, 1990), air temperature, air pressure, relative humidity, and electrostatic charge: the collection efficiency increases as the air temperature increases and the relative humidity decreases (Miller, 1990; Miller and Wang, 1991).

Scavenging of vapour phase PAHs by ice crystals and snow flakes also occurs, but the exact process is not well understood (Czuczwa *et al.*, 1988; Barrie, 1991). This is an important process, particularly for the lower molecular weight PAHs, as some exist partly or even exclusively in the vapour phase owing to relatively high saturation vapour pressures (Andren and Strand, 1981). PAHs in the vapour phase can be directly incorporated into ice crystals by vapour condensation on to the surfaces of individual ice crystals (Scott, 1981). McVeety and Hites (1988) calculated washout ratios of PAHs by rain and snow and found that both precipitation types were inefficient scavengers of vapour phase PAHs. The majority of work on vapour phase scavenging has been directed at understanding the behaviour of inorganic gaseous species such as HCl, HNO_3, NH_3, H_2O_2 and SO_2 (Barrie, 1991).

Overall, the scavenging of particulate PAHs by snow is thought to be more efficient than the scavenging of gaseous PAHs (Thomas, 1986), and it has been estimated that snow flakes have a collision efficiency for particles five times higher than rain drops (Leuenberger *et al.*, 1988). Scavenging of PAHs by snow is thus usually thought to be more efficient than scavenging by rain (Georgii and Schmitt, 1983; Leuenberger *et al.*, 1988). However, McVeety and Hites (1988) measured the washout ratios of individual PAHs in rain and snow and found that while this is true for the lower molecular weight compounds, it does not necessarily apply to the heavier compounds. The washout ratio is a measure of the removal efficiency of PAHs by the rain or snow and is defined as:

$$W_T = C_{p,d+a} / (C_{A,a} + C_{A,g})$$

where: W_T = washout ratio,

$C_{p,d+a}$ = concentration of PAH in precipitation in dissolved plus adsorbed phases (ng l^{-1}),

$C_{A,a}$ = concentration of PAH in atmosphere in adsorbed phase (ng m^{-3}),

$C_{A,g}$ = concentration of PAH in atmosphere in gaseous phase (ng m^{-3}).

A higher value for W_T for an individual compound indicates a more efficient removal from the atmosphere by the process of wet precipitation for that compound.

Table 1.7 shows the values for W_T calculated for the PAHs in rain and in snow by McVeety and Hites (1988). The reduction in the removal efficiency of the larger PAH compounds by snow compared to rain can possibly be explained by the ice crystal growth theory proposed by Scott (1981). As the higher molecular weight PAHs do not have a significant vapour phase component they will therefore not be incorporated in ice crystals by vapour condensation.

Table 1.7 **Washout Ratios (W_T) for Some PAHs by Rain and Snow.**
(from: McVeety and Hites, 1988)

COMPOUND	Rain	Snow
Phenanthrene	790	13,200
Anthracene	6,090	104,000
Fluoranthene	4,810	36,400
Pyrene	3,300	31,400
Benz[a]anthracene	51,500	52,700
Chrysene/Triphenylene	32,100	54,700
Benzo[e]pyrene	135,000	70,000
Benzo[a]pyrene	205,000	75,400
Indeno[123-cd]pyrene	174,000	53,500
Benzo[ghi]perylene	248,000	56,500

If this was the case under all conditions then it would result in a different relative abundance distribution of PAHs in rain compared with snow. The lower molecular weight PAHs would account for a higher proportion of total PAHs in rain than snow, and conversely, the heavier PAHs would be predominant in rain. However, Georgii and Schmitt (1983) found that the relative abundance of individual PAH compounds in precipitation is constant from one event to another over a short period of time, and is not affected by the type and form of precipitation event. They also show that the distribution concentrations of individual PAHs between the dissolved and particulate fractions is constant. In general, as the molecular weight increases, the amount of compound in the dissolved phase decreases. It is evident that there is a need for further research in this area to clarify the process of vapour scavenging of organic compounds by ice crystals and snow flakes.

The addition of PAHs to fallen snow occurs by dry deposition. This is a result of the gravitational precipitation of aerosols on to the snow surface (Thomas, 1986; Simmleit *et al.*, 1986). Some researchers suggest that when measuring wet deposition only, precautions should be taken to sample snow soon after snowfall to reduce the impact of dry deposition (Georgii and Schmitt, 1983). Conversely, it has been proposed that the dry deposition of PAHs to the surface of fallen snow may be negligible, owing to the low surface roughness of the snow pack, which results in the surface being relatively resistant to dry particle deposition (McVeety and Hites, 1988). Thomas (1986) reports that the influence of dry deposition of PAHs to a snowpack is low, and may be balanced by the loss by photodecomposition. However, the study only covered a period of dry deposition of less than two weeks and it is noted that dry deposition could be more significant over a longer time. There appears to be a need for the question of significance of dry deposition of PAHs to be further investigated and clarified.

For example, in one study of the atmospheric flux of PAHs to water surfaces in the Great Lakes region of North America, a value for the ratio of the wet-to-dry deposition flux was estimated to be of the order of 9:1 (Andren and Strand, 1981).

However, in a separate study in the same region, the ratio was estimated to be 1:9 (McVeety and Hites, 1988).

Other than gravitational settling, an additional source of dry deposition of particulate phase PAHs to a snowpack is wind-driven impaction. It has been reported that air permeable snow can act as a mechanical filter for wind-blown airborne particles (Gjessing, 1977).

In summary, the relative importance of wet versus dry deposition in terms of contamination by PAHs is therefore dependent on the distribution of the PAHs between the particulate and vapour phase, the particle size distribution in the atmosphere, precipitation intensity and duration, the aqueous solubilities and chemical reactivities of the individual PAH compounds, and the meteorological conditions pertaining at the time of, and after deposition (Eisenreich, 1981; Thomas, 1986).

1.6.4 The Concentration and Distribution of PAHs in Snow.

Table 1.8 illustrates values for the concentrations of PAHs found in snow. It is evident from this that there have been few quantitative studies of PAHs in snow in recent years, and those that have been undertaken have not studied a consistent suite of compounds.

The absolute concentration of PAHs in snow is affected by factors such as geographical location, meteorological conditions and orographic effects.

Table 1.8 **The Concentration Range of Benzo[a]pyrene and Total PAH Reported in Snow (ng l^{-1}).**

Reference	B[a]P	TPAH	N	Location
1	29±28	341	4	Urban FRG
2	-	2500	9	Urban FRG
3	-	53	7	Rural Western USA
3	-	131	7	Urban Western USA
4	29±11	178	3	Urban FRG
5	3	80	10	Remote Northern USA
6	20	1720	20	Urban Switzerland
7	16	606	7	Urban Switzerland

N = number of PAH in study.
- = Not analysed.

References:
1: Schrimpff *et al.*, (1979)
2: Georgii and Schmitt, (1983)
3: Kawamura and Kaplan, (1986)
4: Thomas, (1986b)
5: McVeety and Hites, (1988)
6: Leuenberger *et al.*, (1988)
7: Czuczwa *et al.*, (1988)

Snows from urban areas may have higher concentrations of PAHs than snow from remote and rural areas (Kawamura and Kaplan, 1986). Schrimpff *et al.* (1979) report a difference in concentration of approximately 4 times between urban samples and rural samples. Georgii and Schmitt (1983) showed that the concentration of PAHs in snow also reduced with increasing distance from a suburban area. McNeely and Gummer (1984) analysed snow samples from Ellesmere Island in the Canadian Arctic for 17 PAHs but they were all below the detection limits (0.02 μg l^{-1}).

The meteorological conditions around the time of snow fall affect the PAH content. Elevated concentrations were recorded in snow that had fallen after a four-day period of no precipitation, characterised by a high pressure weather system (Thomas, 1986). The temperature during and after snowfall will also have an effect as this controls vapour phase partitioning and melting of the snow, which will redistribute PAHs (Simmleit *et al.*, 1986; Thomas, 1986; Simmleit and Herrmann, 1987).

The duration and intensity of the precipitation event also affects the concentration of contaminants in snow. There tends to be an inverse proportionality between the volume of precipitation and the concentration of contaminants (Georgii and Weber, 1960). This has been demonstrated for organic matter, including PAHs (Kawamura and Kaplan, 1986; Georgii and Schmitt 1983). This means that over the period of one precipitation event, the concentration of contaminants decreases with time.

Schrimpff *et al.* (1979) found that the concentration of PAHs in snow in a relatively remote mountain area increased with altitude. This was believed to be a result of orographic uplift of the air mass which causes a strong washout of contaminants on windward slopes as the air ascends (Barrie, 1991).

Some processes can act to remove PAHs from a snow pack. Firstly, melting of snow causes a release of PAHs from the snow, as described earlier. Secondly, photodegradation may result in the chemical transformation of PAHs (Thomas, 1986). Solar radiation may also cause loss of lower molecular weight PAHs by volatilisation (McVeety and Hites, 1988). It is also possible that losses will occur by wind-driven volatilisation.

1.7 Background to the Present Study.

As can be seen from the previous section, PAHs can be considered an important class of micropollutants in snow, which have so far been subjected to a small number studies. There are currently no data available with respect to the concentration of PAHs in snow in Britain. As there are areas in Britain where snow is a seasonally significant meteorological and hydrological feature, research in this area is called for.

This need is substantiated by the results of previous work undertaken in the Cairngorm Mountains of Scotland. Certain episodes of snowfall in this area have been seen to result in the deposition of darkly coloured or 'black snows' (Brimblecombe *et al.*, 1986; Davies *et al.*, 1988; Landsberger *et al.*, 1989). These were typically found to have low pH values and high concentrations of organic carbon (OC). The carbon content of snowfall was found to correlate well with acidity when estimated by reflectance measurements of filtered snowmelt samples, as shown in Figure 1.5 (Davies *et al.*, 1988). The concentration of OC in snow from this area is in the region of 0.02-0.68 mg l^{-1} with corresponding pH values in the range 3.95 to 5.09 (Davies *et al.*, 1992).

Atmospheric soot particles are a rich source of both organic and elemental carbon (OC and EC). OC is defined as the portion that volatilise when heated, or is extractable with solvents, and EC is defined as the nonvolatile, nonextractable fraction (Wolff, 1985). The latter is also sometimes referred to as 'black carbon'. Soot can be a rich source of PAHs and other organic compounds, and therefore the soot content of snow is a significant factor with respect to atmospheric contamination by PAHs (Broman *et al.*, 1988). Soot also has a significant effect on the physical properties of the snowpack. It has been estimated that the spectrally averaged albedo of a snowpack surface can be reduced by 1% by 40 μg elemental carbon (EC) per litre in new snow, and 10 μg EC per litre in coarse grained old snow (Clarke and Noone, 1985). This has important implications for the rate and extent of snowpack melting induced by solar radiation.

Table 1.9 summarises measurements of EC/OC in snows from various locations. The concentration ranges from around 3 μg l^{-1} in remote areas, up to 16000 μg l^{-1} in a highly polluted black snow event in Austria. Analysis of cores from Greenland suggests that the background level of EC in snow is 2 μg l^{-1}, as found in ice of approximate age of 4-6000 years. The significance of EC/OC in snow is further highlighted by the fact that soot can have a PAH content of up to 3% (Lee *et al.*, 1977). If it is assumed that all the EC/OC in snow is soot, then hypothetical maximum values of PAH in snow of 480 μg l^{-1} and 20 μg l^{-1} can be calculated for the black snow events reported by Malissa *et al.* (1989) and Davies *et al.* (1992), respectively.

The chemical characteristics of snowfall in the Cairngorm Mountains are generated in regions dependent on the back trajectories of the air masses with which they are associated (Davies *et al.*, 1992). It is expected that snow resulting from air masses which have formed or passed over regions of high industrial development, such as Eastern Europe and the Midland valleys of England, will have high concentrations of PAHs.

The PAH compounds chosen for this study are the 16 EPA priority PAHs. These are listed in Appendix I, which also shows their molecular structure and gives selected physical and chemical data. They cover a wide range of molecular weights and will be comparable to the majority of contemporary studies of PAHs in the environment.

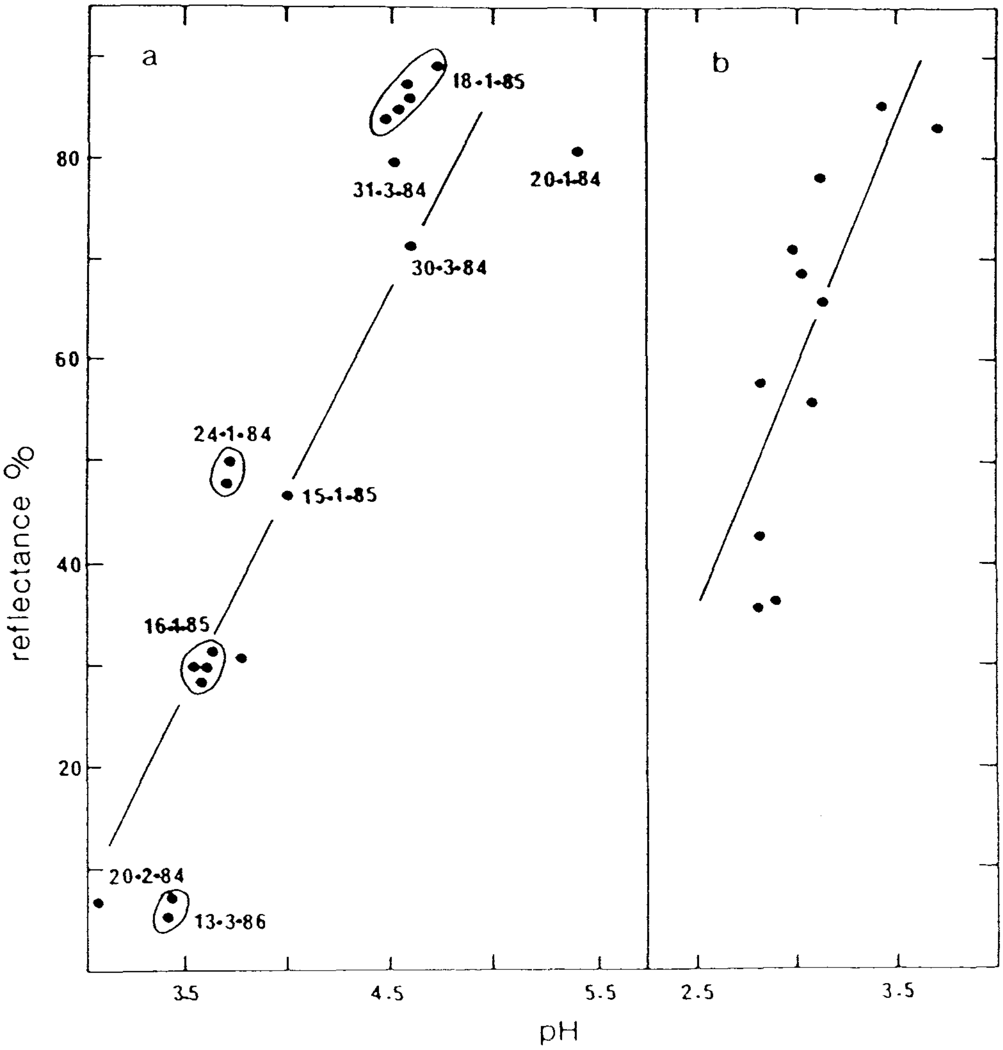


Figure 1.5 **The relationship between filter reflectence and meltwater acidity of 'black' snows from the Cairngorm Mountains, Scotland.**

a) Fresh snowfall, showing dates of fall. Replicate samples are clustered.

b) Snowpit samples.

(from Davies *et al.*, 1988)

Table 1.9 **Concentrations of Elemental and Organic Carbon (EC and OC) in Snow and Ice.**

Ref	Type*	Conc.	Comments
1	EC	0-127 $\mu g\ l^{-1}$	Arctic snowpack samples
2	EC	2.2-25.4 $\mu g\ l^{-1}$	New Mexico and Texas, fr.snow
	EC	1.1 & 2.5 $\mu g\ l^{-1}$	Greenland ice cores+
3	EC	28-210 $\mu g\ l^{-1}$	N.Michigan, USA, fresh snow
	OC	140-1300 $\mu g\ l^{-1}$	N.Michigan, USA, fresh snow
4	EC	4-60 $\mu g\ l^{-1}$	Swedish Arctic, fresh snow
5	EC	16000 $\mu g\ l^{-1}$	Austria, fresh snow
6	OC	20-680 $\mu g\ l^{-1}$	Scotland, fresh snow

* : EC = elemental carbon, OC = organic carbon
+ : represents background concentrations from ice of ages 4000 and 6000 years

References:
1: Clarke and Noone, (1985)
2: Chýlek *et al.*, (1987)
3: Cadle and Dasch, (1988)
4: Noone and Clarke, (1988)
5: Malissa *et al.*, (1989)
6: Davies *et al.*, (1992)

CHAPTER 2: REVIEW OF TECHNIQUES FOR THE ANALYSIS OF POLYCYCLIC AROMATIC HYDROCARBONS

2.1 Introduction.

For the analysis of PAHs, all equipment used for the preparation, handling and storage of samples and standards must be made of glass or metal to ensure that no contamination is imparted to the sample. PTFE (eg. Teflon) is acceptable where its use is unavoidable, but all other polymer and plastic utensils present too high a risk of contamination from leached compounds, and should not be used. Before use, the equipment must be rigorously cleaned to remove any possibility of contamination. All solvents used must be of a high purity to further prevent contamination.

Prior to analysis, the analyte must usually be isolated from the rest of the sample (the 'matrix'). It is also usually desirable, and sometimes essential, when performing trace level analyses, for this process to include a concentration of the analyte.

The PAHs are usually extracted into an organic solvent which is then concentrated, and subjected to a variety of clean-up techniques (ie. to remove unwanted compounds) if necessary. The sample is sometimes transferred to a different solvent to enable a particular analytical technique to be applied.

Various extraction and concentration methods have been applied to the analysis of PAHs in environmental samples. This review deals with those that are most applicable to the analysis of trace levels of PAHs in water and water-borne or atmospheric particulate samples only.

2.2 Sample Preparation.

2.2.1 Extraction of Dissolved Phase PAHs.

It is important to note that the term 'dissolved' is usually operationally defined by the pore size of filter used in a particular study. Also, in some studies the procedures used to extract PAHs from water do not always distinguish between total PAHs and dissolved/particulate PAHs (see: Harrison *et al.*, 1975; EPA, 1982; Kawamura and Kaplan, 1983; Ligocki *et al.*, 1985; SCA-DOE, 1988).

2.2.1.1 Liquid-Liquid Extraction.

Liquid-liquid or solvent extraction entails the vigorous mixing of the water sample with an immiscible organic solvent. The mixing can be carried out by shaking in a separating funnel (Ogan *et al.*, 1979; Furuta and Otsuki, 1983), by agitation and stirring in a collection vessel (McVeety and Hites, 1988), the use of ultrasonic homogenisers (Acheson *et al.*, 1976) or continuous liquid extraction (Goldberg *et al.*, 1973)

The choice of solvent is critical. It must be immiscible with water, have a high solubility for PAHs and have a relatively high degree of volatility to facilitate its reduction once extraction has been completed (Harrison *et al.*, 1975). Suitable solvents include cyclohexane (Furuta and Otsuki, 1983; Bedding *et al.*, 1988), hexane (Ehrhardt and Knap, 1989) and dichloromethane (Acheson *et al.*, 1976; Ogan *et al.*, 1979; Kawamura and Kaplan, 1986). Less frequently used solvents include the C5-C8 alkanes, benzene, chloroform, and carbon tetrachloride (Bartle *et al.*, 1981).

The disadvantages of solvent extraction are as follows: a) large volumes of (often potentially hazardous) chemicals are required; b) the concentration of PAHs by evaporation of the solvent means that any contaminants present in the solvent will be also be concentrated; c) thus solvents of high purity are required, which are expensive to buy or time consuming to prepare; d) the amount of equipment needed and the number of solvent and sample transfers increases the possibility of introducing contamination.

2.2.1.2 Solid Phase Extraction of Dissolved PAHs.

The principle of these types of techniques is that the water sample is passed through a porous adsorbant phase which removes the PAHs from the water. The PAHs are subsequently removed from the adsorbent by solvent elution or thermal desorption.

Activated carbon is one such adsorbent that has been used for the extraction of organic compounds from water. However, the recovery of PAHs from the activated carbon by solvent elution is often low and variable (Borneff and Kunte, 1983). Other adsorbents that have been used for PAH extraction more successfully include: Tenax-GC, a porous polymer based on 2,6-diphenyl-p-phenylene oxide (Leoni *et al.*, 1975; Jones *et al.*, 1976); Amberlite XAD polymer resins (Junk *et al.*, 1974; Kveseth *et al.*, 1982); open pore polyurethane (Navratil *et al.*, 1977; Dasu and Saxena, 1978); C-18 bonded porous silica (Ogan *et al.*, 1978; Takeuchi and Ishii, 1981; Junk and Richard, 1988).

Solid phase extraction has certain drawbacks. The adsorbent material must be thoroughly cleaned before use, to prevent contamination of the sample extract by adsorbed contaminants. It is possible that the material itself can be a source of contamination, as has been shown for activated carbon (Van Rossum and Webb, 1978) and XAD resins (James *et al.*, 1981). In addition, it is possible that irreversible adsorption of the analyte can occur.

The advantages of solid phase extraction are that it usually takes a shorter time than liquid extraction, uses fewer materials and is relatively easy to perform (Ogan *et al.*, 1978). Also, smaller sized samples can be used. C-18 silica has been used extremely successfully for small scale extraction work (<0.5 l sample size) (Junk and Richard, 1988) and micro-scale extraction (1.0 ml sample size) (Takeuchi and Ishii, 1981).

One great advantage of solid adsorbents that merits further investigation and trial is on-line sampling and analysis, as has been attempted with coupled column chromatography (Eisenbeiss *et al.*, 1978; Ogan *et al.*, 1978). This involves pumping the water sample, modified with an alcohol to increase the solubility of PAHs in the water and to promote "wetting" of the adsorbent, through an HPLC pre-column packed with C-18 silica. The pre-column adsorbs the PAHs from the water, and is then switched in-line to the analytical HPLC equipment and the mobile phase is back-flushed through the pre-column, thus eluting the PAHs on to the analytical column. Excellent recoveries have been reported. The great advantage of this type of extraction is that there is minimum handling of the sample, which needs only to be filtered, have the solvent added and then pumped from the filter vessel, all of which can be easily automated. This would greatly simplify analysis of field samples, where ideal laboratory facilities are not always available.

2.2.2 Extraction of Particulate Associated PAHs.

For water samples, the PAHs associated with the particulate phase will normally be present on a filter. The PAHs will be adsorbed onto the particles to varying degrees. A suitable method is therefore required to remove the PAHs from the particles and into a suitable solvent.

2.2.2.1 Soxhlet Extraction.

Soxhlet extraction is the classic technique for extraction of organic compounds from solid samples. The sample needs to be in a granular or particulate form for the technique to be efficient. It is a continuous extraction process, with a pool of purified solvent being continuously cycled through the sample.

Solvents that have been used for the extraction of PAHs using this technique include benzene (Gordon and Bryan, 1973), hexane (Pacyna and Oehme, 1988), cyclohexane (Bjørseth *et al.*, 1979), toluene (Gschwend and Hites, 1981), methanol (Andren and Strand, 1981), chloroform (Readman *et al.*, 1986) and dichloromethane (May and Wise, 1984). Mixtures of different solvents are also commonly used.

Generally, Soxhlet extraction takes a relatively long time to achieve a good recovery efficiency, dependent on the solvent used and the cycle time. Periods of up to 48 hrs have been reported (May and Wise, 1984).

Further disadvantages of Soxhlet extraction are the large volumes of solvent required and the potential loss of analyte owing to volatilisation by hot solvent or thermal degradation (Golden and Sawicki, 1975).

Soxhlet extraction has been successfully used for the extraction of PAHs in sediment (Hites *et al.*, 1980; Readman *et al.*, 1986; Heit *et al.*, 1988) and atmospheric samples (Bjørseth *et al.*, 1979; Andren and Strand, 1981; Pacyna and Oehme, 1988).

2.2.2.2 Ultrasonic Extraction.

Ultrasonic extraction has benefits as an alternative to Soxhlet extraction. This type of extraction involves the sonication of the sample immersed in a suitable solvent. This is done in an ultrasonic bath which generates high-frequency waves (> 25 kHz) through a body of water, which are in turn transmitted to the sample. The high frequency waves energise the solvent and enable it to surround and penetrate the particles and thus solubilise the PAHs.

Ultrasonic extraction has been used to analyse PAHs associated with airborne particles collected on glass fibre filters (Lee and Schuetzle, 1983; Valerio *et al.*, 1986; Nielsen, 1988). Solvents employed have included dichloromethane

(Nielsen, 1988) and cyclohexane (Golden and Sawicki, 1975; Valerio *et al.*, 1986) as the extraction solvent. It has also been applied to the analysis of sediment samples using dichloromethane and methanol (Thompson and Eglington, 1978).

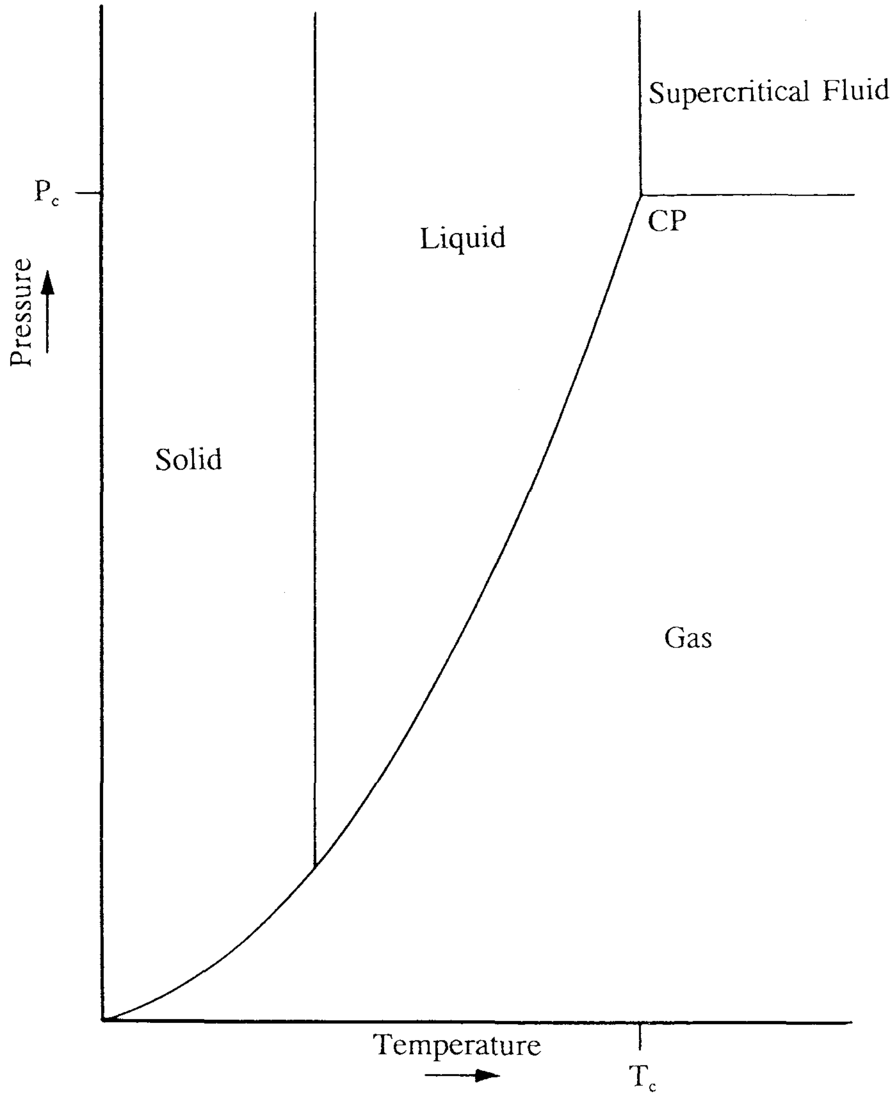
The advantages of ultrasonic extraction over Soxhlet extraction are that the extraction takes a much shorter time (c. 30 min), a smaller volume of solvent is required and there are virtually no losses from volatilisation. In comparative studies of Soxhlet and ultrasonic extraction, the latter technique has been shown to be more efficient (Chatot *et al.*, 1971; Golden and Sawicki, 1975), but depended critically on the solvent used (Chatot *et al.*, 1971).

2.2.2.3 Supercritical Fluid Extraction.

Supercritical fluid extraction (SFE) is a relatively recent development that uses supercritical fluids as the extraction media for the removal of an analyte from a matrix. A gaseous compound can be defined as a supercritical fluid (SCF) when it is under conditions of temperature and pressure that cause it to be compressed to a density which approximates a liquid. It is then a compressible fluid that takes the shape of and fills its container (White and Berry, 1990). Typically, SCFs have densities 100-1000 times greater than their respective gases. The conditions under which SCFs form are determined by the critical temperature (T_c) and pressure (P_c) of the compound in question (see Figure 2.1), which define the critical point (CP) of the compound (Majors, 1991).

SCFs have both gas- and liquid-like properties: they have high diffusivities, and their high densities enable them to dissolve analytes from solid matrices. They also exhibit low surface tension and low viscosity. The properties of SCFs make them rapid and efficient extraction media (Majors, 1991).

Ideally, the sample matrix needs to be in a solid granular or porous form. Liquids can be subjected to SFE if they are immobilised on a solid support. The most commonly used SCF is carbon dioxide. Once the analyte has been extracted into



<u>Figure 2.1</u> <u>Phase diagram illustrating the critical point (CP) and the critical temperature (T_c) and pressure (P_c) that define the physical state of a substance.</u>

the SCF it can be introduced directly to an analytical instrument, trapped on an adsorbant or transferred into a secondary solvent (Pipkin, 1992).

SFE has been successfully used for the extraction of PAHs adsorbed from solution onto glass beads, and also from soils (McNair and Frazier, 1991).

2.2.3 Sample Clean-up.

When the PAHs have been extracted from the sample into a solvent, the extract may need a degree of purification to remove other compounds that interfere in the analytical procedure. This is generally required for samples with a high content of organic material.

The most common forms of sample cleaning are solvent washing, solvent partition, column chromatography and thin layer chromatography. These are discussed below.

Solvent washing techniques involve washing the extraction solvent with immiscible, dilute aqueous solutions of an alkali or acid, to remove acidic or basic compounds respectively (Bartle *et al.*, 1981).

Solvent partitioning involves the transfer of the PAHs from the extraction solvent, hexane for example, into a different solvent, such as dimethylsulphoxide or dimethylformamide, in which the contaminants are not soluble. The second solvent is then modified in some way, such as dilution with water, to enable the PAHs to be back extracted into fresh hexane. This approach has been used for the analysis of PAHs in airborne particulates (May and Wise, 1984).

Column chromatographic techniques utilise the separation of organic compounds on various chromatographic materials to isolate a fraction containing the PAHs. Common materials used include aminosilane (May and Wise, 1984), silica gel (Heit *et al.*, 1988), silica-alumina (Valls *et al.*, 1989), alumina (Gordon and

Bryan, 1973), silicic acid (Hites *et al.*, 1980) and Sephadex LH-20, a lipophilic gel (Gschwend and Hites, 1981). High performance liquid chromatography (HPLC) has also been used to separate and collect the organic fraction of a sample (Nielsen, 1988; Pacyna and Oehme, 1988).

Thin layer chromatography (TLC) can also be used for the separation of PAHs in a complex sample matrix. The extract solvent is reduced to a small volume and spotted on to a TLC plate. The plate is then developed with a suitable solvent and the area containing the PAH fraction is identified with an ultraviolet lamp. The area of coating is scraped off, collected and the PAHs eluted in a solvent. This type of preparative method has been used for several studies of PAHs (De Wiest, 1978; Kawamura and Kaplan, 1983; Merrill and Wade, 1985; Valerio *et al.*, 1986; Greenberg, 1989). For a more complete discussion of TLC techniques for PAH analysis, see Section 2.3.1 below.

2.3 Analytical Techniques for PAH Identification.

Many papers, reviews and books deal with the analytical techniques for PAH compounds (see: Snook *et al.*, 1979; Bartle *et al.*, 1981; Lee *et al.*, 1981; Bjørseth, 1983; Vo-Dinh, 1989). A brief overview of the most suitable and most widely used techniques follows.

2.3.1 Thin Layer Chromatography (TLC).

TLC involves the chromatographic separation of a mixture of PAHs on a solid stationary phase material spread thinly on a supporting plate, usually made of glass or metal.

Several combinations of active coatings and mixtures of eluting solvents are available for the separation of PAHs. The three most commonly used are: alumina with pentane and diethyl ether; cellulose acetate with ethanol, toluene and water; cellulose with dimethylformamide and water (Lee *et al.*, 1981).

Separation can be further enhanced by the application of two dimensional TLC in which the plate is eluted in one direction with a particular solvent and then rotated through 90° and eluted with a second solvent (Lee *et al.*, 1981).

After elution and separation, the PAHs can be identified by comparison with standards, and quantified by *in situ* spectrophotometric scanning (Schrimpff *et al.*, 1979; Simmleit *et al.*, 1986; Thomas 1986a, 1986b; Simmleit and Herrmann, 1987).

The disadvantage of TLC techniques, for preparative work as well as analysis, is the potential loss of PAHs owing to oxidation. PAHs are susceptible to photolytic oxidation when adsorbed on some types of substrates, such as activated silica which is often used in TLC methods (Korfmacher *et al.*, 1980; Lee *et al.*, 1981). On the other hand, TLC offers a relatively fast analysis which allows a large number of samples to be analysed in parallel at a relatively low cost.

2.3.2 Column Chromatography.

Column chromatography was formerly the most frequently applied separation method for PAHs, but improvements in HPLC and gas chromatography (GC) techniques have made column chromatography redundant as an analytical technique for PAHs (Lee *et al.*, 1981). These types of techniques include gel chromatography, predominantly utilising 'Bio-Beads' and 'Sephadex' LH-20 gels (Snook *et al.*, 1979), and also adsorption chromatography, commonly using alumina or silica adsorbents (Lee *et al.*, 1981).

2.3.3 High Performance Liquid Chromatography (HPLC).

HPLC equipment and methodology has undergone rapid advancement over the last twenty years and is now considered equal to GC as a tool for the analysis of PAHs.

The main advantage of this type of analysis is that a wide variety of column packings is available, which offer differing affinities for PAH isomers (May and Wise, 1984). There is also an added degree of selectivity obtained by the choice of the mobile phase. This allows for the separation of isomers such as the benzofluoranthenes, which are not always separated by GC techniques (Grant and Meiris, 1981; May and Wise, 1984).

Further advantages are that the commonly applied detection methods, namely UV-absorption and fluorescence spectrometry, are relatively selective for PAHs, and particularly so when diode array (Dong and Greenberg, 1988) and laser fluorometric (Furuta and Otsuki, 1983) detection techniques are used. They are also non-destructive, allowing the collection of fractions of the effluent for additional analysis. Unlike with GC, HPLC analysis of PAHs is not limited by the low volatility of the higher molecular weight compounds (Fetzer and Biggs, 1987). In addition larger samples can be injected compared to GC (Lee *et al.*, 1981), thus aiding a decrease in the detection limits.

Various column packings and chromatographic conditions can be used for the analysis. The arrangement most commonly used is reverse phase HPLC on chemically-bonded octadecyl (C18) stationary phases using gradient elution techniques. Polar bonded normal phase packings can also be used (Bartle *et al.*, 1981; Lee *et al.*, 1981). Normal phase HPLC is particularly useful for separating PAHs from complex mixtures (May and Wise, 1984).

2.3.4 Gas Chromatography (GC).

In general, gas chromatography is capable of better resolution of PAH compounds than HPLC, but because of volatility limitations this technique is limited to the analysis of PAHs with a ring structure containing six or less rings (Lee *et al.*, 1981; Fetzer and Biggs, 1987).

Currently, fused silica and glass capillary columns, with internal diameters of 0.2

to 0.3 mm and lengths of between 10 to 25 m, are most commonly used for GC analysis of PAHs (Lee and Wright, 1980). The most common coating materials used are non-polar or low polarity coatings. Examples of commercially available materials of these types are SE-52 (methylsilicone gum with 5% phenyl groups) and SE-54 (methylsilicone gum with 1% vinyl and 5% phenyl groups) coatings, respectively (Bartle *et al.*, 1981).

The detection methods most commonly employed for the GC analysis of PAHs are flame ionisation detection (FID) and mass spectrometry (MS). The flame ionisation detector has good linearity of response, sensitivity and reliability (Bartle *et al.*, 1981). However, the disadvantage of the FID is that it is a nonselective detector, thus providing uncertain identification information on compounds detected.

The excellent resolution capability of GC and its compatibility with mass spectrometry make MS a particularly well suited technique for the detection of PAHs (see below).

The electron capture detector (ECD) can also be used for the detection of PAHs, as some PAHs have a relatively high ECD-response (Bartle *et al.*, 1981). When used in parallel, the ECD/FID response ratio has been shown to enhance sensitivity and aid in the resolution of isomers of PAH compounds (Bjørseth and Eklund, 1979).

2.3.5 Mass Spectrometry (MS).

Mass spectrometry is a widely used analytical technique for PAHs. A number of thorough reviews of the application of MS to PAH analysis have been compiled (see: Bartle *et al.*, 1981; Lee *et al.*, 1981; Howard and Mills, 1984; Hites, 1989).

A number of ionisation techniques can be employed, the most common being electron impact (EI) ionisation. As a result of the delocalised electron structure and the inherent stability of PAH molecules, the mass spectra produced by EI ionisation are characteristically dominated by the presence of the molecular ion (M^+), with some fragmentation ions also being formed. Usually, the fragmentation ions are formed by the losses of two hydrogen atoms and the loss of double- or single-charged C_2H_2. These losses result in the production of the $(M-2)^+$, $(M-26)^+$ and $(M-26)^{2+}$ ions, respectively. The $(M-2)^+$ is frequently the second most abundant ion. The double-charged molecular ion (M^{2+}) is also usually present at medium abundance, increasing with the size of the molecule (Hites, 1989).

As a consequence of the formation of few species other than M^+, relatively simple mass spectra are usual, and it is therefore difficult, or sometimes impossible, to distinguish between isomers without the use of additional data, such as GC retention times (Howard and Mills, 1984; Hites, 1989).

Positive and negative chemical ionisation (CI) mass spectrometry produce less complicated spectra than does EI ionisation, and can, in certain cases, be used to distinguish PAH isomers (Howard and Mills, 1984; Hites, 1989).

2.4 Choice of Analytical Technique for Present Study.

Two of the techniques detailed above were available for use in the current study. These were HPLC, with UV-absorbance and fluorescence detection, and GC, with FID and MS detection. Both techniques were subject to a number of constraints, primarily of cost, state of repair and time required for method development and 'trouble-shooting'. Both were employed at different stages of the research, dependent on the particular laboratory facilities and the availability of the instruments.

CHAPTER 3: STUDY SITES AND SAMPLING METHODOLOGY

3.1 Study Sites.

Two major sites were chosen for the study of PAHs in snow: the Cairngorm Mountains in Scotland and the Laurentian Mountains in Eastern Canada. Opportunistic sampling was also undertaken on three occasions in Southern England. Table 3.1 details the dates and nature of all samples taken.

3.1.1 Cairngorm Mountains, Scotland.

Ciste Mhearad (57°06'N, 03°38'W), near the summit of Cairn Gorm in the Cairngorm Mountains is a remote, small (0.4 km^2) mountain catchment at an altitude of about 1080 m a.s.l. (see Figure 3.1). It can accumulate a deep snowpack on top of often saturated and frozen ground. The snowcover of the area is generally characterised by wind-blown surface layers of hard or soft slab and basal layers of coarse, granular snow, with grain diameters > 2 mm. The snowpack often contains ice layers caused by melt-freeze cycles and rain-on-snow events (Ward, 1980; Ward *et al.*, 1985). The annual precipitation for the area is > 2000 mm, of which approximately one-third to one-half falls as snow. Redistribution of the snow by wind is common (Tranter *et al.* 1987).

Ciste Mhearad is an ideal site to study, as it has previously been the subject of a number of snow chemistry studies (Tranter *et al.*, 1986, 1987, 1988; Cooper et al, 1987; Morris and Thomas, 1987; Davies *et al.*, 1988, 1992; Landsberger *et al.*, 1989; Jickells *et al.*, 1992).

The snowfall in this area can sometimes be highly polluted, owing to the long-range atmospheric transport of pollutants. This is dependent on the trajectory of the air mass associated with the deposition of the snow (Abrahams *et al.*, 1988). For the Scottish Highlands, the major pollutant source areas are to the south and the east (Weston and Fowler, 1991). The polluted snows in this region

Table 3.1 **Sample Identification and Characteristics.**

Sample Code		No. (D+P)	Type	Location	Date
QUEBEC	B	10 (5+5)	F	LL	19/12/89
	C	10 (5+5)	F	LL	9/1/90
	D	10 (5+5)	F	LL	7/2/90
	E	10 (5+5)	F	LL	8/2/90
	F	12 (6+6)	F	LL	10/2/90
	G	10 (5+5)	F	LL	11/2/90
	H	10 (5+5)	F	LL	13/2/90
SWIN		6 (3+3)	F^*	SW	10/12/90
SOTON 1		6 (3+3)	F	SN	7/2/91
SOTON 2		6 (3+3)	F	SN	8/2/91
SCOT 1	25/2	6 (3+3)	SP	CG	25/2/91
	27/2	6 (3+3)	F	CG	27/2/91
	27/2	6 (3+3)	SP	CG	27/2/91
	28/2	6 (3+3)	F	CG	27/2/91
	28/2	6 (3+3)	SP	CG	27/2/91
SCOT 2	1/4	6 (3+3)	SP	CG	1/4/91
	2/4	6 (3+3)	SP	CG	2/4/91
	3/4	6 (3+3)	F	CG	3/4/91
	3/4	6 (3+3)	SP	CG	3/4/91
	5/4	6 (3+3)	F	CG	5/4/91
	Total:	150			

No.: D+P = dissolved + particulate
Type: F = fresh snowfall sample;
F^* = c. 24 h old snow pack, sub-surface sample;
SP = snow pit sample.
Location: LL = Lac Laflamme, Québec;
SW = Swindon,;
SN = Southampton;
CG = Cairngorm Mountains.

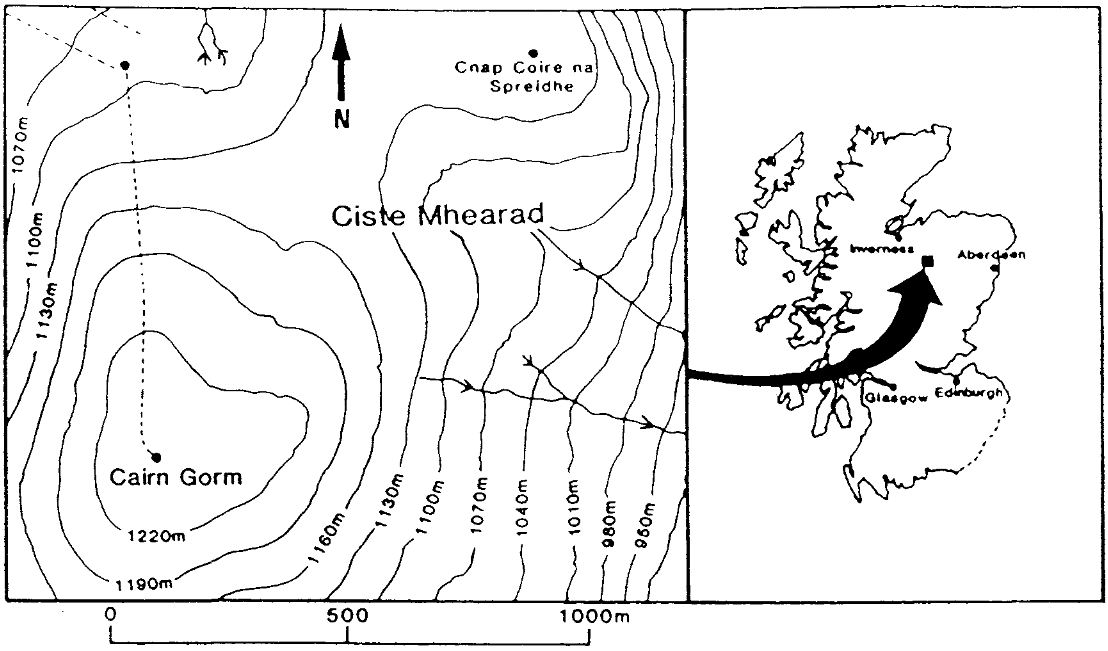


Figure 3.1 **Map showing the location of the Ciste Mhearad study site, Cairngorm Mountains, Scotland.**
(from Davies *et al.*, 1988)

can contain high concentrations of elemental carbon (soot) and metals, such as Pb, V and Zn (Tranter *et al.*, 1985; Abrahams *et al.*, 1988; Landsberger *et al.*, 1989). Such snowfalls are often darkly coloured, termed 'black snows' (see Section 1.6). They can have pH values as low as 3.0 (Davies *et al.*, 1984). In comparison, less polluted snows have pH values of around 4.5. The carbon load, measured as reflectance of filtered particulates from snowmelt, has been demonstrated to correlate linearly with the pH of the snowmelt (Davies *et al.*, 1988) (see Figure 1.6).

3.1.2 Laurentian Mountains, Canada.

The sampling site was at a CAPMoN (Canadian Air and Precipitation Monitoring Network) station at Lac Laflamme, in the Montmorency Forest (47°19'N, 71°07'W). This is in the Laurentides National Park in the Province of Quebec, 80 km north of Quebec city, and is at an altitude of 777 m a.s.l (see Figure 3.2). The mean annual precipitation for the area is 1.4 m, of which about a third is snow. Snow cover usually exists from mid-December to mid-May. The area is dominated by boreal forest and is remote from human influences (Jones, 1987). This area has been the subject of numerous studies of snow chemistry, which have been reviewed by Jones (1987).

3.1.3 Wiltshire and Hampshire, England.

Snow was sampled 3 times in the winter of 1990/91, once in Wiltshire at a rural site, and twice in Hampshire at an urban site (see Figure 3.3). There are no data available for the chemical characteristics of snow for Southern England. Rainfall in the area can be expected to have a mean pH in the range 4.3-4.5 (UKRGAR, 1987).

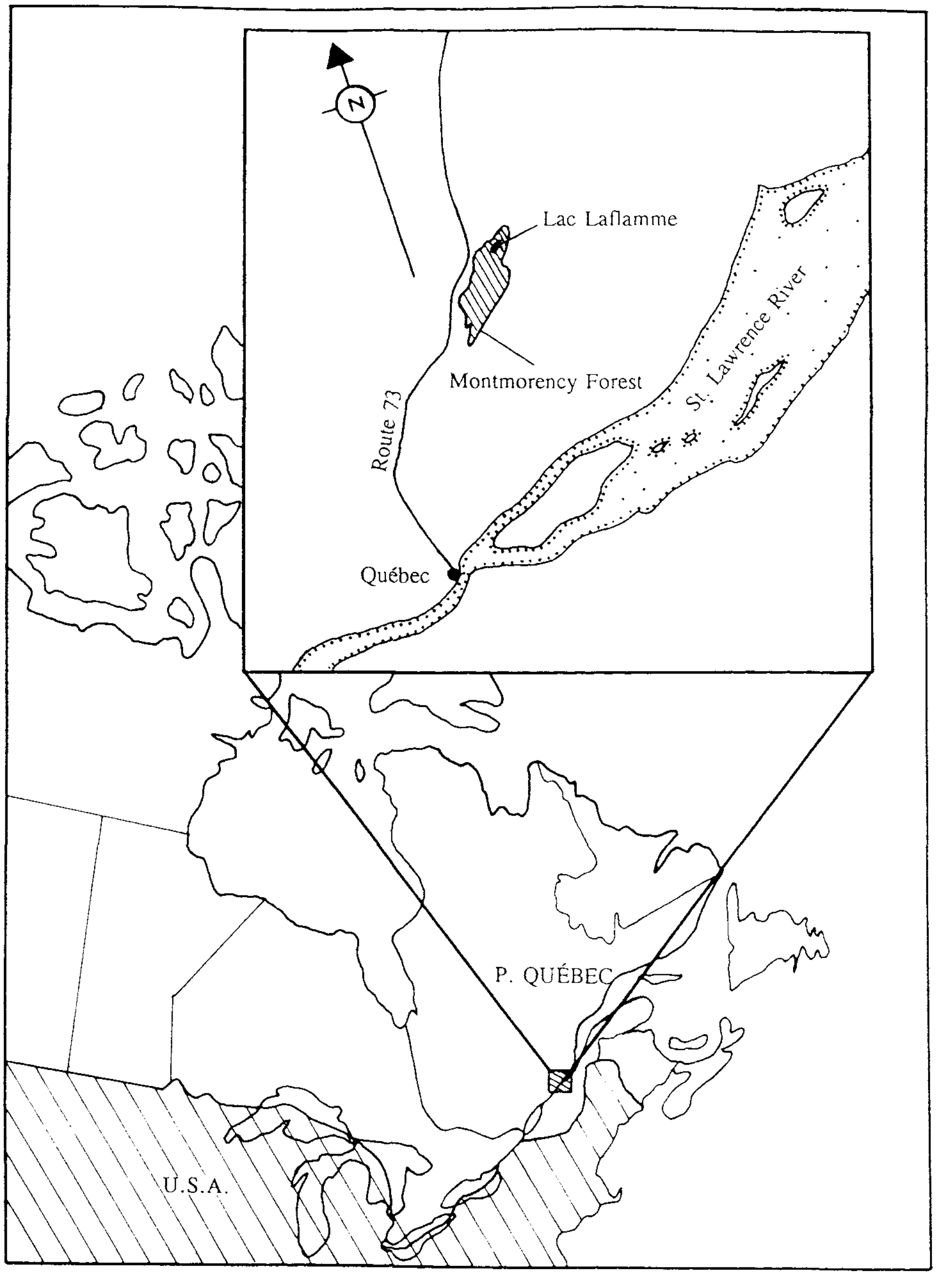


Figure 3.2 **Map showing the location of the Lac Laflamme study site, Québec, Canada.** (from Taylor and Jones, 1990)

Figure 3.3 Map showing the location of Swindon and Southampton, Southern U.K.

3.2 Sampling Equipment.

The requirements for the choice of sampling equipment were dictated in part by the nature of the field work. The equipment used, and the samples taken, had to be easily carried by a person on foot, often in mountainous terrain under adverse weather conditions. The equipment had also to be easy to clean in a field laboratory, and impart no contamination to the samples. For these reasons, three light-weight aluminium canisters were specially constructed for the initial field work in Scotland. These had an approximate volume of 2.5 l each, and were secured with a clip-on lid. Each container had an aluminium disk fitted to a rod handle to allow the snow to be packed down inside. These were cleaned and carried inside the container until the samples were taken. The containers were filled with a pre-cleaned aluminium scoop.

In Canada, the sampling site was approached with the use of motor toboggans and so a larger amount of equipment could be carried. This enabled the use of large (4.5 l), wide-mouthed glass jars for sample collection. These were also filled with a pre-cleaned aluminium scoop. Similar jars were also used for the sampling undertaken in Hampshire and Wiltshire.

For the collection of samples for the determination of major ions and pH, pre-cleaned low-density polyethylene scoops, jars and bags were used.

Full details of all equipment preparation, cleaning and sample preparation are detailed in Sections 4.1 and 4.4.

3.3 Sampling Technique.

All snow samples were collected upwind of the prevailing winds at the time of sampling. All sampling sites were approached on foot, to minimise the possibility of contamination. A full description of the sampling equipment and its preparation is given in Section 4.3.

3.3.1 Scotland.

Samples were collected from either fresh surface layers, when available, or snow pits. On each sampling excursion three samples were taken for the analysis of PAHs, and corresponding samples were taken for the determination of pH and major ions (Cl, SO_4, NO_3, Na, K, Ca and Mg). Samples were taken from snow pits when fresh snow was unavailable. The exact sampling level in the pit was chosen by inspection of the pit wall for distinct layers of snow, some of which were darkly coloured. Such samples will obviously have been affected by a number of factors after deposition, including dry deposition of pollutants and changes caused by melting and leaching of the snowpack, and the results will therefore be open to some uncertainty as to their validity as indicators of atmospheric pollution. However, they will provide some indication of the upper levels of PAH content of polluted snow in the United Kingdom.

Sampling was undertaken over a two-week period in March/April 1989, and also over two two-week periods in February and April 1991. Access to the site was either on foot from the nearest road, about 3 km distant and 500 m lower in altitude, or when weather conditions were favourable, by ski-lift to approximately 1 km from the site, from where the approach was also made on foot.

The samples were immediately taken for initial work-up to a temporary laboratory in the photographic dark room at the Nature Conservancy Council establishment at Achintoul, Aviemore.

3.3.2 Canada.

All samples taken at the Montmorency Forest site were of fresh snowfall. The snow was sampled from the entire depth of the fresh layer, which was always clearly evident on top of the previous snow surface. There were no incidences of discoloured snow.

Typically, five samples from each event were taken for PAH analysis. Samples were also collected for the determination of pH, conductivity, and ammonia and major ion content. An attempt was made to collect a time series of samples throughout a precipitation event by leaving uncovered sampling jars in the open, but this was unsuccessful as insufficient amounts of snow were collected.

Sampling was undertaken at various times during a four month period from November 1989 to February 1990. Samples were either taken immediately to the laboratory at the Institut National de la Recherche Scientifique (INRS) in Québec City for full preparation, or were provisionally worked-up in the laboratory at the INRS Montmorency Forest field station.

3.3.3 Wiltshire and Hampshire.

Opportunistic sampling was undertaken on three occasions in Southern England. On the first occasion (10/12/90), samples were collected from a 24 h old snow pack in a field, c. 250 m from a main road in a rural location. This site is approximately 4 miles North-West of Swindon, Wiltshire (see Figure 3.3).

Sampling of fresh snow was also undertaken in Southampton. Samples of shallow snowfall (c. 3 cm) were taken from the car park of the Oceanography Department at the University (7 and 8/2/91). The samples were taken early in the morning, before the car park had been used.

On all occasions, three samples were taken for PAH analysis, and samples for the determination of pH and major ion content were also collected. The samples were taken immediately to the laboratory at the Department of Oceanography.

CHAPTER 4: ANALYTICAL METHODOLOGY

4.1 Materials and Equipment Preparation.

The solvents used for cleaning, extraction, sample preparation and analysis were: 'AnalaR' grade acetone and dichloromethane, 'HiPerSolv HPLC' grade acetonitrile and 'Pesticide Residue Analysis' grade cyclohexane. 'AnalaR' grade concentrated sulphuric acid (H_2SO_4) and nitric acid (HNO_3) were also used. All were obtained from BDH Ltd.

Organic-free (OF) water was initially prepared by double-distillation. In this process, water is distilled using all-glass equipment from a 10% (w/v) potassium permanganate ($KMnO_4$) solution in 'Milli-Q' (Millipore) deionised water. This ensures that any residual organic matter in the water is oxidatively degraded. However, this was found to be a slow method for producing HPLC solvent and unsuitable for bench-top application, and for the latter part of the investigation OF-water was produced by high intensity UV-irradiation of deionised water. This method produces water with a DOC concentration of $< 0.2\ \mu g\ l^{-1}$ (Jones, pers. comm.).

Before use, all equipment was thoroughly cleaned using a hot water and detergent wash (10% 'Micro'), a rinse in OF-water and then a solvent rinse with acetone followed by dichloromethane. The acetone is used to remove residual water and allow the dichloromethane to fully 'wet' the surface of the object and thus clean it more efficiently.

An alternative cleaning procedure used for objects difficult to wash, such as Pasteur pipettes and small vials, was combustion in a muffle furnace at 400°C for 4 h, followed by solvent rinsing. Alternatively, for volumetric glassware, prolonged soaking (>48 h) in chromic acid, followed by an OF-water rinse and a solvent rinse was employed. Teflon objects, such as jar- and bottle-lid liners, were also cleaned in this way. Chromic acid was prepared by dissolving 50 g of sodium dichromate (Na_2CrO_4) in 50 ml of OF-water and then slowly adding 3 litres of concentrated sulphuric acid (Vogel, 1978). This has to be done with the vessel standing in a sink of cold, running water. This precaution is needed because the hydration of dichromate is a highly exothermic reaction.

Glass fibre filters (Whatman, GF/F) were prepared by wrapping in aluminium foil and then combusting in a muffle furnace at 400°C for 4 h to remove any organic matter. Anhydrous sodium sulphate (Na_2SO_4) was also prepared in this way and then stored in a dessicator.

Equipment used for the sampling and storage of samples for determinations of major ions were prepared by soaking in detergent solution (2% Micro), rinsing with Milli-Q deionised water, then prolonged soaking (c. 1 week) in 50% nitric acid solution, followed by a thorough rinse with Milli-Q water.

4.2 Preparation of Analytical PAH Standards.

Owing to their bio-hazardous properties, great care must be exercised when handling PAHs in their pure form or in concentrated solutions. All handling and weighing of pure PAHs was carried out inside a fume extraction cupboard while wearing protective clothing, including gloves, face mask (to prevent inhalation of PAH dust) and safety spectacles. Any spills were immediately wiped up with tissues which were then disposed of by degradation in chromic acid. Waste solutions of PAHs were disposed of by evaporating the solvent in a fume extraction cupboard and then soaking the container vessel in chromic acid to degrade the PAHs.

Appendix II details the composition of the PAH standard solutions used in this study and referred to below.

For the initial HPLC work, a certified standard of PAHs in acetonitrile was used (Standard Reference Material 1647a), which was obtained from the National

Bureau of Standards (NBS, 1988). This is a solution of 'the EPA 16' PAHs in acetonitrile, and is of a certified composition that is specifically for use as a calibration solution for liquid chromatographic methods for the determination of PAHs. This was diluted to provide a range of concentrations used for the method development and instrument calibration and is referred to as 'NBS' PAH standard.

Because there was a limited quantity of this standard, another standard was prepared containing the same compounds as SRM 1647a. The concentration for each compound was chosen to provide a chromatogram with approximately equal PAH peak heights when analysed with fluorescence detection. This standard is referred to as the 'HPLC Standard' and was prepared according to the DOE-SCA procedure (DOE-SCA, 1988). The appropriate amount of solid PAH (Sigma Ltd. and Aldrich Ltd.) was weighed, dissolved in cyclohexane and then made up to a volume of 100 ml. The exposure to solid PAHs was reduced by minimising the number of transfers of compound to the weighing vessel. These stock solutions were then combined and diluted in acetonitrile to give mixed working standards for HPLC work. The 'GC Standard' was made in a similar way, but by dilution of the stock standard in dichloromethane.

For the work with GC-MSD (see Section 4.6.2), new standards were prepared (MS and MS-Isotope Standards). These contained a wider range of compounds than the previous standards (see Appendix II) and were made by dissolving the solid PAHs directly in dichloromethane. This wider range was used to increase the resolution of detection of PAH isotopes, as the isotopes often elute close together and peak values can sometimes be incorrectly assigned. The isotope standard, used as an internal-standard, was prepared with seven perdeuterated compounds and one ^{13}C-substituted compound. This is essential in GC-MS analysis to correct for injection losses and run-to-run variations. The use of internal-standards and isotopes is given further consideration in Section 4.6.2.

In all cases, the dissolution of PAHs was aided when necessary by ultrasonic agitation of the solutions. Heat was never applied, as this could cause loss by volatilisation of low molecular weight PAHs or thermal degradation.

Once prepared, solutions of PAHs were kept refrigerated at < 4°C and protected from exposure to light by wrapping the glass vessels in aluminium foil. These precautions prevent losses from volatilisation and UV-induced photo-degradation of PAHs.

The GC-MS standards were weighed when they were initially prepared, and after each subsequent use, to ensure that there were no losses of solvent by volatilisation. Any losses were corrected by an addition of solvent. PTFE tape was wrapped around the glass stopper joints of flasks to further help prevent evaporative losses.

4.3 Development of PAH Extraction Techniques.

As with the choice of sampling equipment (see Section 3.2), the initial sample handling and extraction techniques were dictated by field conditions. It is desirable to extract samples for PAH analysis as soon as possible after they have been taken to avoid possible losses caused by chemical reaction, microbial degradation and changes in the phase distribution caused by adsorption-desorption processes and volatilisation. The intention was to filter and extract the snowmelt in the field and store the extract and the loaded filters until they could be fully worked-up in the analytical laboratory. To this end, a convenient and efficient method was required that did not involve the use of a large amount of equipment.

4.3.1 Extraction of Dissolved Phase PAHs.

4.3.1.1 Liquid-liquid Extraction.

The first technique considered was liquid-liquid extraction. This was the first choice because it is a relatively simple manual method requiring basic equipment that is readily cleaned.

Following laboratory assessment (see below), the initial filtered snowmelt samples from the field trip to Scotland in 1989 were extracted by shaking with 20 ml cyclohexane in a separating funnel. However, this method proved unsuitable. It was found that in contrast to the samples of OF-water used in the laboratory, a large quantity of solvent-water emulsion readily formed, which took a long time to fully separate. An additional problem was that the cyclohexane froze when stored at the field accommodation in Scotland (f.p. cyclohexane = 6.5°C). This could lead to a possible fractional concentration effect of any contaminants present in the solvent.

Subsequent solvent extraction was therefore performed using dichloromethane as the extracting solvent, and was based on the UK DOE (DOE-SCA, 1988) and the US EPA Method 610 (EPA, 1982) recommended procedures. Dichloromethane is a better solvent for the extraction of PAH for a number of reasons: i) it is denser than water and so facilitates its separation and removal from the water layer in a separating funnel, and thus facilitates multiple extraction; ii) it is less likely to form an emulsion, as is liable to occur with cyclohexane (Acheson *et al.*, 1976); iii) it has a lower freezing point (-94°C); and iv) it is safer to use, being non-flammable and less toxic. This last point is particularly significant because proper fume extraction facilities were not available in the field laboratory. It was also found that the technique using dichloromethane provided better extraction efficiency than the single-step extraction using cyclohexane, as described below.

In addition to liquid-liquid extraction, two other techniques were considered for the extraction of dissolved PAHs. These were the use of XAD resin for solid phase extraction and on-line HPLC extraction. However, these were shown to be unsuitable, for the reasons stated below.

It was intended to take a minimum of three samples for PAH analysis each day over a sampling period of up to two weeks. It would not have been practical to prepare fresh columns for solid phase extraction each day in the field laboratory, as the potential for contamination of the columns during loading and preparation outside a suitable laboratory is high. Therefore, the use of this technique would have required taking an unreasonably large number of previously prepared extraction columns to the field area.

On-line HPLC extraction is also an unsuitable technique to use outside the analytical laboratory. It is impractical to take an entire HPLC instrument assembly to a field area and to achieve reliable trace analyses in a short time period. However, preliminary trials suggested that this could be a worthwhile technique to pursue and develop further.

4.3.1.2 Assessment of Extraction Using Cyclohexane.

1 litre of OF-water in a separating funnel was spiked with 250 μl of GC-FID PAH standard solution and shaken vigourously to dissolve the PAH. 20 ml of cyclohexane was added to the funnel and the contents were shaken vigourously for 2 min. The funnel was allowed to stand, enabling the mixture to separate into two layers, with the cyclohexane containing the PAH being the less dense upper layer. The separation was usually complete in 15 min. The water was drained out of the funnel and the cyclohexane collected in a 30 ml glass vial. Approximately 5 g of dried Na_2SO_4 was then added to the vial and the contents agitated. This removed any water from the solvent. The cyclohexane was then transferred to a 50 ml pear shaped flask and the vial rinsed with 5 ml of cyclohexane, which was also added to the flask. The cyclohexane was reduced in volume by rotary evaporation to a volume of approximately 2 ml, and transferred to a small pointed vial, graduated to 250 μl. The volume of solvent was further reduced by evaporation under a gentle stream of purified nitrogen gas. The flask was rinsed with 1 ml of cyclohexane and this was added to the vial. The final volume was adjusted to 250 μl, which is the same volume of standard as was originally added to the water. The efficiency of extraction is determined by comparing the FID gas chromatograms of an injection of the extract and one of the same size injection of the original standard. If extraction efficiency is 100 %, the two chromatograms would have equal peak heights. The calculated extraction efficiencies for the

individual PAHs are presented in Table 4.1a. These were calculated according to the formula:

$$E\ (\%) = (H_{ext}/H_{std}) \times 100$$

where: E = extraction efficiency;

H_{ext} = peak height of compound in extract;

H_{std} = peak height of compound in standard.

4.3.1.3 Assessment of Extraction Using Dichloromethane.

200 μl of the HPLC PAH standard was added to 1 litre of OF-water in a separating funnel and shaken energetically to dissolve the PAHs. These were then extracted by vigorously shaking with 40 ml of dichloromethane for 2 min. The mixture was left stand to allow the two layers to separate. The dichloromethane, being denser, sank to the bottom and was easily removed and transferred to a 150 ml round flask. The extraction was repeated a further two times. The extracts were combined and reduced to approximately 10 ml by rotary evaporation, and were then passed through a 10 mm diameter glass column containing 10 g of dried Na_2SO_4 to remove water. Prior to use, the column was cleaned by passing through 3 × 10 ml of dichloromethane. After passing the extract through the column, the flask and column were rinsed with 3 × 5 ml portions of dichloromethane, and all the solvent was combined in a 50 ml pear shaped flask for reduction by rotary evaporation to approximately 1 ml. This was transferred to a small vial, as was 1 ml of dichloromethane used to rinse the flask. The volume was reduced further by evaporation with purified nitrogen gas until the point that it was just dry. 200 μl of acetonitrile was added to allow analysis by HPLC and the calculation of the extraction efficiency as described above, but using peak area. The results are presented in Table 4.1b.

Table 4.1a **Dissolved PAH Extraction Recovery Efficiencies (%) For Method 1.**

Comp.	E1	E2	E3	E4	Mean	s.d.	r.s.d (%)
1	81	68	83	72	76	7	9
2	98	77	90	77	86	10	12
3	102	103	131	113	110	3	12
4	107	93	103	90	98	8	8
5	95	82	87	78	86	7	9
6	105	81	89	76	88	13	14
7	93	78	87	75	83	8	10
8	98	79	88	77	86	10	11
9	84	87	97	67	84	12	15
10	83	83	89	63	80	11	14
11	81	81	86	64	78	10	12
12	84	74	85	63	77	10	13
13	85	73	82	91	83	7	9

(see Appendix II for compound identification of 'GC-FID' standard)

Table 4.1b **Dissolved PAH Extraction Recovery Efficiencies (%) For Method 2.**

Comp	E1	E2	E3	E4	E5	Mean	sd	rsd
1	78	76	69	75	70	74	4	5
2	76	85	80	78	79	80	3	4
3	93	89	84	90	85	88	4	4
4	86	91	88	93	88	89	3	3
5	94	93	89	92	96	93	3	3
6	91	95	89	90	93	92	2	3
7	85	82	87	86	82	84	2	3
8	87	83	90	88	88	87	3	3
9	90	96	85	93	92	91	4	4
10	89	90	85	92	87	89	3	3
11	97	103	99	102	97	100	3	3
12	91	87	93	89	93	91	3	3
13	94	99	96	92	101	96	4	4
14	89	93	87	95	96	92	4	4
15	92	90	89	88	94	91	2	3

(see Appendix II for compound identification of 'GC' standard)

4.3.1.4 Final Choice of Extraction Technique.

Values quoted in the literature for the efficiency of solvent extraction of PAHs from water are quite varied, and differences are reported for the solvents and technique used. In some cases, an efficiency of 100 % is assumed (Ogan *et al.*, 1979). The EPA give values ranging from 78 to 116 % (mean = 93 ± 8 %) for expected efficiency using EPA protocol method 610 for PAH in municipal and industrial waste waters, but state that the final values of PAHs should be expressed uncorrected for extraction efficiency (EPA, 1982). Conversely, the U.K. Department of the Environment state that it may be necessary to make corrections for recovery when the analysis is applied to waters with a high level of suspended solids (DOE-SCA, 1988). It is sometimes not stated in literature whether or not reported values have been corrected for extraction efficiency.

Schrimpff *et al.* (1979) determined the extraction efficiencies for 4 PAH from snowmelt using liquid-liquid extraction and expressed the final results corrected by this factor but without stating the actual values. Furuta and Otsuki (1983) report values for the extraction efficiency of benzo[k]fluoranthene, benzo[a]pyrene and benzo[ghi]perylene from water with cyclohexane as being 96, 89 and 100 % respectively. Kawamura and Kaplan (1983 and 1986) give an overall value of 80 % extraction efficiency for 16 unspecified PAHs in rain and snowmelt using liquid-liquid extraction with dichloromethane. McVeety and Hites (1988) report an overall efficiency value of 71 ± 13 % for 10 PAH from rain samples and Simmleit *et al.* (1986) report a value of 95 % for 3 PAH from snowmelt. Both also used dichloromethane for the extraction.

From Tables 4.1a and 4.1b it can be seen that the extraction efficiencies obtained with both methods are comparable to those given in the literature. However, the values reported for the dichloromethane extraction are higher, with an overall mean value of 89 ± 6 %. These are comparable with the values from the literature quoted above, and are acceptable for application.

The final adopted method was therefore as follows: 40 ml of dichloromethane was added to the emptied melting vessel and shaken, then transferred to the emptied filtering flask and shaken, and then added to the separating funnel containing the snowmelt. This rinsing is performed to minimise losses of PAHs by adsorption onto the surface of the glassware. The separating funnel containing the water and the solvent was then vigorously shaken by hand for 2 min and excess pressure, caused by the volatilisation of the solvent, was vented every 15 sec. The contents were then left to settle for a minimum of 15 min, or until the water and solvent layers had fully separated. The solvent and any remaining small amount of the emulsified layer was then drained off. The solvent extraction was repeated with a further two volumes of solvent and the extracts combined.

4.3.2 Extraction of Particulate Phase PAHs.

Ultrasonic extraction was chosen as the technique for the extraction of the particulate phase PAH. This decision was made on the basis of the speed of extraction and the economy of solvent use.

The efficiency of this extraction technique could not be quantitatively determined owing to the difficulty and expense of obtaining a certified standard of PAHs in a particulate sample matrix representative of a filtered snowmelt sample. However, a snowmelt particulate sample was obtained specifically to assess the extraction technique. After filtering, the glass fibre filter was placed in a 50 ml centrifuge tube with 30 ml of dichloromethane. This was supported in an ultrasonic bath with the solvent surface at the same level as the water. Ice was placed in the water to prevent the water and sample being heated and causing potential losses from volatilisation. The ultrasonic extraction was monitored by measuring the fluorescence of the dichloromethane at 254 nm excitation and 375 nm emission wavelengths at 5 min intervals. These wavelengths are optimum for the measurement and estimation of total PAH content (Waters, 1988). The results are illustrated in Table 4.2 and Figure 4.1. From these it can be seen that maximum fluorescence, and hence maximum PAH extraction, was obtained after 30 min.

Table 4.2 **Particulate Phase PAH Extraction Efficiency.**

Time (min)	Fluorescence (arb. units)
0	18
5	57
10	89
15	89
20	91
25	92
30	92
35	91
40	91

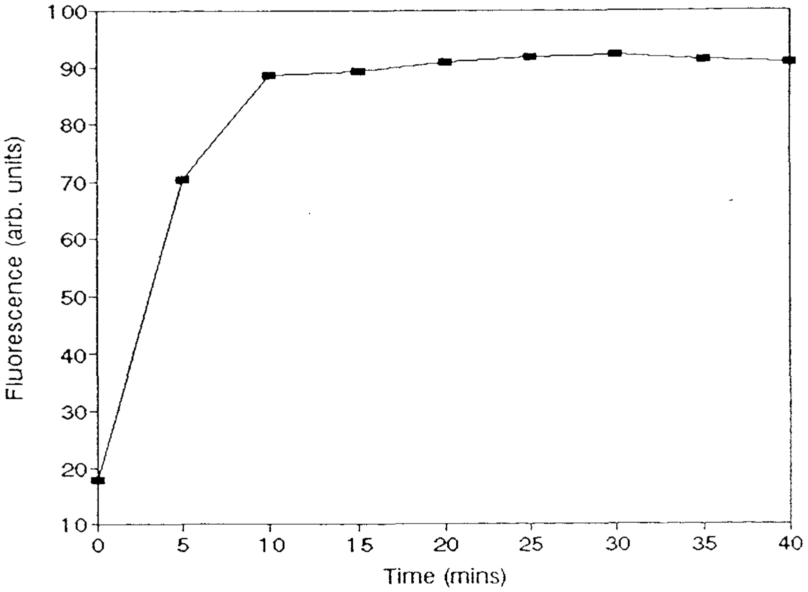


Figure 4.1 Efficiency of extraction of particulate phase PAHs by ultrasonication.

4.4 Sample Preparation.

4.4.1 Preparation of Samples for PAH Analysis.

The snow was transferred from the aluminium canisters to 5 l glass jars and immersed in a water bath at a temperature of 50°C. The samples collected in glass were placed directly in the water bath. The samples were periodically agitated to facilitate melting and to ensure that they were not unduly warmed. When they were completely melted they were immediately removed from the water bath and a maximum of 1 l of snowmelt was filtered using all-glass filtering apparatus (Millipore) and a combusted GF/F glass fibre filter (Whatman). These have a nominal pore size of 0.7 μm. A hand pump was used to apply a vacuum to the filter vessel to aid the flow of water through the filter.

The filters were placed in a glass vial, sealed with either a teflon-lined or aluminium foil-lined screw top. The filtered snowmelt was transferred to a 1 l separating funnel and extracted as described in Section 4.3.1.4.

Blanks were prepared in parallel with samples to check for any introduction by contamination. This involved performing the sample preparation under the same field conditions, without snowmelt and using solvent only for the dissolved phase extraction method, and an unused GF/F filter. The blank 'extract' solvent and filter were then treated in the same way as the sample extracts and filters.

4.4.1.1 Dissolved Phase PAHs.

The extracts from the Scottish samples were stored in 150 ml amber glass bottles, sealed with Teflon-lined lids, and transported to the analytical laboratory, where they were transferred to a 150 ml round-bottomed flask. The bottles were transported inside insulated cool boxes which were kept cold with frozen cooler blocks. For all other field samples, the solvent was drained directly into the round-bottomed flasks.

In the laboratory, the combined 120 ml of solvent in the flask was subjected to an initial volume reduction by rotary evaporation to a volume of approximately 10 ml. This was passed through a 10 mm diameter glass column containing 10 g of anhydrous sodium sulphate to remove any water from the sample. The column was rinsed three times with 10 ml dichloromethane immediately before use.

After the extract had been dried, the flask and the column were rinsed with 3 aliquots of 5 ml of solvent, and the solvent was combined in a 50 ml pear-shaped flask. This was reduced by rotary evaporation to a volume of approximately 1 ml. It was then transferred to a small glass vial, in which it was reduced in volume further by a steady stream of nitrogen gas passed through purifying cartridges (Chrompak) to remove moisture and organic contamination. The pear-shaped flask was twice rinsed with 1 ml of solvent which was added to the vial. The sample was then evaporated until just dry. 1 ml of the solvent used for the particular analytical technique employed was then added, and the vial sealed with an airtight screw cap with a teflon lining. The solvents used were acetonitrile for HPLC analysis and dichloromethane for GC analysis. Immediately prior to GC-MS analysis, the extract was further reduced to a volume of 100 μl by nitrogen gas blow-down, and using narrow-bore glass-liners to hold the sample inside the vials.

4.4.1.2 Particulate Phase PAHs.

The filters were transferred to a 40 ml glass centrifuge tube and 30 ml of dichloromethane added. They were subjected to ultra-sonication for 30 min in an iced water sonicator and then centrifuged at 1500 r.p.m. for 5 min. The solvent was decanted and placed in a 50 ml pear-shaped flask and prepared in the same way as described above for the dissolved phase samples.

4.4.2 Preparation of Samples for Other Analyses.

The samples collected for inorganic determinations were melted in the water bath.

The samples were filtered through a 0.45 μm cellulose acetate filter (Millipore) using a Nalgene filter unit and hand-operated vacuum pump. Subsamples were then taken and the sample pH and conductivity were determined (see Section 4.5.3.3). Two aliquots of 50 ml each were placed in pre-cleaned polyethylene bottles for major ion determination (see Section 4.5.3.3). That to be used for cation analysis was acidified with 500 μl of 50% v/v nitric acid (HNO_3). Both were kept refrigerated until they reached the laboratory where they were either analysed immediately or frozen for later analysis. In Canada, a third aliquot of 50 ml was taken for the determination of ammonium by flow injection analysis.

4.5 Development of Analytical Techniques.

Two analytical methods were used in this study for the analysis of PAHs, namely HPLC and GC. HPLC was initially the preferred choice because this was the only method available at the laboratory in Canada.

4.5.1 High Performance Liquid Chromatography.

4.5.1.1 Apparatus and Instrumentation.

In Canada, the equipment used was a Waters Model 600 HPLC Multisolvent Delivery System with a Waters Model 490 Programmable Multiwavelength UV-Visible Detector and a Perkin-Elmer LS-4 Programmable Fluorescence Spectrometer Detector. The latter can be programmed to change detection parameters at set times during the analysis, and hence optimise the detection. Data acquisition was performed by a Nelson Analytical 900 Series interface. The analytical column used was a Vydac 201TP54 octadecyl silica (ODS) reverse phase column (5 μm, 4.6 × 250 mm), which was eluted with continuously helium-sparged acetonitrile and OF-water, using a solvent gradient. A Bio-Rad ODS-10 Micro-guard column (10 μm, 4.6 × 40 mm) was fitted to protect the analytical column. However, owing to limited access to the instrument and the length of time needed for method development, it was decided to seal the extracts from the

Canadian samples and ship them back to Southampton for analysis. Standard solutions and blank samples were shipped with the extracts to check for losses or contamination during transit.

In Southampton, the HPLC equipment consisted of a Waters Model 501 dual pump solvent delivery system with a Perkin-Elmer LS-5 Programmable Fluorescence Spectrometer Detector. This detector is virtually identical to the LS-4. Data acquisition and detector instrument control were automated using a Perkin-Elmer Model M3600 Data Station with Perkin-Elmer Computerised Luminescence Spectroscopy (PECLS) software. For method development work with high concentration standards, a Waters Model 455 UV-visible LC Spectrophotometer set at 354 nm was used down line from the LS-5. Separation was achieved with a Vydac 201TP54 ODS column as described above. This was protected with a custom-built guard column (30 × 4 mm) containing Li-Chrosorb RP-18, 5 μm ODS. Solvent gradient elution with helium-sparged acetonitrile and OF-water was automatically controlled by computer using 'Flowmaster' pump control software (Waters Corp.).

4.5.1.2 Procedure.

An injection of extract or standard was made via a Rheodyne Model 7125 six-port injector fitted with a 20 μl sample loop. An injection of 80 μl was made to ensure that the sample loop was fully flushed and completely filled with sample. The sample was then introduced to the system by rotating the valve, thus switching the loop into the solvent delivery route, and flushing the sample into the analytical column. After 2 min, the valve was reset to the load position and flushed with 3 × 100 μl of acetonitrile and then with air (Ogan *et al.*, 1979). This flushing was also performed before the first analysis of each run to ensure replication of injection conditions.

The sample was eluted by an acetonitrile and OF-water gradient elution using the following gradient conditions: hold at 50% acetonitrile for 3 min, increase to

100% acetonitrile over 32 min and hold for 10 min. The system was then equilibrated by reducing the solvent to 50% acetonitrile over 15 min and holding at this for 10 min before the next injection is made. This is done to ensure uniform solvent conditions at the start of each analysis. The solvent volumetric flow rate throughout the run was 1.5 ml min^{-1}. It was found that continuous sparging of the HPLC delivery solvents with helium was necessary to maintain uniform solvent conditions. This is given further detail in Section 4.5.1.4, below.

The LS-5 fluorescence spectrometer was programmed with a wavelength programme to optimise detection (see below). At the PAH concentrations used in the standard and anticipated in the samples (a range of 1.5 to 40 pg μl^{-1}), UV-visible detection was too insensitive.

The solvent delivery and the detector control programmes were both initiated manually as the sample loop was switched in-line. Data acquired with PECLS were stored on computer disks which allowed data manipulation and inter-analysis comparisons to be performed at a later time.

4.5.1.3 Optimisation of Experimental Conditions.

The first task was to achieve adequate chromatographic separation of the compounds. This was achieved by making successive analyses of standards and changing the delivery solvent gradient between each run until an acceptable chromatogram is produced. For a given PAH eluting at a given time, if the cumulative proportion of acetonitrile to OF-water is increased up to that time, then the PAH will elute quicker, and *vice versa*. Manipulation of the solvent gradient therefore produces changes in the chromatogram profile by changing the retention times of the compounds. This process of optimisation resulted in the gradient described in Section 4.5.1.2. This work was performed using UV-visible detection and high concentration standards, as the fluorescent detector could not be used to its fullest abilities until the retention times of each compound were determined by analysing single compound standards. The resulting chromatographic conditions were capable of fully separating the 15 PAHs of interest.

For the fluorescence detector, the optimum wavelength for each compound was determined by measuring the combined emission and excitation spectra of solutions of the individual PAHs using automated synchronous fluorescent scanning. Optimum wavelength values for the fluorescence detection of individual PAHs and examples of fluorescence spectra of PAHs are available in the literature (Das and Thomas, 1978; Eisenbeiss *et al.*, 1978; Ogan *et al.*, 1978, 1979; Grant and Meiris, 1981; Furuta and Otsuki, 1983; May and Wise, 1984; DOE-SCA, 1985; Dong and Greenberg, 1988; Baek *et al.*, 1991). However, these values sometimes exhibit a wide range in the quoted values for a particular PAH. This is primarily owing to the fact that the characteristics of the fluorescence spectra of a compound (and also the fluorescence intensity) are dependent on the matrix in which the compound is present (Willard *et al.*, 1988), and none of the available data referred to PAHs in solution in acetonitrile. Variations in instrument parameters will also affect the values reported. For these reasons it was decided to determine accurate values for the optimum excitation and emission wavelengths for the PAHs of interest dissolved in acetonitrile, using the detector to be employed for the analysis. This would ensure that the values acquired would most accurately reflect the conditions under which the PAHs were being measured in the fluorescence detector flow-cell.

This was done by replacing the flow-cell on the detector with a cuvette holder that could accept 10 mm quartz cuvettes. Solutions of individual PAHs in acetonitrile were placed in the cuvettes. A pre-scan of the sample was then performed. During this process, the excitation wavelength is set at 230 nm and the emission fluorescence is repeatadly measured across a range of 250 to 600 nm, with the excitation wavelength increasing by increments of 10 nm each time. This identifies the approximate region of wavelength conditions under which maximum fluorescence is obtained. The wavelengths are then determined by repeating the above process with a resolution of 1 nm for each wavelength. This resulted in the determination of wavelengths that yield maximum fluorescence for each compound in solutions of acetonitrile, and these are shown in Table 4.3.

These wavelengths, when combined with the known retention times of each compound, enabled the LS-5 to be programmed to tune to the optimum wavelengths for a time 'window' during which the compound in question eluted. Table 4.4 lists the wavelengths and times of wavelength change used in the detection of the PAHs in this study. In most cases, compromise wavelength pairs had to be used for two or more compounds to prevent peaks from being only partially quantified. This is because the detector could not always change wavelengths quickly enough between closely eluting compounds to ensure that the target compounds were detected. Also, run-to-run variations introduced a small but critical change to some retention times, resulting in detection errors. Compromise wavelengths were chosen by studying the spectra of the grouped compounds and selecting wavelengths that gave an overall optimal response level for each compound.

Table 4.3 **Optimum Fluorescence Excitation and Emission Wavelengths Determined for 16 PAHs in Acetonitrile.**

Compound	$\lambda_{(excitation)}$	$\lambda_{(emission)}$
	(nm)	(nm)
Naphthalene	268	326
Acenaphthylene	250	364
Acenaphthene	244	400
Fluorene	249	309
Phenanthrene	242	364
Anthracene	241	401
Fluoranthene	250	459
Pyrene	230	390
Benz[a]anthracene	270	389
Chrysene	255	381
Benzo[b]fluoranthene	250	437
Benzo[k]fluoranthene	233	411
Benzo[a]pyrene	249	406
Dibenz[ah]anthracene	276	396
Benzo[ghi]perylene	285	414
Indeno[1,2,3-cd]pyrene	288	503

Table 4.4 HPLC Fluorescence Detector Programme.

Time (mins)	Excitation wavelength (nm)	Emission wavelength (nm)	Compounds detected (see below)
0.0	270	325	1
12.9	250	375	2,3,4
20.5	240	425	5,6,7
29.0	260	385	8,9
34.5	290	460	10,11,12,13,14,15
45.0	RESET	RESET	

For identification of compounds detected, see Appendix II.

4.5.1.4 Trouble-shooting.

A problem was encountered during the earliest stage of method development, when 'Milli-Q' water was being used as an HPLC solvent. This had been prepared with a Millipore 'Organex' filter to remove organics, and had previously been successfully used in the same laboratory as a delivery solvent for amino acid analysis by HPLC. The symptoms encountered were high column back-pressure occurring with an inferior resolution of PAHs and a large 'hump' appearing in the UV-visible chromatogram. On inspection, the column end-frit was found to be partially blocked with a residue, believed to be an accumulation of organic contaminants from the solvent(s). The frit was cleaned by ultrasonication in 5 M nitric acid, followed by OF-water then acetonitrile. Following this, OF-water produced in the laboratory was used as a delivery solvent, and the problem did not recur.

When the retention times of the individual PAHs were being determined by injection of single compound standards , it was noted that the chromatogram of an injection of a 'pure' acenaphthylene standard also contained a second peak in the position where acenaphthene would be, if it were present. Further analysis showed that the acenaphthylene source was in fact contaminated with acenaphthene. It was therefore decided to exclude acenaphthylene from future standards to prevent the introduction of a bias to the determination of acenaphthene. The cause of this error is the difficulty in preparing 100 % pure acenaphthylene, and this effect has also been noted by Ogan *et al.* (1979).

Once the solvent delivery and detector parameters had been optimised, the analytical technique required calibrating. However, during this process it was noted that in successive analyses of the same standard, the peak areas of each compound gradually decreased.

The first suspected cause was sample loss owing to adsorption of PAHs to particles of dirt in the injector assembly. This was dismantled and cleaned by ultrasonication in acetone, dichloromethane and then acetonitrile. However, this did not solve the problem.

The effect still existed when the Vydac column was replaced with a new 'Chromspher-PAH' (Chrompak Ltd.) column (150 × 4.6 mm), thus eliminating a faulty column as the cause. If there had been a chemical change in the column packing, PAHs could have become irreversibly bonded to the active sites of the packing material.

The next suspected cause of this effect was oxygen quenching of fluorescence. Initially, the delivery solvents were degassed by sparging with helium for 20 min at the beginning of each day of analysis. Sparging is necessary to remove dissolved gases from the solvents, as they can otherwise be released following compression under pressures of up to 3000 p.s.i.in the HPLC pumps (Bakalyar *et al.*, 1978). This can result in bubbles of gas causing blockages in the pumps or tubing, preventing the flow of solvent at the desired rate or composition. To test for the occurence of oxygen quenching, four analyses of a standard were made after sparging once, and then another analysis was performed after the solvents had been re-sparged. This next analysis showed an increase in peak areas, thus showing that quenching was occurring. The most obvious cause of this quenching was the redissolution of oxygen from the air (Fox and Stanley, 1976; Bakalyar *et al.*, 1978). This effect is specific to oxygen and has been shown not to be attributable to nitrogen, argon, carbon dioxide, hydrogen and nitrous oxide (Bakalyar *et al.*, 1978).

To overcome this affect, a continuous sparging system was devised and constructed. This enabled the solvents to be sparged at the beginning of each day for 20 min, and then kept under a head pressure of 5 p.s.i. of helium to prevent oxygen from redissolving in the solvents.

Further problems were encountered when it was noticed that the retention times were decreasing, which could have prevented successful detection. Possible causes were faulty pump check valves, leading to a slow increase in the relative proportion of acetonitrile to OF-water, or a change in ambient temperature affecting solvent viscosity and hence flow rate.

The two pumps were dismantled, and the metal parts and sapphire ball valves were cleaned by ultrasonication in 5 M nitric acid, OF-water and then acetonitrile. One draw-off valve was also replaced, as it was found to be faulty, and all the solvent tubing was replaced with new Teflon tubing.

The reproducibility of the pumps delivery performance was tested by using OF-water and a copper sulphate ($CuSO_4$) solution (6.25 g l^{-1}). This is a blue solution which can be monitored by measuring the absorbance of the HPLC effluent at 240 nm with the UV-Visible detector. Copper sulphate is not retained by the column packing, and so the solution behaves in the same way as OF-water. The $CuSO_4$ solution was used as one solvent and OF-water as the other for the test. They were pumped through the system in a "saw tooth" pattern (see Figure 4.2a) and the effluent was monitored.

It was found that the absorbance profile matched the programmed gradient profile, but with a slight delay. However, it was reproducible, showing that run-to-run solvent delivery should be constant. The $CuSO_4$ solution was then used in place of acetonitrile in the solvent gradient used for PAH analysis (see Figure 4.2b). Note that there is a delay between the programmed profile and the actual profile, as shown by points A_1 and A_2, and B_1 and B_2, which should be equally aligned. It can be seen that there is a difference of 5 min between each point in a pair. The time between runs was therefore lengthened to ensure an adequate equilibration was achieved. If true equilibration was not achieved, it would result in "excess" acetonitrile left in the system, and so cause the compounds being analysed to elute quicker.

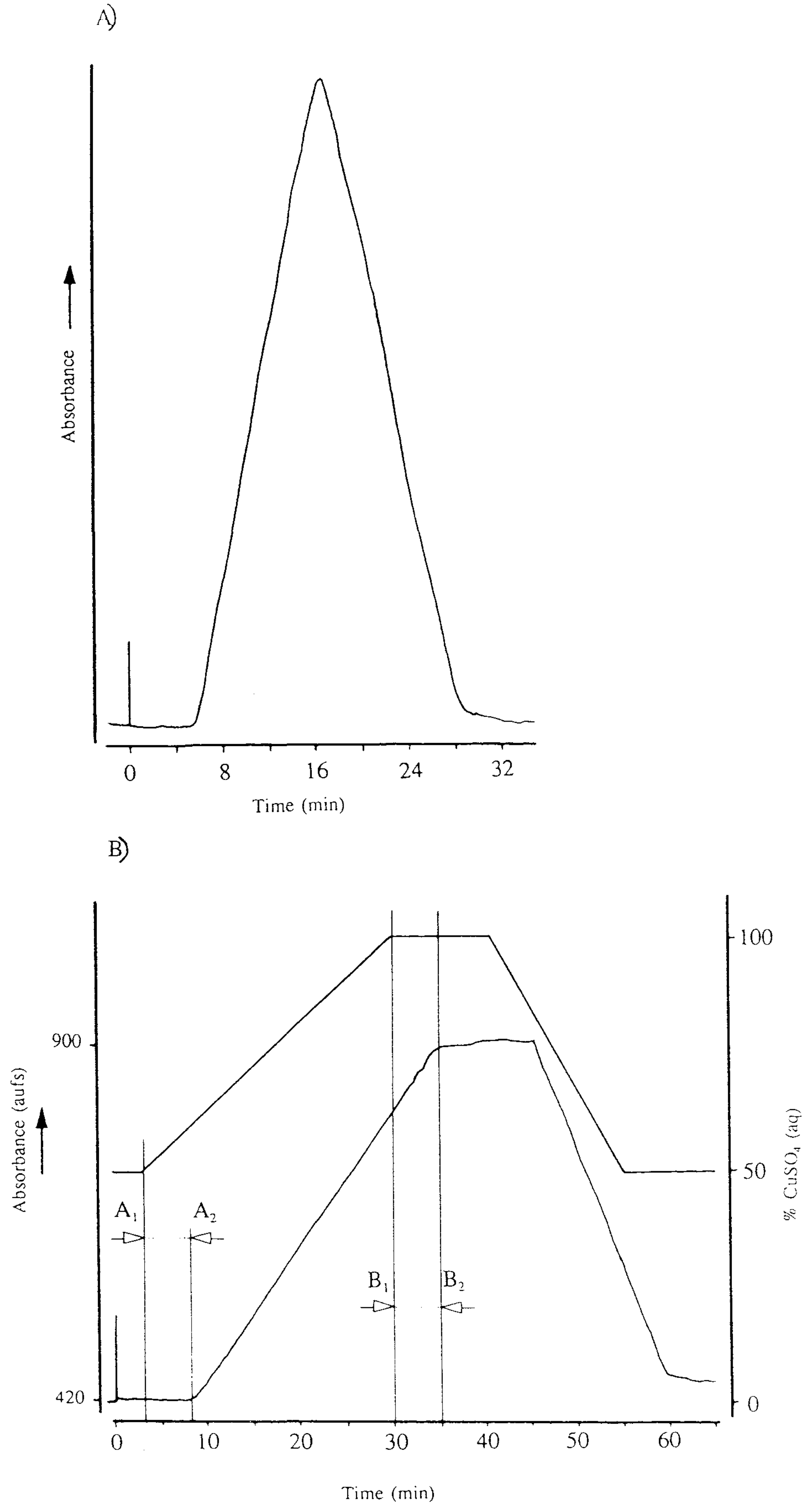


Figure 4.2 Profiles of absorbance at 240 nm by $CuSO_4$ solution when substituted for HPLC delivery solvent.
A) 0 to 100 % $CuSO_4$ in 15 min then 100 to 0 % in 15 min.
B) $CuSO_4$ solution substituted for acetonitrile in HPLC gradient. Upper trace is programmed gradient (right-hand y-axis), lower trace is actual gradient (left-hand y-axis). See text for explanation of A_1, A_2, B_1 and B_2.

The 5 min delay period represents the transit time of a non-retained solute (t_M) and can be used to calculate the dead volume of the system (V_M), as follows:

$$V_M = F_c \times t_M$$

where F_c = volumetric flow rate (1.5 ml min^{-1}).

From this, the dead volume is calculated to be 7.5 ml. The implication of this is that this is the volume of solvent that is present in the system between the pumps and the detector at any one instant, and consequently the volume of solvent that needs to be mixed from isocratic conditions before an effect is registered at the detector.

Following the tests with copper sulphate, the HPLC system was cleaned by pumping OF-water through it overnight at a rate of 0.1 ml min^{-1}.

To further check the performance, the effect of temperature was investigated by surrounding the column with a water jacket to keep it at a constant temperature of 30°C. Surprisingly, this appeared to have minimal effect on the retention times and the precision of retention times of individual PAHs. The cause of this apparent independence of retention times with temperature could possibly be attributed to inconsistencies in solvent delivery and a slow deterioration of the column condition. Other workers have since stressed the importance of maintaining a constant column temperature to ensure consistent analyses, and recommend temperatures in the region of 15°C (Scrimshaw, pers.com.; Förster, pers.com.).

The changes mentioned above improved the precision of peak retention times to a level that was sufficient to permit calibration of the system and to perform the analysis of dissolved phase PAHs in the samples from Canada. However, the system performance deteriorated towards the end of these analyses, and the HPLC method was not capable of successfully analysing the more complex samples of particulate phase PAH extracts.

4.5.1.5 Calibration and Precision.

The HPLC was calibrated using the HPLC standard at 8 different concentrations (see Table 4.5), and peak area was used to quantify detector response. The calibration curves for all compounds were found to be linear over the entire concentration range, and regression analysis for individual peaks showed a minimum correlation (R^2) of 99.5% (see Table 4.6 and Figure 4.3).

For each set of analyses, a standard was analysed at the beginning and end of each group of sample extracts (usually 5 samples per group). The average detector response for each peak from these two runs was used to calibrate the sample peak response. This assumes that the detector response is linear over the entire range of analysis.

The extract concentration is calculated as follows:

$$C_x = (A_x/A_s) \times D \times C_s$$

where:
C_x = concentration of PAH 'x' in sample extract (μg ml^{-1}),
A_x = mean area of PAH 'x' peak in sample extract (n=5),
A_s = mean area of PAH 'x' peak in standard solution (n=2),
D = dilution factor of standard (0.03),
C_s = concentration of PAH 'x' in stock standard (μg ml^{-1}).

and the final sample concentration is calculated by:

$$S_x = (C_x \times V_e)/(S_v \times 1000)$$

where:
S_x = concentration of PAH 'x' in snowmelt (ng l^{-1}),
V_e = final volume of extract (1000 μl)
S_v = volume of snowmelt extracted (l)
1000 = unit conversion factor to ng.

Table 4.5 HPLC Calibration Data - Peak Areas.

Conc*	Compound+						
	1	2	3	4	5	6	7
1	10	--	--	9	13	--	--
2	15	6	9	18	18	17	--
3	24	12	16	27	27	30	16
4	35	15	20	33	36	41	35
5	43	17	25	53	50	45	59
10	94	34	49	99	86	103	135
20	189	72	98	199	172	174	218
30	279	112	141	301	277	267	340

Conc*	Compound+							
	8	9	10	11	12	13	14	15
1	7	11	8	9	4	4	6	--
2	10	21	16	15	9	6	6	--
3	14	27	26	23	18	11	17	6
4	18	37	31	28	21	16	22	8
5	29	64	49	42	39	24	45	9
10	61	119	91	76	76	44	92	19
20	113	231	175	150	142	88	175	35
30	178	357	266	227	222	138	270	58

-- : below detection limit
+ : see Appendix II for compound identification of 'HPLC' standard
* : relative concentration × 10^{-3} standard concentration

Table 4.6 **HPLC Regression Data.**

for: [PAH] = aX + b
where: X = peak area, and
[PAH] = relative concentration of PAH*

Compound	a	b	R^2 (%)
Naphthalene	0.11	0.25	99.95
Acenaphthene	0.27	0.27	99.85
Fluorene	0.21	-0.28	99.92
Phenanthrene	0.10	0.23	99.93
Anthracene	0.11	-0.05	99.73
Fluoranthene	0.11	-0.48	99.63
Pyrene	0.09	0.39	99.82
Benz[a]anthracene	0.17	0.32	99.78
Chrysene	0.08	0.32	99.83
Benzo[b]fluoranthene	0.11	0.05	99.91
Benzo[k]fluoranthene	0.13	-0.10	99.94
Benzo[a]pyrene	0.13	0.05	99.76
Dibenz[ah]anthracene	0.22	0.04	99.87
Benzo[ghi]perylene	0.11	0.08	99.69
Indeno[123-cd]pyrene	0.53	0.07	99.53

* : relative concentration × 10^{-3} standard concentration

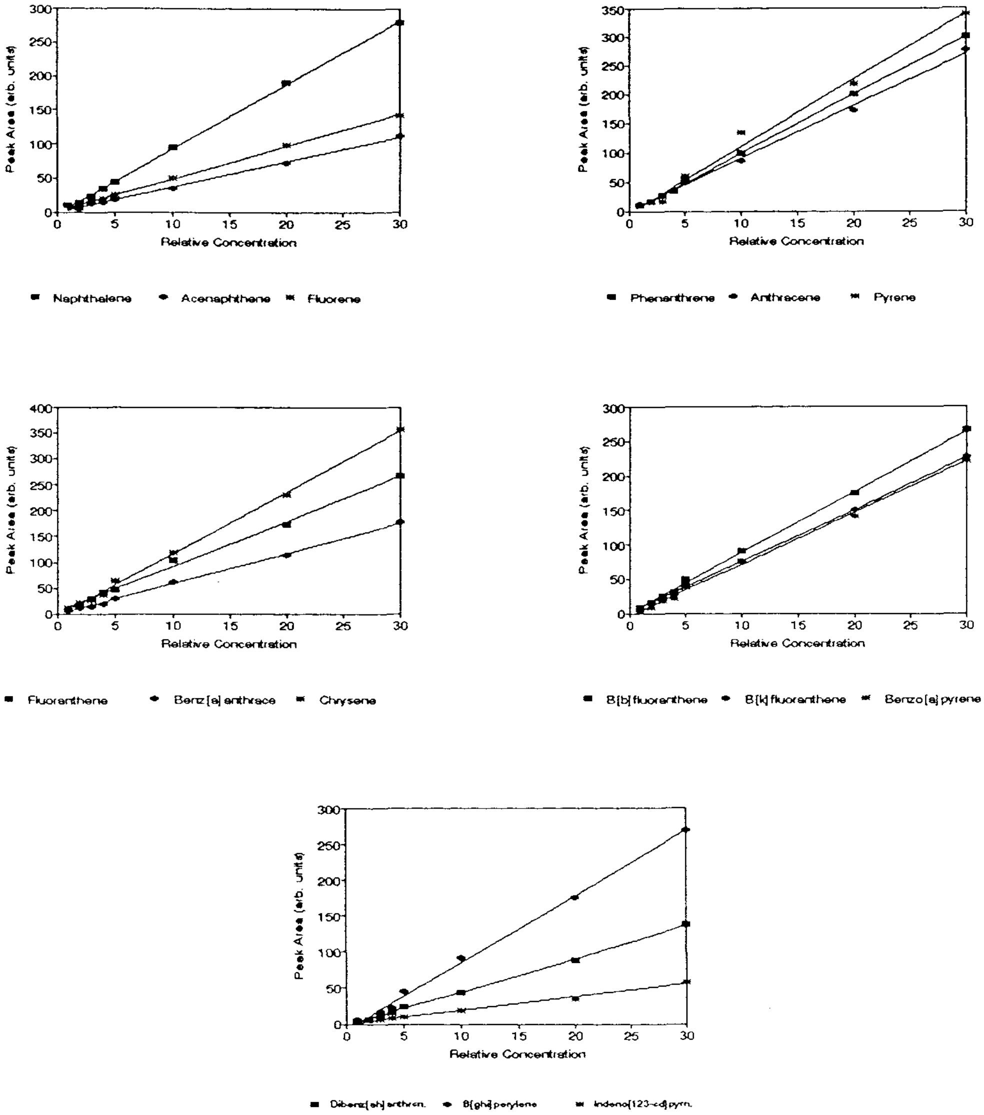


Figure 4.3 HPLC calibration curves for HPLC PAH standard.

Precision of peak area determination was calculated by analysing an HPLC standard five times in succession. The results obtained are shown in Table 4.7. The coefficient of error, or residual standard deviation (RSD), ranges from 0.8 to 5.6%.

Detection limits for each compound were defined by peak heights that had a signal-to-noise (S/N) ratio of 3. The absolute detection limits and the method detection limits are shown in Table 4.8.

4.5.2 Gas Chromatography.

4.5.2.1 Apparatus and Instrumentation.

The initial work using GC was performed on a Varian Series 3700 which was fitted with a 20 m × 0.32 mm i.d. retention gap. This was connected *via* a zero dead-volume connector to a 12 m × 0.22 mm i.d. fused silica capillary analytical column. The carrier gas was nitrogen (1.5 ml min^{-1}). Flame ionisation detection (FID) was used with hydrogen (30 ml min^{-1}) and air (250 ml min^{-1}) for the fuel. On-column injection was employed (Grob and Grob, 1978) using a capillary needle syringe.

Whilst this method proved acceptable for the analysis of standards and spiked OF-water extractions, it was unsuitable for environmental samples. The FID is not in any way selective for PAHs and the initial samples were too complex to allow satisfactory resolution and detection of PAHs. Therefore, this method was not used and is not given any further consideration.

Table 4.7 **HPLC Precision Data - Peak Area.**

Compound	1	2	3	4	5	Mean	sd	rsd%
Naph	502	512	515	495	492	500	9	1
Acenaph	828	829	829	817	808	820	8	1
Flrn	588	613	613	612	616	610	10	2
Phen	292	292	291	286	291	290	2	1
Anth	174	164	169	170	160	170	5	3
Flrnth	428	424	423	418	417	420	4	1
Pyr	979	999	982	970	970	980	11	1
BaA	434	432	427	418	419	430	7	2
Chrys	573	587	592	588	599	590	9	1
BbF	429	433	437	422	421	430	6	1
BkF	407	386	379	376	380	390	11	3
BaP	352	351	344	324	337	340	10	3
DBA	87	85	85	82	86	85	1	2
BghiP	246	244	244	234	240	240	4	2
IP	22	19	22	20	21	20	1	6

Table 4.8 **HPLC Detection Limits.**

Compound	Absolute D.L. (pg/inj)	Method D.L. ($ng\ l^{-1}$)
Naphthalene	85.0	4.30
Acenaphthene	1100.0	56.00
Fluorene	630.0	31.00
Phenanthrene	16.0	0.79
Anthracene	6.2	0.31
Fluoranthene	69.0	3.40
Pyrene	26.0	1.30
Benz[a]anthracene	23.0	1.20
Chrysene	9.0	0.45
Benzo[b]fluoranthene	35.0	1.70
Benzo[k]fluoranthene	17.0	0.85
Benzo[a]pyrene	28.0	1.40
Dibenz[ah]anthracene	140.0	7.00
Benzo[ghi]perylene	45.0	2.30
Indeno[123-cd]pyrene	320.0	16.00

In the latter part of the study, 2 GC-MS instruments were available for use. The first of these was a Perkin-Elmer Ion Trap Detector (ITD) coupled to a Perkin-Elmer Series 8500 GC. The ITD is a mass selective detector that operates on the principles of mass spectrometry (see Section 2.3.5). A schematic diagram of the ITD is shown in Figure 4.4, and its operation is described below.

The effluent from the GC, comprising of helium carrier gas and vapourised sample, passes through a heated open-split interface and transfer line. The open-split interface is a gas-pressure interface between the GC (+ve pressure) and the ion trap (-ve pressure). It's function is to ensure a constant flow of helium into the ion trap under all conditions of flow rate and temperature. From the transfer line, the effluent then enters the ion trap. This is kept under a vacuum (c. 10^{-3} Torr He, 10^{-6} Torr sample) by a turbomolecular pump and a rotary-vane pre-pump. Inside the ion trap, the sample molecules are ionised by accelerated electrons produced by thermionic emission from a heated, charged filament. The resulting positive sample ions are then trapped in an electrical field created by the ion trap electrodes (the top and bottom end cap and the ring electrodes). Inside this field at the storage voltage, most ions have stable oscillations and are held, but as the RF (radio frequency) voltage on the ring electrode is increased, these oscillations become more unstable with increasing mass-to-charge ratio. This causes the ions to be selectively emitted from the ion trap, and a representative portion of these strike the electron multiplier. One such ion will cause the dislodgement of one electron from the wall of the electron multiplier, and as this passes down the electron multiplier it causes more electrons to be emitted, resulting in an electron current signal which is then processed by the ITD circuitry and software. Typically, 10^5 electrons are produced from one ion impact.

This data is used to provide a mass spectrum of the ions present in the trap during one scan (i.e. one full range ramp of the RF voltage on the ring electrode). The available total scan range is from 20 to 650 atomic mass units (a.m.u.) with a resolution of 1 a.m.u. The ITD operation and data management is controlled by PC. Data acquisition by the ITD was delayed for 15 min to allow the solvent to

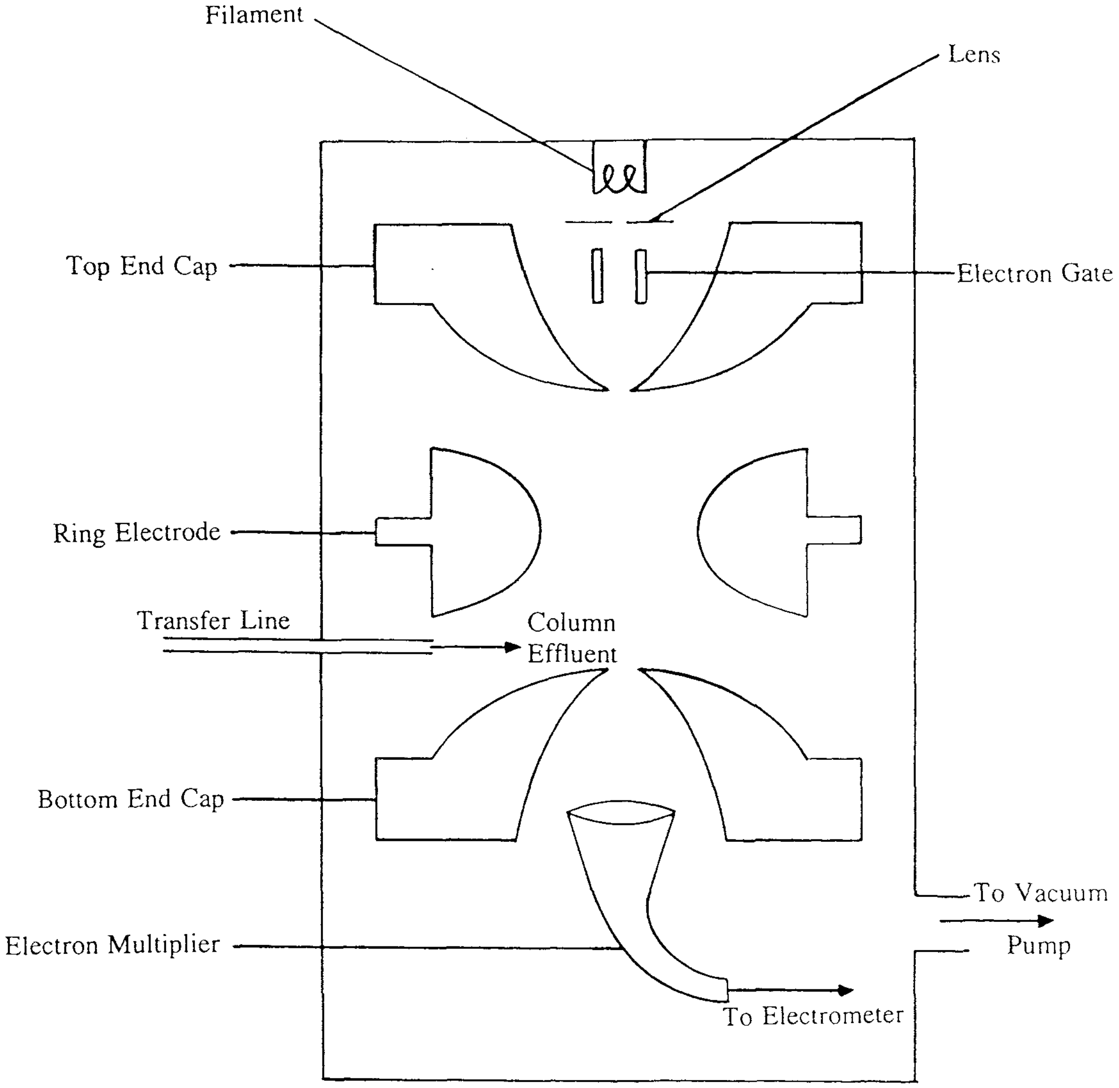


Figure 4.4 Schematic diagram of the Ion Trap Detector (ITD).

flush out of the system, thus preventing the detector being overloaded and damage occurring to the filaments and electron multiplier.

The GC was equipped with a 50 m × 0.25 mm i.d. fused silica capillary column (SGE Ltd.) with a 0.5 μm BP5 stationary phase coating. The sample was introduced by splitless injection (2 min split-vent valve delay), and eluted with high purity He (0.8 ml min^{-1} vol. flow rate) using the following temperature gradient: hold at 40°C for 4 min, ramp at 25°C min^{-1} to 150°C, and then at 12°C min^{-1} to 250°C and hold for 15 min. The injector port was operated at 275°C. The transfer line, open-split interface, exit nozzle and ion trap manifold were operated at a temperature of 200°C.

Numerous defaults and failures developed with this instrument, and despite a considerable investment of time and money it was never working sufficiently well enough to enable the successful analysis of any samples.

The second GC instrument used was made available at the Chair of Hydrology, University of Bayreuth, Germany. This was a Hewlett-Packard 5970 Series Mass Selective Detector (MSD). The operation of this is similar in principle to the ITD discussed above. The MSD was coupled to a Hewlett-Packard 5890-A GC, and both were PC-controlled with Hewlett-Packard 'MS Chem Station' software. The analytical column used was a 60 m × 0.25 mm i.d. fused silica capillary column (J&W Ltd.) with a 0.25 μm SE-54 stationary phase coating, and the carrier gas was high purity He. The sample was introduced by splitless injection (2 min split-vent valve delay), and eluted using the following temperature gradient: hold at 50°C for 2 min, ramp at 15°C min^{-1} to 110°C, then at 7°C min^{-1} to 300°C and hold for 32 min. The injector port and transfer line were maintained at 280°C and 290°C respectively. Data acquisition by the MSD was delayed for 15 min to allow the solvent to flush out of the system, thus preventing the detector being overloaded and damage occurring to the filaments and electron multiplier.

4.5.2.2 Procedure.

Immediately prior to analysis, the 1 ml sample extracts were reduced to a volume of 100 μl by evaporation with a stream of purified nitrogen gas. Then a 50 μl spike of the MS-Isotope diluted by a factor of 6000 was added to each sample for identification and calibration purposes (see Section 4.5.2.4), thus giving a total volume of 150 μl. The resulting approximate concentration of each isotope in the mixture was 100 pg μl^{-1}. The standards used to measure precision and response factors were prepared in the same way.

Splitless injection was employed, with a split-vent valve delay time of 2 min. The samples were introduced into the injection port by a slow, hot needle, 'sandwich' injection technique. This involves drawing 1 μl of dichloromethane solvent into the syringe body, followed by 1 μl air and then 1 μl of sample. The entire load is then drawn up into the syringe body and the needle is placed in the injection port for approximately 5 s, after which the plunger is depressed over a 2 s period. The plug of solvent ensures that all of the sample is transferred from the syringe into the injector port. This slow technique better transfers the sample into the port, as quicker injections can result in rapid volatilisation of the solvent which causes an excessive increase in pressure inside the port. This can lead to part of the sample being lost by leaking from the injection port, or part of the sample being forced back into the syringe. This would produce a loss of sample and an unrepresentative transfer of the sample constituents onto the column, and thus introduce an unrepeatable error to the procedure.

4.5.2.3 Optimisation of Experimental Conditions.

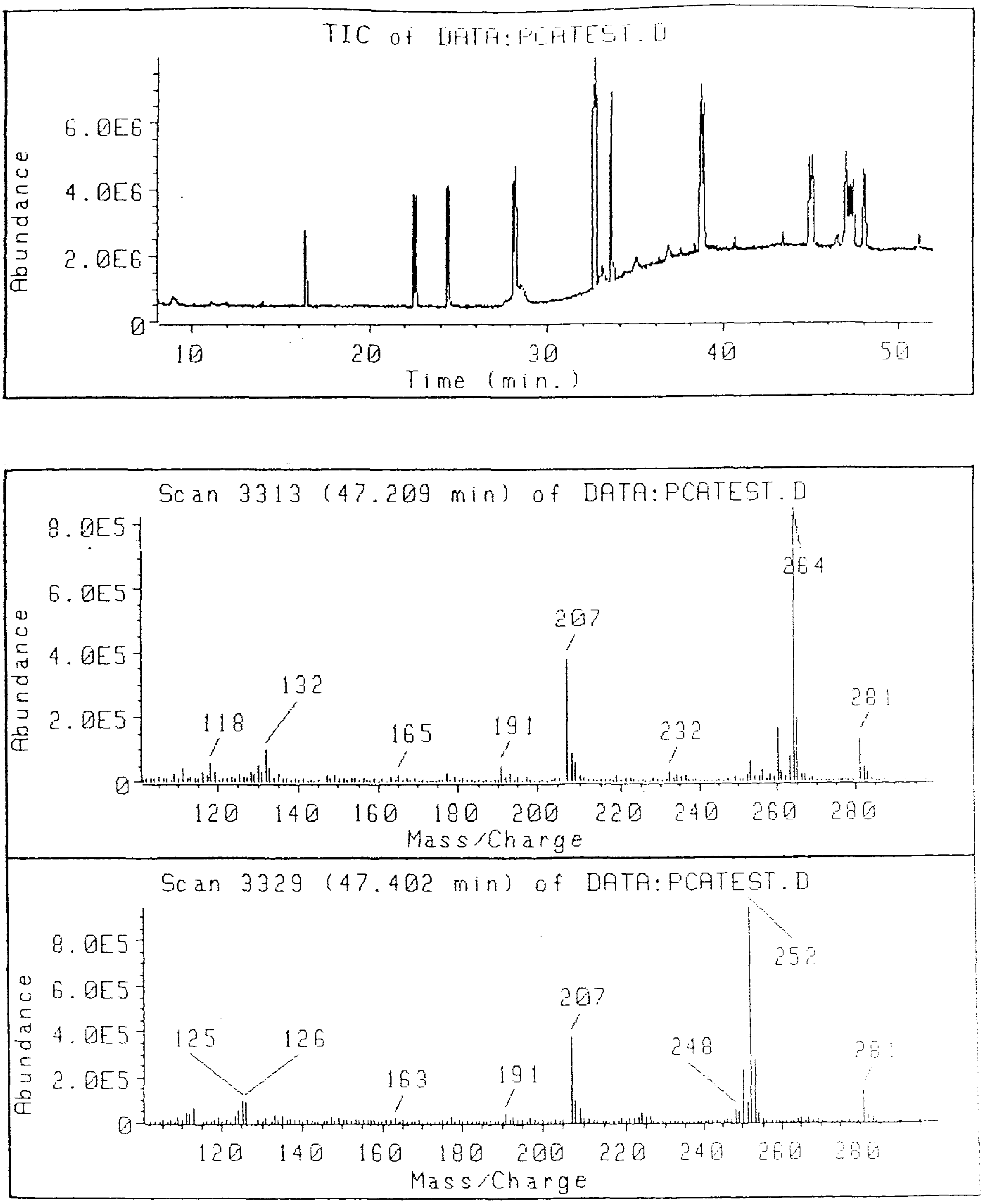
The optimum GC operating conditions were obtained by making repetitive analyses of a standard PAH solution and changing the temperature gradient between each analysis. Higher temperatures and steeper temperature/time gradients lead to shorter retention times, and *vice versa*. The temperature gradient can therefore be manipulated to produce an optimum separation of the compounds. The instrument parameters finally used were capable of separating 18 peaks from a mixture of 19 compounds. The isomers dibenz[ac]anthracene and dibenz[ah]anthracene eluted as one peak.

Once the optimum GC conditions have been determined, the operation of the detector can be optimised. For both detectors, this required the retention times and the major ions in the mass spectrum of each compound to be known. The detector response for the most abundant ion for each compound is used for quantification purposes.

This information was obtained by analysing standard solutions in full scan mode, during which the detector scans across the range of 50 to 300 a.m.u. at a rate of 4 scans s^{-1}. This data is used to produce a total ion chromatogram (TIC) (Figure 4.5a). This is a construction of a conventional chromatogram using the data for all ions detected in the scan mass range.

The detector operating software is then used to obtain a mass spectra of the compound responsible for each peak in a TIC, and so the retention time and major ions for each compound can be determined. An example of such a mass spectrum for benzo[a]pyrene and benzo[a]pyrene-d12 are shown in Figure 4.5b. The major ions used for the quantification and calibration of each compound are given in Table 4.9.

With this knowledge, the MSD and ITD were operated in the multiple ion detection (MID) mode. In this mode, the ITD will scan only a specified, discrete group of ions, rather than a continuous mass range. This makes the detection more sensitive as more scans of the ions of interest are performed in any given time period. This process was made even more sensitive for the MSD as the ion scan range could be specified to change at given times during the run, thereby allowing the detector to monitor only two ions at a time (the detection and calibration ions, see Table 4.9).



<u>**Figure 4.5a and b**</u> <u>**Total ion chromatogram (TIC) of 'MS' PAH standard and mass spectra of benzo[a]pyrene and benzo[a]pyrene-d12.**</u>

Table 4.9 **Detection and Calibration Ions Used for GC-MSD Analysis.**

Compound	Calibn. Ion No.	Detecn. Ion	Calibn. Ion No.
Naphthalene		128	1
Naphthalene-d8	1	136	
Acenaphthene		153	2
Acenaphthene-d10	2	164	
Fluorene		166	3
Fluorene-d10	3	176	
Phenanthrene		178	4
Anthracene		178	4
Anthracene-d10	4	188	
Fluoranthene		202	5
Fluoranthene-d10	5	212	
Pyrene		202	5
Benz[a]anthracene		228	6
Chrysene		228	6
Chrysene-d12	6	240	
Benzo[b]fluoranthene		252	7
Benzo[k]fluoranthene		252	7
Benzo[e]pyrene		252	7
Benzo[a]pyrene		252	7
Benzo[a]pyrene-d12	7	264	
Perylene		252	7
Indeno[123-cd]pyrene		276	7
Dibenz[ah]anthracene		278	7
Benzo[ghi]perylene		276	8
^{13}C-Benzo[ghi]perylene	8	288	
Anthanthrene		276	7

A graphics report produced by the MSD of an analysis of the MS PAH standard spiked with the MS-isotope standard is shown in Figure 4.6. This shows the TIC and also the single ion chromatograms for each ion analysed (n.b. ^{13}C-benzo[ghi]perylene (ion m/z 288) was not present in this particular analysis).

4.5.2.4 Calibration and Precision.

The analyses were calibrated with the use of an internal-standard solution of seven perdeuterated and one ^{13}C-substituted PAH isotopes (see Appendix II). These isotopes are purely artificial and not naturally occurring, and therefore there is no possibility of their occurence in the sample material.

The purpose of spiking the samples with the isotopes is to aid in unequivocal detection of the PAHs (in combination with retention time data), and also to quantify the detector response.

The method of quantification by internal-standards results in accurate corrections being made for variations in detected analyte for each separate injection. These variations can be caused by adsorption, degradation or leakages during the injection and column transfer processes. This technique uses the principal that the known amount of standard isotope in the sample behaves in exactly the same way, and is subjected to exactly the same conditions, as the analyte (McVeety and Hites, 1988). PAHs can be susceptible to a highly significant degree of discrimination during the injection of samples into GC injection ports (Pecher, pers. comm.).

This fact is well illustrated by the peak area data from 6 analyses of one PAH standard solution by GC-MSD (Table 4.10). It can be seen that for all compounds there is a high error, as measured by the relative standard deviation (RSD). This error ranges in value from 22 % for naphthalene to 69 % for indeno[123-cd]pyrene. It is interesting to note that the RSD values increase with increasing

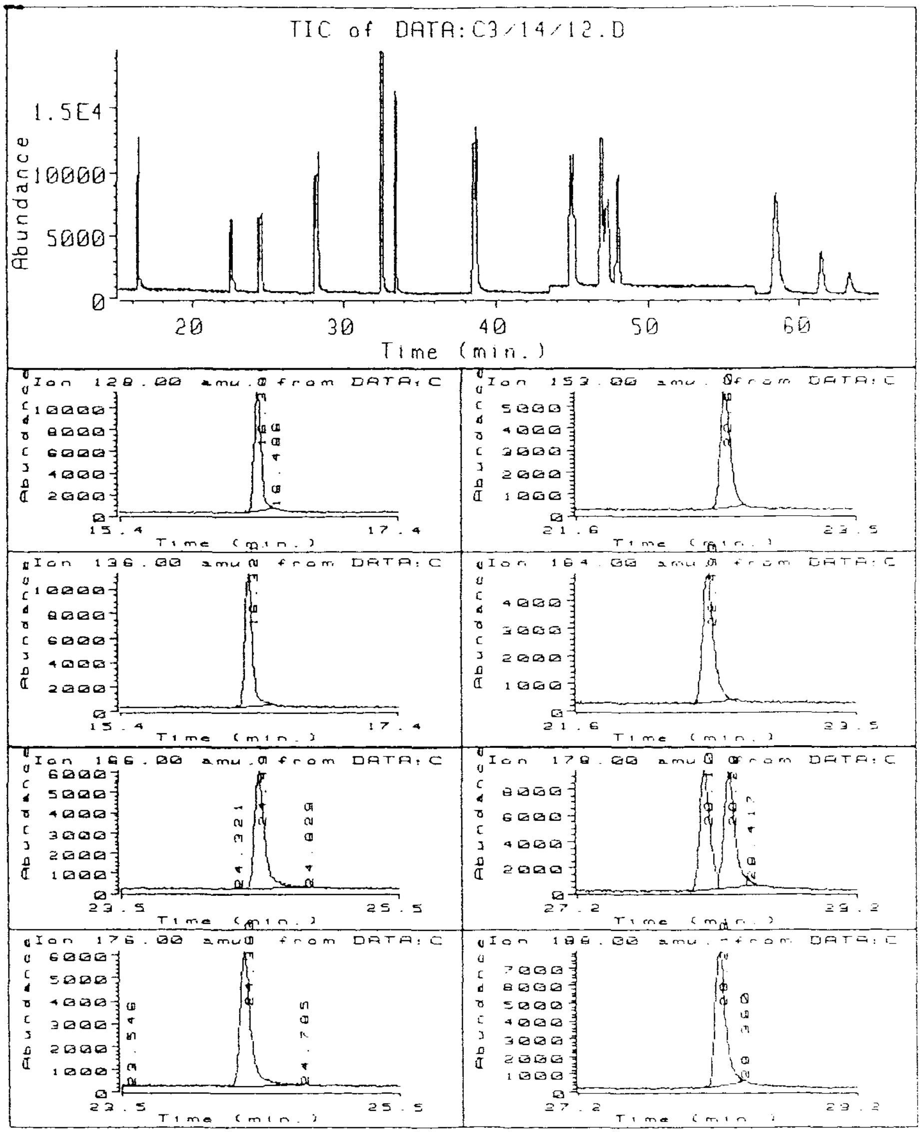


Figure 4.6 **MSD out-put showing typical analysis of a PAH standard, with TIC and single ion chromatograms.** (cont. overleaf)

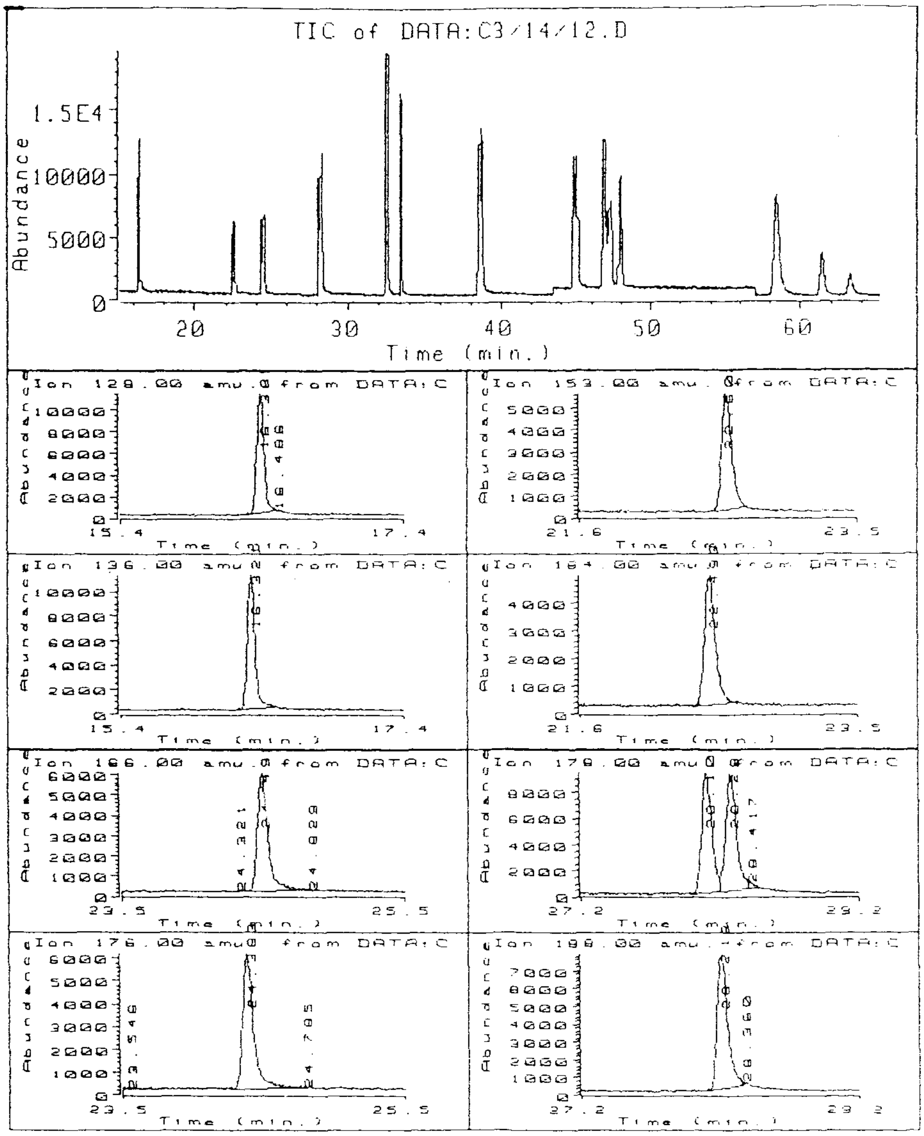


Figure 4.6 MSD out-put showing typical analysis of a PAH standard, with TIC and single ion chromatograms. (cont. overleaf)

Table 4.10 **GC-MSD Peak Area Precision Data.**

(see Appendix II for identification of GC-MS standard)

PAH	1	2	3	4	5	6	Mean	s.d.	r.s.d.
1	462070	228750	388189	404108	381074	331091	365880	79319	22%
2	316442	154358	252154	256048	244458	208835	238716	53971	23%
3	361781	171966	299405	327595	303601	218380	280455	71210	25%
4	543161	208156	452972	451942	436069	291391	397282	123171	31%
5	582134	222342	472897	512335	485620	296735	428677	138368	32%
6	850963	232304	720520	663230	759713	371421	599692	242678	40%
7	970762	253959	804410	742632	835318	433104	673364	272129	40%
8	729993	88167	496304	572265	721116	324238	488681	247691	51%
9	852151	119563	539261	589919	791313	380884	545515	270182	50%
10	932607	96809	613476	608162	840786	370594	577072	307092	53%
11	1084656	113820	626317	736569	920724	475374	659577	342843	52%
12	1256300	163308	807968	766966	1088376	548025	771824	389006	50%
13	796297	68468	465703	526797	708136	317009	480402	264729	55%
14	1011726	112238	635812	685334	923322	430929	633227	329391	52%
15	987425	57721	442069	572179	674075	194026	487916	336097	69%
16	1400724	79948	626662	857049	975149	446802	731056	455972	62%
17	734936	51333	365350	434899	563729	221837	395347	242730	61%
18	375479	32098	195204	254517	256303	88438	200340	124575	62%

molecular weight, and further analysis shows that this relationship exhibits a high degree of linearity ($R^2 = 96$ %), as illustrated in Figure 4.7. This suggests that the discrimination is controlled by an absorption process, with the less volatile PAHs being more readily absorbed. Possible sites for absorption are the injector port liner, contamination particles in the injector port and the column, other active sites on the column coating, caused by chemical degradation, and also the syringe needle. This phenomena has serious implications for the analysis of PAHs by GC techniques that do not employ internal-standard calibration.

For the quantification of individual PAHs in the samples, the response factor (RF) for the isotope-PAHs to standard PAHs in the same solution needed to be known. These were calculated according to the formula:

$$RF = (A_{ix} \times C_{nx})/(C_{ix} \times A_{nx})$$

where: A_{ix} = area of isotope-PAH 'x' peak in the standard,
C_{nx} = concentration of PAH 'x' in the standard (pg μl^{-1}),
C_{ix} = concentration of isotope-PAH 'x' in the standard (pg μl^{-1}),
A_{nx} = area of PAH 'x' peak in the standard.

The RFs for each compound were calculated on a daily basis from the analysis of a spiked standard solution at the start of each set of analyses.

These values were used to calculate the concentration of each compound in the injected extract using the following formula:

$$C_x = RF \times (C_{isx}/A_{isx}) \times A_x$$

where: C_x = concentration of PAH 'x' in the extract (pg μl^{-1}),
C_{isx} = concentration of spiked isotope-PAH 'x' in the extract (pg μl^{-1}),

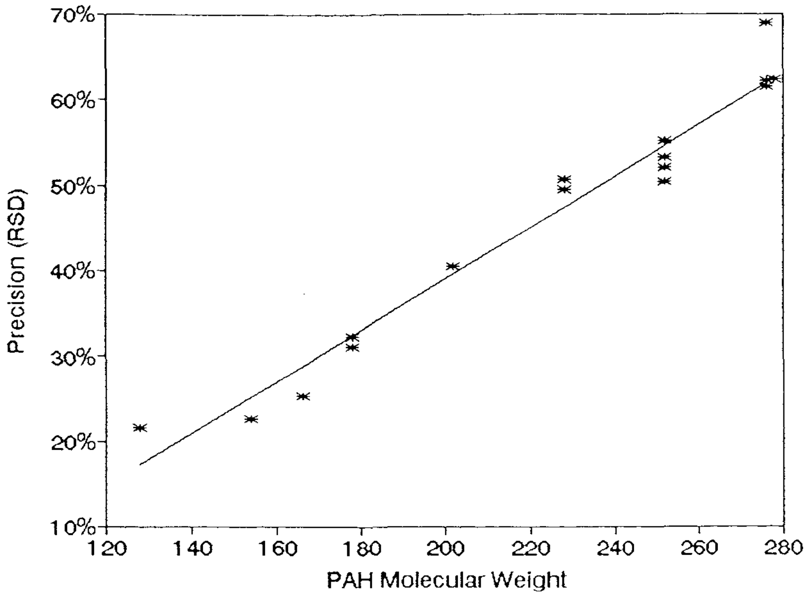


Figure 4.7 **The relationship between the precision of peak area determinations and molecular weight for PAHs analysed by GC-MSD.**

A_{isx} = area of spiked isotope-PAH 'x' peak in the extract ($pg\ \mu l^{-1}$),

A_x = area of PAH 'x' peak in the extract.

The final sample concentration is calculated by:

$$S_x = (C_x \times V_e)/(V \times 1000)$$

where:
S_x = concentration of PAH 'x' in snow ($ng\ l^{-1}$),
V_e = final volume of extract (150 μl),
V = volume of snowmelt extracted or filtered (l),
1000 = unit conversion factor.

The detection limit for each compound was calculated from visual inspection and manual integration of a chromatogram of the lowest concentration standard used (50 $pg\ \mu l^{-1}$). The detection limit is defined as the concentration of a compound which would produce a peak with a height equal to a signal-to-noise ratio of 3, assuming that a linear relationship exists between peak height and compound concentration. The values calculated for the absolute detection limits and the method detection limits are shown in Table 4.11.

4.5.3 Other Analyses.

4.5.3.1 Determination of Major Cations.

Calcium (Ca^{2+}) and magnesium (Mg^{2+}) were determined by flame atomic absorption spectroscopy (FAAS). Sodium (Na^{+}) and potassium (K^{+}) were determined by flame atomic emission spectroscopy (FAES). Both FAAS and FAES were performed using a Pye-Unicam SP9 Spectrophotometer. An air-acetylene flame was used for atomisation. The absorption by Ca^{2+} and Mg^{2+} were measured at wavelengths of 422.7 nm and 285.2 nm respectively, with respective cathode lamp currents of 10 and 4 mA. The intensity of emission by Na^{+} and K^{+}

Table 4.11 GC-MSD Detection Limits.

Compound	Absolute D.L. (pg μl^{-1})	Method D.L. (ng l^{-1})
Naphthalene	2.0	0.6
Acenaphthene	2.0	0.6
Fluorene	2.0	0.6
Phenanthrene	2.0	0.6
Anthracene	2.0	0.6
Fluoranthene	2.0	0.6
Pyrene	2.0	0.6
Benz[a]anthracene	2.0	0.6
Chrysene	2.0	0.6
Benzo[b]fluoranthene	5.0	1.5
Benzo[k]fluoranthene	5.0	1.5
Benzo[e]pyrene	5.0	1.5
Benzo[a]pyrene	7.0	2.1
Perylene	6.0	1.8
Indeno[1,2,3-c,d]pyrene	2.0	0.6
Dibenz[ac+ah]anthracene	10.0	3.0
Benzo[g,h,i]perylene	5.0	1.5
Anthanthrene	10.0	3.0

were measured at wavelengths of 589.0 nm and 766.5 nm respectively. For both FAAS and FAES the bandpass was set at 0.1 nm.

Acidified samples (see Section 4.4.2) of filtered snowmelt were modified by the addition of a releasing agent ($La(NO_3)_3$) and an ionisation suppressant (CsCl). The releasing agent prevents Ca^{2+} and Mg^{2+} forming insoluble and thermally stable chemical complexes that would prevent them being fully atomised and accurately quantified (Welz, 1985). Conversely, Na^+ and K^+ are easily atomised and can be partially ionised in the flame, which prevents their accurate determination. Therefore, an addition of CsCl is made to suppress ionisation (Welz, 1985). Blanks and standards were also acidified and modified in the same way.

Depending on the sample concentration, 250 or 500 μl of sample was introduced into the flame by aspiration through a custom-built micro-volume aspirator. The output from the SP9 was channelled through a chart recorder, and the resulting peak heights from each aspiration were used for quantification. The accuracy and precision of these determinations are ± 5% (Welz, 1985).

4.5.3.2 Determination of Major Anions and Ammonium.

Sulphate (SO_4^{2-}), chloride (Cl^-) and nitrate (NO_3^-) were determined by ion chromatography using a Dionex Model 4000i Ion Chromatograph. No pre-treatment of the filtered samples prior to analysis was necessary.

Ammonium was determined using a flow-injection analyser (Technicon Instruments Corp.). This is an automated procedure that uses the Berthelot Reaction, in which a blue coloured compound is quantitatively formed when a solution of an ammonium salt is added to sodium phenoxide, followed by the addition of sodium hypochlorite. A solution of potassium sodium tartrate and sodium citrate is added to the sample stream to prevent the precipitation of calcium and magnesium hydroxides. Absorbance of light at 630 nm is used to determine the concentration of ammonium.

4.5.3.3 Determination of pH and Conductivity.

The pH of the samples was measured using either an Orion SA250 portable meter, with a Ross combination electrode and automatic temperature compensator, or an Accumet Model 955 portable pH meter (Fisher Scientific Ltd.). The meters were calibrated with buffer powder solutions of pH 4.00 and 9.00 (BDH Ltd.).

Electrical conductivity of snowmelt was measured in Canada using a Model HI8033 conductivitymeter (HANNA Instruments).

CHAPTER 5: RESULTS

Owing to the problems encountered with the analytical facilities on the one hand, and the limited time available for use of the MSD on the other, only a small number of the total samples available were successfully analysed for PAHs. Those that were analysed are:

i) QUEBEC B-H (36 extracts, dissolved phase only),
ii) SCOT 1 (30 extracts, dissolved and particulate phases),
iii) SOTON 1 (6 extracts, dissolved and particulate phases).

The first set were analysed by HPLC, and the remaining two by GC-MSD.

It is important to note that where mean values are reported, values calculated to be less than the method detection limit for each compound are recorded as zero. All values reported are uncorrected for extraction efficiency.

5.1 Scotland

5.1.1 PAH Concentrations

The concentrations of 19 PAHs were determined in the dissolved and particulate phases for a total of 30 sample extracts. The values obtained for each sample extract are shown in Table 5.1. The mean, standard deviation and residual standard deviation (N=3) for each compound in each sample group are shown in Table 5.2. Mean concentrations above zero for individual compounds range from 0.9 to 270 ng l^{-1} in the dissolved phase for acenaphthene and phenanthrene, respectively, and from 0.6 to 580 ng l^{-1} in the particulate phase for naphthalene and fluoranthene, respectively. The total dissolved and the total particulate mean PAH concentrations range from 70 to 780 ng l^{-1} and 30 to 2700 ng l^{-1}, respectively, with overall total (dissolved + particulate) PAH concentrations of between 100 and 3500 ng l^{-1}.

Table 5.1

PAH Concentrations for SCOT 1 Sample Extracts.

DISSOLVED PAH CONCENTRATIONS

Compound	Concentration		(ng/l)												
	25/2/1D	25/2/2D	25/2/3D	27/2/1D	27/2/2D	27/2/3D	27/2/4D	27/2/5D	27/2/6D	28/2/1D	28/2/2D	28/2/3D	28/2/4D	28/2/5D	28/2/6D
Naphthalene	0	1	12	10	9	12	6	9	6	4	27	25	2	10	6
Acenaphthene	0	0	0	0	0	0	0	0	0	0	1	2	3	0	3
Fluorene	4	3	11	10	10	14	3	6	4	6	17	13	4	5	3
Phenanthrene	64	51	123	167	210	244	22	29	29	219	287	289	15	16	11
Anthracene	3	1	7	9	11	12	3	4	4	11	14	14	0	0	0
Fluoranthene	159	67	167	152	231	206	22	27	30	213	248	246	10	9	7
Pyrene	119	40	86	59	91	78	18	21	23	96	102	106	3	6	4
B(a)Anthracene	44	6	15	9	17	9	8	12	11	12	13	0	0	0	0
Chrysene	137	28	56	26	76	40	26	31	31	56	58	63	15	7	4
B(b)Flnthn	117	10	31	35	36	24	33	42	28	44	50	33	21	26	22
B(k)Flnthn	74	0	13	2	14	0	0	0	0	0	0	14	0	0	1
B(e)Pyrene	42	5	8	10	14	0	9	13	11	11	13	12	0	0	0
B(a)Pyrene	40	3	0	6	9	0	6	0	8	7	3	8	5	0	0
Perylene	6	0	0	0	0	0	0	0	0	0	0	0	0	0	0
I(123-cd)P	9	0	0	0	0	0	0	0	0	0	0	0	0	0	0
DB(ac + ah)Anth	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
B(ghi)P	0	0	0	0	15	0	0	0	0	0	16	0	0	0	0
Anthanth	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0

PARTICULATE PAH CONCENTRATIONS

Compound	Concentration		(ng/l)												
	25/2/1P	25/2/2P	25/2/3P	27/2/1P	27/2/2P	27/2/3P	27/2/4P	27/2/5P	27/2/6P	28/2/1P	28/2/2P	28/2/3P	28/2/4P	28/2/5P	28/2/6P
Naphthalene	18	2	0	0	2	0	0	0	0	0	0	0	0	0	0
Acenaphthene	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Fluorene	13	8	8	4	10	3	0	0	1	16	11	16	1	1	0
Phenanthrene	152	107	109	65	128	38	4	2	3	326	376	303	4	4	4
Anthracene	9	5	6	5	9	5	0	0	0	20	16	13	0	0	0
Fluoranthene	225	269	270	174	312	243	8	6	4	565	643	529	3	3	2
Pyrene	121	176	184	106	186	148	6	4	3	344	381	304	2	2	2
B(a)Anthracene	15	58	82	37	78	89	6	6	4	107	109	101	0	0	0
Chrysene	65	181	188	112	213	194	12	13	9	337	342	315	2	3	0
B(b)Flnthn	4	173	155	95	173	134	27	33	28	272	278	201	17	19	19
B(k)Flnthn	0	128	94	57	118	92	7	7	7	150	153	134	0	2	1
B(e)Pyrene	35	51	56	40	72	57	10	12	11	109	110	84	0	0	0
B(a)Pyrene	8	41	55	35	64	56	6	9	8	79	65	60	1	0	0
Perylene	0	0	5	6	9	8	0	0	0	12	5	10	0	0	0
I(123-cd)P	6	25	89	49	91	81	10	10	8	200	225	0	2	0	0
DB(ac + ah)Anth	0	0	23	17	9	18	0	0	0	41	37	24	0	0	0
B(ghi)P	13	19	136	68	123	98	16	18	15	186	208	190	3	0	0
Anthanth	0	0	0	0	4	16	0	0	0	0	0	0	0	0	0

Table 5.2 Mean Sample Group PAH Concentrations, Standard Deviations and Residual Standard Deviations for SCOT 1 Samples.

DISSOLVED PAH CONCENTRATIONS

Compound	25/2D/O	s.d.	r.s.d.	27/2D/O	s.d.	r.s.d.	27/2D/F	s.d.	r.s.d.	28/2D/O	s.d.	r.s.d.	28/2D/F	s.d.	r.s.d.
1 Naphthalene	4.4	6.9	155%	10.0	1.5	15%	7.0	1.6	22%	19.0	13.0	67%	5.9	3.9	67%
2 Acenaphthene	0.0	0.0	—	0.0	0.0	—	0.0	0.0	—	0.9	0.8	95%	2.1	1.8	88%
3 Fluorene	5.9	4.6	77%	11.0	2.2	19%	4.3	1.2	28%	12.0	5.8	48%	4.0	1.4	35%
4 Phenanthrene	80.0	38.0	48%	210.0	39.0	19%	27.0	4.2	16%	270.0	40.0	15%	14.0	2.7	19%
5 Anthracene	4.1	3.0	72%	11.0	1.6	15%	4.0	0.5	13%	13.0	1.3	10%	0.0	0.0	—
6 Fluoranthene	130.0	56.0	43%	200.0	41.0	20%	26.0	3.7	14%	240.0	20.0	8%	8.8	1.6	19%
7 Pyrene	82.0	40.0	49%	77.0	16.0	21%	21.0	2.7	13%	100.0	4.8	5%	4.3	1.4	33%
8 B(a)Anthracene	22.0	20.0	93%	12.0	4.8	41%	10.0	1.9	18%	8.6	7.5	87%	0.0	0.0	—
9 Chrysene	74.0	57.0	77%	47.0	26.0	55%	29.0	3.0	10%	59.0	3.6	6%	8.6	5.8	67%
10 B(b)Flnthn	53.0	57.0	108%	32.0	6.2	20%	34.0	7.3	21%	43.0	8.8	21%	23.0	2.8	12%
11 B(k)Flnthn	29.0	39.0	136%	5.4	7.8	146%	0.0	0.0	—	4.6	8.0	173%	0.0	0.0	—
12 B(e)Pyrene	18.0	21.0	114%	7.7	7.0	91%	11.0	1.6	14%	12.0	0.9	8%	0.0	0.0	—
13 B(a)Pyrene	14.0	23.0	158%	4.7	4.3	92%	4.4	3.9	90%	6.2	2.7	43%	0.0	0.0	—
14 Perylene	2.0	3.4	173%	0.0	0.0	—	0.0	0.0	—	0.0	0.0	—	0.0	0.0	—
15 I(123-cd)P	3.1	5.4	173%	0.0	0.0	—	0.0	0.0	—	0.0	0.0	—	0.0	0.0	—
16 DB(ac+ah)Anth	0.0	0.0	—	0.0	0.0	—	0.0	0.0	—	0.0	0.0	—	0.0	0.0	—
17 B(ghi)P	0.0	0.0	—	5.1	8.8	173%	0.0	0.0	—	5.3	9.2	173%	0.0	0.0	—
18 Anthanth	0.0	0.0	—	0.0	0.0	—	0.0	0.0	—	0.0	0.0	—	0.0	0.0	—
TOTAL	520.0			630.0			180.0			780.0			71.0		

PARTICULATE PAH CONCENTRATIONS

Compound	25/2P/O	s.d.	r.s.d.	27/2P/O	s.d.	r.s.d.	27/2P/F	s.d.	r.s.d.	28/2P/O	s.d.	r.s.d.	28/2P/F	s.d.	r.s.d.
1 Naphthalene	7.0	10.0	145%	0.6	1.0	173%	0.0	0.0	—	0.0	0.0	—	0.0	0.0	—
2 Acenaphthene	0.0	0.0	—	0.0	0.0	—	0.0	0.0	—	0.0	0.0	0%	0.0	0.0	—
3 Fluorene	9.6	3.2	33%	5.7	3.5	61%	0.0	0.0	—	15.0	3.4	23%	0.6	0.5	87%
4 Phenanthrene	120.0	25.0	20%	77.0	46.0	60%	2.9	1.0	35%	340.0	37.0	11%	4.0	0.1	2%
5 Anthracene	6.6	2.0	31%	6.0	2.3	38%	0.0	0.0	—	17.0	3.3	20%	0.0	0.0	—
6 Fluoranthene	250.0	25.6	10%	240.0	69.0	28%	6.3	2.0	32%	580.0	58.0	10%	2.7	0.5	20%
7 Pyrene	160.0	26.0	21%	150.0	40.0	27%	4.4	1.9	43%	340.0	39.0	11%	1.9	0.2	13%
8 B(a)Anthracene	45.0	26.0	57%	61.0	21.0	34%	5.3	1.1	20%	110.0	4.2	4%	0.0	0.0	—
9 Chrysene	140.0	69.0	48%	170.0	54.0	31%	11.0	1.7	15%	330.0	14.0	4%	1.6	1.4	88%
10 B(b)Flnthn	110.0	93.0	84%	130.0	39.0	29%	30.0	3.2	11%	250.0	43.0	17%	18.4	1.3	7%
11 B(k)Flnthn	74.0	66.0	90%	89.0	31.0	34%	6.9	0.3	5%	150.0	10.0	7%	0.0	0.0	—
12 B(e)Pyrene	47.0	11.0	23%	57.0	16.0	29%	11.0	0.8	7%	100.0	15.0	15%	0.0	0.0	—
13 B(a)Pyrene	35.0	24.0	70%	51.0	15.0	29%	8.5	0.6	7%	68.0	9.6	14%	0.0	0.0	—
14 Perylene	1.8	3.2	173%	7.6	1.6	21%	0.0	0.0	—	8.8	3.7	42%	0.0	0.0	—
15 I(123-cd)P	40.0	43.0	108%	74.0	22.0	30%	9.1	1.2	13%	140.0	120.0	87%	0.6	1.0	173%
16 DB(ac+ah)Anth	7.6	13.0	173%	15.0	5.3	36%	0.0	0.0	—	34.0	8.8	26%	0.0	0.0	—
17 B(ghi)P	56.0	69.0	124%	96.0	27.0	28%	17.0	1.5	9%	190.0	12.0	6%	0.0	0.0	—
18 Anthanth	0.0	0.0	—	6.8	8.2	121%	0.0	0.0	—	0.0	0.0	—	0.0	0.0	—
TOTAL	1100.0			1200.0			110.0			2700.0			30.0		

The mean concentrations of PAHs in each phase for each sample group are illustrated in Figure 5.1. The PAH number of the X-axis refers to the number of the compound in the MS standard (see Table 5.1 for identification of PAH numbers).

Tables 5.3a and b show the mean percentage distribution of each compound in the dissolved and particulate phases for snowpack and fresh snow samples, and this information is illustrated in Figures 5.2a and b. The mean distribution in the dissolved phase for both sets ranges from 100 % for acenaphthene to 0 % for dibenz[ac+ah]anthracene and anthanthrene.

5.1.2 Supplementary Chemical Data

The pH and major cation concentrations for the samples referred to above are shown in Table 5.4 and illustrated in Figure 5.3. Data for major anion concentrations are not available.

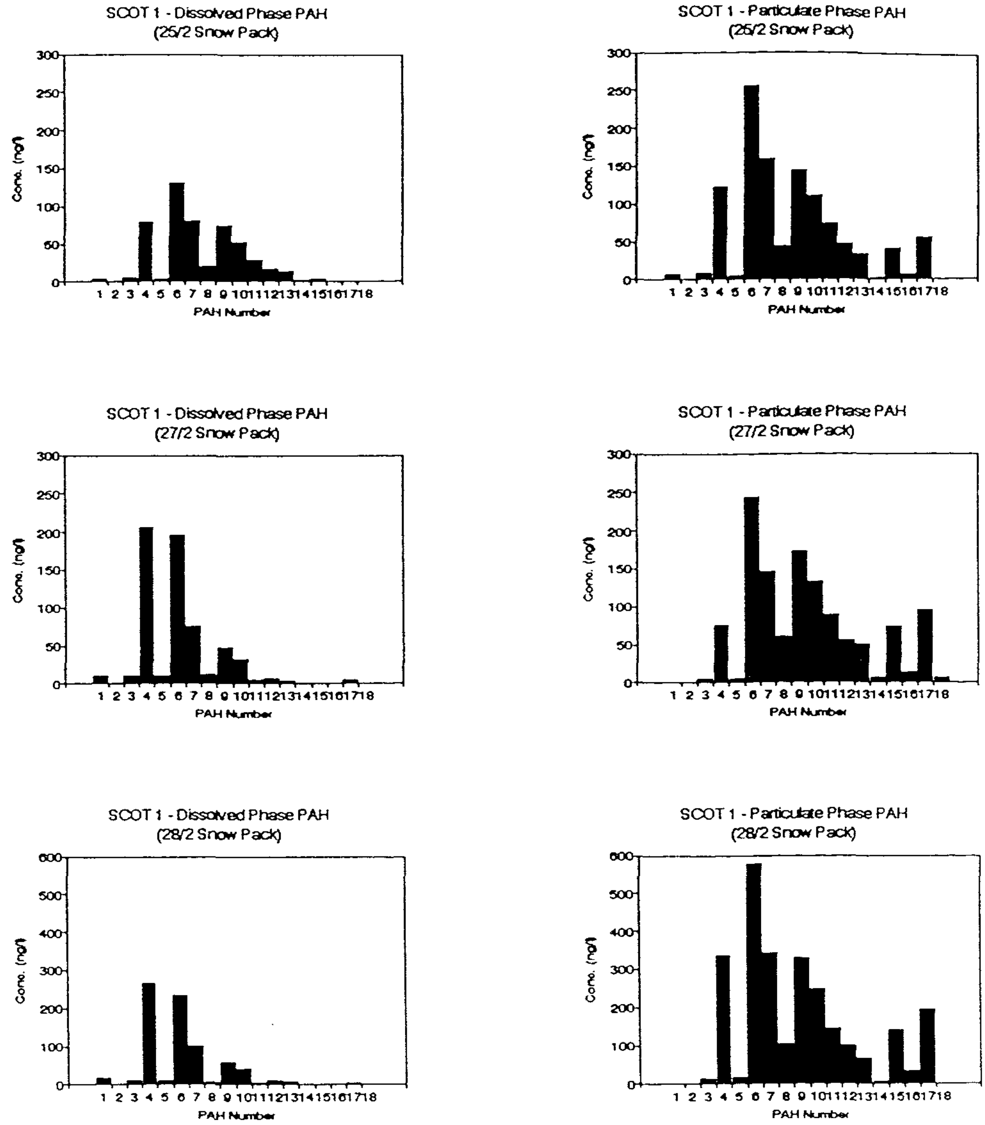
5.1.3 Meteorological Data

No meteorological data for these samples are available.

5.2 Canada

5.2.1 PAH Concentrations

The concentrations of 15 PAHs were determined in the dissolved phase for a total of 36 sample extracts. Particulate phase extracts were not analysed. The mean, sample standard deviation and residual standard deviation (N=5, except for 'F' where N=6) for each compound in each sample group are shown in Table 5.5. Mean concentrations above zero for individual compounds range from 0.3 for anthracene, to 130 ng l^{-1} for fluorene. The total dissolved mean PAH concentration ranges from 1.0 to 240 ng l^{-1}.



SCOT 1 - Dissolved Phase PAH (25/2 Snow Pack)

SCOT 1 - Particulate Phase PAH (25/2 Snow Pack)

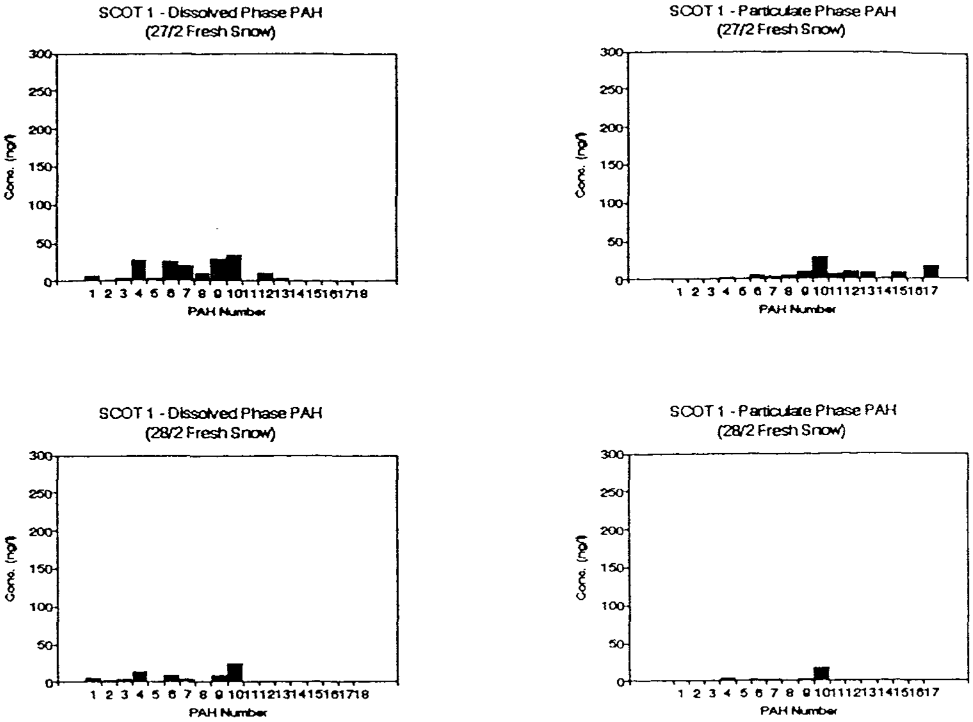
SCOT 1 - Dissolved Phase PAH (27/2 Snow Pack)

SCOT 1 - Particulate Phase PAH (27/2 Snow Pack)

SCOT 1 - Dissolved Phase PAH (28/2 Snow Pack)

SCOT 1 - Particulate Phase PAH (28/2 Snow Pack)

Figure 5.1 PAH concentrations for SCOT 1 samples.
(continued overleaf)



SCOT 1 - Dissolved Phase PAH (27/2 Fresh Snow)

SCOT 1 - Particulate Phase PAH (27/2 Fresh Snow)

SCOT 1 - Dissolved Phase PAH (28/2 Fresh Snow)

SCOT 1 - Particulate Phase PAH (28/2 Fresh Snow)

Figure 5.1 (continued)

Table 5.3a+b PAH Phase Distribution Data for SCOT 1 Samples.

SCOT 1 - SNOW PACK SAMPLES

	Compound	% Dissolved Phase									% D	% P
1	Naphthalene	0%	29%	100%	100%	83%	100%	100%	100%	100%	79%	21%
2	Acenaphthene								100%	100%	100%	0%
3	Fluorene	23%	26%	58%	69%	52%	83%	26%	62%	44%	49%	51%
4	Phenanthrene	30%	32%	53%	72%	62%	87%	40%	43%	49%	52%	48%
5	Anthracene	28%	23%	56%	66%	57%	72%	36%	45%	50%	48%	52%
6	Fluoranthene	41%	20%	38%	47%	43%	46%	27%	28%	32%	36%	64%
7	Pyrene	49%	19%	32%	36%	33%	35%	22%	21%	26%	30%	70%
8	B(a)Anthracene	74%	9%	20%	20%	19%	11%	10%	11%	0%	19%	81%
9	Chrysene	68%	13%	23%	19%	26%	17%	14%	15%	17%	24%	76%
10	B(b)Flnthn	97%	5%	17%	27%	17%	15%	14%	15%	14%	25%	75%
11	B(k)Flnthn	100%	0%	12%	3%	11%	0%	0%	0%	9%	15%	85%
12	B(e)Pyrene	54%	8%	12%	19%	16%	0%	9%	10%	12%	16%	84%
13	B(a)Pyrene	84%	6%	0%	14%	12%	0%	8%	5%	12%	16%	84%
14	Perylene	100%		0%	0%	0%	0%	0%	0%	0%	13%	88%
15	I(123-cd)P	61%	0%	0%	0%	0%	0%	0%	0%		8%	92%
16	DB(ac+ah)Anth			0%	0%	0%	0%	0%	0%	0%	0%	100%
17	B(ghi)P	0%	0%	0%	0%	11%	0%	0%	7%	0%	2%	98%
18	Anthanth					0%	0%				0%	100%

SCOT 1 - FRESH SNOW SAMPLES

	Compound	% Dissolved Phase						% D	% P
1	Naphthalene	100%	100%	100%	100%	100%	100%	100%	0%
2	Acenaphthene	100%		100%				100%	0%
3	Fluorene	82%	86%	100%	100%	100%	82%	92%	8%
4	Phenanthrene	78%	80%	74%	84%	93%	92%	84%	16%
5	Anthracene				100%	100%	100%	100%	0%
6	Fluoranthene	76%	77%	76%	73%	82%	87%	78%	22%
7	Pyrene	58%	78%	69%	74%	83%	90%	75%	25%
8	B(a)Anthracene				59%	66%	74%	66%	34%
9	Chrysene	88%	72%	100%	68%	71%	77%	79%	21%
10	B(b)Flnthn	55%	57%	53%	54%	56%	49%	54%	46%
11	B(k)Flnthn		0%	51%	0%	0%	0%	10%	90%
12	B(e)Pyrene				47%	52%	52%	50%	50%
13	B(a)Pyrene	91%			40%	0%	48%	45%	55%
14	Perylene							---	---
15	I(123-cd)P	0%			0%	0%	0%	0%	100%
16	DB(ac+ah)Anth							---	---
17	B(ghi)P	0%			0%	0%	0%	0%	100%
18	Anthanthrene							---	---

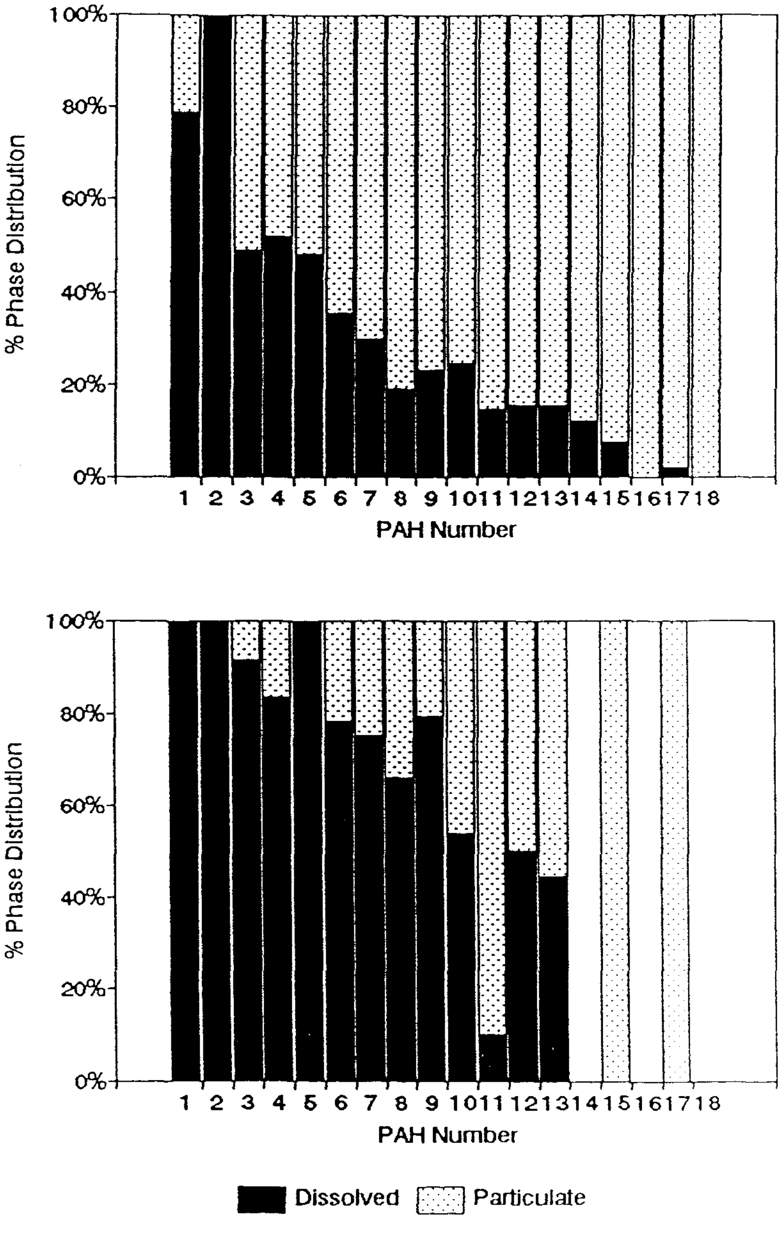
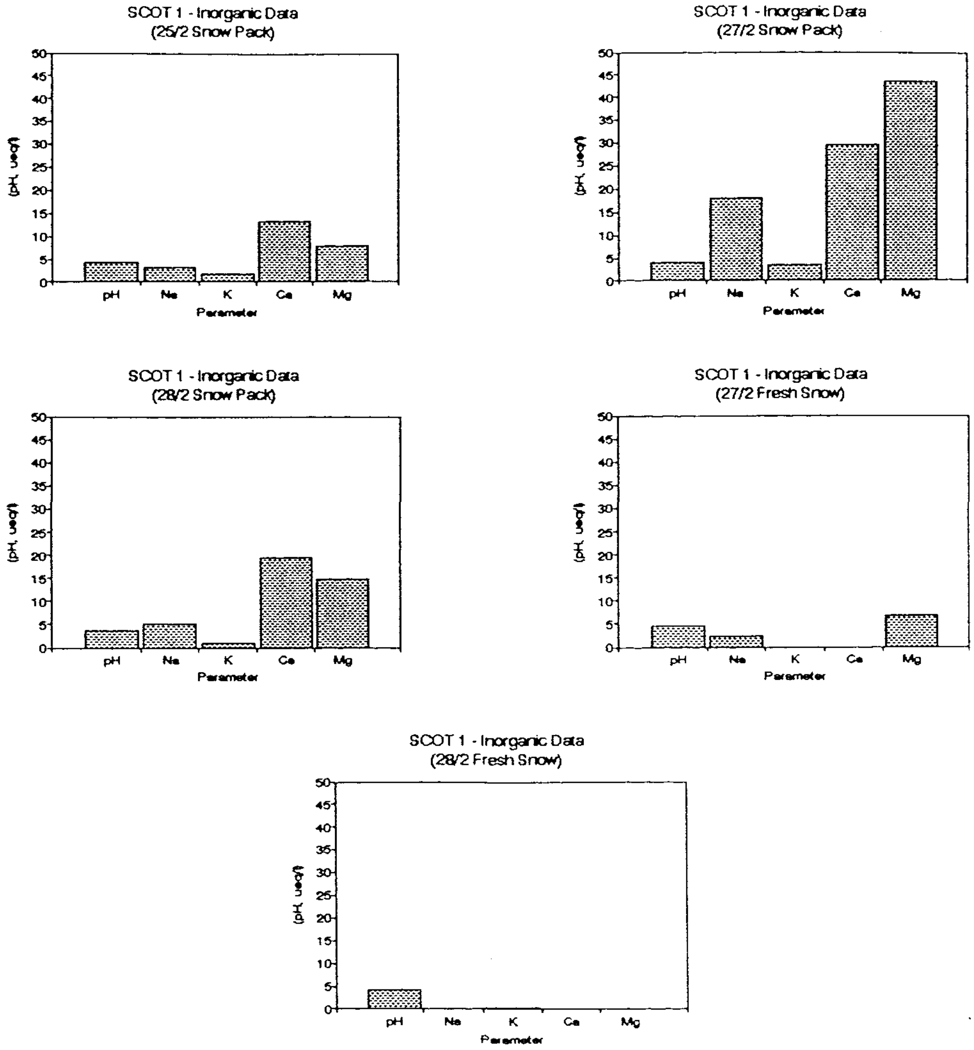


Figure 5.2a+b PAH phase distribution for SCOT 1 samples.
a) Top = Snow pack samples
b) Bottom = Fresh snow samples
(see Table 5.2 for PAH number identification)

Table 5.4 Inorganic Chemical Data for SCOT 1 and SOTON 1 Samples.

Sample	pH	Na (ueq/l)	K (ueq/l)	Ca (ueq/l)	Mg (ueq/l)
SOTON 1	4.50	18.0	1.1	82.0	9.4
SOTON 2	4.20	18.0	0.4	37.0	7.1
25/2/O	4.10	3.0	1.9	13.0	8.0
27/2/O	3.90	18.0	3.4	29.0	44.0
27/2/F	4.50	2.3	0.0	0.0	6.7
28/2/O	3.70	5.0	0.9	19.0	15.0
28/2/F	4.40	0.0	0.3	0.0	0.0


SCOT 1 - Inorganic Data (25/2 Snow Pack)

SCOT 1 - Inorganic Data (27/2 Snow Pack)

SCOT 1 - Inorganic Data (28/2 Snow Pack)

SCOT 1 - Inorganic Data (27/2 Fresh Snow)

SCOT 1 - Inorganic Data (28/2 Fresh Snow)

Figure 5.3 Inorganic data for SCOT 1 samples.

Table 5.5 Mean Sample Group Dissolved PAH Concentrations for QUEBEC Samples.

	Compound	Mean B	s.d.	r.s.d.	Mean C	s.d.	r.s.d.	Mean D	s.d.	r.s.d.	Mean E	s.d.	r.s.d.	Mean F	s.d.	r.s.d.	Mean G	s.d.	r.s.d.	Mean H	s.d.	r.s.d.
1	Naphthalene	0.0	0.0	—	0.0	0.0	—	0.0	0.0	—	6.4	5.8	91%	0.0	0.0	—	0.0	0.0	—	0.0	0.0	—
2	Acenaphthene	0.0	0.0	—	0.0	0.0	—	0.0	0.0	—	0.0	0.0	—	0.0	0.0	—	0.0	0.0	—	88.0	80.1	91%
3	Fluorene	0.0	0.0	—	40.0	38.0	95%	91.0	25.0	27%	0.0	0.0	—	0.0	0.0	—	130.0	50.0	40%	110.0	33.5	31%
4	Phenanthrene	3.7	0.8	22%	4.5	1.5	33%	11.0	1.5	13%	5.8	0.8	14%	0.0	0.0	—	7.2	3.3	46%	7.5	2.2	29%
5	Anthracene	0.0	0.0	—	0.3	0.3	91%	0.0	0.0	—	0.0	0.0	—	0.0	0.0	—	0.0	0.0	—	0.0	0.0	—
6	Fluoranthene	0.0	0.0	—	11.0	6.5	60%	18.0	2.9	16%	0.0	0.0	—	0.0	0.0	—	17.0	6.6	39%	16.0	6.0	37%
7	Pyrene	0.0	0.0	—	6.1	2.5	41%	9.1	2.2	24%	0.0	0.0	—	0.0	0.0	—	11.0	3.7	34%	8.3	1.5	19%
8	B[a]anthracene	0.0	0.0	—	0.0	0.0	—	0.0	0.0	—	0.0	0.0	—	0.0	0.0	—	0.0	0.0	—	0.0	0.0	—
9	Chrysene	1.2	0.3	27%	3.7	1.4	38%	5.8	1.0	18%	2.2	0.7	34%	1.0	0.4	43%	15.0	6.8	45%	7.5	2.4	32%
10	B[b]fluoranthene	0.0	0.0	—	8.1	10.0	123%	2.4	2.1	86%	0.0	0.0	—	0.0	0.0	—	12.0	7.1	59%	4.7	1.8	38%
11	B[k]fluoranthene	0.0	0.0	—	0.0	0.0	—	0.0	0.0	—	0.0	0.0	—	0.0	0.0	—	2.5	1.6	64%	0.9	0.3	32%
12	B[a]pyrene	0.0	0.0	—	0.0	0.0	—	0.0	0.0	—	0.0	0.0	—	0.0	0.0	—	0.0	0.0	—	0.0	0.0	—
13	DB[ah]anthracene	0.0	0.0	—	0.0	0.0	—	0.0	0.0	—	0.0	0.0	—	0.0	0.0	—	0.0	0.0	—	0.0	0.0	—
14	B[ghi]perylene	0.0	0.0	—	0.0	0.0	—	0.0	0.0	—	0.0	0.0	—	0.0	0.0	—	0.0	0.0	—	0.0	0.0	—
15	I[123-cd]pyrene	0.0	0.0	—	0.0	0.0	—	0.0	0.0	—	0.0	0.0	—	0.0	0.0	—	0.0	0.0	—	0.0	0.0	—
	TOTAL	5.0			74.0			140.0			16.0			1.0			190.0			240.0		

The mean concentrations of PAHs for each sample group are illustrated in Figure 5.4. The PAH number of the X-axis refers to the number of the compound in the HPLC standard (see Table 5.5 for identification of PAH numbers).

5.2.2 Supplementary Chemical Data

The data for sample pH, conductivity and major anion and cation concentrations are shown in Table 5.6 and illustrated in Figure 5.5.

5.2.3 Meteorological Data

The estimated back-trajectories of the air masses passing over Lac Laflamme for the time period immediately preceding each sampling event are shown in Figures 5.6a to 5.6g. These were supplied by the Atmospheric Environment Service of Environment Canada and show the trajectories for air-masses at levels corresponding to air pressures of 850, 925 and 1000 mbar.

5.3 England

5.3.1 PAH Concentrations

The concentrations of 19 PAHs measured in snowfall from one event in Southampton are shown in Table 5.7. The mean values, the sample standard deviation, residual standard deviation (N=3) and phase distribution are shown in Table 5.8. Mean concentrations above zero for individual compounds range from 7 to 370 ng l^{-1} in the dissolved phase for benzo[k]fluoranthene and phenanthrene, respectively, and from 4 to 800 ng l^{-1} in the particulate phase for anthanthrene and fluoranthene, respectively. Acenaphthene was not detected in any of the samples. The overall total (dissolved + particulate) PAH concentration is 6900 ng l^{-1}.

The mean concentrations of PAHs are illustrated in Figure 5.7. The PAH number of the X-axis refers to the number of the compound in the GC-MS standard (see

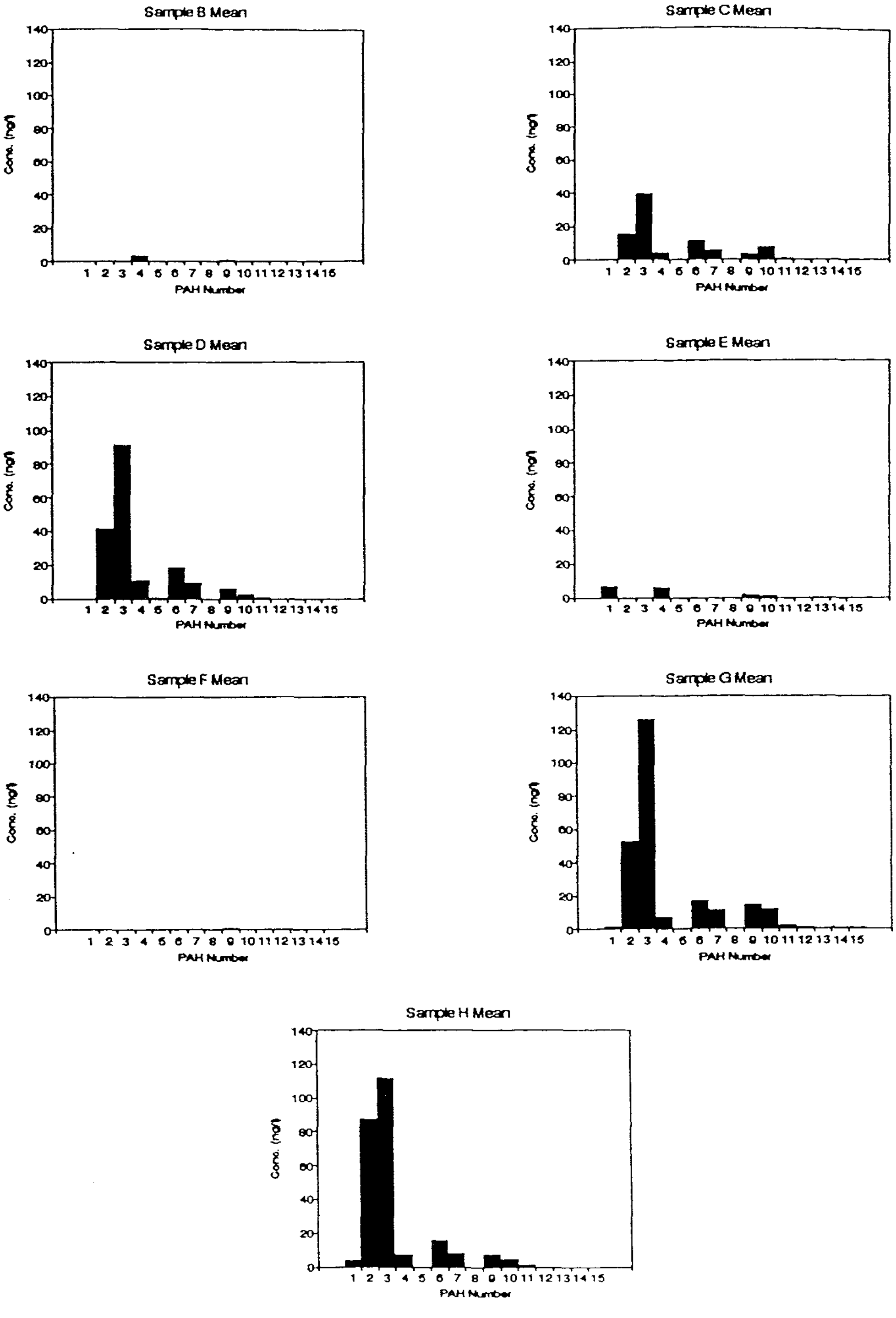


Figure 5.4 **Dissolved PAH concentrations for QUEBEC samples.**
(see Table 5.5 for PAH number identification)

Table 5.6 Inorganic Chemical Data for QUEBEC Samples.

(units: pH; μmohs; μeq/l)

	SAMPLE						
	B	C	D	E	F	G	H
pH	4.70	---	4.20	4.60	5.00	4.50	4.60
Cond.	16.0	---	25.0	13.0	17.0	58.0	40.0
Cl	5.6	3.7	6.1	4.7	5.8	2.7	1.8
NO3	33.0	39.0	45.0	21.0	18.0	62.0	29.0
SO4	11.0	16.0	48.0	21.0	3.3	18.0	16.0
NH4	7.0	19.0	20.0	10.0	7.3	4.3	7.3
Na	5.5	3.9	3.1	2.3	5.0	2.3	1.9
K	2.3	7.2	1.0	0.9	1.1	1.0	0.4
Ca	4.0	2.5	6.3	1.9	1.6	1.9	1.6
Mg	0.7	7.4	1.3	0.7	0.5	0.7	0.4

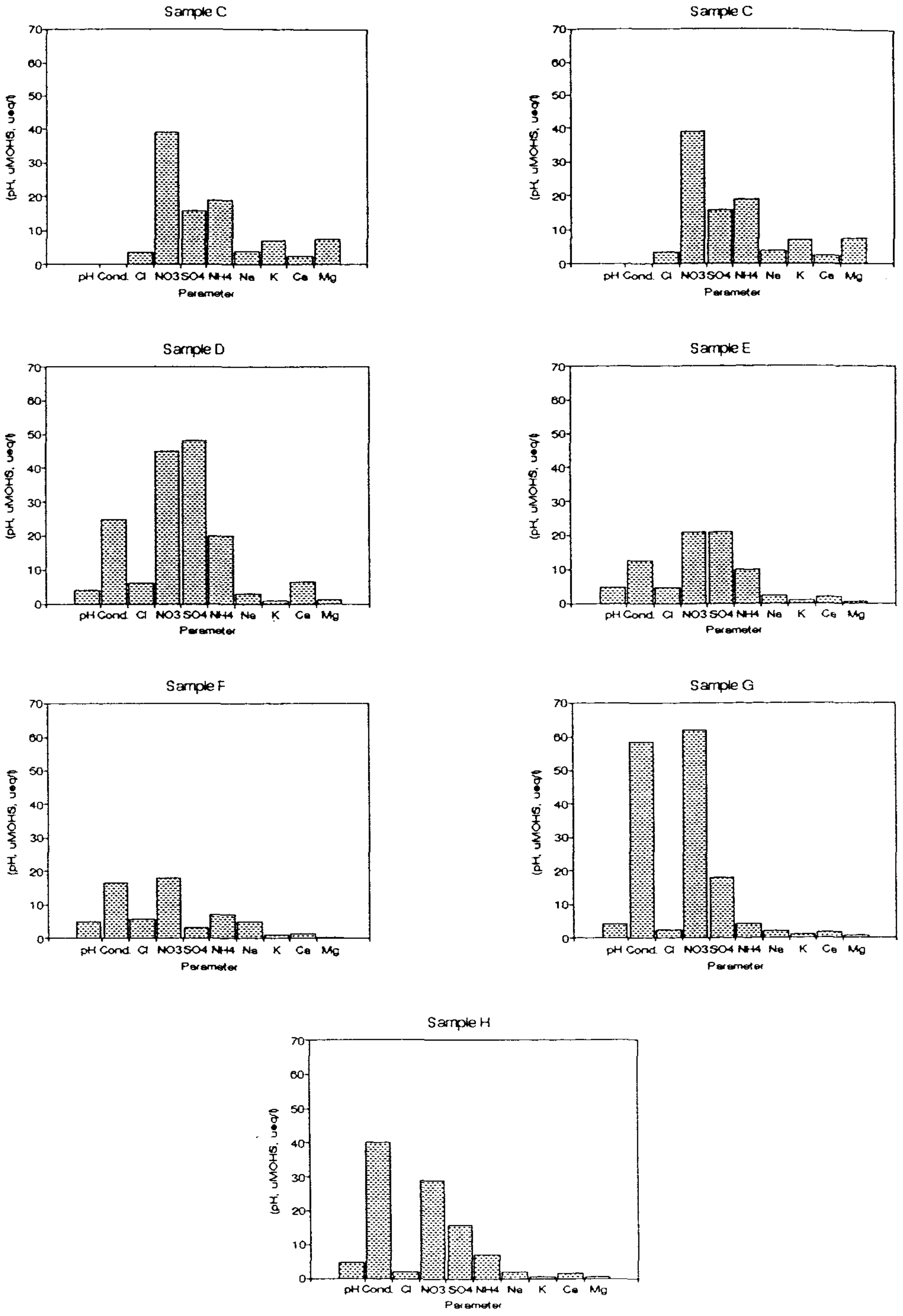


Figure 5.5 Inorganic data for QUEBEC samples.

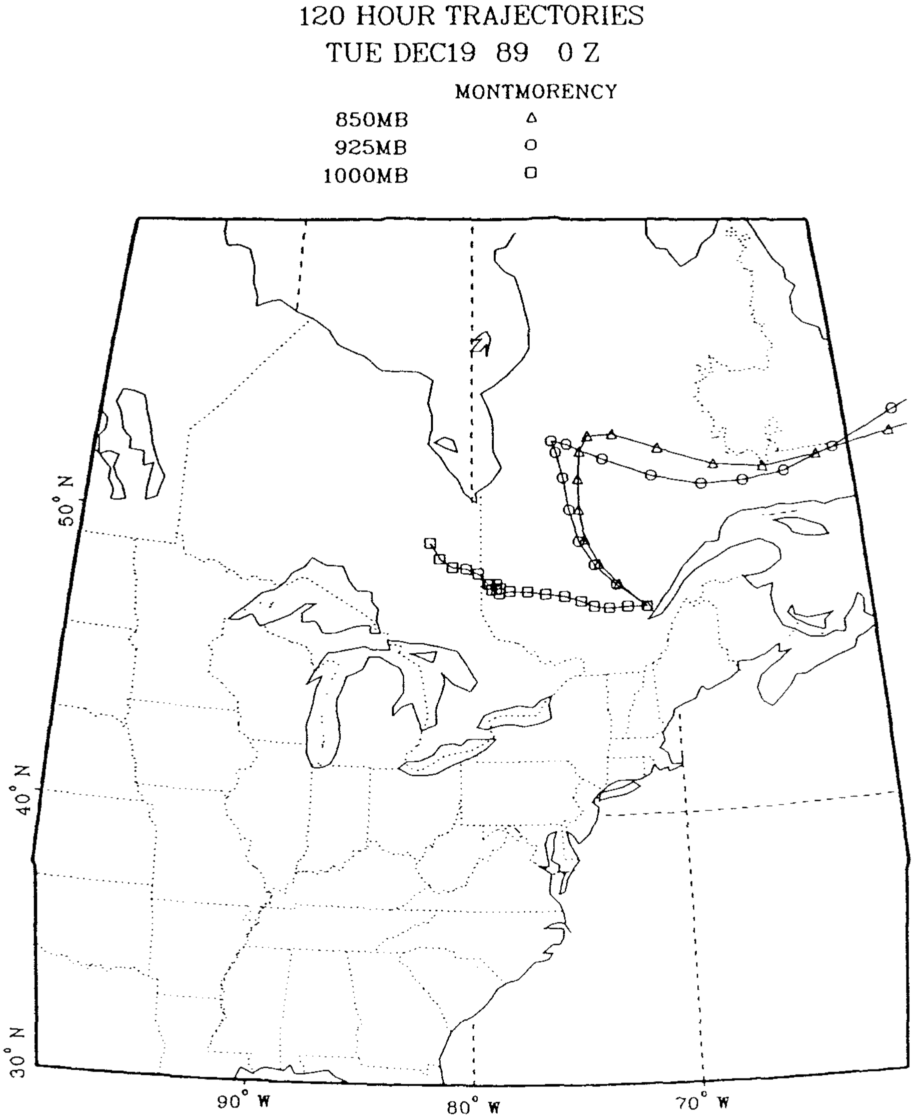


Figure 5.6a Air-mass back-trajectories for QUEBEC-B.

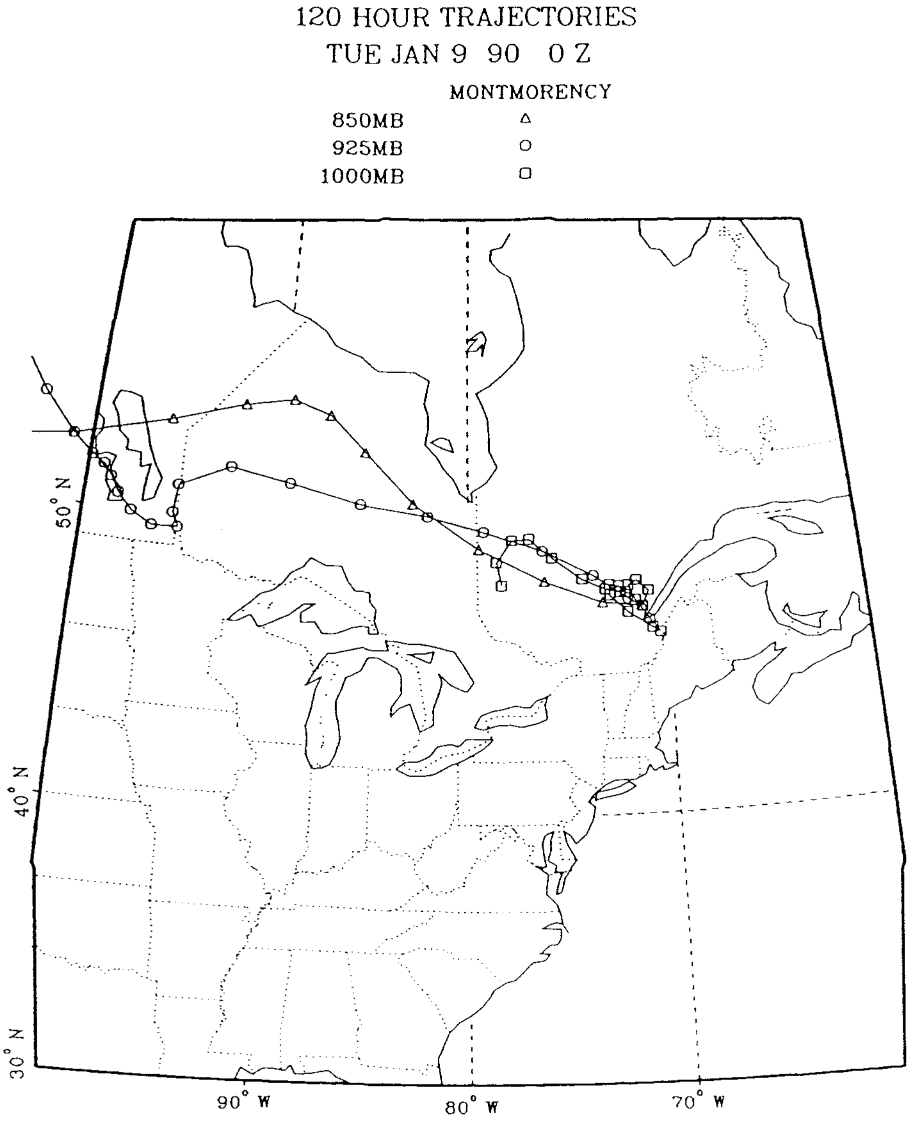


Figure 5.6b Air-mass back-trajectories for QUEBEC-C.

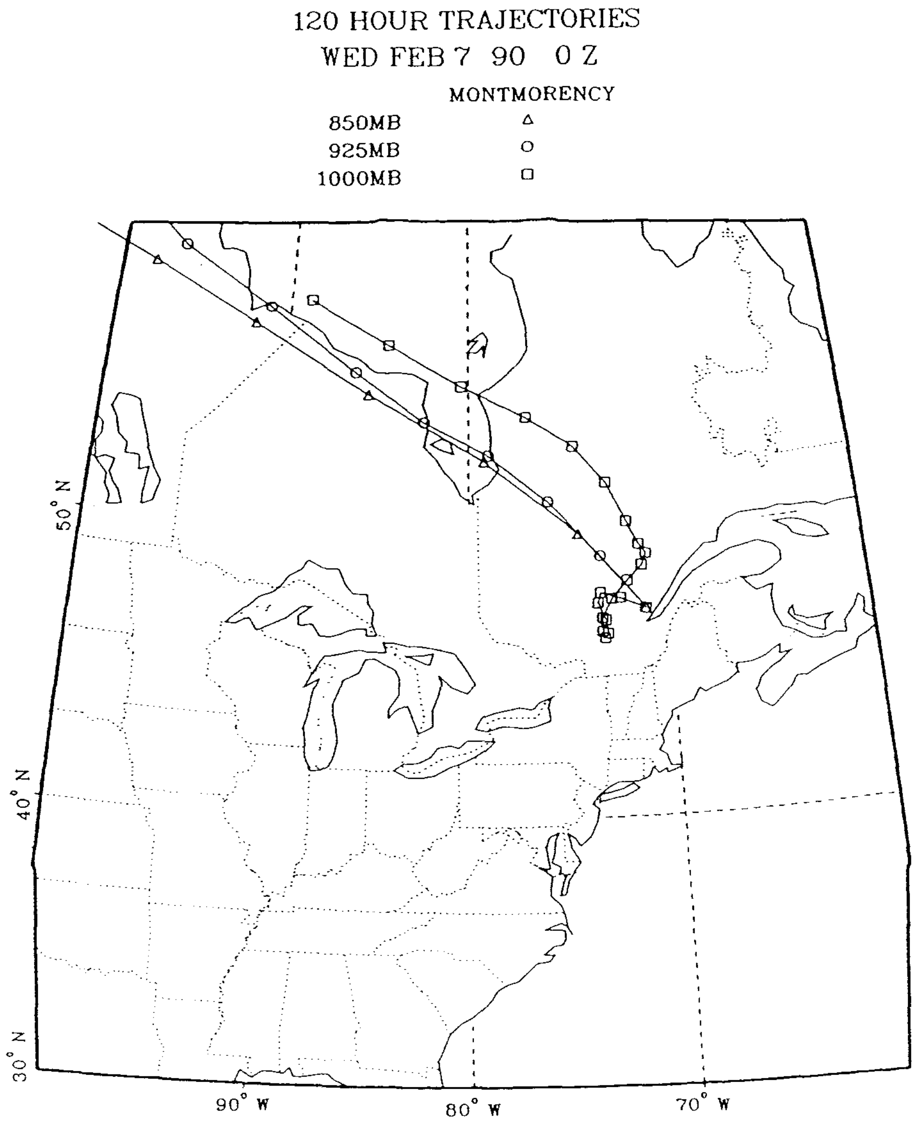


Figure 5.6c Air-mass back-trajectories for QUEBEC-D.

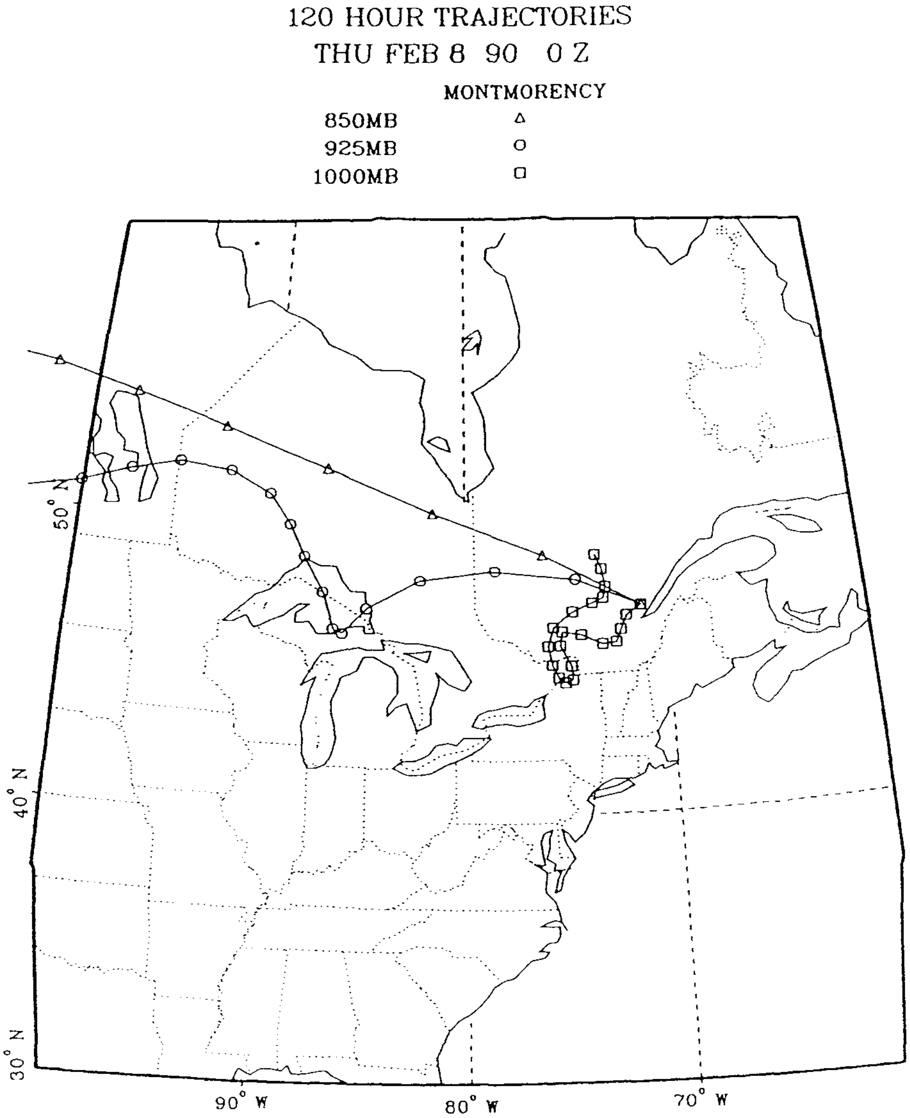


Figure 5.6d Air-mass back-trajectories for QUEBEC-E.

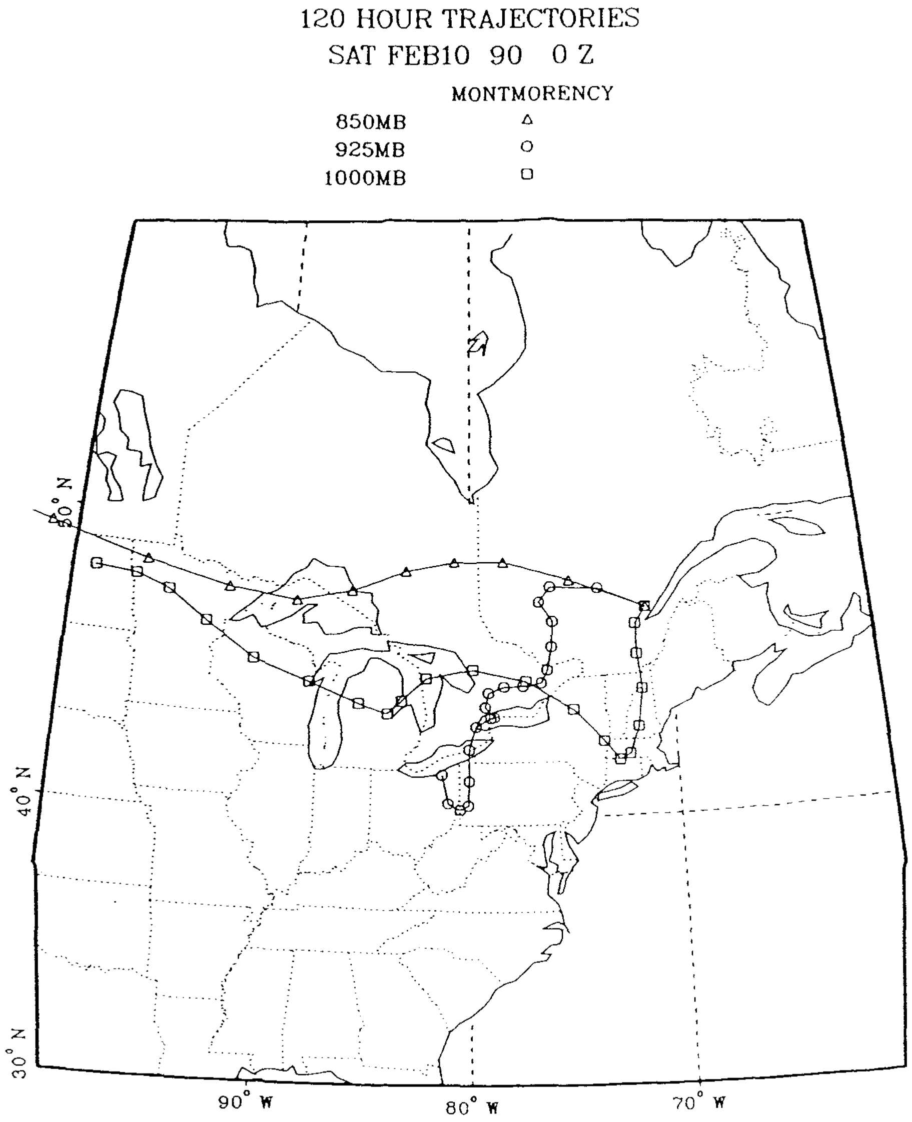


Figure 5.6e Air-mass back-trajectories for QUEBEC-F.

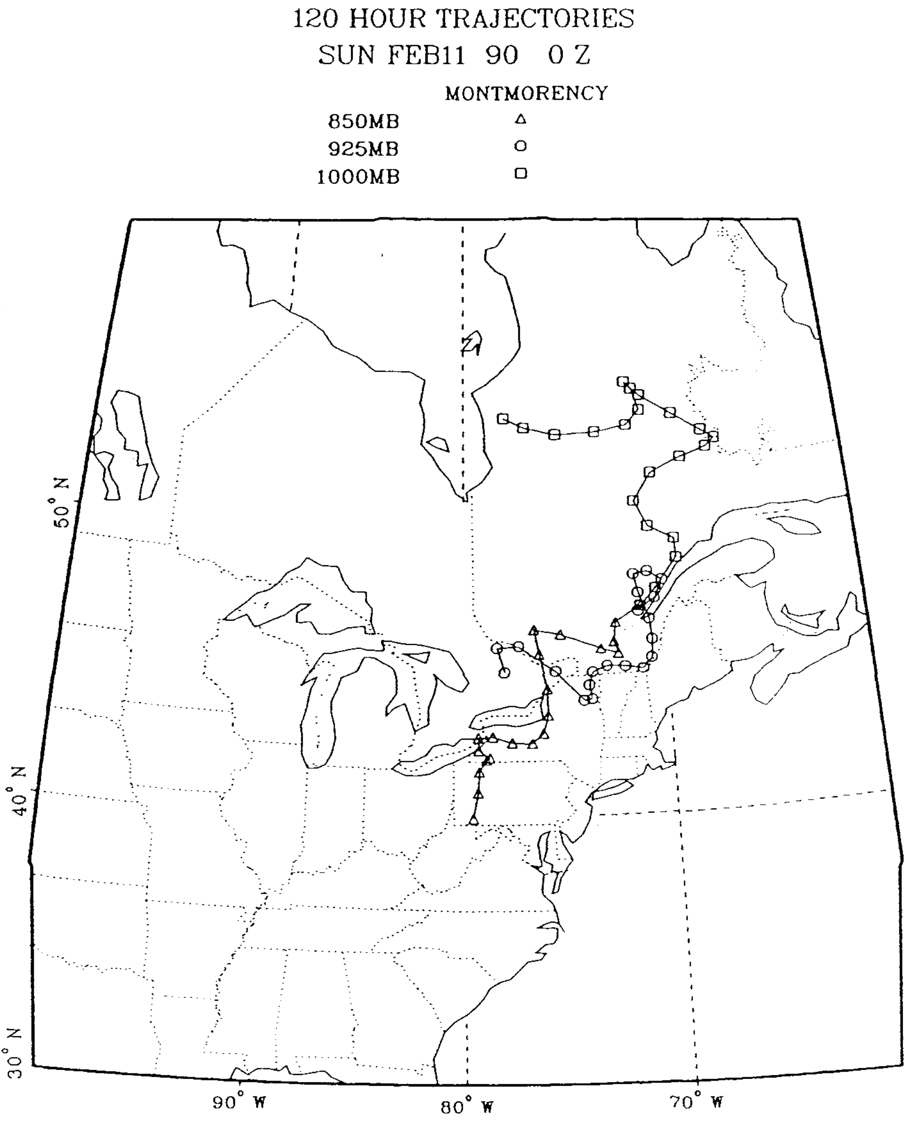


Figure 5.6f Air-mass back-trajectories for QUEBEC-G.

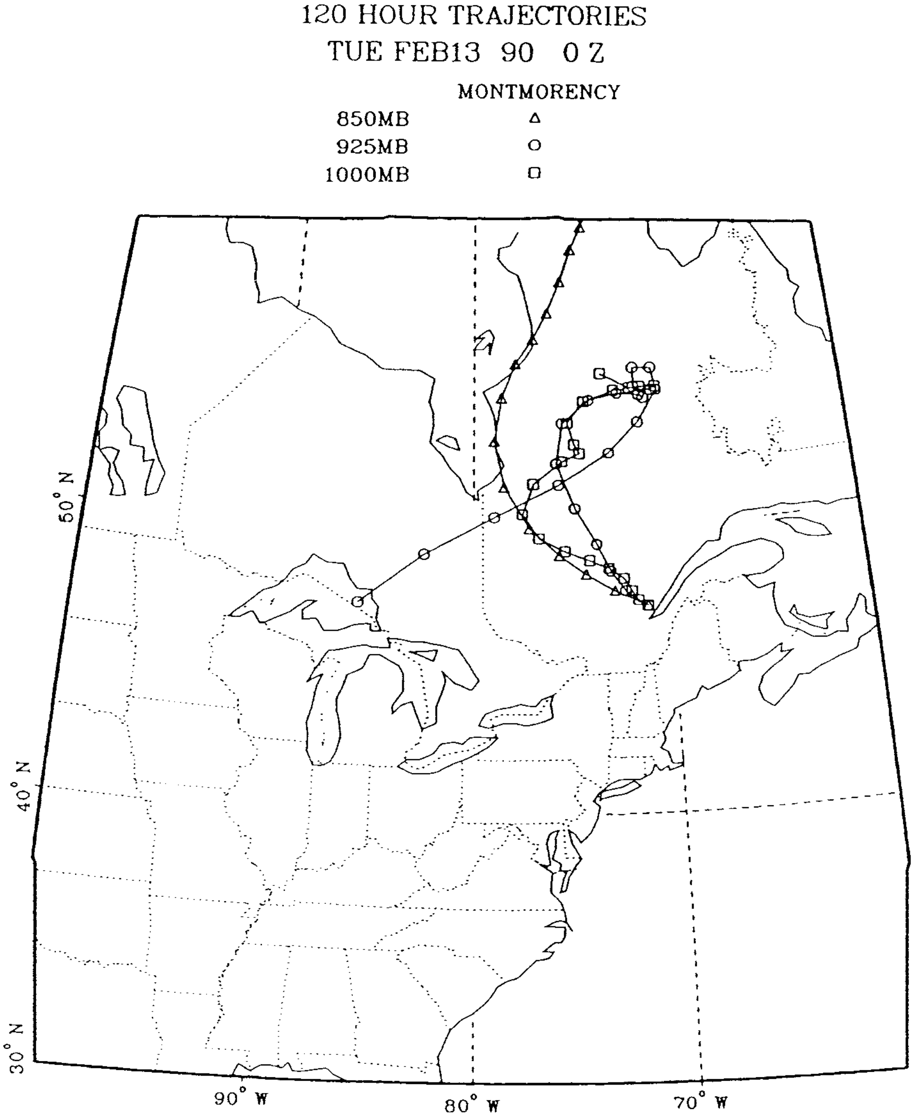


Figure 5.6g **Air-mass back-trajectories for QUEBEC-H.**

Table 5.7 PAH Concentrations for SOTON 1 Samples.

Compound	Concentration (ng/l)					
	1D	2D	3D	1P	2P	3P
Naphthalene	80	86	111	0	0	0
Acenaphthene	0	0	0	0	0	0
Fluorene	68	65	83	0	43	12
Phenanthrene	366	324	428	144	891	139
Anthracene	0	19	17	25	109	32
Fluoranthene	286	238	311	341	1747	317
Pyrene	176	160	187	254	1389	249
B(a)Anthracene	25	23	18	206	635	185
Chrysene	67	64	72	560	1039	461
B(b)Flnthn	0	26	0	518	1040	428
B(k)Flnthn	0	11	9	334	743	266
B(e)Pyrene	0	11	15	258	668	219
B(a)Pyrene	0	0	0	224	754	174
Perylene	0	0	0	39	181	36
I(123-cd)P	0	0	0	131	466	148
DB(ac+ah)Anth	0	0	0	0	130	39
B(ghi)P	0	0	0	364	950	323
Anthanth	0	0	0	0	13	0
	1067	1026	1250	3398	10799	3028

Table 5.8 Mean PAH Concentrations, Standard Deviations, Residual Standard Deviations and PAH Phase Distribution Data for SOTON 1 Samples.

	Compound	Mean D	s.d.	r.s.d.	Mean P	s.d.	r.s.d.	Mean T	% D	%P
1	Naphthalene	92	17	18%	0	0	---	92	100%	0%
2	Acenaphthene	0	0	---	0	0	---	0	0%	0%
3	Fluorene	72	10	13%	18	23	123%	90	80%	20%
4	Phenanthrene	370	52	14%	390	433	111%	760	49%	51%
5	Anthracene	12	10	87%	56	47	84%	68	18%	82%
6	Fluoranthene	280	37	13%	800	819	102%	1100	25%	73%
7	Pyrene	170	13	8%	630	656	104%	800	21%	79%
8	B(a)Anthracene	22	3	15%	340	254	75%	360	6%	94%
9	Chrysene	70	4	6%	690	309	45%	760	9%	91%
10	B(b)Flnthn	9	15	173%	660	330	50%	670	1%	99%
11	B(k)Flnthn	7	6	87%	450	258	57%	460	1%	98%
12	B(e)Pyrene	8	8	90%	380	249	65%	390	2%	97%
13	B(a)Pyrene	0	0	---	390	321	82%	390	0%	100%
14	Perylene	0	0	---	85	83	97%	85	0%	100%
15	I(123-cd)P	0	0	---	250	189	76%	250	0%	100%
16	DB(ac+ah)Anth	0	0	---	56	67	118%	56	0%	100%
17	B(ghi)P	0	0	---	550	351	64%	550	0%	100%
18	Anthanth	0	0	---	4	7	173%	4	0%	100%
	Totals:	1100			5700			6800		

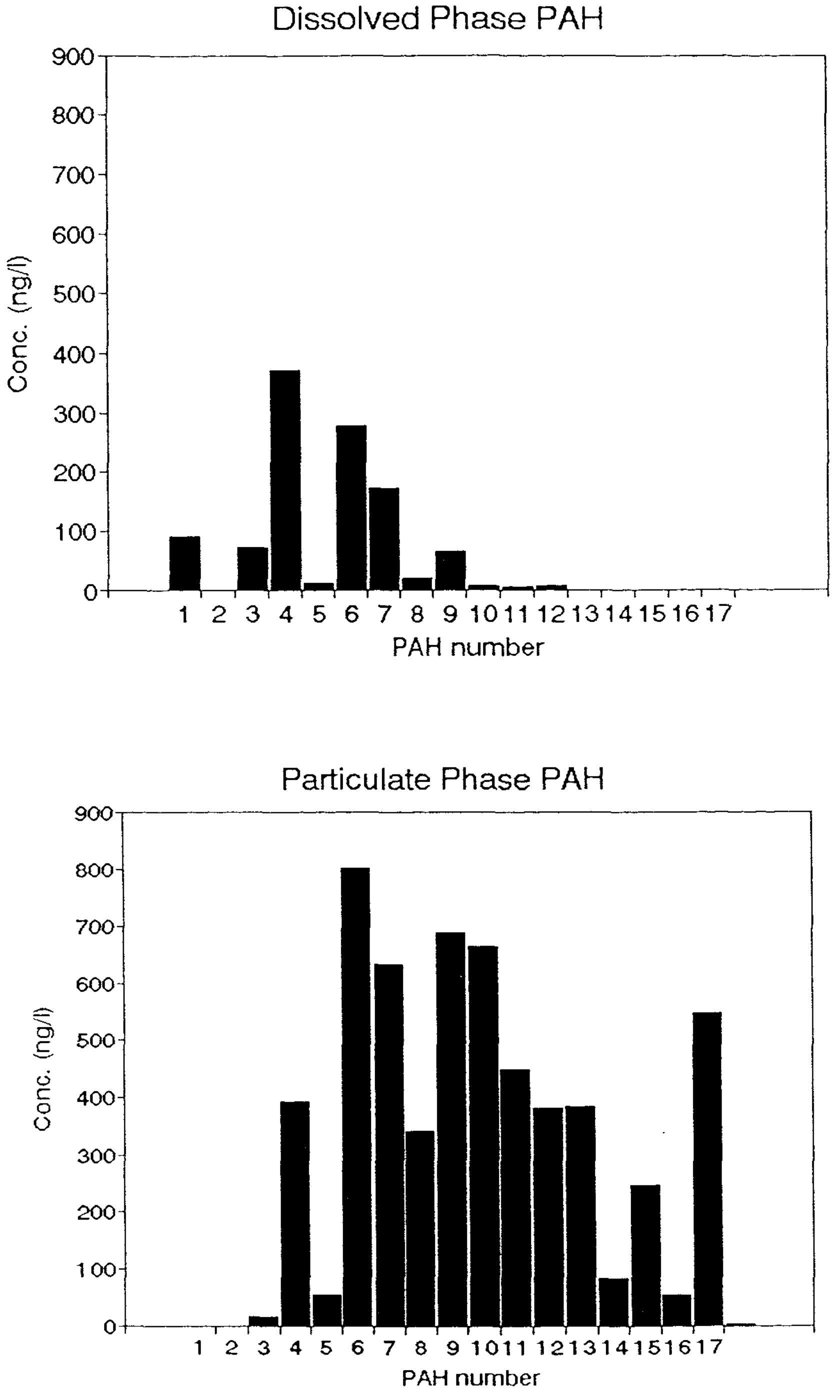


Figure 5.7 **PAH concentrations for SOTON 1 samples.**

Table 5.7 for identification of PAH numbers).

Table 5.8 shows the mean percentage distribution of each compound in the dissolved and particulate phases, and this information is illustrated in Figure 5.8. The mean distribution in the dissolved phase ranges from 100 % for naphthalene to 0 % for benzo[a]pyrene through to anthanthrene.

5.3.2 Supplementary Chemical Data

The pH and major cation concentrations for SOTON 1 are shown in Table 5.4 and illustrated in Figure 5.9. Data for the major anion concentrations are not available.

5.3.3 Meteorological Data

No meteorological data for these samples are available.

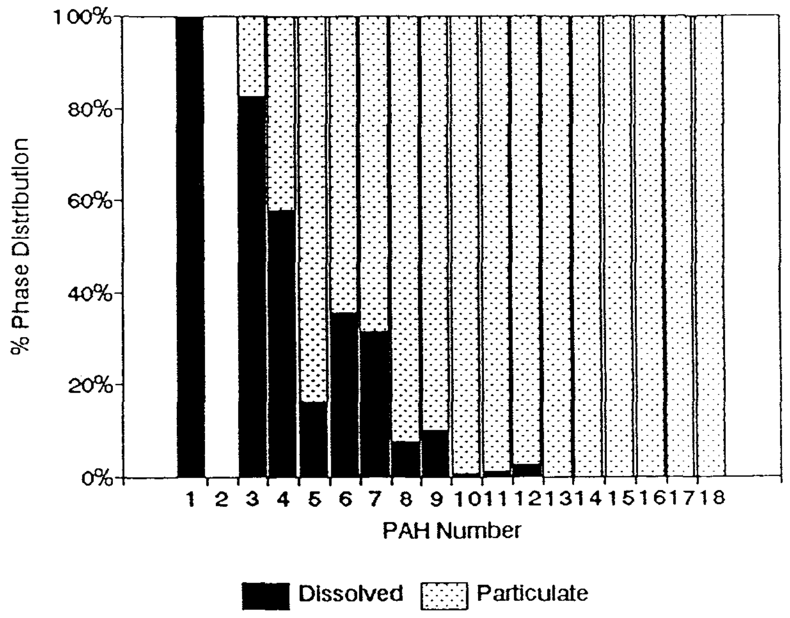


Figure 5.8 **PAH phase distribution for SOTON 1 samples.**
(see Table 5.8 for PAH number identification)

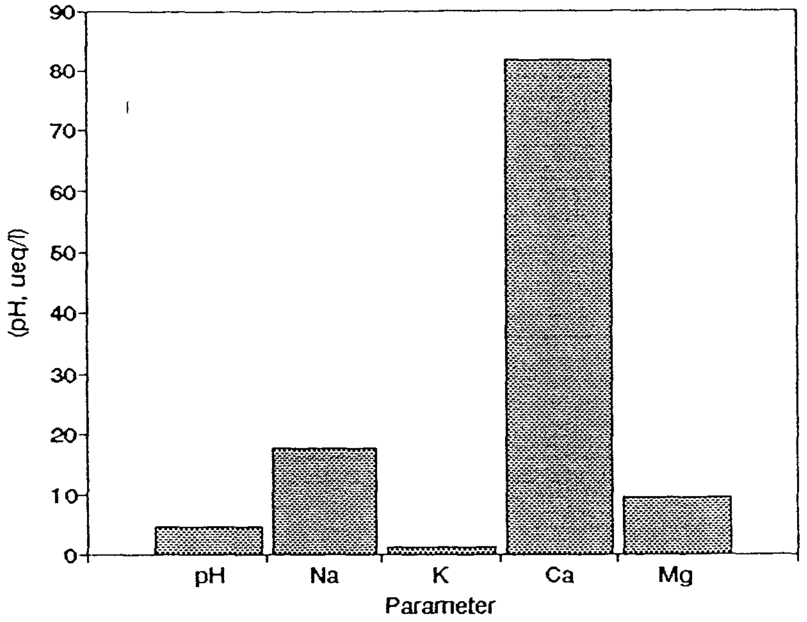


Figure 5.9 Inorganic data for SOTON 1 samples.

CHAPTER 6: DISCUSSION

6.1 Introduction.

Interpretation of the data set is constrained by its limited extent. This is a consequence of the factors mentioned at the beginning of the preceding chapter, namely the difficulties encountered with the analytical facilities, and limited time. However, a number of useful observations can still be made.

Of the 19 PAHs analysed, the concentrations in snow of 4 of them have not previously been reported (see Table 1.6 and references therein). In addition, benzo[b]fluoranthene and benzo[k]fluoranthene have not previously been reported as separate compounds. Perylene has previously been reported present in snow, but was not quantified (Lunde *et al.*, 1977). Also, there are no existing data available for the concentrations of any PAHs in snow from the U.K.

The PAH data available can be divided into three major groups:

i) aged snow samples from snowpacks in Scotland,
ii) fresh snow samples from Scotland and Southampton,
iii) the dissolved phase PAH only from fresh snow in Canada.

At this stage is essential to note that few other studies have investigated the separate dissolved and particulate phases of the PAH content of snow, and of those that have, only one provides detailed information on the separate dissolved and particulate concentrations (Leuenberger *et al.*, 1988). All other studies have reported total-PAH content. Therefore, where comparisons with other data are made, these shall concern total-PAH (dissolved + particulate phase) concentrations, unless otherwise specified. To avoid confusion, the sum of the dissolved and particulate phase concentrations shall be referred to as the 'total-PAH', and the sum of all the total-PAH concentrations for each compound shall be represented by 'ΣPAH':

ie. ΣPAH = [naphthalene] + [acenaphthene] + ... + ... + [anthanthrene].

Many studies do not report individual PAH concentrations. It is therefore difficult or impossible to compare ΣPAH values where a different and non-inclusive suite of PAHs has been investigated. For example, Kawamura and Kaplan (1988) report ΣPAH concentrations for 7 PAHs, 3 of which are alkyl-PAHs, and are therefore not considered in the current work. As the contribution of the remaining 4 PAHs (which are included in the present study) to the total is not given, it is somewhat arbitrary to compare the ΣPAH concentrations to the ΣPAH in this study. Where inter-study comparisons are made, they shall refer to studies that include similar PAH distributions, or shall be limited to comparisons of individual compounds.

An important feature of the whole data set that needs to be highlighted is the wide range of relative standard deviations for the concentrations of PAHs. These range from 2 to 173 % for the Scottish snows (see Table 5.2). These are most likely a result of the chemically heteogeneous nature of snow, and are not attributable to an analytical artefact. Tranter *et al.* (1987) report coefficients of variation for the major ions in fresh snowcover and aged snow samples of up to 144 and 200 %, respectively, dependent on the assumed distribution type (ie. normal or log-normal distribution).

6.2 Snowpack Samples, Scotland.

6.2.1 Absolute PAH Concentrations.

All of the samples in this group are from evidently discoloured layers of the snowpack in Ciste Mhearad. This area is often subject to episodes of highly discoloured, 'black' snowfall (Davies *et al.*, 1984, 1988, 1992; Landsberger *et al.*, 1989).

The ΣPAH concentrations in the snowpack samples are relatively high (1600, 1800 and 3500 ng l^{-1}). These levels are similar to the values measured in snow from urban areas in Frankfurt, Germany (Georgii and Schmitt, 1983) and near Zürich, Switzerland (Leuenberger *et al.*, 1988). Mean values reported from these two sites are 2500 ng l^{-1} and 1720 ng l^{-1}, respectively.

The mean concentrations of total benzo[a]pyrene in the snowpack samples (49, 56 and 74 ng l^{-1}) are all higher than those reported in the literature for snow samples (see Table 1.8).

These relatively high values may at first seem surprising for a remote, sub-arctic mountain catchment such as Ciste Mhearad. However, this site is best classified as 'rural' in terms of much of its precipitation chemistry, owing to the episodic anthropogenic pollution events that affect it (Davies *et al.*, 1984; Landsberger *et al.*, 1989). Other snowfall from this site has previously been demonstrated to have a high acidity, and can also contain high, anthropogenic concentrations of trace metals, such as Pb, Cu, Zn and Cd, that are similar to typical urban concentrations (Tranter *et al.*, 1986; Abrahams *et al.*, 1988; Davies *et al.*, 1992). Such incidences of pollutant deposition can be attributed to the long-range transport of the pollutants in air-masses from source regions, such as Eastern Europe (Davies *et al.*, 1992; Jickells *et al.*, 1992).

6.2.2 Relative Abundance Distribution.

The relative concentration distribution of individual PAHs in the snowpack is remarkably constant for both the dissolved and the particulate phase (see Figure 5.1). When the mean individual total-PAH concentrations are ranked by abundance, the order of the first five (most abundant first) is: fluoranthene, phenanthrene, pyrene, chrysene and benzo[b]fluoranthene. This is exactly the same order as shown by the data of Leuenberger *et al.* (1988) for snow from an urban site, and very similar to the data of McVeety and Hites (1988) for snow from a remote site which has the order: phenanthrene, fluoranthene, pyrene, chrysene/triphenylene, benzo[e]pyrene. Benzo[b]fluoranthene was not analysed in the latter study. Further consideration of the relative distribution patterns is given in Sections 6.2.4 and 6.4.1, below.

6.2.3 Dissolved/Particulate Phase Distribution.

The dissolved/particulate phase partitioning of PAHs in the snowpack samples is as expected: *ie*. the lower molecular weight compounds are predominantly present in the dissolved phase, and the higher molecular weight compounds in the particulate phase (Georgii and Schmitt, 1983; Leuenberger *et al.*, 1988). This is given further consideration in Section 6.4, below.

6.2.4 Possible Source Indications.

The pattern of PAH distribution described in Section 6.2.2 is consistant with those PAH distributions found in world-wide ocean sediments (Hites *et al.*, 1980a), and is indicative of an anthropogenic combustion source (Laflamme and Hites, 1978; Heit *et al.*, 1981, 1988; Tan and Heit, 1981). In particular, fluoranthene, pyrene and chrysene are associated with combustion sources (Hites *et al.*, 1980; Heit *et al.*, 1988). For remote marine and lacustrine sediments, the primary PAH input is *via* atmospheric deposition of small particles (< 1 μm) that have undergone long-range transport (Hites *et al.*, 1980a; Gschwend and Hites, 1981).

The ratio of fluoranthene-to-pyrene can be used as a crude indicator of combustion source, with values of 0.6, 1.0 and 1.4 being indicative of automobile, wood smoke and coal combustion emissions, respectively (Hangebrauck *et al.*, 1967; Giger and Schaffner, 1978; Lee *et al.*, 1977). The ratios present in the snowpack samples are: 1.6, 1.9 and 1.9. However, as noted in Section 1.5.1, any conclusions made about these values must be treated with caution, since the effects of mixing of PAHs from different sources and the differential rates of chemical degradation of PAHs may also affect the ratios.

Without additional information on alkyl-PAH homologues, other classes of hydrocarbons, trace metals and meteorological conditions at the time of precipitation, it is difficult to make specific conclusions as to the source of the PAHs in the snowpack (see: Hites *et al.*, 1980a, 1980b; Heit *et al.*, 1981; Tan and Heit, 1981; Kawamura and Kaplan, 1986).

6.3 Fresh Snow Samples, Scotland and Southampton.

6.3.1 Absolute PAH Concentrations.

The ΣPAHs concentrations in the fesh snowfall samples from Scotland are significantly lower than those in the snowpack samples. However, it should be remembered that the snowpack samples represent visibly discoloured layers, and none of the fresh snow samples from Scotland were observed to be discoloured.

The ΣPAH concentrations are 100 and 290 ng l^{-1}. These are an order of magnitude less than the ΣPAH values for the snowpack samples. The concentrations are of a similar order of magnitude to a study of snowfall from a remote site in Northern USA (McVeety and Hites, 1988).

The concentrations of benzo[a]pyrene in the Scottish samples (13.0 and 0 ng l^{-1}) are lower than those reported for urban areas (Schrimpff *et al.*, 1979; Thomas, 1986b; Leuenberger *et al.*, 1988; Czuczwa *et al.*, 1988). McVeety and Hites report a benzo[a]pyrene concentration of 3 ng l^{-1} in snow from a remote site in Northern USA.

Perylene, dibenz[ac+ah]anthracene and anthanthrene were not detected in either the dissolved or particulate phase in Scotland.

The samples of fresh snow from Southampton have very high PAH concentrations. The ΣPAH concentration is 6800 ng l^{-1}, which is comparable to a maximum total of 6000 ng l^{-1} reported for 9 PAHs (8 in common with this study) in snow from a densely urbanised area in Frankfurt, Germany (Georgii and Schmitt, 1983).

The mean benzo[a]pyrene concentration in snow from Southampton is 390 ng l^{-1}, which is accounted for solely by the particulate phase. This is an order of magnitude higher than concentrations in snow from urban areas reported in the literature (see Table 1.8) and is comparable to a maximum concentration found in rain water in the Netherlands (see Table 1.5).

Acenaphthene was not detected in either phase in any of the samples from Southampton.

6.3.2 Relative Abundance Distribution.

The order of relative abundance of PAHs in the fresh snow samples from Scotland shows the same five compounds as for the snowpack samples, although the order is different, being: benzo[b]fluoranthene, chrysene, phenanthrene, fluoranthene and pyrene (see Section 6.2.2).

For the Southampton samples, the most abundant compounds are: fluoranthene, pyrene, chrysene and phenanthrene, benzo[b]fluoranthene and benzo[ghi]perylene.

6.3.3 Dissolved/Particulate Phase Distribution.

Both sets of samples exhibit the expected phase distribution pattern (see Section 6.2.3, above, and Section 6.4, below), but the samples from Scotland exhibit elevated dissolved phase percentages compared with the Southampton sample and the snowpack samples from Scotland (see Figures 5.2a,b and 5.8). This is further discussed in Section 6.4, below.

6.3.4 Possible Source Indications.

The relative distribution pattern of PAHs in all of the fresh snow samples is also suggestive of a combustion source for the PAH content of the snow (see Section 6.2.4, above).

The mean fluoranthene-to-pyrene ratios for the two Scottish sample groups are 1.3 and 2.0. The former value may therefore be indicative of coal combustion. However, the same limitations as mentioned above apply to the interpretation of these values.

The mean fluoranthene-to-pyrene ratio for the Southampton samples is 1.4, which may be indicative of a coal combustion source, subject to the limitations discussed above.

6.4 Comparison of Snowpack and Fresh Snow PAH Content.

6.4.1 Absolute PAH Distributions.

For the SCOT1 samples, the dissolved phase ΣPAH concentrations are lower than the particulate phase ΣPAH for the snowpack samples, but are higher in the fresh snow. If this is also the case at the time of deposition of the 'black' snow, then it implies that there is a relative loss of dissolved phase PAHs between the time of deposition and subsequent metamorphism of the snow within the pack.

A number of processes could account for the loss of dissolved PAHs. The dissolved phase PAHs in the fresh snow are predominantly the lower molecular weight compounds. These have higher P_o values (see Section 1.5.4 and Table 1.3), are therefore more volatile and hence are more susceptible to loss from the snowpack by revolatilisation to the atmosphere. This process has previously been suggested for the apparent loss of trace-organochlorines from annual snow-ice layers in the Canadian Arctic (Gregor, 1991), but as yet, no empirical investigations into the occurence of this effect have been undertaken.

Another potential cause of this apparent enrichment of particulate phase PAHs is the loss of dissolved phase PAHs by elution from the snowpack by melt- and/or rainwater. This would preferentially remove the dissolved phase PAH, and the particle-bound PAHs would undergo relative concentration in the remaining snowpack, as demonstrated by Schöndorf and Herrmann (1987) and Simmleit *et al.* (1986).

Dry deposition will also cause a relative enrichment of the higher molecular weight compounds, as these compounds have a higher aerosol concentration relative to the lower molecular weight compounds (Yamasaki *et al.*, 1982; Baker and Eisenreich, 1990). The process of dry deposition of trace-organics to snow surfaces has not been researched in any great detail. The results of this study suggest that dry deposition may be an important factor in the addition of PAHs to snow surfaces and their relative distributions in aged snow and snowpacks.

6.4.2 Relative PAH Abundances.

The abundance distributions of the individual PAH concentration values were analysed using Spearman's rank correlation coefficient (r'). This provides a measure of the similarity of rank order between two sets of data. Values of r' are normalised to fall between +1.0 and -1.0, where +1.0 indicates a perfect correspondence between the ranks, -1.0 indicates a perfect inverse relationship, and zero indicates that the two sets of ranks are independent.

This type of analysis was applied to test the similarity of abundance distributions of PAHs between each sample set in the dissolved phase (D), in the particulate phase (P) and in the total (D+P) PAH content. From such an analysis, an r' value of +1.0 would indicate that for two sets of data, the individual PAHs exhibit the same order of rank of abundance. Table 6.1 shows the r' values obtained. 1, 2 and 3 refer to the three snowpack data sets and 4 and 5 refer to the fesh snow data sets. All values given are significant at the 1 % level, except for P5 v P4, which is not significant at the 10 % level.

As mentioned in Section 6.2.2, it can be seen that the PAH distributions in the snowpack samples are similar. The dissolved PAH ranks for the snowpack data (D1, D2 and D3) produce coefficients of 0.88, 0.83 and 0.95, and the particulate

Table 6.1 **Spearman's Rank Correlation Coefficients (r') for SCOT1 Samples.**

	D2	D3	D4	D5
D1	0.88	0.83	0.84	0.62
D2		0.95	0.88	0.72
D3			0.90	0.78
D4				0.75

	P2	P3	P4	P5
P1	0.93	0.97	0.68	0.70
P2		0.95	0.75	0.61
P3			0.67	0.71
P4				0.32

	T2	T3	T4	T5
T1	0.96	0.95	0.54	0.91
T2		0.99	0.54	0.89
T3			0.53	0.87
T4				0.63

Key:

D = dissolved phase PAH
P = particulate phase PAH
T = total PAH
1 = 25/2/O
2 = 27/2/O
3 = 28/2/O
4 = 27/2/F
5 = 28/2/F

PAH data (P1, P2 and P3) yields coefficients of 0.93, 0.97 and 0.95. The corresponding r' values from the ΣPAH data set (T1, T2 and T3) are 0.96, 0.95 and 0.99. These results show that there is a similar order of PAH abundances in each phase and the ΣPAH concentrations.

The two data (*ie*. D5 v D4, P5 v P4 and T5 v T4) for the fresh snow samples show less similarity in their PAH abundance order. The calculated r' values for similarity of rank for the dissolved, particulate and ΣPAH abundances between the two samples are 0.75, 0.32 and 0.63, respectively.

The second fresh snow sample (*ie*. 5) shows a relatively high degree of similarity of ΣPAH abundance order to the snowpack samples (*eg*. compare T5 and T1, r' = 0.91). However, the abundance order between the dissolved and the particulate phases of the fresh snow and snowpack samples shows less similarity (*eg*. compare P5 and P1, r' = 0.70, and D5 and D1, r' = 0.62).

Further examination of r' values for the data set shows that for the aged snow, the particulate fraction is predominantly responsible for the ΣPAH abundance pattern, whereas for fresh snow, the dissolved phase has a greater influence.

6.4.3 PAH Phase Distributions.

The overall phase distribution of PAHs in all of the snow samples is as expected, with the dissolved phase being dominated by lower molecular weght compounds and the particulate phase by higher molecular weight compounds (Georgii and Schmitt, 1983). However, comparison with the data relating to fresh snow reported by Leuenberger *et al.* (1988) shows that the distribution of the dissolved phase in the Scottish snowpack samples is significantly lower to their findings, whereas the fresh snow samples from Scotland show a similar phase distribution pattern. This effect could be accounted for by the relative enrichment of particles in the snowpack suggested in Section 6.4.1, above, in relation to the differences in ΣPAH values for the snowpack and fresh snow. The fresh snow sample from

Southampton shows a similar phase distribution pattern to the snowpack samples, but should be considered as a sample with totally separate characteristics, as discussed below.

The phase distribution data of the SCOT1 samples was subjected to Spearman's rank correlation coefficient analysis. The average percent phase distributions for both the dissolved and particulate phases in each snow type (*ie.* fresh or snowpack), expressed as a percentage of the total, were used for the analysis, and the results are shown in Table 6.2. The results indicate that the rank order of %-distribution values is the same for the dissolved and the particulate phases in both snow types, and that for the same snow type, the dissolved and particulate phase ratios are the inverse of each other: *ie.* the same compounds predominate in each case of snow type and phase.

6.4.4 PAH Content and Snow Acidity.

When the snowpack samples and the fresh snow samples from Scotland are examined together, it can be seen that higher ΣPAH values tend to coincide with the lower pH values (see Tables 5.2, 5.4 and 5.7). When these two variables are plotted against each other, it appears that there is an association between the two, which regression analysis suggests may be linear ($R^2 = 90\%$) (see Figure 6.1). This is consistant with the findings of Davies *et al.* (1988), who show that a linear relationship between snow acidity and particulate organic carbon content (see Section 1.7 and Figure 1.5).

However, it is clearly evident that the sample of fresh snow from Southampton does not fit this proposed association, as this has pH andΣPAH values of 4.5 and 6800 ng l^{-1}, respectively. This suggests that this snow has distinctly different chemical and source characteristics.

The possible association of PAHs with acidic deposition is evidently an area that requires further investigation. Bjørseth *et al.* (1979) found that high

Table 6.2 **Spearman's Rank Correlation Coefficients for SCOT1 Phase Distribution Data.**

	FD	FP	AD
FP	-1.00		
AD	0.97	-0.97	
AP	-0.97	0.97	-1.0

Key:

F = fresh snow
A = aged snow
D = dissolved phase
P = particulate phase

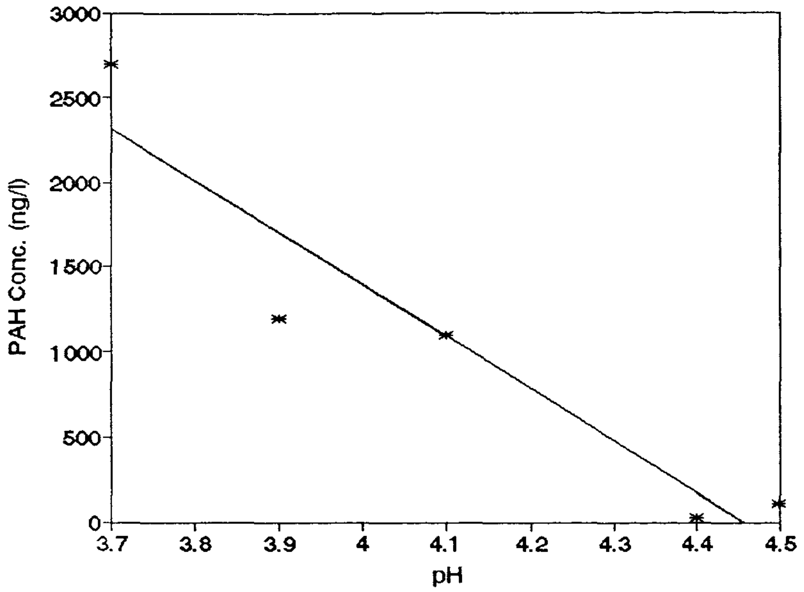


Figure 6.1 **Snow pH v PAH concentration for SCOT 1 snowpack and fresh snow samples.**

concentrations of PAH in winter air in Scandinavia coincided with high concentrations of SO_4^{2-}, an important contributor to precipitation acidity, and Gschwend and Hites (1981) suggest that the PAH flux into the northeastern USA reflects the strength of the same combustion sources as those responsible for acid rain. However, Heit *et al.* (1988) found that although the PAH flux to lake sediments showed a positive correlation with SO_2 and NO_x in some instances, this was not true for all sources. They conclude that the hypothesis proposed by Gschwend and Hites (1981) is not necessarily true, owing to differences in regional emissions.

6.4.5 Benzo[a]pyrene and ΣPAH Content.

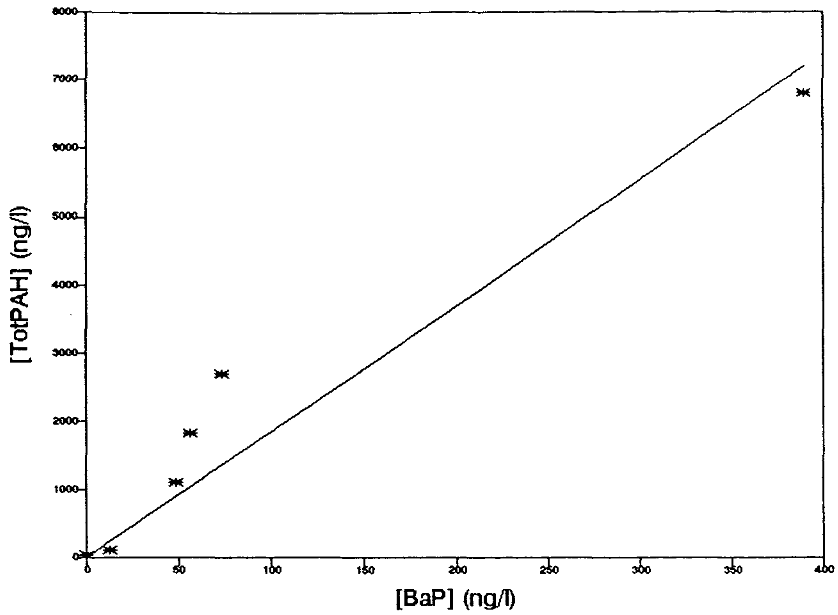
It is often stated that the benzo[a]pyrene (BaP) content of a sample can be used as an indication of total PAH content (eg: Herrmann, 1978; Siebert *et al.*, 1978; Lamparczyk *et al.*, 1988). Regression analysis of the SCOT1 and SOTON data shows that a possible association exists between the BaP and ΣPAH concentrations, which has an R^2 value of 94 %, significant at the 1 % level (see Figure 6.2).

6.5 Fresh Snow Samples, Québec.

Only values for the dissolved phase PAHs are available for the samples from Québec, and so discussion of the significance of PAH distribution patterns or concentration levels are not possible, as the overall PAH content is not known.

6.5.1 Absolute PAH Concentrations.

The dissolved ΣPAH are relatively low; the concentrations range from 1.0 to 240 ng l^{-1}. This compares with a dissolved ΣPAH concentration of 600 ng l^{-1} calculated for 12 common PAHs in snow from an urban site (Leuenberger *et al.* 1988). Benz[a]anthracene, benzo[a]pyrene, dibenz[ah]anthracene, benzo[ghi]perylene and indeno[1,2,3-cd]pyrene were not detected in any of the



$$\Sigma PAH = 17(\pm 2)[BaP] + 470(\pm 340)$$

$$R^2 = 94\%$$

Figure 6.2 **Regression analysis of ΣPAH on benzo[a]pyrene.**

samples (see Table 4.8 for detection limits).

6.5.2 Relative Distribution.

Fluorene is overall the most abundant PAH (max. concentration = 130 ng l^{-1}). This may contribute a major part to the ΣPAH content, as fluorene can be expected to be present predominantly in the dissolved phase. Leuenberger *et al.* (1988) measured a dissolved phase concentration of 16 ng l^{-1} and a particulate phase concentration of 1.6 ng l^{-1} for this compound in snow (ie. D = 91 %).

6.5.3 Air-mass Back-trajectory Analysis.

The back-trajectories of the air-masses passing over the sample site immediately prior to the time of snow deposition are shown in Figures 5.6a to 5.6g, and discussed in relation to the dissolved ΣPAH concentrations below. It is necessary to state that back-trajectory analyses are often subject to large error margins (Sykes and Hatton, 1976) that increase with increasing distance from the point of origin (Davies *et al.*, 1992). Also, there are no data available for the amount of deposition for each event. This is an important consideration as the concentration of pollutants in precipitation is inversely proportional to the amount of precipitation (Georgii and Weber, 1960; Georgii and Schmitt, 1983). Air-mass back-trajectories should therefore only be used as an approximate indicator of the region of air mass origin.

Whilst taking these limitations into account, it can be expected that the samples with the higher dissolved ΣPAH values will be associated with air-masses passing over industrialised and urbanised regions, which implies the areas to the West and South, and the Great Lakes region of North America in particular. The trajectories considered for the indication of pollutant transport are the 850 and 925 mbar trajectories (Pacyna and Oehme, 1988 and Colin *et al.*, 1989, respectively).

The dissolved ΣPAH (DΣPAH) concentrations and the air-mass origin region indications of the two trajectories are summarised below, subject to the limitations discussed above:

Sample B

DΣPAH = 5.0 ng l^{-1}

850 mbar: North Atlantic

925 mbar: North Atlantic

Summary: Good agreement: would expect a low PAH concentration from an air-mass from the indicated region, owing to the scarcity of PAH emission sources.

Sample C

DΣPAH = 74.0 ng l^{-1}

850 mbar: West

925 mbar: Westerly, from North West

Summary: Possible PAH source in urbanised West Canada.

Sample D

DΣPAH = 140.0 ng l^{-1}

850 mbar: North West/Arctic

925 mbar: North West/Arctic

Summary: Unexpectedly high PAH value.

Sample E

DΣPAH = 16.0 ng l^{-1}

850 mbar: West/North West

925 mbar: West/Great Lakes

Summary: Unexpectedly low PAH value, particularly considering the 925 mbar trajectory which is indicated as passing close to the industrialised regions surronding Lakes Superior and Michigan, and the site of smelting works at Sudbury, E.Ontario.

Sample F

DΣPAH = 1.0 ng l^{-1}

850 mbar: West/ Great Lakes region

925 mbar: South West/Northern USA

Summary: Unexpectedly very low PAH value. The trajectory data suggests that the air mass has passed over highly urbanised and industrialised regions, therefore predicting a high PAH value.

Sample G

DΣPAH = 190.0 ng l^{-1}

850 mbar: South West/ Northern USA

925 mbar: Southerly, from West

Summary: Good agreement between PAH concentration and indicated source region.

Sample H

DΣPAH = 240.0 ng l^{-1}

850 mbar: North/Arctic

925 mbar: complicated trajectory, possible Westerly origin

Summary: the high PAH concentration could be a result of an air-mass source indicated to be in the Southern Ontario/Lake Superior region.

It can be seen that the air-mass trajectory interpretation is somewhat ambiguous. However, only half of the data pertaining to the PAH concentrations are available, and a better interpretation may be possible when the particulate phase PAH data are also included. A knowledge of the amount of precipitation is also required to allow better interpretation.

CHAPTER 7: CONCLUSION AND RECOMMENDATIONS FOR FURTHER RESEARCH

7.1 Conclusion.

A sampling methodology and sample extraction protocol was developed for the investigation of dissolved and particulate phase PAHs in snow. The sampling methodology took into account the need to work in inhospitable environments, often under adverse weather conditions. An extraction method was developed that could be performed under non-ideal field-laboratory conditions. Reproducible and contamination-free sample preparation was achieved.

Two analytical techniques for trace-level organic analysis were used for the determination of PAHs. These were HPLC with fluorescence detection and GC with MS detection. The latter technique involved the use of stable-isotopes for calibration purposes.

Both analytical techniques were optimised for the trace-level analysis of a maximum of 19 PAH compounds in snow. Typical method limits of detection achieved for individual compounds are ≤ 1.0 ng l^{-1}. Of the compounds investigated, 4 have not previously been reported in snow.

The sample preparation and analytical techniques developed are applicable to the study of other classes of trace-organic contaminants in snow.

A total of 75 sample extracts were analysed from three contrasting sites. These were: i) a remote, sub-arctic, mountain catchment in the Cairngorm Mountains, Scotland; ii) an urban site in Southampton, Southern UK; iii) a boreal forest site in the Laurentian Mountains, Québec, Canada.

The data obtained suggest that the common source of PAHs in all of the snow samples is combustion processes.

Aged snowpack samples from the Cairngorm Mountains, Scotland, were found to have PAH concentrations similar to those reported for urban areas in Germany and Switzerland (Georgii and Schmitt, 1983; Leuenberger *et al.*, 1988). This is similar to findings from the same area for the occurence of trace-metals in snow (Davies *et al.*, 1988, 1992).

Fresh snowfall samples from Scotland were found to have concentrations similar to those reported in snow from a remote location (McVeety and Hites, 1988).

There exists at least an order of magnitude difference in PAH concentrations between the values for fresh snowfall and aged snow, for both individual PAH and ΣPAH concentrations.

PAHs were determined in both the dissolved and the particulate phases. Only one previous investigation is known of that has studied the detailed distribution of PAHs in the dissolved and particulate phases of snow. This is somewhat surprising, as the behaviour of PAHs in the environment is strongly influenced by their association with particulate matter. Therefore, an understanding of the phase distribution of PAHs is desirable.

For fresh snow in the Cairngorm area, the proportion of PAHs in the dissolved phase was found to be significantly higher than in the aged snow samples. This can be explained by post-deposition processes which cause a relative loss of the lower molecular weight PAHs from the snowpack. These compounds have higher volatilities and higher aqueous solubilities, and are therefore more susceptible to losses by revolatilisation to the atmosphere and leaching of the snowpack by melt- and/or rainwater. In addition, dry deposition to the snowpack surface will produce a relative increase in the particle bound PAH fraction. The relative extent of the latter process is currently largely unknown.

The PAH distribution patterns in the aged snow samples from Scotland were shown to be similar for each phase when analysed by abundance ranking. Fresh snow samples exhibited less similarity in PAH distributions between the two phases.

The differences in the absolute amounts and relative phase distribution patterns in snow from Ciste Mhearad suggest that sampling of the snowpack from this site may not be a useful indicator of the seasonal flux of PAHs to snowcover, as there is evidence that post-depositional processes cause major changes in the PAH distributions.

Some evidence of an association between snow acidity and PAH content for the snow from Scotland was obtained. Data from snowfall from the urban site in Southampton did not fit this crude relationship. Differences in the chemical nature of fresh snow samples from Scotland and Southampton can be attributed to differences in the source of particulates and the proximity of the sorces. It can be expected that the urban samples will contain particulate matter of a larger size distribution, and these particles will therefore have had a shorter atmospheric residence time.

The data for PAH content of snow from Scotland and Southampton suggests that the benzo[a]pyrene content of a sample may be indicative of the total PAH content, as is often stated in the literature. However, a more extensive data set is required to improve the accuracy and precision of this hypothesis.

The data set for PAHs in the fresh snow samples from Canada is incomplete, comprising of dissolved phase PAH concentration values only. These are similar in magnitude to those for fresh snow in the Cairngorm Mountains. Application of air-mass back-trajectory analysis to provide an indication of source regions for the PAHs detected yielded ambiguous results. This analysis should be improved when the data for the particulate phase PAHs are available.

Despite the limitations of the extent of the data set obtained, it remains a significant contribution to the existing literature on trace-organic contamination in snow, and PAHs in snow in particular.

7.2 Recommendations for Further Research.

The principal weakness of this research project was the difficulty in attaining reliable analytical methods for the determination of trace-level PAH concentrations. A large proportion of the time available was spent developing these methods. As a consequence, the full potential of the sample set was not achieved. All of the elements of interest identified in the study would benefit from a more extensive data set.

In particular, a clearer understanding of the PAH deposition in fresh snow to the Ciste Mhearad catchment under varying meteorological conditions is required to clarify the relative magnitudes of the dissolved and particulate PAH fraction at time of deposition. This would also enable the proposed relationship between snow acidity and PAH content to be better evaluated.

Additionaly, an investigation at the same site of post-depositional processes that effect PAHs in snow is called for. This would enable the evaluation of the accumulation of PAHs and the flux of PAHs from the snowpack upon melting to be estimated.

Other aspects identified as desirable to include in similar studies in the future are:

i) The analysis of the particulate fraction characteristics, *ie*. the particle size distribution and the chemical composition of individual particulate fractions.

ii) The analysis of other classes of organic compounds, in addition to trace-metals. This additional information would improve the estimation of PAH source regions and processes (Lunde *et al.*, 1977; Schrimpff *et al.*, 1979; Kawamura and Kaplan, 1986; Valerio *et al.*, 1986; Czuczwa *et al.*, 1988).

iii) A more extensive sampling regime should ideally also be undertaken, with more samples from each event being collected, as has been effected in previous snow chemistry studies in the area (see Tranter *et al.*, 1987; Landsberger *et al.*, 1989; Davies *et al.*, 1992; Jickells *et al.*, 1992).

Whilst values for pollutant concentration are useful indicators of the extent of pollution, estimations of pollutant flux values provide information on the rates of pollution.

The Ciste Mhearad site would be a suitable location for a study of this nature. It represents a hydrologically well-defined, sub-arctic catchment, with simple input and output processes: ie. atmospheric precipitation and outflow from one major stream. It would be an ideal site in which to conduct a mass balance study of the geochemistry of PAHs in a remote, sub-arctic environment, similar to that undertaken by McVeety and Hites (1988) for a low-level lacustrine system. Such a study would entail the determination of the PAH content of the atmosphere (vapour and particulate phases), dry precipitation, wet precipitation (rain and snow), snowmelt, stream- and soilwater, and soil. As mentioned above, sampling of the 'seasonal' snowpack may not provide a good indication of total seasonal PAH accumulation in snow, owing to the effects of post-depositional processes.

For the analysis of PAHs, the use of GC-MS with isotope-PAH standards for recovery and calibration purposes is the prefered choice. This would enable the samples to be spiked with the isotopes prior to extraction, and thereby ensure that corrections were made on each separate sample for recovery efficiency, in addition to quantitatively calibrating the PAH analysis.

APPENDIX I

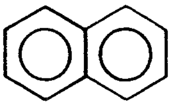
PAH Compounds Studied

Key:

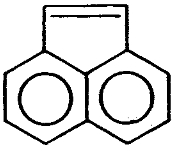
Compound Name
Molecular Weight
Melting Point (°C)
Boiling Point (°C)

pd = partially decomposes
sub = sublimes
--- = not available
(data from Bjørseth, 1982)

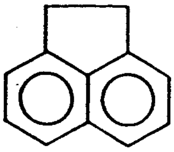
Naphthalene
128.19
81
218



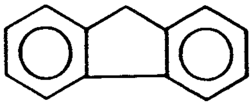
Acenaphthylene
152.21
93
c.270 pd



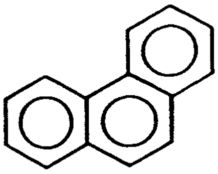
Acenaphthene
154.21
96
279



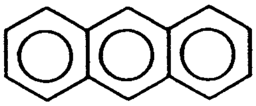
Fluorene
166.23
117
294



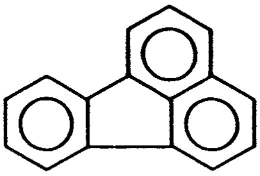
Phenanthrene
178.24
101
338



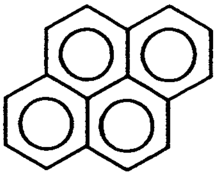
Anthracene
178.24
216
340



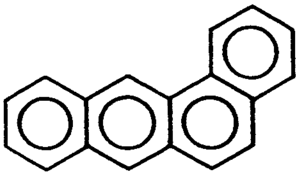
Fluoranthene
202.26
111
383



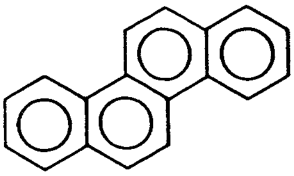
Pyrene
202.26
156
393



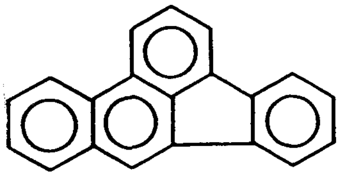
Benz[a]anthracene
228.30
162
435 sub



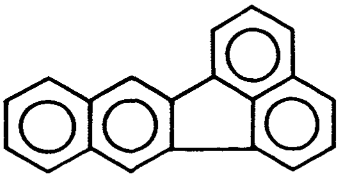
Chrysene
228.30
256
441



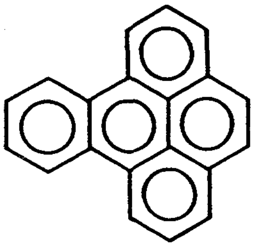
Benzo[b]fluoranthene
252.32
168
481



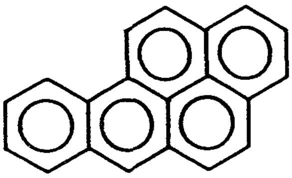
Benzo[k]fluoranthene
252.32
217
481



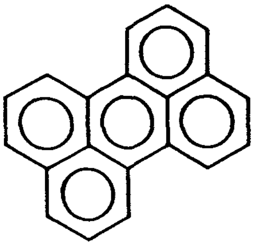
Benzo[e]pyrene
252.32
179
493



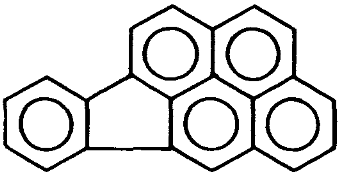
Benzo[a]pyrene
252.32
177
496



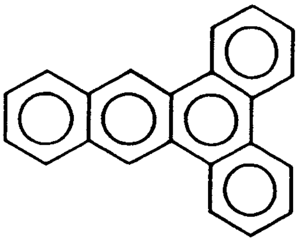
Perylene
252.32
278



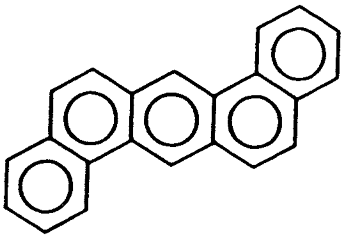
Indeno[1,2,3-cd]pyrene
276.34



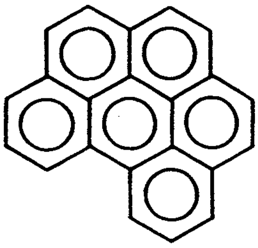
Dibenz[a,c]anthracene
278.36
205



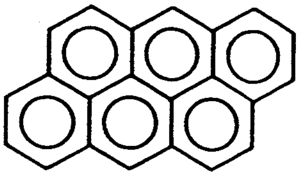
Dibenz[a,h]anthracene
278.36
270



Benzo[ghi]perylene
276.34
278



Anthanthrene
276.34



APPENDIX II - PAH ANALYTICAL STANDARDS

With the exception of Table II.1, all values are expressed to 2 s.f. See note (*) below.

Table II.1 NBS PAH Standard.

Compound		Concentration (μg ml^{-1})*
1	Naphthalene	19.9 ± 0.4
2	Acenaphthylene	15.9 ± 0.2
3	Acenaphthene	19.6 ± 0.5
4	Fluorene	4.76 ± 0.06
5	Phenanthrene	3.37 ± 0.02
6	Anthracene	0.771 ± 0.004
7	Fluoranthene	7.68 ± 0.07
8	Pyrene	8.25 ± 0.02
9	Benz[a]anthracene	3.82 ± 0.02
10	Chrysene	3.62 ± 0.02
11	Benzo[b]fluoranthene	4.08 ± 0.05
12	Benzo[k]fluoranthene	4.61 ± 0.02
13	Benzo[a]pyrene	4.82 ± 0.03
14	Dibenz[ah]anthracene	3.72 ± 0.05
15	Benzo[ghi]perylene	3.75 ± 0.02
16	Indeno[1,2,3-cd]pyrene	4.32 ± 0.08

* : Concentration values cited in: "National Bureau of Standards Certificate of Analysis, Standard Reference Material 1647a - Priority Pollutant Polycyclic Aromatic Hydrocarbons (in Acetonitrile)". The listed uncertainties are ± two standard deviations of the determined values and include both within and between analytical method differences (NBS, 1988).

Table II.2 HPLC and GC Standards.

Compound		HPLC	GC
		Concentration ($\mu g\ ml^{-1}$)	
1	Naphthalene	9.70	2.40
2	Acenaphthene	52.00	0.87
3	Fluorene	37.00	1.40
4	Phenanthrene	2.00	2.00
5	Anthracene	0.71	2.00
6	Fluoranthene	7.80	2.00
7	Pyrene	3.60	2.20
8	Benz[a]anthracene	1.70	3.40
9	Chrysene	1.40	5.60
10	Benzo[b]fluoranthene	3.90	3.90
11	Benzo[k]fluoranthene	1.60	4.40
12	Benzo[a]pyrene	2.70	13.00
13	Dibenz[ah]anthracene	7.90	5.30
14	Benzo[ghi]perylene	5.10	11.00
15	Indeno[1,2,3-cd]pyrene	7.60	7.20

Table II.3 GC-FID PAH Standard.

Compound		Concentration (μg ml^{-1})
1	Fluorene	420
2	Phenanthrene	390
3	Anthracene	430
4	Fluoranthene	500
5	Pyrene	350
6	Benz[a]anthracene	380
7	Chrysene	560
8	Benzo[a]pyrene	660
9	Dibenz[ah]anthracene	630
10	Benzo[ghi]perylene	170
11	Benzo[a]fluorene	490
12	Perylene	430
13	Benzo[e]pyrene	320

Table II.4 MS PAH Standard.

Compound		Concentration (μg ml^{-1})
1	Naphthalene	100
2	Acenaphthene	99
3	Fluorene	100
4	Phenanthrene	100
5	Anthracene	100
6	Fluoranthene	100
7	Pyrene	110
8	Benz[a]anthracene	93
9	Chrysene	100
10	Benzo[b]fluoranthene	100
11	Benzo[k]fluoranthene	100
12	Benzo[e]pyrene	120
13	Benzo[a]pyrene	90
14	Perylene	120
15	Indeno[1,2,3-cd]pyrene	92
16	Dibenz[ac]anthracene	110
17	Dibenz[ah]anthracene	110
18	Benzo[ghi]perylene	110
19	Anthanthrene	87

Table II.5 MS Isotope PAH Standard.

Compound		Concentration (μg ml^{-1})
1	Naphthalene-d8	55
2	Acenaphthene-d10	56
3	Fluorene-d10	58
4	Anthracene-d10	58
5	Fluoranthene-d10	68
6	Chrysene-d12	56
7	Benzo[a]pyrene-d12	49
8	^{13}C-Benzo[ghi]perylene	56

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