Institute of Environmental and Biological Sciences

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Polychlorinated Biphenyls (PCBs) and Polycyclic Aromatic Hydrocarbons (PAHs) in UK Air and Deposition.

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I dedicate this thesis to my wife
Valerie

Abstract

Air concentrations and deposition fluxes of PCBs and PAHs are presented for 1991 and 1992 at four UK urban centres (London, Manchester, Cardiff and Stevenge). Sampling was also carried out throughout 1993 at a rural location in NW England (Hazelrigg). This monitoring programme, part of the toxic organic micropollutants survey (TOMPS), has provided the first extensive data sets for PAHs and PCBs in the UK urban and rural atmosphere.

Atmospheric PCBs and PAHs were sampled every other week at each of the sites using High-Volume air samplers, equipped with glass fibre filters to collect particulate and polyurethane foam plugs to serve as vapour adsorbents. Bulk deposition was collected every month. Furthermore, atmospheric PCBs were sampled every day at the rural site, between March and June 1994, in a preliminary attempt to investigate the influence of separate meteorological episodes.

At the four urban sites mean annual ΣPAH concentrations ranged from approximately 60 - 150 ng m^{-3}, while the mean ΣPCB concentration ranged from 500 - 1500 pg m^{-3}. These concentrations are the same order of magnitude as contemporary concentrations reported in other urban areas on an international basis. The lighter, predominantly vapour phase PAHs of fluorene and phenanthrene and the lower chlorinated PCB congeners, 28 and 52, dominate the atmospheric profile for both sets of compounds respectively. ΣPAH concentrations were actually greater in the Hazelrigg atmosphere (~ factor 2) than in Manchester. This was due to significantly higher concentrations of fluorene and phenanthrene. This site and another rural site in the NW England are under the influence of local sources. Added to this, volatilisation of these lighter compounds from secondary sources such as sediments/soils/vegetation may explain the elevated concentrations during the warmer summer months. Principal components analysis highlighted the dominance of these lighter compounds in the rural atmosphere over the urban atmospheres. At Hazelrigg the ΣPCB concentrations were lower than the urban sites by a factor of between 3-4, reflecting the lack of point sources in the rural environment.

Seasonal variations were evident for the heavier PAH in both the urban and rural atmosphere. This was characterised by elevated concentrations in the winter, possibly due to increased fuel consumption for residential heating. The lighter compounds in the urban atmosphere did not show the seasonal cycling evident in the rural atmosphere, probably due to the masking effect of increased primary emissions in the winter. The ΣPCB concentrations showed elevated concentrations in the summer at all of the sites, the vapour phase concentrations of several prominent congeners being correlated with temperature. The more chlorinated congeners showed an increased cycling amplitude from winter to summer than the less chlorinated congeners. This

may be due to them being more readily exchangeable between surfaces and the atmosphere, than the lower chlorinated congeners.

Partitioning between the particulate and vapour phases for the PAHs and the PCBs appears to be controlled mainly by temperature and a compound's volatility. Total suspended particulate plays a lesser role, the partitioning behaviour (calculated partition coefficients at 20°C) for six indicator congeners being similar in both the Manchester and Hazelrigg atmospheres. As surface area available for sorption is more important than just particulate concentration it is postulated here that the amount of area available at the earth's surface, particularly if covered by vegetation, will play a more important role in vapour phase sorption/desorption than atmospheric particulate.

Meteorological episodes typified by high pressure anti-cyclonic systems resulted in elevated particulate phase ΣPCB and ΣPAH concentrations in the Cardiff and Manchester atmospheres respectively. The use of air mass back trajectories identified three separate air masses at the Hazelrigg site, when ΣPCB concentrations varied significantly from the sampling mean. The lack of profile differences between these air masses (originating from different areas) indicate similar sources to the atmosphere, or similar processes that occur during transport that result in a uniform profile.

The mean ΣPAH deposition flux varied from ~5 $\mu g\ m^{-2}\ d^{-1}$ at the urban sites to ~2 $\mu g\ m^{-2}\ d^{-1}$ at the rural site. The mean ΣPCB deposition flux varied from ~0.8 $ng\ m^{-2}\ d^{-1}$ at the urban sites to ~0.2 $ng\ m^{-2}\ d^{-1}$ at the rural site. Comparison with fluxes reported at rural/remote sites in north America would suggest that Hazelrigg and a site in the Lake District in NW England represent semi-urban areas; it seems that greater distances away from urban centres are required before 'true' rural fluxes are obtained.

Large differences in air concentrations between phenanthrene and the heavier benzo[a]pyrene were not matched by a similar difference in deposition fluxes. Phenanthrene has an air concentration a factor of ~30 greater than benzo[a]pyrene, yet its deposition flux is only a factor of ~2 higher. The deposition sampler may be biased against vapour phase collection, however, evidence suggests that lighter PAH may be more susceptible to photolytic degradation than the heavier compounds. The PCBs, unlike the lighter PAHs, are deposited at a similar rate relative to their air concentrations. Using source inventory data, PAH and PCB annual releases into the UK atmosphere were estimated, and a simple mass balance was determined for the UK environment using the derived depositional fluxes.

Acknowledgements

I would like to acknowledge the Department of the Environment for funding the TOMPS programme and NETC, through Peter Coleman, who gave me access to the London and Stevenage data sets.

Vicky Burnett deserves a special mention for her time and effort in setting up the analytical procedures used in this thesis. Also thanks to Keith Waterhouse for his invaluable technical support in the labs, and excellent company in the hills!

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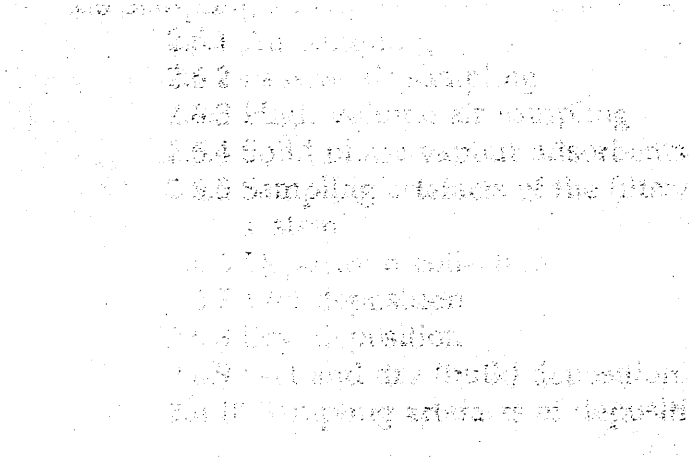
Finally and most importantly, I would like to thank Professor Kevin Jones for giving me the opportunity to better myself, and be part of a first class research group. His encouragement, drive and good humour have made the last four years extremely enjoyable.



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Chapter 1

Introduction

1.1 General Introduction

Over the last 25 years interest has grown in the cycling and effects of persistent organic chemicals in the environment. Much of this attention has focussed on the semi-volatile organic compounds (SOCs), whose chemical and physical properties have resulted in their presence in every environmental compartment. These compounds, particularly the organochlorines, are generally produced anthropogenically and considered to be xenobiotics - that is, chemicals not produced by nature. The term SOC covers an enormous range of chemicals found in the environment with vapour pressures ranging from 10^{-1} - 10^{-10} Pa. This wide range in vapour pressures and diverse physical-chemical properties has made this group of organic compounds ubiquitous around the globe, providing a challenge to understanding the processes that control their movement and accumulation. Certain broad groups like the polycyclic aromatic hydrocarbons (PAHs), and industrially produced chemicals like the pesticides, polychlorinated biphenyls (PCBs), phthalate esters and the by-products of pesticide production and waste incineration, the dioxins and furans, are of particular interest due to their persistence and toxicity. In this thesis the presence and behaviour in the atmosphere of two of these groups

of compounds, the PCBs and PAHs, were studied.

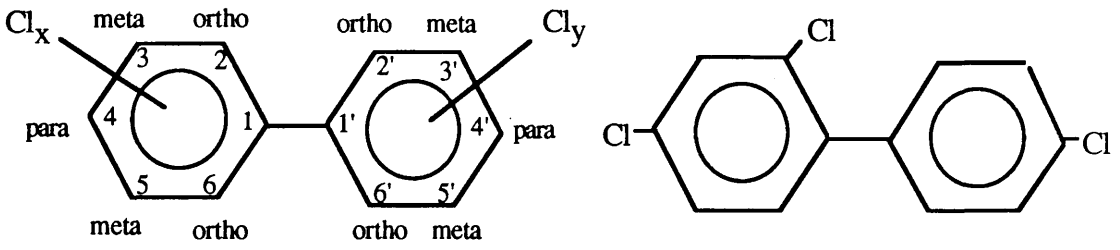
Most of the contemporary releases into the environment of these compounds are directly into the atmosphere, from where the contaminants will migrate, breakdown or be deposited onto terrestrial or aquatic surfaces. In other words, the atmosphere acts as a highly dynamic medium for these compounds, and although concentrations may be orders of magnitude lower than those found in soil or sediments, the atmosphere is of key importance in transporting these chemicals. Therefore, the role of the atmosphere and the behaviour of these contaminants within it must be fully understood if we are to predict the movement, processes and ultimate sinks. Both the PCBs and the PAHs are included in the UK-DoE Red List of priority organic contaminants and the US-EPA priority list of pollutants, and described in more detail in the following sections.

1.2 Polychlorinated biphenyls (PCBs)

PCBs were first synthesised industrially in the US in 1929 by an $FeCl_3$-catalysed chlorination of a biphenyl ring. This reaction produces a mixture of individual PCB compounds or congeners, the composition of the mixture depending on the proportion of chlorine to biphenyl. Theoretically over 200 PCB congeners can exist, which differ in the number and position of chlorine atoms on the biphenyl ring. Figure 1.1 denotes the parent PCB structure (a) and an example of an individual congener, number 28 (b). The

numbering scheme was developed by Ballschmiter and Zell (1980) who numbered all 209 congeners according to the number and position of chlorine atoms. The numbering scheme has been accepted by the International Union of Pure and Applied Chemistry (IUPAC) and PCBs are commonly referred to by their IUPAC numbers.

Figure 1.1 PCB structure



a) Parent PCB chemical structure

b) 2, 4, 4' - trichlorobiphenyl (IUPAC congener #28)

The individual numbered congeners fall into homologue groups according to the number of chlorine atoms around the biphenyl structure. For example, congener 28 is an example of a trichlorobiphenyl as it possesses three chlorine atoms. Table 1.1 presents the distribution of PCBs by level of chlorination. From these homologue groups, thirty individual congeners, covering a wide degree of chlorination, were analysed in this thesis.

Industrial PCB mixtures were classified according to the amount of chlorine present. For example, Aroclor mixtures (the trade name given by the American chemical company Monsanto) were marked with a four figure

number i.e. Aroclor 1248, the 12 denoting the number of carbon atoms, while the 48 refers to the percentage of chlorine (by weight) present in the mixture. Other trade names for technical PCB mixtures include Clophen (Bayer, Germany), Phenoclor (Prodelec, France) and Kanechlor (Kanegafuchi, Japan).

Table 1.1 Distribution of PCBs by level of chlorination (Jones et al., 1991).

PCB homologue	Molecular formula	Number of isomers
Monochlorobiphenyl	$C_{12}H_9Cl$	3
Dichlorobiphenyl	$C_{12}H_8Cl_2$	12
Trichlorobiphenyl	$C_{12}H_7Cl_3$	24
Tetrachlorobiphenyl	$C_{12}H_6Cl_4$	42
Pentachlorobiphenyl	$C_{12}H_5Cl_5$	46
Hexachlorobiphenyl	$C_{12}H_4Cl_6$	42
Heptachlorobiphenyl	$C_{12}H_3Cl_7$	24
Octachlorobiphenyl	$C_{12}H_2Cl_8$	12
Nonachlorobiphenyl	$C_{12}HCl_9$	3
Decachlorobiphenyl	$C_{12}Cl_{10}$	1

The unusually high chemical stability and electrical resistance of PCBs, together with their low volatility and resistance to degradation at high temperatures led to a range of industrial applications. These can be categorised into 'closed' or 'open' (dissipative) uses. Examples of closed uses include their use in capacitors and transformers as dielectric fluids, hydraulic fluids in mining equipment and as heat transfer and vacuum pump fluids. Open uses include flame retardants, plasticisers and additives to cement, plasters, casting agents, lubricating and cutting oils and use in printing inks.

According to Harrad *et al.* (1994) peak production in the UK occurred in the late 1960's resulting in approximately 40,000 tonnes being sold in the UK between 1954-1977. It was only in the mid-1960's that PCBs were first identified in environmental samples (Jensen, 1972) and that awareness was raised of the hazards posed by PCBs to biota and their accumulation in the foodchain. Due to their occurrence in the environment and the human health risks posed by PCBs (reviewed by Safe (1994)), restrictions on the manufacture and use have been imposed by most countries. PCBs are classified as probable/possible carcinogens to humans by the International Agency for Research in Cancer (IARC). However, other health effects such as immunosuppression, reproductive and development toxicity, modification of endocrine pathways and neurotoxicity have been reported in a variety of mammals (Safe, 1994) and current concerns and research is focussing on these, rather than carcinogenesis.

For the UK, restricted use was imposed in 1976 (APARG, 1995) with only certain 'closed' systems still in operation, such as large transformers and capacitors. Since their first production in the UK in 1954, PCBs have entered the environment through both point and diffusive sources such as from landfill sites, spillages from transformers and capacitors, production of refuse derived fuel, incineration of PCB waste and the recovery of contaminated scrap metal to name but a few. With the advancement of analytical techniques, environmental PCB concentrations are now reported on an individual congener basis rather than being reported as a commercial

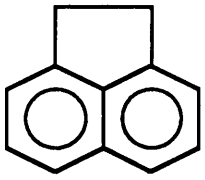
mixture (i.e. Aroclor mix). This was an important step forward since the congener pattern or profile in environmental samples will not be the same as that of the profile of the original commercial mixtures.

1.3 Polycyclic aromatic hydrocarbons (PAHs)

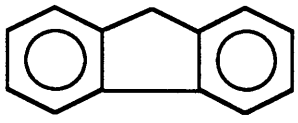
PAHs are formed mainly as a result of pyrolytic processes, notably the incomplete combustion of organic materials. PAH can be formed in any incomplete combustion or high temperature pyrolytic process involving fossil fuels, or more generally, materials containing C and H (Baek *et al.*, 1991). PAHs consist of two or more fused benzene rings in linear, angular or cluster arrangements resulting in several hundred compounds having been identified from combustion sources (Menichini, 1992). From this huge number the US-EPA prioritised 16 on the grounds of human health effects. These have been found to have the highest animal carcinogenic and mutagenic loading according to the IARC (1983; 1987). For this reason there is a wide interest in PAH emission sources, environmental levels and human exposures.

On a global scale PAHs are not only derived from anthropogenic sources but also from natural sources such as forest/prairie fires and volcanic activity. However, in industrialised countries - particularly in the urban environment - anthropogenic sources make by far the greatest contribution to the environmental burden. Figure 1.2 presents the chemical structures

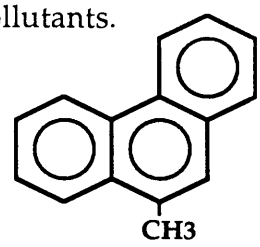
Figure 1.2 Chemical structures of the polycyclic aromatic hydrocarbons analysed in this study. *US-EPA priority pollutants.



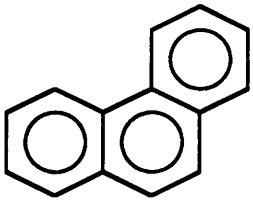
Acenaphthene (ACE) *



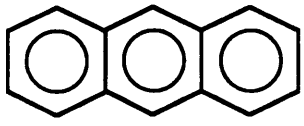
Fluorene (FLU) *



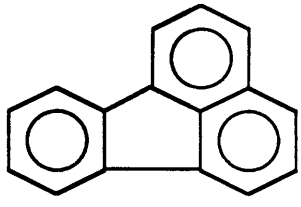
1-methyl phenanthrene (MPHE)



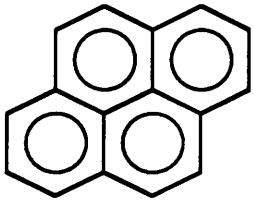
Phenanthrene (PHE) *



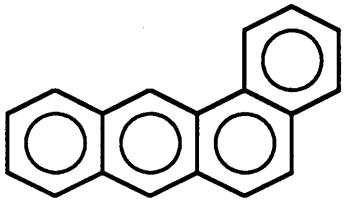
Anthracene (ANTH) *



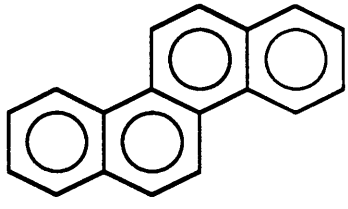
Fluoranthene (FLUO) *



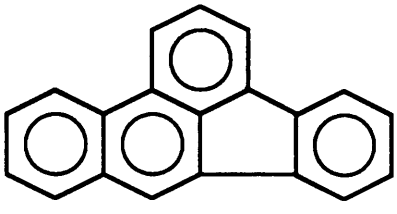
Pyrene (PYR) *



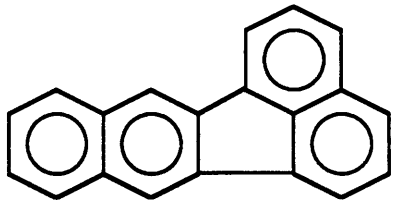
Benz[*a*]anthracene (BENZANTH) *



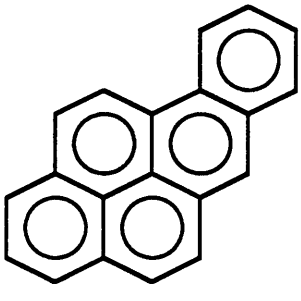
Chrysene (CHRY) *



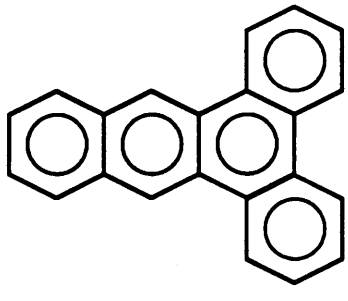
Benzo[*b*]fluoranthene (B[b]F) *



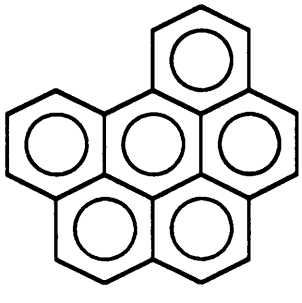
Benzo[*k*]fluoranthene (B[k]F) *



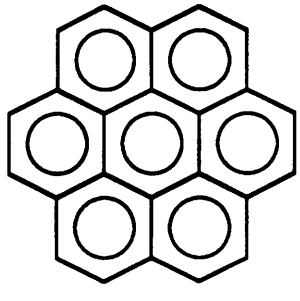
Benzo[*a*]pyrene (B[a]P) *



Dibenz[*ac*]anthracene (D[ac]A) *



Benzo[*ghi*]perylene (B[ghi]P) *



Coronene (COR)

and names of 15 PAHs examined in this thesis. All these compounds will be referred to by their abbreviated names (presented in brackets in Figure 1.2), and range from the two-ringed acenaphthene (ACE) to the heavier seven-ringed coronene (COR). Of these compounds benzo[a]pyrene (B[a]P) is one of the most studied and carries the highest carcinogenic rating (IARC, 1987). Health concerns regarding PAHs focus on their metabolic transformation by terrestrial and aquatic organisms into mutagenic, carcinogenic and teratogenic agents such as dihydrodiol epoxides. These metabolites bind to and disrupt DNA and RNA, which is the basis of tumour formation.

There are numerous anthropogenic sources of PAHs, particularly in the contemporary urban environment. Major sources include the combustion of organic based materials for energy supply, either stationary sources such as power stations and domestic heating, or mobile sources like cars, trains and aircraft. Incineration of municipal solid waste (MSW), sewage sludge, clinical waste and chemical waste also provide major sources of PAHs to the environment. Unregulated fires such as recreational fires, waste wood and tyre burning are also likely to make a significant contribution to the environmental loading (Wild and Jones, 1995).

1.4 Aims of study

This thesis intends to establish ambient atmospheric concentrations of PCBs and PAHs. Little or no systematic collection of data on these compounds

had been undertaken in the UK prior to this study. This has allowed comparisons to be made with other studies on an international basis and was envisagd by the Department of the Environment (DoE) as influential in forming legislative criteria for air quality guidelines. Temporal and spatial variations in PAH and PCB concentrations have been investigated at four urban sample sites and at a rural location.

The vapour-particle partitioning in the atmosphere has also been examined. By studying this distribution for individual compounds the dominance of the vapour or particulate phase for different compounds under different conditions can be established, which has implications for transport and depositional processes. Depositional fluxes of these compounds have also been measured in both the urban and rural environment and have been used in conjunction with source inventories to establish mass balances to the UK environment.

Meteorological episodes of unusually high contaminant loading have been investigated at the sampling locations. The influence of meteorological factors on contaminant loading and behaviour in the atmosphere has been assessed by running an intensive (high resolution) air sampling programme at the rural location. Air mass back trajectories would be calculated to help explain contaminant loading.

Finally, by identifying and quantifying source compartments within one of

the urban areas, the cycling nature of a prominent vapour phase PCB congener (PCB 52) could be predicted. A simple box model invoking temperature as the controlling factor for volatilisation from these compartments has been utilised to predict concentrations over an annual time scale.

1.5 Thesis layout

To explain the presence of SOCs in the general atmosphere and the processes affecting them, Chapter 2 presents a review of the sources of PAHs and PCBs to the UK atmosphere, vapour-particle partitioning and the physical-chemical properties governing the atmospheric behaviour of these contaminants. Atmospheric residence times and depositional processes are also discussed, together with atmospheric and depositional sampling strategies.

Chapter 3 details the methods and analytical procedures for the sampling and analysis of atmospheric PAHs and PCBs. The sampling was part of the Toxic Organic MicroPollutants Survey (TOMPS) funded by DoE. This chapter describes the sampling regime, site locations and methodology, including quality control and assurance criteria for the generated data.

Chapters 4 and 5 present the PCB and PAH data respectively for the five TOMPS sites and discuss seasonal cycling, vapour particle partitioning and

spatial variations of these compounds.

Chapter 6 looks into the meteorological effects on contaminant loading in the atmosphere and discusses several meteorological episodes identified in the TOMPS data. Furthermore, a high resolution sampling study is presented which looks into short term changes in atmospheric concentrations of PCBs. Meteorological data and air mass back trajectories are applied to help in the explanation of these short term fluctuations.

Chapter 7 utilises a model developed by Pankow (1993) to explain the vapour phase concentrations of one compound, a tetrachlorinated biphenyl, (PCB 52) in the urban atmosphere of Manchester. This model assumes temperature to be the governing factor controlling the atmospheric concentration, defining volatilisation from a series of compartments within the box as the primary sources.

Chapter 8 examines the depositional fluxes of both PCBs and PAHs measured at each of the sample sites. Using contemporary data on emissions from recently compiled source inventories simple, mass balances are developed for the UK. Discrepancies between annual emissions and deposition are explored.

Chapter 9 concludes the major points from this thesis and recommends those areas needing further research.

1.6 Units and concentrations

Atmospheric concentrations of PCBs and PAHs are reported in this thesis as mass per unit volume of air (i.e. ng m^{-3} or pg m^{-3}), where ng = 10^{-9} g and pg = 10^{-12} g. To keep with the convention of standard SI measurements of substances in solids or liquids, it would be much better to report air concentrations as mass per unit mass of air (i.e ng g^{-1}). However this unit is rather difficult to perceive and increases with altitude and temperature.

Another way of commonly expressing concentrations of atmospheric contaminants is by volume per unit volume (also known as the volume mixing ratio), expressed as parts per million by volume (ppmv) or parts per billion (10^{-9}) by volume (ppbv). The mixing ratio can be calculated from the contaminant concentration by the following equation:-

$$\text{ppbv} = \frac{\text{ng m}^{-3} \times Vo}{M} \times \frac{T}{To} \times \frac{Po}{P}$$

Where M is the compound's molecular mass and Vo is the molar volume of an ideal gas (22.4×10^{-3} m^3 mol^{-1}) with standard temperature (To) 273 K and pressure (Po) 101.3 Pa. T is the ambient temperature and P the ambient pressure during the sampling period. Thus, a mixing ratio is useful in that it is independent of temperature and pressure, and allows a direct comparison of one contaminant with another in terms of number of molecules in the

atmosphere.

Semi-volatile compounds such as the PCBs and PAHs exist both in the vapour and particulate phases making the use of volume mixing ratios limited; it is inappropriate to report particulate phase concentrations as volume per unit volume measurements. However, because of their abundance in the vapour phase, global PCB concentrations have in some cases been reported in this manner, particularly for comparison with other vapour phase organic contaminants (Standley and Hites, 1991). In this thesis the particulate and vapour phase data are always reported as mass per unit volume of air.

Chapter 2

Semi-volatile Organic Compounds in the Atmosphere: A Review

2.1 Sources to the atmosphere

As discussed in Chapter 1 the SOCs studied in this thesis are the PCBs and the PAHs. Both these groups of compounds are ubiquitous in the global atmosphere and have many differing sources. PAHs are continually produced and emitted to the atmosphere from combustion sources, whereas PCBs are no longer manufactured or put to new uses within the UK. PCBs are released into the atmosphere either from point sources, such as landfill sites and waste incinerators, or by re-volatilisation from surfaces, such as soil, vegetation and water.

2.1.1 PAH sources

Much of the PAH input to the global atmosphere arises from forest fires and volcanic activity (Nikolaou *et al.*, 1984) as well as from the biogenic production of some individual PAHs such as perylene (Sanders *et al.*, 1993). However, emissions from human activities are the predominant source, particularly in industrialised countries such as the UK. Atmospheric

releases are considered to be from two main combustion categories. The first is combustion of materials for energy supply (i.e. oil, petrol, gas, coal, wood etc.), and the second is combustion for waste minimalisation such as waste incineration (Wild and Jones, 1995). Peters *et al.* (1981), cited in Baek *et al.* (1991), estimated for the US that 26 % of atmospheric emissions were from residential heating and 23 % from mobile sources (i.e. petrol and diesel engines). Interestingly different countries have varying emission patterns. For example, Ramdahl *et al.* (1983) estimated that industrial processes contribute to 69 % of total atmospheric emissions in Norway, yet only 24 % in the US. As Baek *et al.* (1991) pointed out there may be large uncertainties in estimating emission factors in this way, but certainly it is clear that centres of dense population, where energy consumption is at its highest, are a significant source of atmospheric PAHs.

For the UK, Wild and Jones (1995) have attempted to budget the various PAH sources to the environment including the atmosphere. The emission of PAH from the burning of fuels for energy can be spilt into stationary and mobile sources. Stationary sources include the burning of fuel for heating and power generation (i.e. coal, oil, gas). Wild and Jones (1995) estimated that domestic heating results in 600 tonnes of ΣPAH (Σ = 16 PAH) being released into the atmosphere per annum. Coal and oil fired power stations, as well as industrial oil users, release approximately 5.8 tonnes of PAH while industrial emissions i.e. refineries, tyre production, aluminium smelting etc. are estimated to emit ~18 tonnes per annum. The burning of

wood is thought to contribute around ~4 tonnes per annum of PAH to the atmosphere. However, all of these estimates are hampered by large uncertainties over the vapour phase emissions, which effectively excludes the lower molecular weight PAHs, resulting in an underestimation of the true amount released from this source.

Mobile sources make a significant contribution to the PAH loading in the atmosphere. With the increase in motor vehicle numbers the emission of PAHs to the atmosphere, particularly the urban atmosphere, is significant. It is estimated that at least 60 tonnes of PAH per annum are produced from leaded and unleaded petrol car emissions. Diesel driven vehicles (i.e. heavy goods vehicles, buses, vans etc.) add a further 19 tonnes of PAH to the atmosphere. The projected increase in diesel vehicles (QUARG, 1993b) and the rise in the use of unleaded fuel (higher aromatic content [Baek *et al.*, 1992]) may result in increased PAH emissions to the atmosphere.

Other sources of PAH to the atmosphere include incineration of municipal, chemical, clinical and sewage sludge waste. The ash that results from this incineration contains a significant amount of PAH but, more importantly, stack emissions release PAHs to the atmosphere. These emissions will be highly variable, depending on feedstock, incinerator design and combustion conditions. On the basis of a plant working 12 hours a day with a rate of disposal of 9 tonnes of refuse per hour, (Davis *et al.*, 1976), then Wild and Jones (1995) suggest an estimated 56 kg of PAH are emitted annually from

UK incinerators.

Other PAH sources, which are unquantifiable, include unregulated fires such as forest and heathland fires as well as recreational fires, and the unregulated burning of tyres, wood and other waste. A potentially important source to the atmosphere is the soil to air volatilisation of previously deposited PAHs, particularly of the low molecular weight more volatile compounds. Although this area is poorly understood, Park *et al.* (1990) found that 30 % of naphthlene (two ringed PAH) added to soil was lost by volatilisation, while for other PAHs volatilisation was negligible. The importance of volatilisation losses for the low molecular weight PAHs has been implicated in sewage sludge amended soils (Wild and Jones, 1993).

2.1.2 PCB sources

PCB sources to the atmosphere are subject to similar uncertainties as the PAHs. As described in Chapter 1, PCBs were produced in technical mixtures classified according to the percentage of chlorine present in the mixture. In the UK and most other western countries the use of PCBs was severely restricted or banned by the early 1980's (Jones *et al.*, 1991). However, substantial stocks may still be tied up in industrial applications such as the dielectric fluids in transformers and capacitors (the so called 'closed uses'). These are either broken up, resulting in the release of PCBs directly to the environment or disposed of by incineration. Other uses were more

dissipative, the so called 'open uses'. Examples include the use of PCBs as plasticisers, fire retardants and agents in printing inks. Many of these PCB-associated products have ended up in landfill sites which may now be releasing PCBs to the atmosphere through volatilisation or on wind blown particles. Fugitive atmospheric emissions of PCBs have been measured around several landfill sites (Lewis *et al.*, 1985; Hermanson and Hites, 1989). Other point sources include stack emissions from clinical and chemical waste incinerators (Murphy *et al.*, 1985), and the release from scrap metal recovery processes. Harrad *et al.* (1994) attempted to budget the PCBs in the UK environment and detailed the major sources and their contribution to the UK atmosphere. The primary source was considered to be soil-derived, with approximately 88% of the atmospheric burden coming from soils. Leaks from transformers and capacitors contribute ~9% to the atmospheric loading, while the production of refuse derived fuel and the recovery of contaminated scrap metal contribute some 3% to the atmospheric burden. In general, since the end of production, PCBs have become widely distributed between the various environmental compartments due to the many diffusive and point sources. Over recent months studies emphasising the potential role of vegetation as a significant sink and source to the atmosphere for a variety of SOCs have been published (Simonich and Hites, 1994, Welsch-Pausch *et al.*, 1995). This has raised some uncertainties, in the case of the PCBs, over the dominance of soil as a source to air estimated by Harrad *et al.* (1994). Movement of PCBs from any compartment such as soil, water and vegetation will result in a transfer to the atmosphere.

2.2 Fate of SOCs in the atmosphere

SOCs in the atmosphere will be distributed between the atmospheric particulate and vapour phases according to the physical conditions (temperature and particulate loading) of the ambient atmosphere and the physical-chemical properties of the compounds in question. This vapour-particle partitioning plays an important role in determining the behaviour and fate of atmospheric SOCs. For example, it affects photo- and chemical degradation rates and also determines the relative importance of dry and wet deposition processes for a certain compound. The three main factors which determine a chemical's fate in the atmosphere are, its vapour pressure, water solubility and chemical reactivity.

2.2.1 Vapour pressure and water solubility

The SOCs including pesticides, PAHs, PCBs and PCDD/Fs have vapour pressures ranging from 10^{-4} - 10^{-11} atms (10^{-1} - 10^{-7} Pa) at ambient temperatures (Mackay *et al.*, 1992). A compounds volatility (as measured by its vapour pressure) will affect its atmospheric fate. Bidleman *et al.* (1986) deduced that SOC volatility, expressed by vapour pressure, is the dominating factor governing adsorption to air particulate matter. This vapour-particle partitioning will ultimately decide a compound's fate and will be discussed in more detail later.

The solubility of a compound will determine how readily it will dissolve in

rain, in cloud droplets and water surfaces. The dissolution of a compound into water is determined by Henry's Law. Henry's Law states that the vapour pressure of a solute is proportional to its concentration (Heys, 1981), the proportionality constant is the Henry's Law constant (H).

$$P = HC$$

Where P = partial pressure of a gas and C = concentration of a dissolved gas. H or K_H is therefore effectively an air-water partition co-efficient calculated from the ratio of vapour pressure of a compound to its water solubility, expressed in units of atm (Pa) m^3 mol^{-1} at 25 ^oC, or if divided by RT, the gas constant (R= 82E-6 m^3 atm K^{-1} mol^{-1}) and a particular temperature (T=K) ,it becomes dimensionless (Standley and Hites, 1991). Henry's Law constant is a function of temperature only for a particular gas-solvent system. However, each gas-solvent system has a unique Henry's constant. Henry's law breaks down when partial pressures exceed 5-10 atm and/or when the dissolved concentration exceeds 3 mol %. However, for environmental contaminants considered here, the aqueous solubilities and vapour pressures of the pure substances are very low. Water solubilities, vapour pressure, Henry's Law constants and K_{ow} (octanol-water partitioning co-efficients) are given in Table 2.1 for selected PAHs, PCBs and PCDD/Fs. Henry's Law constants do not necessarily show a simple linear pattern like water solubility and vapour pressure, when plotted against molecular descriptors like molecular weight. For example, systematic variation of K_H

Table 2.1 Physicochemical properties for selected PAHs, PCBs and PCDD/Fs.
(Shiu et al., 1988; Mackay et al., 1992)

Compound	MW (a) g/mol	P (b) Pa (25 oC)	Water Sol. (c) g/m3 (25 oC)	H (d) Pa m3/mol	log Kow (e)
PAH					
ACE	154	1.52	3.8	12.2	3.92
PHE	178	0.113	1.1	3.24	4.57
ANTH	178	0.077	0.045	3.96	4.54
FLUO	202	0.0087	0.26	1.04	5.22
CHRY	228	0.00011	0.002	0.065	5.86
B[b]F	252	0.000029	0.0015	2.36	5.80
B[k]F	252	0.000011	0.00081	0.016	6.00
B[a]P	252	0.000021	0.0038	0.046	6.04
COR	300	0.000022	0.00014	0.00042	6.50
PCB					
28	258	0.034	0.037	27.0	5.60
52	292	0.012	0.04	43.5	5.83
101	326	0.0024	0.017	31.7	6.30
138	361	0.00017	0.002	24.9	6.69
153	361	0.00012	0.003	17.6	6.76
180	395	0.00013	0.0005	34.2	7.13
Tetra-CB	292	0.095	0.043	24.6	5.93
Hexa-CB	361	0.0011	0.0035	31.5	6.75
Octa-CB	430	0.000078	0.00021	38.1	7.11
PCDD/Fs					
2,3,7,8-TCDD	322	0.00012	0.000019	3.3	6.81
2,3,7,8-TCDF	306	0.0002	0.00042	1.5	6.14
2,3,4,7,8- PeCDFs	340	0.000017	0.00023	0.5	6.55
1,2,3,4,7,8-HxCDDs	391	0.0000014	0.0000044	4.5	7.80
1,2,3,4,6,7,8-HpCDFs	409	0.00000057	0.0000014	1.4	7.42
OCDD	460	0.00000095	0.000000074	0.7	8.21

(a) = Molecular weight, MW (mean values reported for the separate homologue groups)
(b) = Vapour pressure,P (mean value)
(c) = Water solubility (mean value)
(d) = Henry's Law constant, H (mean value)
(e) = Log Kow: logarithmic value of the octanol-water partitioning co-efficient. (mean value)

values does not occur with change in molecular weight of PCBs (i.e. Cl number) (Burkhard *et al.*, 1985). However, the PCDDs do show a variation in K_H values with a fall of a factor of 1.6 per chlorine added, as a result of the decrease in vapour pressure (by 8) and solubility (by 5) (Shiu *et al.*, 1988). If K_H is sufficiently high for a certain compound, vapour dissolution into droplets is neligible; in other words the compound experiences liquid phase resistance. Conversely a low K_H results in a compound experiencing vapour phase resistance and the compound will prefer the liquid phase. Henry's Law constants generally increase with increased temperature, primarily due to the temperature dependency of chemical vapour pressures; solubility is much less affected by the changes in temperature normally found in the environment.

2.2.2 Chemical reactivity

A compound's reactivity in the atmosphere, along with its vapour-particle partitioning, will determine its residence time. For SOCs the major transformation processes include, photolysis or photo-oxidation, oxidation by reaction with hydroxyl radicals, ozone or other oxidising agents and re-arrangements to other structures. For many of the SOCs, the distribution between the particle and vapour phases has a significant effect on its atmospheric reactivity. Aged air masses have been found to be enriched with the particle-bound more chlorinated PCDD/Fs (Eitzer and Hites 1989; Tysklind *et al.*, 1993), probably due to volatilisation of the less chlorinated

compounds and their subsequent photolysis. For the PCBs, the reverse is found to be the case. In aged air masses the less chlorinated congeners were found to prevail, possibly due to the loss of chlorines from the heavier compounds by photolysis (Atlas and Giam, 1981). Laboratory studies have been undertaken to observe reaction rates of vapour state PCBs and PCDD/Fs with OH radicals, O_3 and NO_3 radicals (Atkinson, 1987; Kwok *et al.*; 1994). Kwok *et al.* (1994) calculated atmospheric lifetimes of gaseous PCDD/Fs to be in the order of 1 to 4 days, the OH radical reaction being the dominant tropospheric loss process. Bunce *et al.* (1989) found that mono-chlorinated biphenyls have a half-life of several days when exposed to direct solar degradation. Atmospheric residence times will be dealt with in more detail in Section 2.4.1.

Chemical reactions of PAH in the atmosphere are important because such reactions appear to be one of the major removal processes and because the products of the reactions may in some instances be more toxic than the parent PAH (Nikolaou *et al.*, 1984). The major atmospheric loss mechanism for the more volatile vapour phase PAHs is by reaction with the OH radical (Atkinson and Aschmann, 1987; Arey *et al.*, 1989; Kwok *et al.*, 1994). Vapour phase reactions with N_2O_5 and/or the OH radical in the presence of NO_x results in the formation of nitro derivatives (nitroarenes). Since the OH radical-initiated reaction is a daytime process and the N_2O_5 reaction is a night-time process, diurnal variations have been observed in the volatile nitroarenes (Arey *et al.*, 1989). Calculated rate constants indicate that the OH

radical and NO_3 radical reactions will be the dominant atmospheric loss processes for phenanthrene, and that the overall atmospheric lifetime of vapour phase phenanthrene will be ≤ 1 day (Kwok *et al.*, 1994). The reactivity of particulate associated PAH has been more thoroughly investigated. Over the last 15 years studies on the transformation of reactive PAH on particles have been undertaken, in particular, reactions with gases such as nitrogen dioxide (NO_2), sulphur trioxide (SO_3) and ozone (O_3) (Pitts *et al.*, 1978; Butler and Crossley, 1981, Lindskog *et al.*, 1985; Yokley *et al.*, 1986). Degradation of the heavier multi-ringed PAH such as benzo[a]pyrene has been found to depend not only on the concentration of the above gases but also on the relative humidity and the nature of the sorbent particulate. Behymer and Hites (1988) found that the photolytic process is independent of PAH structure and dependent on the physical and chemical properties of the particulate. Using different types of fly ash, Behymer and Hites (1988) found that the substrates that stabilise reactive PAH are black or gray in colour and have a significant carbon content. Dark substrates adsorb the most light and prevent the light from getting to the PAH. The stabilisation of PAH associated with certain types of particulate will result in increased atmospheric residence times and hence promote long range transport.

2.2.3 Vapour - particle partitioning

Vapour - particle partitioning of SOCs in the atmosphere was first described by Junge (1977), who used the gas-solid, linear Langmuir isotherm theory

which states that the rate of adsorption of a compound to a surface is proportional to the compound's vapour pressure and the amount of surface area available:

$$\phi = c\theta/(P + c\theta) \qquad (2.1)$$

Where ϕ is the fraction of the total atmospheric concentration of a compound sorbed to the aerosol, P is the vapour pressure of that compound, θ is the concentration of the aerosol surface area ($cm^2\ cm^{-3}$ air) and c is a parameter depending upon the sorbate molecular weight, surface concentration necessary for monolayer coverage and the heat of desorption of that compound. Junge's approach to gas-particle partitioning proved difficult. However, since finding the concentration of an aerosol surface area ($cm^2\ cm^{-3}$ air) to parameterise the distribution process proved to be a difficult task, Yamasaki *et al.* (1982) got around the problem by assuming that the surface area is linearly related to the total suspended particulate (TSP $\mu g\ m^{-3}$) in the atmosphere. By using TSP, Junge's isotherm approach could be applied through the use of a compound- and temperature-dependent thermodynamic partition coefficient of the form:-

$$K = \frac{A}{F/TSP} \qquad (2.2)$$

A and F represent the equilibrium concentrations of a compound in the vapour and particulate phase respectively ($ng\ m^{-3}$). F is typically defined as

the filter retained concentration and A the adsorbent retained concentration of an air sampling system. The adsorbent is typically located downstream of the filter in any air sampling system. SOC air sampling is discussed in Section 2.6. The quantity F/TSP (ng μg^{-1}) represents the thermodynamic activity on/in the particulate matter. The constant K can be viewed as the equilibrium ratio of A to F/TSP, i.e. as the equilibrium ratio of the concentration of a compound in the gas phase to that in/on the particulate matter. Yamasaki *et al.* (1982) chose to invert Equation (2.2) to show that an increasing partition coefficient, K, denotes decreasing partition to the solid phase. Although this is the inverse of the usual convention for parameterising a two compartmental system the partition coefficient K_p is now usually expressed as:-

$$K = \frac{F/TSP}{A} = \frac{F}{A(TSP)} = K\text{-}1 \qquad (2.3)$$

Various studies have been selected which can be divided up into three distinct observations to support Equation (2.3) in validating vapour-particle distributions of SOCs in the atmosphere.

Observation 1: The compound dependent K_p values, at typical ambient temperatures, for a range of PAHs have been found to be remarkably similar in different cities including: Osaka, Japan (Yamasaki *et al.*, 1982), Portland, OR (Ligocki and Pankow, 1989) and Chicago, IL (Cotham and Bidleman, 1992).

Observation 2: At a certain temperature, such as 20 °C, a linear relationship was found between log K_P and log P°_L [where log P°_L is the sub-cooled liquid vapour pressure of that compound] (Foreman and Bidleman, 1987). This experimental data supports the theory of Pankow (1987), where Kp should correlate with compound vapour pressure at a certain temperature.

Observation 3: Log K_P plotted against inverse temperature (1/T) (T = Kelvin) for a variety of PAHs sampled in Osaka (Yamasaki *et al.*, 1982) gave sufficient linearity to determine the heats of desorption (Hd) [from the slope of the line]. The same plots carried out for PAHs sampled in Chicago IL air produced similar Hd values (Kreiger and Hites, 1994).

The use by Yamasaki *et al.* (1982) of TSP as a surrogate measurement of the amount of surface area available for adsorption by vapour phase molecules is therefore acceptable for the Langmuir isotherm approach and allows the use of Equation (2.3). Furthermore, the partition coefficient K_P is a strong function of atmospheric temperature (which affects a compound's volatility) and when K_P is plotted vs. 1/T then the linear regression takes the form (Pankow, 1987) :-

$$-\text{Log } K_P = m/T + b \qquad (2.4)$$

Where m and b are the slope of the line and the Y- intercept respectively. These are effectively thermodynamic expressions of the partitioning process.

Several studies have found strong correlations between log (F/TSP)/A and 1/T for a range of SOCs. T is taken as the ambient temperature during the sampling event. Hoff *et al.* (1992b) examined the partitioning for a variety of pesticides and found that there was increased sorption to particulate matter with decreasing temperature for cis-chlordane, γ–HCH, 4,4'-DDT and endosulphan (the slope of the line depending on the compound). Interestingly, no apparent correlation was noted for α-HCH and heptachlor, indicating that these compounds remain wholly in the vapour state at ambient temperatures.

Pankow (1987) predicted that the value of m and b obtained by the linear regression over some ambient temperature range will be given by:-

$$m = Hd/2.303R - T_{amb}/4.606 \qquad (2.5)$$

$$b = \log (A_{tsp}t_o/275\,[M/T_{amb}]^{0.5}) + 1/4.606 \qquad (2.6)$$

Where Hd is the heat of desorption (KJ mol^{-1}) from a surface, R is the gas constant and T_{amb} (K) is the centre of the ambient temperature range for the regression. For b (the Y-intercept) A_{tsp} is the surface area of the total suspended particulate ($cm^2\ cm^{-3}$), t_o is the molecular vibration time (s) and M is the molecular weight (g mol^{-1}). The slope and the intercept are therefore strongly dependent upon Hd and the surface area of the particulate

(sorbent) A_{tsp} respectively. Heats of desorption (from atmospheric particulate surfaces) have been calculated from plots of log (F/TSP)/A vs. 1/T for a variety of SOCs, including PAHs (Yamasaki *et al.*, 1982, Kreiger and Hites, 1994), organochlorine pesticides (Cotham and Bidleman, 1992; Hoff *et al.*, 1992b) and PCBs (Bidleman *et al.*, 1986; Hoff *et al.*, 1992b).

The thermodynamic approach was utilised by Storey and Pankow (1991), who studied the partitioning of PAHs to several model aerosols (graphitic carbon, sodium chloride, silica and alumina) as well as standard urban particulate matter (UPM). Good agreement between log $K_{p,s}$ vs. 1/T plots for the graphitic carbon aerosol and UPM supports the theory that partitioning to atmospheric aerosol is adsorptive and non-specific in nature. $K_{p,s}$ was a surface area corrected K_p, derived for the different aerosols from Equation (2.6). Agreement between UPM and the other three sorbents, however, was not as good as with graphitic carbon, indicating that different aerosol compositions may affect the vapour to particulate partitioning.

Pankow (1991) improved the simple linear regression (SLR) plots (Log Kp vs. 1/T) for individual compounds, to derive a common factor for a whole compound class such as the PAHs. This was done on the basis that similar compounds sorbing to the same particulate matter should possess very similar Y-intercepts [b value, Equation (2.4)]. This common y-intercept regression (CYIR) uses a mean b value, calculated from individual compounds, to plot the regression. For a class of compounds such as the

PAHs, the use of a common b value (or Y intercept) has proved more reliable in evaluating heats of desorption. These in turn are more highly correlated with the heats of vapourisation derived from laboratory experiments.

2.2.4 Deviations from true vapour - particle partitioning

Discrepancies in the non-specific adsorption characterising vapour - particle partitioning for SOCs have been highlighted. Variations in log K_p vs 1/T plots for a class of compound derived from field data taken at different locations and times do occur. For example Hd values calculated for PAHs collected in Osaka, Japan in 1982 (Yamasaki *et al.*, 1982) differ slightly from Hd values calculated from PAHs collected in Indianapolis, IN in 1994 (Krieger and Hites, 1994). These differences are put down to thermodynamic variability such as differences in the amount of atmospheric particulate present and hence the sorbing surface area available (Pankow and Bidleman, 1992). Temperature is the only environmental factor taken into account in the partitioning model of SOCs. However, recent work has highlighted humidity as having a low, but significant effect on the partitioning of PAHs to the particulate (Lee and Tsay, 1994); that is increased water vapour condenses on the particulate reducing SOC adsorption. Cotham and Bidleman (1992) found that high temperatures (~30 ^{o}C) and high relative humidities reduced SOC sorption to particulate matter. Secondly, and perhaps more importantly, the sampling system artefacts can result in F and

A (Equation (2.3)) not representing their true atmospheric values, resulting in a biased K_P (Bidleman *et al.*, 1986). Details of sampling artefacts are discussed in Section 2.6. Furthermore, it is now considered that there is a non-exchangeable PAH fraction retained within atmospheric aerosol. This fraction is released in soxhlet extraction procedures resulting in a biased particulate loading, compared to the true exchangeable particulate-PAH fraction in the atmosphere (Bidleman *et al.*, 1986).

The partitioning between the particle and vapour phases is therefore dependent on the volatility of a compound, the ambient temperature (and humidity to some degree) and the amount of particulate matter present (i.e. the surface area available), which will differ between an urban and rural atmosphere. Hence the V/P partitioning will, in the long term, determine a compound's fate in the atmosphere, since those compounds found mainly associated with the particulate are more susceptible to depositional processes and shorter atmospheric residence times. On the other hand compounds with a significant vapour phase fraction, although least affected by depositional processes, may be prone to photochemical transformation. Certainly the elucidation of a compound's distribution at ambient temperatures allows the fate of that compound to be predicted.

2.3 The role of atmospheric particulate matter

Particulates in the air consist of very small solid- or liquid-suspended droplets and are generally classified according to size. Table 2.2 lists the general particulate types and sizes. The origins, sizes and removal pathways are discussed in detail in Twomey (1979). Large or coarse particles with diameters (d) greater than 2 - 2.5 μm are produced by mechanical means such as aeolian weathering of soils, sea spray, volcanic activity and release from plants (e.g. pollen and spores). The smallest particles, $d < 0.1$ μm, are known as Aitken nuclei, which arise from gas to particle conversion. This range contains most of the total number of particles, but little mass. The lifetimes of Aitken nuclei are short because of rapid coagulation. Mid-sized, or accumulation mode particles (0.1 μm $< d < 2$ μm) are also produced by gas to particle conversion and by coagulation of Aitken nuclei.

Table 2.2 Types of suspended particulates in the atmosphere (Wellburn, 1991).

Type	Nature	Size (diameter) (μm)
Grit	Solids, settle out quickly	> 500
Dust	Solids, settle more slowly	2 - 500
Smoke†	Gas-borne solids	< 2
Mist†	Liquid droplets	0.1 - 2
Aitken nuclei	Solid or liquid droplets	< 0.1

† Accumulation mode particles

The accumulation mode, which comprises most of the surface area and about half the mass of urban air particulate matter, is an important one for air pollutants (Bidleman, 1988). Compared with coarse particles,

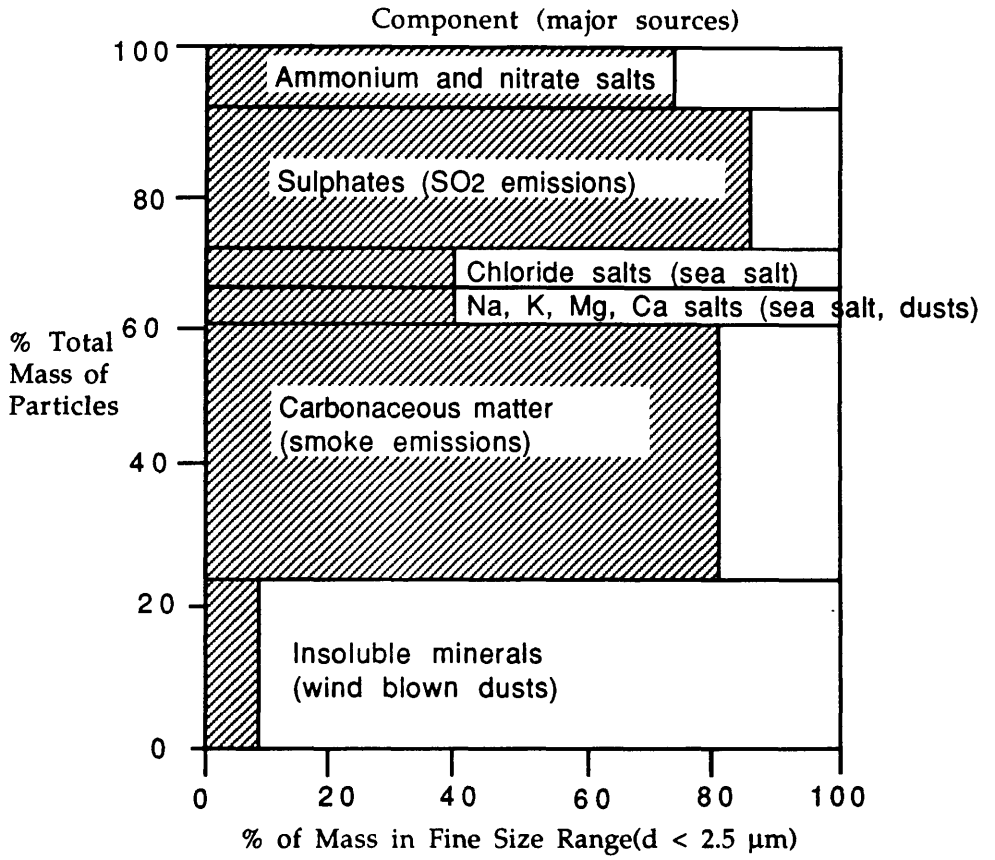
accumulation-mode particles contain high levels of organic compounds, soluble inorganic species (e. g. sulphate, nitrate and ammonium) and many trace metals. Accumulation-mode particles are too small to undergo rapid gravitational settling and they are more slowly removed by rain and dry deposition. As a result, their atmospheric lifetimes and potential for transport over long distances are greater. Residence times of 7 - 30 days have been quoted (QUARG, 1993).

2.3.1 Nature of urban aerosol and sampling

Over the last 40 years the nature of urban aerosol has changed, in the 1950's and 1960's smoke played a major role in the pollution of UK towns and cities. At the time, it largely comprised of carbonaceous soot from coal burning. However, with the decline of domestic coal combustion due to the Clean Air Act of 1956 (Boubel *et al.*, 1994), the concentrations of black sooty smoke fell. Conversly, concentrations of secondary particulate pollutants such as ammonium sulphate increased due to increased sulphur dioxide emissions over Europe.

In recent years growth in the number of diesel vehicles, which can emit black smoke, has led to some increase in the blackness of smoke at heavily trafficked sites, and it is diesel engines rather than coal combustion which are now the major source of black smoke particles in the UK (QUARG, 1993). The composition of typical urban aerosol is presented in Figure 2.1.

Figure 2.1 Composition of atmospheric aerosol collected in Leeds (1982/3). (QUARG, 1993)



Simple measurement of atmospheric particulate is carried out by gravimetrically determining a filter before and after air sampling. The mass difference is reported as the total suspended particulate (TSP - $\mu g\ m^{-3}$). A widely used method in the UK is the black smoke method, where air is drawn through a white filter on which the particles produce a stain, the darkness of which is measured using a portable reflectometer. However, the method does not consider other, non-coloured, particulate. With the increasing concern over particulate matter $\leq$ 10 μm in diameter (PM_{10}), many studies have fractionated the particulate according to size using a

cascade impactor connected to the air sampling apparatus.

2.3.2 SOCs and atmospheric particulate

Urban atmospheric particulate (regarded as the urban aerosol) is strongly influenced by anthropogenic sources. In the early 1980's the airborne toxic elements and organic subtances (ATEOS) programme was set up in New Jersey, USA, to study airborne particulates in different urban locations within a city, as well as a semi-rural background site (Lioy and Daisey, 1985). Species measured included those associated with inhalable particulate matter (IPM) and included extractable organic matter from which PAHs and volatile organic compounds (VOCs) were examined. IPM (particles < 15 μm diameter) includes PM_{10} which can deposit in the tracheobronchial region of the lungs and is implicated in human health effects (Pope *et al.*, 1992). At each of the locations within the city IPM comprised of mainly mineral matter, such as secondary sulphate and suspended soil (~70 %). Contributions from motor vehicles were ~10 % at each of the sites while contributions from industry and other combustion sources varied depending on site location. Interestingly, pollution episodes were found to influence the composition of the organic fraction of the urban aerosol. During these periods, increased concentrations of extractable organic matter were observed at all of the sites, including the semi-rural site. Diurnal variations in particulate loading have been observed, particularly for PM_{10}. This bears some similarity to the traffic-dominated pattern for CO

emissions, indicating that traffic is a significant source of particulate. Moreover, work carried out in Los Angeles (Rogge *et al.*, 1993) found that internal combustion engines burning mineral fuels contribute > 21 % of the primary fine particulate organic carbon emitted to the atmosphere.

SOCs have been widely studied in atmospheric particulate, particularly the PAHs because of their combustion derived sources (Behymer and Hites, 1988; Baek *et al.*, 1992). More importantly, the distribution of SOCs (mainly the PAHs) have been examined in the various particle sizes (Katz and Chan, 1980; Pistikolopoulos *et al.*, 1990; Handa *et al.*, 1980). These studies report that particulate bound PAHs are located on the small accumulation-mode particles (d < 2μm). Katz and Chan (1980) reported that the particle size range of ≤ 1.1 to 3.3 μm contained between 72 - 89 % of the particulate PAHs. Similarly, although there is less data on the organochlorines, Kaupp *et al.* (1994) found approximately 90 % of the PCDD/Fs associated with small particles, < 1.35 μm in diameter. This is significant in terms of both human exposure and atmospheric transport, since accumulation-mode particles have relatively long residence times in the atmosphere.

In this thesis atmospheric particulate was determined as TSP collected on a filter and reported as μg m^{-3} of air. A high volume air sampler (Hi-Vol) described in Section 2.6 was fitted with a modified PM_{10} head. This was installed simply to be a more efficient collector of general atmospheric particulate over the conventional pyramidal Hi-Vol head. The baffles and

collecting shims were removed from the PM_{10} head to allow all particulate sizes access to the collecting filter. Collecting and analysing atmospheric particulate allows examination of the partitioning between the solid and vapour phases for a particular compound. Seasonal variations in this distribution can be followed, as well as spatial differences such as between urban and rural particulate, where time and dilution may have an effect on the aerosol.

2.4 Atmospheric transport

SOCs in the atmosphere are either adsorbed to particulate matter of different size ranges when emitted from the source or present in the vapour phase and can, during the course of time, undergo association with aerosols as they are transported. Since the atmospheric input is of major importance for the distribution of SOCs to the terrestrial and aquatic ecosystems, it is important to monitor their transport from sources and any subsequent compositional changes.

The atmospheric transport of SOCs has long been recognised as the mechanism resulting in the global distribution of many of these anthropogenic compounds. Long range transport from local and regional sources is governed by the spatial pattern of discharge and by the structures of global atmospheric flow. For example, acid deposition in parts of Scandinavia is due to transport of acidic pollutants from western Europe

(Irwin and Williams, 1988). Similarly, atmospheric transport is responsible for the movement of SOCs from sources to remote areas. Atlas and Giam (1981) discovered PCBs, DDT, dieldrin, chlordane and two phthalate ester plasticizers in the atmosphere of a remote Pacific atoll, far removed from industrial and human activity. The very nature of transport through the atmosphere results in the atmosphere acting as a significant source to remote areas through the mechanisms of deposition. Certainly in the upper Great Lakes region of the USA the atmospheric input of PCBs constitutes the greatest source to Lakes such as Superior, Michigan and Huron (Eisenreich *et al.*, 1981; Swackhamer and Armstrong, 1986; Murray and Andren, 1992).

2.4.1 Residence times

In the atmosphere as well as in the oceans the mobility of sparsely water soluble, semivolatile compounds will be mainly regulated by the ratio of particle bonded to non-particle bonded molecules. The ratio is regulated in the atmosphere by the surface of particles offered per volume unit and the mean temperature of the specific environment (Junge, 1977) and has been discussed in Section 2.2.3. The adsorbed portion will follow the transport routes of the aerosols, which - after aggregation - will deposit to surfaces (wet or dry) and have shorter residence times than the vapour phase component.

Ballschmiter and Wittlinger (1991) reviewed the global distribution of SOCs and assumed that the residence time of molecules depended on their

vapour - particle partitioning and particle residence times. The residence time (days) of a compound is predicted by dividing the particle residence time by the partition ratio ø (Equation 2.1, Section 2.2.3) at a mean tropospheric temperature. With a general particle residence time of between 6 to 9 days, those compounds with partition ratios of < 0.01 are predicted to have residence times of between 190 - 600 days. This is applicable for the lower molecular weight more volatile compounds such as the di and tri-chlorinated biphenyls and the pesticides HCH and HCB with vapour pressures of 10^{-2} - 10^{-3} Pa, and helps explain the ubiquitous global distribution of these compounds. Using this partitioning approach Manchester-Neesvig and Andren (1989) suggested a residence time of ~100 days for PCBs (averaged across 38 congeners covering the major homologue groups). Chemical transformation will certainly reduce residence times of atmospheric SOCs (ie ≤ 1 day for phenanthrene (Kwok *et al.*, 1994) but even with a particle residence time of 6 days and a wind speed range of 5 - 15 km/h, a particulate bound compound has a range of 720 - 2200 km at ground level, and probably further at greater heights due to higher wind velocities.

2.4.2 Long range transport

Since the 1970's reports have documented the SOC transport over oceans away from source areas. For example, elevated DDT levels have been found over the northern Indian Ocean (Tanabe and Tatsukawa, 1980) and western Pacific (Tanabe *et al.*, 1982). PCBs and polychlorinated camphenes (e.g.

toxaphene) were found in N. Atlantic air carried from N. America (Bidleman and Olney, 1974; Bidleman *et al.*, 1981). The movement of SOCs have been tracked from where they were generated (sources) to remote environments. For example, Bjorseth *et al.* (1979) found that the particlulate-bound PAH loading in the atmosphere of southern Norway occurred mainly in air masses having crossed the UK or the European continent. Similarly Masclet *et al.* (1988) measured both vapour and particle-bound PAH in a remote site on Corsica in the Mediterranean and found elevated concentrations in air masses tracked from north and western Europe. Importantly, they found that many of the vapour phase concentrations were determined by the source area only and that they remained high relative to the concentrations in the industrial zone from where the air was derived.

The use of meteorological data to establish back trajectories to allow the tracking of pollutants has also been applied to the Artic region. Growing concern in the 1980's over the prolification of SOCs in the polar atmosphere led to several studies where air samples were collected along with meteorological data to establish air mass direction. Oehme and Manø (1984) sampled various polychlorinated compounds including pesticides such as DDT, the HCH isomers and HCB as well as several pentachlorobiphenyls at the Arctic islands of Bear and Hopen. The concentration profiles for the measuring station at Bear Island during the autumn of 1982 showed two distinct maxima, with different compound composition. The comparison of the results with the trajectories calculated for this period gave a strong

indication of long range transport from Europe (first maxima) and the USA/Asia (second maxima). Further evidence of long range transportation of organochlorines and PAH have been confirmed by Patton *et al.* (1991) and Oehme (1991). Although pinpointing specific events or pollution episodes has had some success in the Arctic region, identifying sources is difficult due to the distances travelled and the time involved to move from source to polar region. Recently Wania and Mackay (1993) proposed a theory where compounds with vapour pressures in a certain low range may preferentially accumulate in the polar regions. A process of global fractionation may be occurring in which organic compounds become latitudinally fractionated, 'condensing' at different ambient temperatures dependent on their volatility. Certainly the patterns of environmental distribution of organochlorines in the higher latitudes appear to support this theory (Barrie *et al.*, 1992).

On a synoptic scale western Europe, in particular the UK, is affected by a variety of air masses. These bring different weather types to the UK, with the predominance of unstable westerly fronts (Musk, 1988). In contrast, high pressure anticyclones (characterised by clear skies and low winds) can persist over the UK blocking westerly depressions resulting in stable conditions with continental influences. In this thesis the use of back trajectories is incorporated to determine the direction of an air mass and hence reveal its importance as an influence on SOC loading.

2.5 Atmospheric deposition

Although it is now established that many of the SOCs are widely distributed in the global atmosphere (Ballschmiter, 1991; Iwata *et al.*, 1993), contamination of remote terrestrial and aquatic surfaces has occurred through depositional processes. As described by Ballschmiter (1991) the extent of deposition from the troposphere to the earth or ocean surface regulates the spreading of pollutants into unpolluted areas of the world as a consequence of the long range atmospheric transport. As the earth's surface is 71% water then it is probable that the deposition of anthropogenic compounds from contaminated air masses occurs mainly at sea, particularly as the mean global precipitation pattern favours deposition over the oceans. Unlike deposition to terrestrial surfaces the mixing process to deeper water layers (at least to 20-50 meters) will be relatively fast, resulting in the oceans acting as a transport medium (like the atmosphere) and also as a source, with compounds transported to remote regions or re-entering the atmosphere through volatilisation. The distribution of persistent organochlorines in oceanic air and surface seawater was thoroughly investigated by Iwata *et al.* (1993) with estimations of gas-exchange fluxes across the air-water interface in various global locations. Importantly, deposition of organochlorines has become evident in the remote polar regions (Tanabe *et al.*, 1983; Gregor and Gummer, 1989).

On a regional basis SOC deposition is an important source to terrestrial and aquatic ecosystems. Assessment of regional air and water quality and

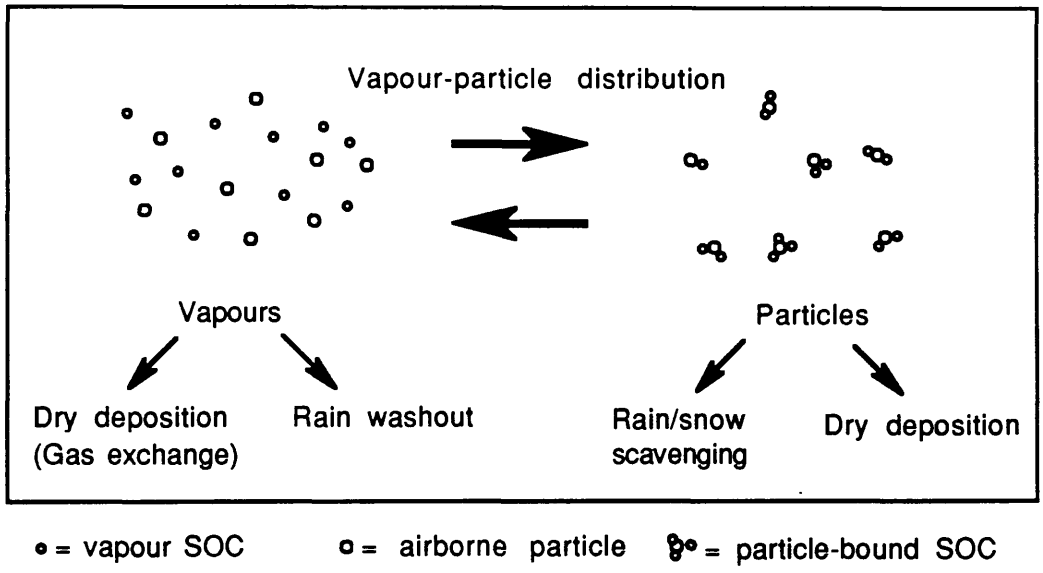
implementation of clean air legislation and risk management programmes requires an understanding of depositional processes and the quantification of contaminant deposition to surfaces. In the Great Lakes region of North America where several of the Lakes are in the vicinity of major emission sources, deposition of SOCs to these water bodies has been the focus of much research. Eisenreich *et al.* (1981) reviewed the depositional processes of SOCs to these water surfaces, emphasising the importance of the vapour - particle distribution in affecting deposition. For an organic compound this can either be through wet or dry deposition. The importance of dry deposition as a source of SOCs to lake surfaces was acknowledged by both Eisenreich *et al.* (1981) and later by McVeety and Hites (1988), who noted that the dry aerosol deposition for selected PAHs was greater than wet removal processes by a ratio of 9:1.

2.5.1 Depositional processes

The distribution of airborne organics between vapour and particle phases strongly affects atmospheric removal processes. For the more volatile compounds such as the di-, tri- and tetra-chlorinated biphenyls and the low molecular weight three-ring PAHs that exist predominantly in the vapour phase, depositional processes and rates will differ from the particulate-bound fraction. The two main types of atmospheric removal processes discounting chemical transformation are wet and dry deposition. A schematic diagram is presented in Figure 2.2 showing the various

depositional pathways for vapours and particle-bound organics.

Figure 2.2 Depositional processes which deposit SOCs to the earth's surface (adapted from Bidleman (1988)). SOCs partition between the vapour and particle phase, precipitation scavenges both of these matrices. Dry deposition of particles is also a significant removal process for SOCs.



2.5.2 Wet and dry deposition

Precipitation events scavenge contaminant-laden particles by incorporating the particles into rain drops, either during droplet formation or as the droplet falls through the air column (Ligocki *et al.*, 1985a). Vapour phase contaminants are removed from the atmosphere as a result of partitioning across the water droplet surface followed by dissolution into the bulk liquid. Non-reactive vapours (i.e. vapour phase SOCs) are scavenged by precipitation according to Henry's Law, if equilibrium between the vapour and aqueous phases is attained (Ligocki *et al.*, 1985a, b). Slinn (1978) predicted that a falling raindrop should attain equilibrium with a trace

organic vapour in a ~10 m fall. As an example from the work of Leister and Baker (1994) wet depositional fluxes (F_{wet} - μg m^{-2} $month^{-1}$) can be calculated from a volume-weighted monthly SOC concentration ($[SOC]_{vwm}$, μg m^{-3}):

$$[SOC]_{vwm} = [\Sigma C_{[SOC]i} Vi] / [\Sigma Vi]$$

$$F_{wet} = [SOC]_{vwm} (\tau)$$

Where $C_{[SOC]i}$ is the SOC concentration in each individual rain event, Vi is the volume of precipitation and τ is the precipitation rate (m^3 m^{-2} $month^{-1}$). The extent of wet scavenging for a compound is given by the 'washout ratio' (W) which is the concentration in rain (ng L^{-1}), divided by the concentration in air (ng m^{-3}). The particle washout ratio is given by Wp and the vapour phase washout ratio is given by Wv expressed as:-

$$Wv = RT/H$$

Where R is the gas constant and H is the Henry's Law constant for that compound at a certain temperature, T. If the fraction present in the particulate phase is defined as ø, then the overall washout ratio is given by (Ligocki *et al.* 1985b):-

$$W = Wv(1 - ø) + Wpø$$

In general, washout efficiency is enhanced as the volatility of a species is reduced, probably due to particle washout being the primary removal mechanism for these compounds. Eitzer and Hites (1989) calculated gas and particle washout ratios for the dioxin and furan homologue groups in Bloomington, IN. Plots of Wv and Wp against compound vapour pressure showed a strong correlation for Wv and a lack of correlation for Wp, the latter indicating that particle washout is a physical process acting on the particle and, therefore, all the compounds bound to the particle are affected similarly. Wv was found to increase significantly with decreasing vapour pressure i.e. as the Henry's constants decreased, compounds became more susceptible to washout.

SOCs are removed from the atmosphere during dry periods by dry particle deposition and by vapour exchange between the atmosphere and water and terrestrial surfaces. Dry particle deposition rates of SOCs depend upon the aerodynamic size distribution and upon micrometeorological conditions (Slinn, 1983). Although dry particle deposition rates are very difficult to measure directly, modelled and experimentally derived particle deposition velocities have been derived for various SOCs including PAHs (McVeety and Hites, 1988), PCDD/Fs (Koester and Hites, 1992) and PCBs (Holsen *et al.*, 1991). Monthly dry particle fluxes ($F_{part.\ dry}$, $\mu g\ m^{-2}\ month^{-1}$) can be estimated by:-

$$F_{part.\ dry} = [SOC]_{part.}\ Vd$$

Where $[SOC]_{part}$ is the measured particle SOC concentration ($\mu g\ m^{-3}$) and Vd is the estimated dry deposition velocity (m $month^{-1}$).

Gaseous contaminants actively exchange between the atmosphere and water and atmosphere and terrestrial surfaces at a rate proportional to their concentration gradients (Mackay, 1986). Gaseous fluxes of SOCs have been examined over water bodies such as in the Great Lakes region of North America. Leister and Baker (1994) used the following equation to derive gaseous fluxes to the Chesapeake Bay area on the eastern seaboard (Maryland) :-

$$F_{gas,\ dry} = K_{OL}([SOC]_{diss.} - [SOC]_{gas}/H)$$

Where $F_{gas,\ dry}$ is the SOC flux resulting from gas exchange ($\mu g\ m^{-2}\ month^{-1}$), K_{OL} is a mass transfer coefficient expressed on a liquid phase concentration basis (cm $month^{-1}$), H is the Henry's Law constant (Pa $m^{-3}\ mol^{-1}$) and $[SOC]_{diss.}$ and $[SOC]_{gas}$ are the concentration of SOC dissolved in surface water ($\mu g\ L^{-1}$) and in the atmospheric gas phase (ng m^{-3}) respectively. Baker and Eisenreich (1990) and Hoff *et al.* (1992a) found that the vapour exchange of SOCs is highly dynamic, with volatilisation during the warmer summer months offsetting efficient deposition during the cooler, winter months.

Monitoring deposition for SOCs in urban areas is less extensively studied, but for the PCBs and PAHs depositional fluxes are expected to be orders of magnitude higher. Holsen *et al.* (1991) determined dry deposition PCB fluxes in Chicago air and found them to be three orders of magnitude higher than in remote areas of the USA. In this thesis bulk deposition (wet and dry) was collected monthly from both urban sites and a rural location. By calculating deposition fluxes simple mass balances could be derived for the UK environment, annual release data for PAHs and PCBs was obtained from contemporary source inventories.

2.6 Sampling strategies for atmospheric SOCs

2.6.1 Air sampling

Examples of air sampling for SOC have been reported as early as the 1950's (Waller, 1952) when benzo[a]pyrene (3,4-benzpyrene), a high molecular weight PAH, was collected on filter paper. In this case air was drawn from outside a building by means of a small electric pump coupled to a gas meter so that the volume of air aspirated could be measured. Filter papers were also analysed for other airborne pollutants such as SO_2 and black smoke shading. Early measurements of airborne pesticides were carried out using impingers, gas bubblers and columns packed with solid adsorbents (Yule *et al.* 1971; Miles *et al.*, 1970; Stanley *et al.*, 1971). These methods were developed for use in agricultural areas or to monitor insecticide drift during forest spraying operations where concentrations in the atmosphere tended

to be high and the volume of air required for a sample relatively small, of the order of 5 - 50 m^3 (Bidleman and Olney, 1974). In areas well away from point sources, where time and atmospheric dilution result in greatly reducing the concentration of an airborne compound, large volumes of air need to be sampled to obtain detectable levels. There are two ways in which a sufficient volume of air can be sampled, one of which is passive air sampling (non-active) and the second is high volume air sampling (active).

2.6.2 Passive air sampling

Passive air sampling is a non active technique of sampling large volumes of air (up to millions of m^3). The earliest techniques involved leaving pre-cleaned screens (nylon mesh) coated in a neutral oil or lipid such as silicone oil or glycerin to collect atmospheric particulates for the subsequent analysis of pesticides (Risebrough *et al.*, 1968). However, this technique does not fully address the vapour phase component; Risebrough *et al.* (1968) could not detect any PCBs on their screens, when exposed to the north east Atlantic trade winds, and correctly presumed that they persist mainly in the vapour state. With the improvement of analytical techniques, coated screens (now usually made of Teflon™ or polypropylene) have been used to assess particle associated SOC deposition. Dry depositional fluxes of PCBs have been measured in Chicago air by Holsen *et al.* (1991) using a Mylar-covered plate, while PCDD/Fs have been analysed in fog by collecting fog water droplets on a Teflon wire mesh and allowing the water to run down into a

glass collecting vessel (Czuczwa *et al.*, 1989) (SOC deposition collection will be discussed later). Various matrices have been employed for passive air sampling, including plants (Buckley, 1982; Thomas *et al.*, 1985; Strachan, 1988; Schreiber and Schönherr, 1992), glass (Weistrand *et al.*, 1992) and semipermeable membrane devices (SPMDs) (Petty *et al.*, 1993). Since Klein and Weisgerber (1976) suggested that terrestrial plants accumulate airborne PCBs, studies have been undertaken on the long term accumulation of SOCs in mosses and lichens (Bacci *et al.*, 1986) and plant leaves with a high waxy cuticle content such as pine needles (Strachan *et al.*, 1994). This type of sampling in which the SOCs diffuse into the waxy plant surfaces gives a good indication of tropospheric contamination. Their contents in plant samples collected in 26 areas around the globe have now established a global distribution pattern for a variety of pesticides (HCB, DDT and its metabolites) (Calamari *et al.*, 1991). Semipermeable membrane devices (SPMDs), consisting of a neutral lipid (triolein) enclosed in polyethylene layflat tubing, have been demonstrated to be highly efficient passive air samplers (Petty *et al.*, 1993). These devices readily sequester lipophilic organic contaminants from the vapour phase and are increasingly being used in ambient air monitoring programmes (Lead *et al.*, unpublished). However, their use is limited at present by the uncertainties over the effects of temperature, freezing etc. on the uptake kinetics.

2.6.3 High volume air sampling

High Volume air samplers (Hi-Vols) are active samplers in that they pump air through a filter system. With a Hi-Vol system particulate associated compounds are collected on a precombusted glass- or quartz-fibre filter and an adsorbent behind the filter is used to retain the vapour phase component. Unlike the air sampling system used by Waller (1952) in central London (mentioned above) they are separate units incorporating an air pump/motor, air flow regulator and the sampling head. These samplers are of aluminium construction with the sampling head protected by a roof or specialised air inlet. A self contained detachable sampling head allows easy removal of the filter/sampling matrix with a reduced risk of handling contamination. The use of Hi-Vols was pioneered in the 1970's with the routine sampling of particulate bound SOCs in a variety of sampling locations (Gordon and Bryan, 1973; Faoro, 1975; Gordon, 1976). The extension of the Hi-Vol to sample gas phase SOCs came about with the use of solid adsorbents as a vapour trap. Olney and Bidleman (1974) incorporated polyurethane foam (PUF) plugs (situated behind the filter in the sampling head) to sample vapour phase PCBs in the marine atmosphere of the eastern Atlantic. PUF had originally been used to extract PCBs from seawater (Gesser *et al.*, 1971) but was found to be compatible with high volume air sampling since it offered little resistance to the passage of air. Several other adsorbents (discussed later) along with PUF are now routinely used in sampling the vapour phase component of SOCs in the atmosphere.

2.6.4 Solid phase vapour adsorbents

The use of solid adsorbents for the trapping of organic vapours has long been recognised; one of the earliest applications was the use of activated charcoal in gas masks during World War One (Thain, 1980). A number of different adsorbents have been used for trapping (physical adsorption processes i.e. Van der Vaals' forces) atmospheric vapour phase SOCs. These include Florisil™, porous glass beads, silica gel, polyurethane foam (PUF) and two types of porous resin, Tenax and XAD-2. Table 2.3 presents details of each adsorbent type and quotes PCB collection efficiencies. Advantages and drawbacks of each adsorbent are commented on. PUF which is cut into cylindrical plugs (length ~7 cm) and inserted behind the filter is the most commonly used adsorbent for ambient air monitoring schemes. Selection of a particular adsorbent should depend on the compound(s) to be sampled. Billings and Bidleman (1980) showed that hexachlorobenzene (HCB) was poorly retained by PUF yet the low molecular weight PCB (Aroclor 1016) was effectively trapped. In several cases where more volatile SOCs, such as pesticides like HCB and the hexachlorocyclohexane isomers (HCH) have been sampled, then Florisil™ and silica gel cartridges have been utilised because of their greater adsorbing efficiency (Lane *et al.*, 1992; Ballschmiter and Wittlinger, 1991). Several studies have used XAD-2 resin as the solid adsorbent to collect PCBs (Doskey and Andren, 1979; Hollod and Eisenreich, 1981; Tanabe *et al.*, 1983) and PCDD/Fs (Turrio-Baldassarri *et al.*, 1994). Tenax has also been used to trap vapour phase PAHs (Baek *et al.*, 1992). The use of

Table 2.3 Adsorbents used in the Hi-Vol collection of vapour-phase SOCs

Adsorbent	Structure	Collection efficiency (PCBs)	Advantages	Disadvantages
Florisil™	Mg_2SiO_3	100%[1]	Highly efficient adsorbent Easy to pre-clean[2]	Large pressure drop across the column makes it difficult to include in Hi-Vol operations.[2]
Silica gel	-SiOH	-	Low easily controlled blank, good mechanical properties[8]	Adsorbing efficiency reduced under humid conditions.[9]
Porous glass beads	20/80 mesh	100%[3]	Highly efficient adsorbent of lighter congeners[3]	Lack of applications within the literature, adsorbing efficiency affected by high humidity.[7]
PUF	polyurethane foam density 0.022 g cm^{-3}	75-100%[1]	Low cost, very easy to use Does not restrict air flow[4]	Use of single PUF plug can result in breakthrough of more volatile species, two plugs should be used[5].
Amberlite XAD-2	porous styrene (20/50 mesh) (divinylbenzene copolymer)	92-100%[3]	Efficient adsorbent of lighter compounds (ie more volatile pesticides)[5]	Pre-extraction procedure to obtain clean blanks (PCBs) requires several consecutive extractions.[3, 6]
Tenax	polymer (60/80 mesh) of 2,6-diphenyl-*p*-phenylene oxide	100%[5]	"	Soluble in polar solvents. Like XAD-2 the resin can be partially decomposed by NOx in the air stream.[6]

[1] Giam *et al.* (1975)
[2] Doskey and Andren (1979)
[3] Bouchertall and Duinker (1986)
[4] Bidleman and Olney (1974)
[5] Billings and Bidleman (1983)
[6] Hanson *et al.* (1981)
[7] Duinker and Bouchertall (1989)
[8] Wittlinger and Ballschmiter (1987)
[9] Thain (1980)

the adsorbent/filter setup in Hi-Vol air samplers has now become well established for the sampling of airborne SOCs, and have been used successfully for the sampling of PCBs, PAHs and PCDD/Fs (Manchester-Neesvig and Andren, 1989; Eitzer and Hites, 1989; Holoubek *et al.*, 1992). In this thesis all air sampling was carried out using a Hi-Vol air sampler incorporating PUF adsorbent (2 plugs) behind a glass fiber filter (GFF). GFFs were found to have a greater filtration efficiency of submicron particles (99.1 - 99.9 %) than cellulose filters (98.0 %) (John and Reischl, 1978). PUFs were selected because of their good vapour collecting efficiency, the relative ease of pre-clean up, their cheapness and availability.

2.6.5 Sampling artefacts of the filter/adsorbent system

By separating the particulate component on the filter and the vapour component on the adsorbent, the vapour/particulate ratio (V/P) can be operationally defined as the adsorbent/filter ratio (A/F) (Bidleman, 1988). Depending on how temperature and vapour concentrations change during the collection period, volatilisation losses (known as blow-off) or adsorption gains of SOCs to the particles on the filter may take place (Van Vaeck *et al.*, 1984; Bidleman, 1988; Hart *et al.*, 1992). The A/F ratio can be positively biased relative to the true vapour-particle partitioning ratio if adsorption of vapour phase molecules onto the filter or onto particles collected on the filter is the dominant artefact, or it can be negatively biased by blow off of sorbed compounds off the particles. Blow off losses are considered to be the

more dominant process (Van Vaeck *et al.*, 1984; Bidleman, 1985). Chemical change can also occur for molecules collected on the filter, degradation of benz[a]pyrene (a high MW, 5-ring PAH) has been observed due to the reaction with gas phase components such as O_3 and NO_2 (Peters and Seifert, 1980; Pitts *et al.*, 1980). These artefacts cause A/F to differ from the true V/P. Alterations to the Hi-Vol system have been carried out to examine these problems (Van Vaeck *et al.*, 1984; Hart *et al.*, 1992). Adsorption of vapour phase molecules onto the filter matrix can be partially compensated by using two filters, one behind the other; the amount collected on the back filter is subtracted from the amount collected on the front filter to correct for the filter's vapour phase adsorption (Hart and Pankow, 1994). Van Vaeck *et al.* (1984) developed an Integrated Gas Phase-Aerosol Sampling System (IGPHASS) which incorporated (1) a cascade impactor (which fractionates collected particulate according to size) backed by an adsorbent Tenax cartridge, (2) a conventional Hi-Vol sampling head (filter/adsorbent [Tenax]) and (3) a specialised (vapour phase only) sampling head. This specialised sampling head was designed to eliminate the particle blow-off contribution made to the vapour phase component by having ten separate GFFs aligned above a single Tenax cartridge (via 10 tubes). During the course of a sample day there would be 10 changes to a fresh, unloaded, filter by closing one tube and opening another. In using this combined system the overall atmospheric concentration is evaluated and the concentrations in the various particle sizes and the true vapour phase concentrations can be determined. Of significance, is that the degree of blow off in a conventional

sampling head was deduced for a series of organics including PAHs. Van Vaeck *et al.* (1984) concluded that (1) blow off contributions decrease gradually with increasing molecular weight within a compound class. (2) Blow off from particles is temperature dependent; for the PAHs, significant blow off is found for the benzofluoranthenes in the summer and yet only up to the chrysene/benz[a]anthracene pair in the winter. (3) PAH blow off is enhanced by higher sampled air volumes (1000's m^3). (4) The blow off artefact is negligible for low molecular weight, volatile, PAHs because their vapour-particulate distribution is shifted to the vapour phase. Blow off artefact is negligible here because of the minor concentrations on the particles. Likewise the high MW PAHs show little blow off due to their dominance on the particulate phase. The blow off artefact is most marked for intermediate compounds which have roughly equal distributions between the vapour and particulate phases, in the case of the PAHs this is from pyrene to chrysene.

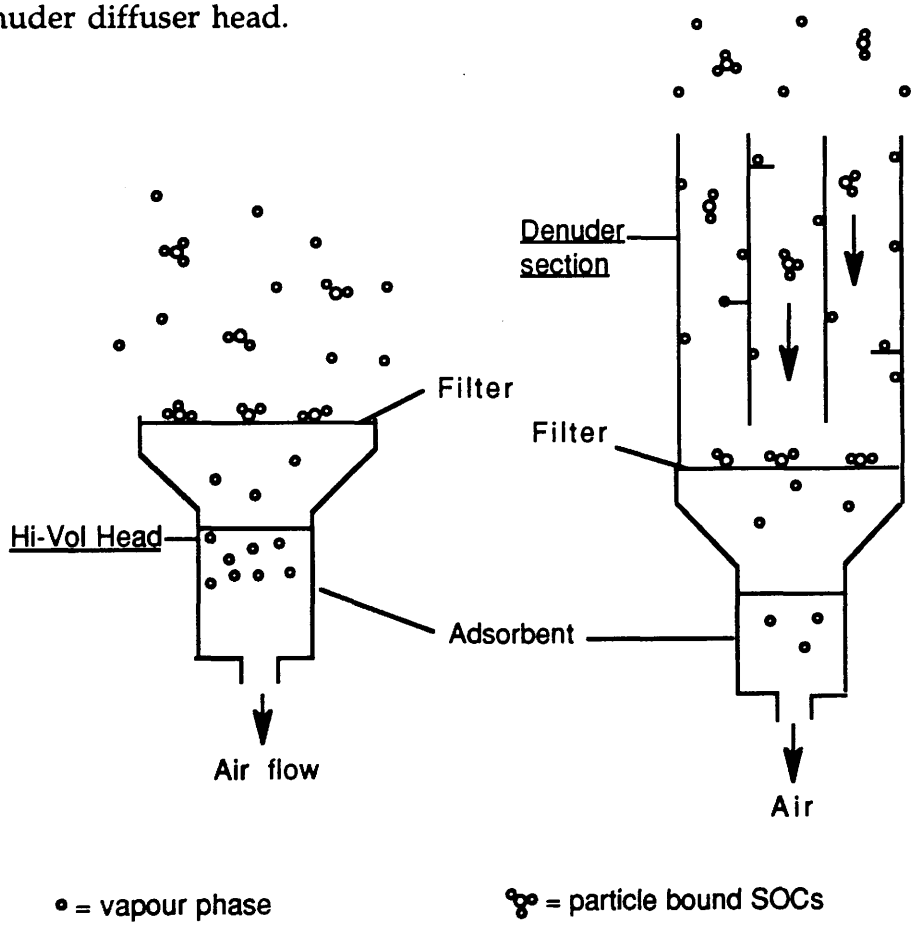
An important aspect in using solid adsorbents to sample vapour phase SOCs is to assess the collection efficiency of the adsorbent involved. The collection efficiency of a solid adsorbent bed depends on the volatility of the organic compound being sampled and the total volume of air pulled through the bed. Simon and Bidleman (1979) found the PCB retention volume for PUF adsorbent by introducing a PCB spike onto the top of fifteen 1 cm thick PUF slices and eluting with a stream of clean air. The PCB moved through the column as chromatographic bands, with the band penetration clearly related

to air volume. Therefore sample breakthrough must be taken into account when selecting an adsorbent type, the compounds to be sampled and the volume of air to be passed through the adsorbent. The most effective way to check for sample breakthrough in the field is to separately analyse front and backup adsorbent traps. Billings and Bidleman (1983) found that PUF (1 plug, 7.6 cm long) efficiently collected heavy PCB (Aroclor 1254), chlordane and toxaphene effectively over an entire air volume range of 300 - 1600 m^3 with negligible breakthrough to the backup trap. The lighter PCB mix Aroclor 1016, was more efficiently collected by Tenax than PUF, but breakthrough out of the backup PUF was not evident. This mixture of di- and trichlorobiphenyls was effectively retained within a 2-plug PUF trap. The air sampling work presented in this thesis was carried out with a 2-plug PUF trap. Breakthrough of a PCB spike was not evident when the first and second PUF (after a 500 m^3 of air) were analysed separately in a break-through experiment discussed in Chapter 6.

Further modification of the filter/adsorbent system has come about with the development of the diffusion denuder to avoid the sampling artefacts of the Hi-Vol. Particulate and vapour SOCs are pulled through the denuder section, which is a series of parallel tubes or concentric cylinders that have walls coated with a solid adsorbent or a high boiling liquid. Vapours diffuse to the denuder walls and are stripped from the air stream. Particles diffuse slowly compared with the residence time of air in the denuder and pass through to be collected by a filter behind the denuder. SOCs are partially

stripped from the particles on the filter by the vapour free air stream, but the volatilised SOCs are collected in an adsorbent trap behind the filter. Thus the sum of SOCs on the filter and backup trap represents the particle bound fraction in ambient air. An illustrative diagram of a diffusion denuder and a Hi-Vol sample head are presented in Figure 2.3. Complete removal of vapours by the denuder is essential to the success of this method.

Figure 2.3 SOC sampling using a standard Hi-Vol sampling head and a denuder diffuser head.



The drawback of diffusion denuders is that they can only sample at fairly low rates (1 - 20 L/min) in relation to Hi-Vols (100 - 1000 L/min), (Coutant *et*

al., 1992; Lane *et al.*, 1992). The low flow rate is required to maintain both laminar flow and a suitable residence time in the denuder tube to allow diffusion of vapour phase molecules to the walls. Comparisons of a denuder sampler with a filter/PUF sampler (low volume) showed no significant differences (vapour and particle) in total PCB concentrations (Krieger and Hites, 1994). Interestingly, the heats of desorption calculated from the vapour-particle partitioning of 14 PAHs, measured with a denuder sampler (Krieger and Hites, 1994), were comparable (r = 0.81) to those sampled with a standard filter/PUF Hi-Vol set up (Yamasaki *et al.*, 1982). This shows that the Hi-Vol A/F ratio is a reasonable indicator of the true atmospheric V/P ratio for PAHs.

2.6.6 Deposition collection

In Section 2.5 the various depositional pathways for SOCs are presented; basically they can be split into wet and dry deposition. Deposition sampling has developed to sample either one or the other, or both together as bulked deposition. Galloway and Likens (1976) recommended that inert surfaces be used in the collection of organics in precipitation. Glass, stainless steel, aluminium and Teflon™ have all been used as collecting surfaces (Likens *et al.*, 1983; Mazurek *et al.*, 1987; Meyers and Hites, 1982; Strachan and Hunealt, 1984). Plastics other than Teflon™ are not suitable for trace organic work because they may introduce contamination into the sample or cause losses by adsorption to the plastic surface. Even with inert surfaces one of the

problems associated with deposition collectors is that collected compounds can be lost due to adsorption on the sides of the funnel and collecting vessel (Franz *et al.*, 1991).

2.6.7 Wet deposition

Examples of wet deposition studies on PAHs, PCBs and PCDD/Fs are provided by McVeety and Hites (1988), Murray and Andren (1992) and Eitzer and Hites (1989) respectively. Basically wet deposition samplers consist of a collecting vessel (glass) connected to a collecting surface (usually funnel shaped), via a tube to provide elevation. This elevation promotes the collecting surface away from local topographical irregularities and also prevents insplash from surrounding surfaces (Sevruck, 1993). Wet only samplers are often incorporated with an automatic lid which opens at the onset of a precipitation event (rain sensor) and closes at its cessation (Brun *et al.*, 1991). To reduce adsorption losses to the collecting vessel a solid adsorbent can be added either to the top of the collecting vessel or incorporated in the tubing, upstream of the main vessel. Thus compounds are scavenged directly from the precipitation as they enter the collecting vessel and losses due to adsorption or volatilisation (from the collected sample) are kept to a minimum. XAD and Tenax have been used as the adsorbent in several precipitation studies (Strachan and Huneault, 1984; Pankow *et al.*, 1984). An automatic rain sampler with a large Teflon-coated collection surface (0.89 m^2) was developed by Pankow *et al.* (1984). This

surface was efficiently closed upon the cessation of a rain event, the lid (Teflon coated) being operated by a motor, controlled by a rain sensor. No portion of the sampler was above the collection surface, dry deposition which may have accumulated on the exterior of the sampler could not be splashed onto the Teflon sheet. This sheet was formed into a funnel shape, the collected water ran down into a glass jar, where, upon reaching a certain level, was pumped through a series of Tenax Adsorption/Thermal Desorption (ATD) cartridges for analyte extraction. This sampler design has been successfully used by Czuczwa *et al.* (1988) and Murray and Anders (1992). Horstmann and McLachlan (1994) found that if only the water in the collecting vessel of a simple rain collector were to be analysed then the wet deposition of PCDD/F would be under estimated by a factor of four, due to adsorption losses to the funnel and the vessel walls. They developed a sampler in which the precipitation first passes through a glass fibre filter, which removes much of the particulate material, and then through an XAD cartridge where the compounds were extracted. A solvent sprinkler system was later developed to rinse the funnel immediately after a rain event to remove adsorbed compounds.

Not all wet deposition is efficiently sampled by the apparatus mentioned above. For example, several studies have sampled fog for pesticides (Glotfelty *et al.*, 1987), PCDD/Fs (Czuczwa *et al*, 1989) and PAHs (Leuenberger *et al.*, 1989) using 'strand' collectors which rely on wind blown drops, or condensation of water droplets onto a mesh, or closely packed vertical

filaments. Capel *et al.* (1991) incorporated the use of Teflon™ screens (wire lattice) to sample urban fog events. Air was pulled onto the screens by means of a fan (the air flow was smoothed by a baffle), the fog droplets condensed onto the screens and ran down onto a Teflon coated tray, and then into a glass collecting vessel for subsequent analysis.

2.6.8 Dry deposition

The dry depositional pathway of SOCs is an important contributor to terrestrial and aquatic surfaces, earlier methods of sampling involved leaving oil coated screens facing into the wind to trap particles. McClure and LaGrange (1977) and Heesen *et al.* (1979) collected dry deposition on mineral oil-coated plates. After the exposure period the oil was scraped off and analysed. The use of coated surfaces to collect dry deposition is preferred, as dry surfaces can result in re-suspension of previously deposited material and lead to underestimations in the amount of actual deposition (Christensen *et al.*, 1979). Murphy (1981) suggested that the use of non-polar oils actively scavenge vapour PCBs from the air as well as particles and hence over estimate dry deposition. He recommended the use of polar fluids to cover inert surfaces for deposition sampling. Holsen *et al.* (1991) erected Mylar covered PVC plates with sharp leading edges to collect dry deposition of PCBs in Chicago air, the Mylar was covered with a high MW polar grease (Apezion L) to trap airborne particulates.

2.6.9 Wet and dry (bulk) deposition collectors

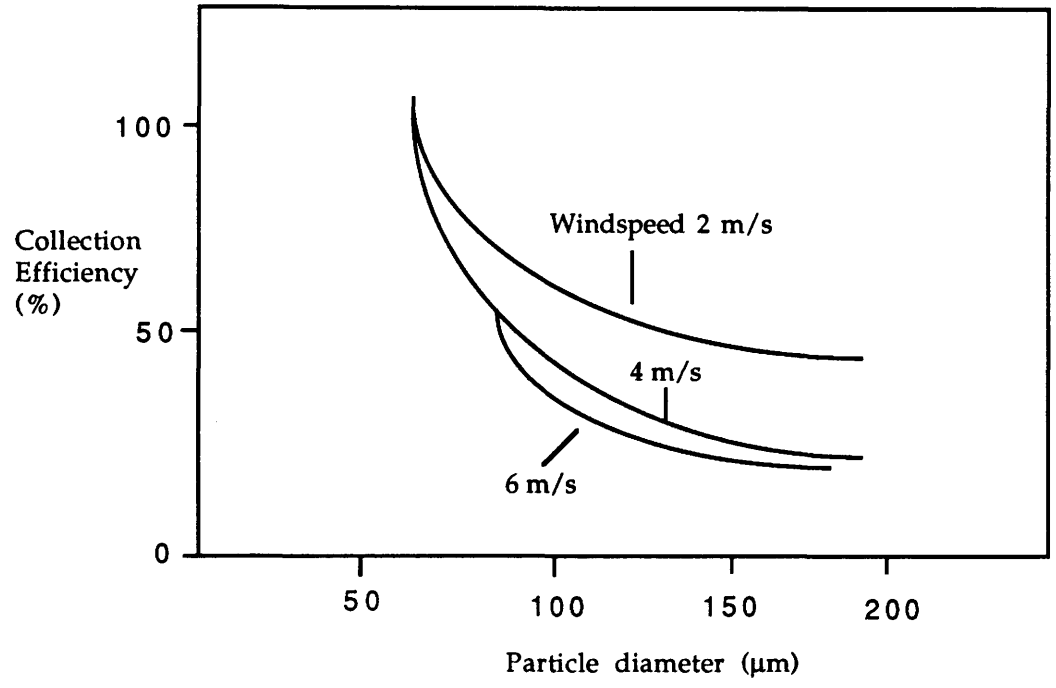
If a net depositional flux of a compound is required, then both wet and dry deposition need to be collected. Gardner (1993) developed a sampler that collected both wet and dry deposition of PAHs separately. The wet deposition was collected via a stainless steel funnel into a 5L glass collection vessel. With cessation of a rain event the funnel was covered over automatically by the dry deposition collector. This was basically a polished stainless steel tray (0.307 m^2) with a 3 cm lip. The tray was filled with water, the level maintained by a 1L constant head pressure water reservoir. The use of water as a dry deposition collecting surface was used in this case as a surrogate for a lake surface. Christensen *et al.* (1979) found that pans filled with water or ethylene glycol-water collected 1.5 - 3 times as much organochlorine dry deposition as did a dry surface (where deposition could be re-suspended). Deposition collected for this thesis was bulked (both wet and dry) using a deposition gauge provided by Warren Spring Laboratory (Clayton *et al.*, 1992). This sampler was similar to wet deposition samplers used by McVeety and Hites (1988), except that an automated cover was excluded so that dry deposition could be sampled between rain events. Basically the gauge consisted of a 5 L glass collecting vessel connected to an elevated Teflon coated aluminium frisbee (0.04 m^2) via 1.75 m Teflon tube; any deposition would therefore only come into contact with Teflon or glass. The glass vessel was positioned in a lagged plastic container fitted with a thermostat to prevent freezing (a diagram is presented in Figure 3.1 in

Chapter 3).

2.6.10 Sampling artefacts of deposition collectors

An area of uncertainty in sampling lies in the efficient collection of deposition, in particular the quantitative collection of precipitation. Any exposed surface of the sampler will disrupt the air flow around it and, depending on design, could result in the inefficient collection of atmospheric aerosol. Sevruk (1993) reported that the deformation of the wind field above the precipitation gauge orifice increased windspeed and turbulence, resulting in small particles falling leeward of the precipitation gauge. The use of a wind shield helps to reduce the wind speed over the collecting surface, hence increasing the collection efficiency. Sampler design is important for maintaining collection efficiency, in particular the collecting surface thickness, shape and rim height. The depth of the collecting surface has been found to effect particle collecting efficiency (Hall and Waters, 1986). Most collectors are funnel shaped with a large depth; Hall and Waters (1986) found that the particle collecting efficiency was greatly improved when a shallow collecting gauge was used. An inverted frisbee was found to have the right depth and aerodynamic design to be an efficient collector over other designs [(i) simple flat disc, (ii) British Standard Deposit gauge]. Figure 2.4 shows the collection efficiency (%) of selected particle sizes over various windspeeds for the 'inverted frisbee' design.

Figure 2.4. Particle collection efficiency (%) for the frisbee over various wind speeds (Hall and Upton, 1988).



Due to its efficient collecting properties a spun aluminium Teflon coated 'inverted frisbee' was selected for the collecting surface of the deposition samplers used in this thesis. A stainless steel wire mesh was placed into the bottom of the frisbee to reduce splash out of impacting precipitation. The inverted frisbee design was successfully used for dry deposition sampling of PCDD/Fs by Koester and Hites (1992). The artefact produced by adsorption of SOCs to the surfaces of the sampler has been recognised and has led to the use of inert materials, in particular Teflon because of its low friction, non static properties. However, recent work has shown that Teflon surfaces adsorb PCBs (Murphy and Sweet, 1994). In the comparison of a stainless steel collecting surface to a Teflon coated surface Murphy and Sweet (1994) found that multiple rinses of the Teflon surface with methanol showed high

amounts of PCBs even in the third methanol rinse. Furthermore, rinses with methanol while the surface was isolated from the atmosphere with a polyethylene glove bag, also showed the presence of high amounts of PCBs. This adsorbing problem with PCBs can be put down to the wetting properties of Teflon. Precipitation beads on its surface and only runs off when sufficiently large droplets are formed. During precipitation events of low intensity the water remains in contact with the Teflon for long periods of time. In addition, solvents will also bead when used to rinse the surface, or if large volumes are used there will be sheet-flow resulting in a short contact time. These complications caused by the wetting surface of the Teflon make it difficult to reproducibly rinse it's surface. These problems with Teflon were only highlighted after the TOMPS sampling campaign was underway. Nevertheless, the derived depositional fluxes were comparable to other studies, details of depositional fluxes being presented in Chapter 8.

Chapter 3

Methods and materials

3.1 Introduction

This chapter describes the protocol for ambient atmospheric sampling and deposition collection for a long term sampling programme of urban and rural air. Included in this Chapter are the analytical procedures and the quality assurance/controls for data generation.

3.2 Sampling protocol

The Toxic Organic MicroPollutants Survey (TOMPS) was initiated and funded by the Department of the Environment (DoE) and administered by the former Warren Spring Laboratory. Administration is now carried out by the National Environmental Technology Centre. The aim of this programme is to measure ambient atmospheric concentrations and deposition rates of selected semi-volatile organic contaminants within several urban sites, later extended to a rural or background site.

Four urban sites were included in the study: London, Manchester, Cardiff and Stevenage. The rural site was located at Hazelrigg, near the Bowland fells in north Lancashire; details of the sites are presented in Table 3.1. At the

Table 3.1 Details of the sample sites* and operation.

Site	Location	Operation and analysis
London	On the roof of the Department of the Environment Headquarters, Westminster, central London.	Operated and maintained by the Warren Spring Laboratory. Analysis of PAHs and PCBs by GC-MSD (Analysis of PCBs restricted to 8 congeners:- IUPAC Nos. 28, 52, 77, 110, 101, 153, 138, 180).
Cardiff	On the roof at the University of Cardiff, city centre.	Operated and maintained by ReChem Environmental Research. Analysis carried out by Lancaster University using HPLC-fluorescence detection for PAHs and GC-ECD for PCBs (conformation by GC-MSD).
Manchester	On the roof of the law courts in Manchester city centre.	Operated and maintained by Lancaster University. Analysis of PAHs and PCBs also carried out by Lancaster University.
Stevenage	On the roof of Warren Spring Lab located near the centre of this light industrial town.	Operated by Warren Spring Lab. samples analysed by WSL as well.
Rural site (Hazelrigg)	Ground level at the environmental field station of Lancaster University near the Trough of Bowland, north Lancashire.	Operated by Lancaster University. Samples analysed by Lancaster University.

* Detailed maps of the urban site locations are given in Clayton *et al.* (1992).

four urban sites the sampling equipment was located at roof top height, approximately 25 m high. Here the air was well mixed in relation to street level and well away from localised sources. At the rural location the sampling equipment was placed at ground level. As a prerequisite to site selection all air samplers and deposition gauges were at least 2 m away from any obstruction, the sites were selected to be away from any vents, flues or chimneys. Plates 3.1 and 3.2 show the Manchester and Hazelrigg sampling sites respectively.

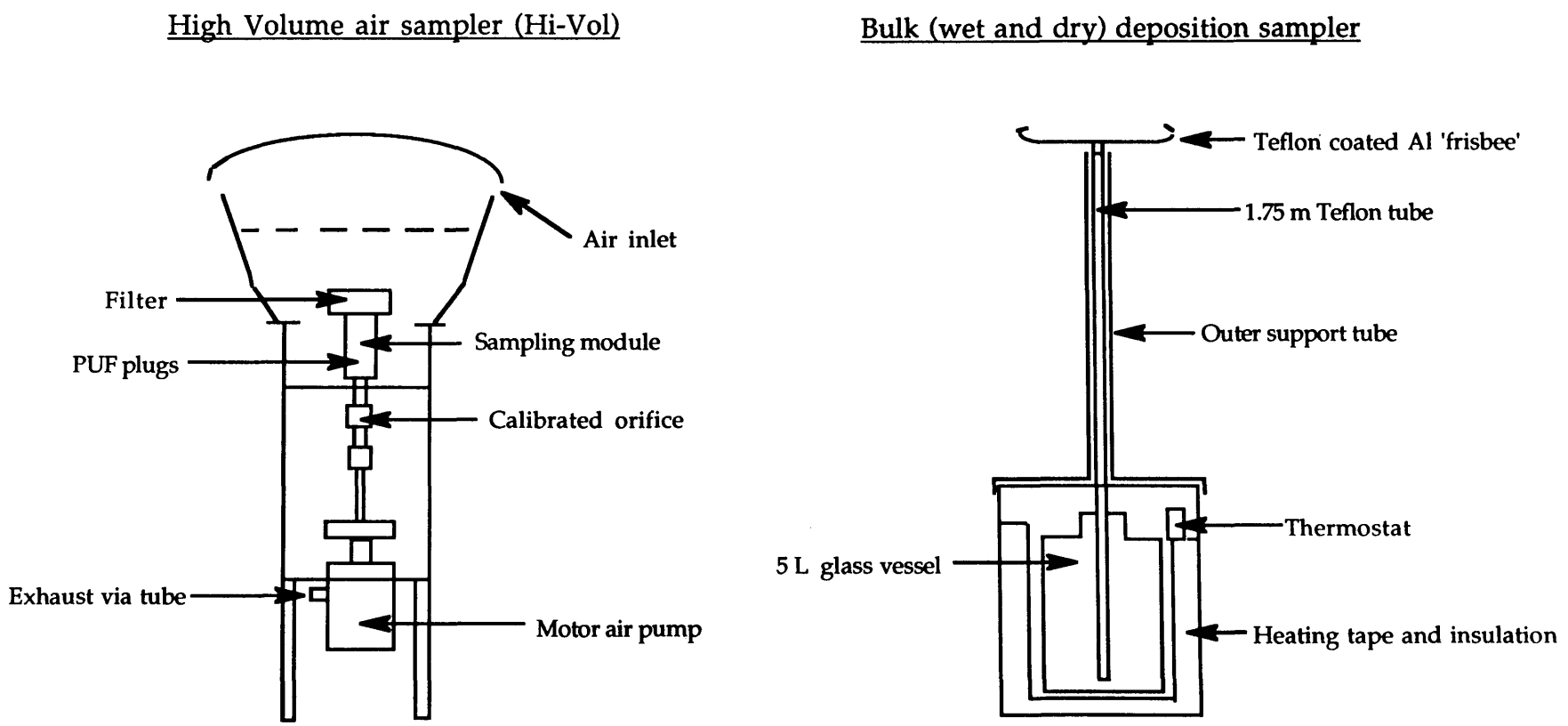
3.2.1 High-Volume Air Sampler

Air sampling was undertaken using a General Metal Works Inc. (OH, USA) PS-1 High Volume Air Sampler (Hi-Vol). These were of aluminium construction and consisted of a sampling head supported on a body holding the motor (pump), Magnehelic manometer gauge and timer unit (an example of a Hi-Vol is displayed in Figure 3.1). Prior to installation at a working site the instrument was first calibrated using a U-tube manometer. A calibration curve displayed in Figure 3.2 depicts air flow (m^3 min^{-1}) against air pressure settings (inches H_2O). The volume of air aspirated is calculated from the length of time that the Hi-Vol is running, and the mean aspiration rate over this period. During a sample period the manometer setting would fall according to the particulate loading on the filter. The mean value between the start and finish manometer reading is used to derive the flow rate from the calibration curve. Although this is a simple

Plate 3.1 Manchester TOMPS sampling site (roof top location), featuring a Hi-Vol and two deposition collectors.

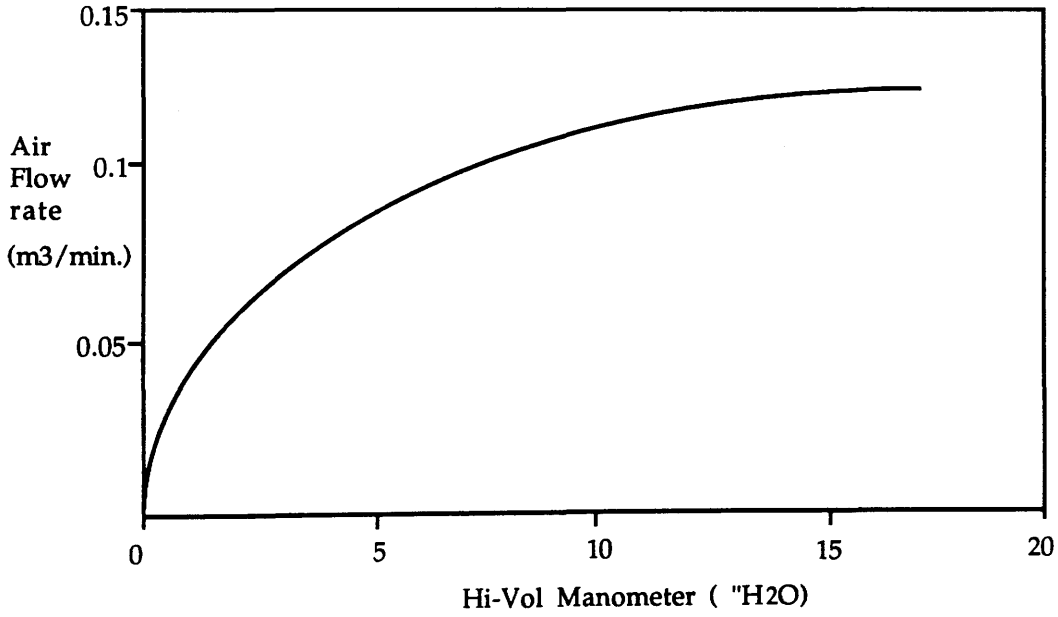
Plate 3.2 Hazelrigg, TOMPS rural sampling site, situated near Lancaster in NW England.

Figure 3.1 Diagram of Hi-Vol air sampler and deposition collector used at the sample sites of this study.



way of finding the volume of air aspirated, it assumes that the drop off rate is linear. For a short sampling period this is acceptable, but for longer periods of over a week, then this method can lead to inaccuracies in calculating the volume of air actually sampled. To improve the accuracy, the manometer reading was recorded every 100 seconds using a Grant Instrument Data Logger (8-bit Squirrel), linked to a pressure transducer. The information was down loaded from the 'Squirrel' to a computer were the change in manometer reading could be observed with time, and the volume of air aspirated could be accurately determined.

Figure 3.2 Calibration curve for Hazelrigg Hi-Vol.



3.2.2 Deposition gauge

The deposition gauge consisted of a 5 L glass collecting jar which was kept in a lagged plastic container with a thermostat to prevent freezing. Inserted

into the neck of the jar was a 2 m Teflon tube onto which a Teflon-coated inverted metal frisbee deposition collecter was fitted. The Teflon tube was shrouded with a plastic pipe which was connected to the lid of the plastic container. This gave support to the whole structure and protected the tube and the jar. A diagram of the deposition gauge is presented in Figure 3.1.

3.2.3 Sampling procedure

Sampling commenced at the four urban sites in January 1991 and is ongoing. This thesis will discuss data up to the end of December 1992. Sampling ceased at the Stevenage site in April 1992. The rural sample site started operation in December 1992 and is also ongoing. Data will be presented here for the first year (i.e. to the end of December 1993). Appendix 1 presents the sample week numbers and corresponding dates for each site. Data from all the sites is publically available (Clayton *et al.*, 1992). Analysis for three of the sites was done at Lancaster (Manchester, Cardiff and Hazelrigg) and forms the main focus of this work. However, data from the other sites, London and Stevenage, have also been included for comparative purposes.

At each site an air sample was taken over a seven day period. The Hi-Vol was set at a specified aspiration rate (manometer - 10 "H_2O) and the timer unit set to run the motor for 30 minutes in every hour. This resulted in approximately 500 m^3 of air being sampled each week. This volume was selected as appropriate due to previous studies conducted in both urban and

rural atmospheres where the sampling volumes were in the order of hundreds of m^3 for PAHs (Arey *et al.*, 1989; Foreman and Bidleman, 1990), PCBs (Bidleman and Olney, 1974; Doskey and Andren, 1981) and PCDD/Fs (Eitzer and Hites, 1989). PCBs and PAHs were analysed on alternate weeks to the PCDD/Fs, so that over the period of one year, at any one site, 26 samples were analysed for PCBs and PAHs and 26 for PCDD/Fs.

Total deposition was collected once a month with no differentiation between wet and dry deposition. This resulted in 12 monthly samples each year. Each sample consisted of a 5 L jar containing water and particulate matter, a quarter PUF plug used for pulling through the Teflon tube in order to clean it, and 100 mL of pesticide-grade hexane used to rinse the frisbee and the tube.

3.3 Analytical protocol

3.3.1 Pre-sampling preparation

Each Hi-Vol was equipped with a sampling module. This module held a circular 10 cm diameter Whatman GF/A filter (pore size 1.5 μm) and two in line polyurethane (PUF) foam plugs (vapour trap). The module could be removed as a single unit to prevent handling contamination. The filters were baked at 450 ^oC for 14 h prior to module construction and gravimetrically weighed after cooling. The PUF plugs were pre-extracted in

dichloromethane (DCM) for 16 h, loosely wrapped in aluminium foil, and air dried in a clean air cabinet. The dried PUF plugs were placed into a pre-cleaned glass sleeve which fitted into the module behind the filter head. An aluminium plate was screwed into place over the exposed filter, and aluminium foil was wrapped over the rear air vent to avoid contamination when the modules were being transported.

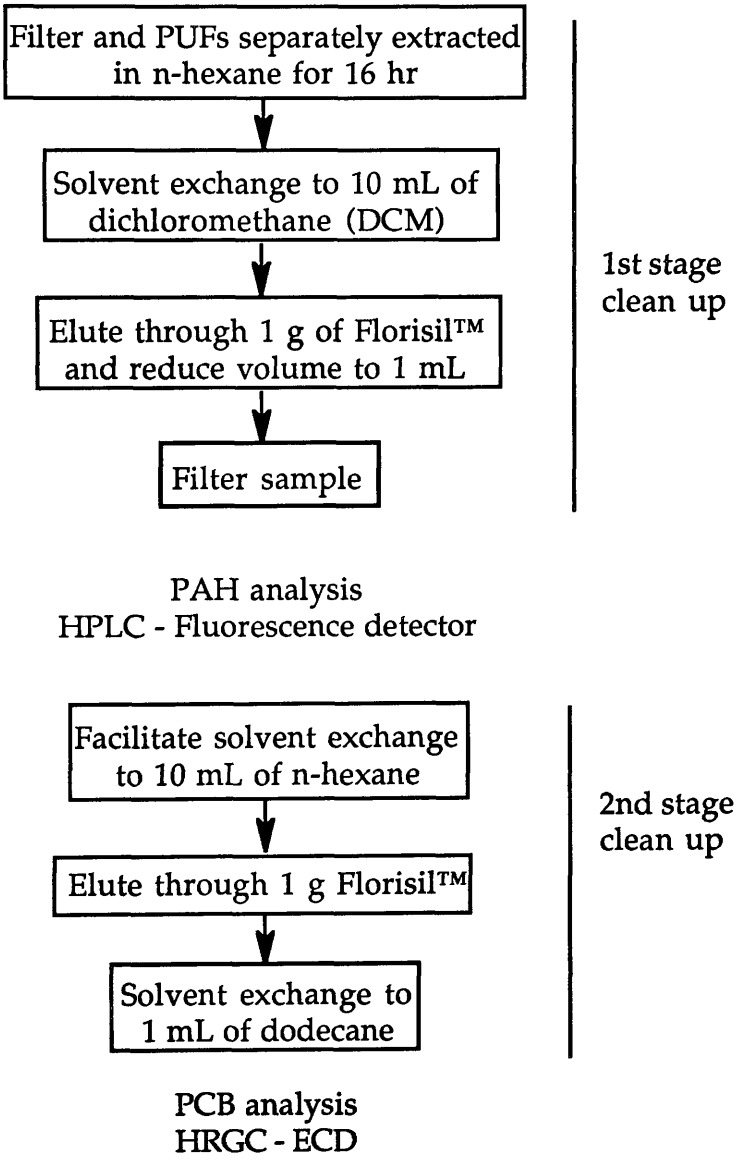
The 5 L jar of the deposition sampler was rinsed with DCM and MilliQ® water prior to its transport to the field. 25 mL of 5% copper sulphate solution was added to the jar as an algicide. Similarly, the inverted metal frisbee and anti-splash mesh were thoroughly rinsed in DCM. A plastic cover was taped over the frisbee when in transport to and from the field or when in storage.

3.3.2 First stage sample clean up

Air samples. A schematic diagram showing the steps taken for atmospheric sample clean up is presented in Figure 3.3. Basically this involved solvent extraction followed by solid phase extraction using open column adsorption chromatography to remove interfering contaminants from the analyte.

The sampling module was dismantled in the clean air cabinet and the PUFs were wrapped separately in aluminium foil. The filter was placed into a desiccator for 24 h and then re-weighed to obtain the mass of the collected particulate or total suspended particulate (TSP). TSP concentrations ($\mu g\ m^{-3}$)

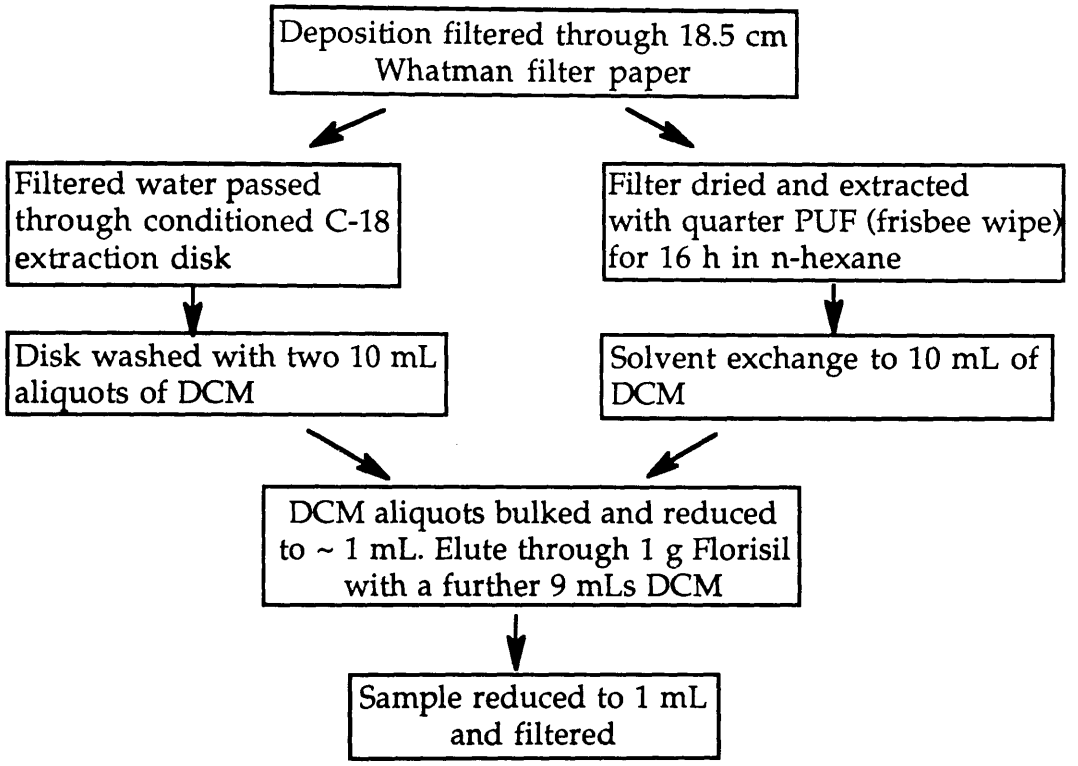
Figue 3.3. Flow chart showing the various stages in sample clean up and analysis of air samples.



are presented for the Manchester, Cardiff and Hazelrigg sites in Appendix 1. The filter was wrapped in aluminium foil and placed into a plastic bag, along with the PUF plugs and stored at 4 °C prior to analysis. Samples were stored for no longer than 1 month before analysis. Kloster *et al.* (1992) found sample integrity to be preserved for PAHs after 4 months of storage at room temperature. The PUF plugs and the glassfibre filters were extracted separately in a 6-place Büchi soxhlet using pesticide-grade hexane (Rathburns Ltd.). The extraction was run for 16 h, before being taken down to near dryness and removed from the soxhlet. Extracts were then quantitatively transferred to 10 mL glass vials, using several DCM washings (to facilitate solvent exchange). The volume was then gently reduced to 1 mL on a heating block (at 35 °C) under nitrogen. The 1 mL extract was then passed through 1 g of Florisil™ (60-100 mesh) packed into a glass pasteur pipette and eluted with 9 mL of DCM. This volume was then reduced again to 1 mL, passed through a 0.5 µm syringe filter and transferred to Hewlett Packard (HP) 2 mL chromatography vials for analysis of PAHs.

Deposition samples. A schematic diagram showing deposition sample clean up is presented in Figure 3.4. The first step involved filtering the water through a 18.5 cm Whatman paper filter to remove large particulate material. This filter was carefully air dried in a clean air cabinet and soxhlet extracted along with a quarter PUF plug used to wipe the interior of the metal frisbee. PAHs and PCBs were extracted wih pesticide-grade n-hexane for 16 h. Like the air samples, the deposition samples underwent a solvent

Figure 3.4 Flow chart showing the various stages in clean up and analysis of deposition samples.



exchange to DCM after soxhlet extraction. The filtered water was conditioned with 5 mL of methanol/L of water. This was then filtered through a pre-treated C-18 Empore disk which retained organic compounds from the water sample. The C-18 disk was subsequently washed with two 10 mL aliquots of DCM; these were added to the DCM from the filter paper and PUF extract and evaporated under a gentle stream of nitrogen. Clean up by column chromatography followed the same procedure as the air samples. In the case of deposition samples each Florisil™ column had ~0.2 g of anhydrous sodium sulphate added to the column to remove any water left within the sample.

3.3.3 Second stage sample clean up

Air and deposition samples. After PAH analysis the 1 mL of DCM extract was then gently evaporated under nitrogen and solvent exchanged back into 1 mL of hexane. This was eluted through 1 g of Florisil™ with a further 9 mL of hexane. This volume was gently evaporated under a nitrogen stream to approximately 5 mL. 1 mL of dodecane (Aldrich Inc.) was added and the volume further reduced until 1 mL of dodecane was left (evaporative losses of dodecane were considered to be negligible relative to hexane). The final extract volume of dodecane, was transferred to a 2 mL HP vial for analysis of PCBs.

3.4 PAH analysis

The analytical techniques employed in the determination of PAHs are high resolution gas chromatography (HRGC) and high performance liquid chromatography (HPLC). At Lancaster the HPLC system was used. Both these methods have different detection systems which can be utilised.

HRGC. Two types of detection systems are used for PAH analysis, the first is flame ionisation detection (FID) and the second is mass selective detection (MSD). FID has good sensitivity but responds to a wide array of organic compounds and therefore has low selectivity, resulting in chromatographic interferences. MSD is a highly selective detection method and gives unambiguous quantification of individual compounds; this detection is now widely used for PAH analysis.

HPLC. UV/Vis diode array detectors are commonly used in PAH analysis where the UV profile, scanned over a range of wavelengths, provides characteristic fingerprints for individual compounds. This system is ideal for matrices where PAH concentrations are relatively high, as it has a low sensitivity compared to the other detectors. A second detection system used in conjunction with HPLC, is Fluorescence detection, which is a highly selective and sensitive technique and can only be applied to compounds that fluoresce. Basically a PAH is exposed to UV radiation of a given wavelength and the fluorescent light emitted is detected. Due to its highly sensitive

nature this system is suitable for PAH analysis in atmospheric samples, where concentrations are low relative to other matrices.

HPLC-fluorescence detection. At Lancater PAH sample analysis was performed by HPLC with fluorescence detection. This consisted of a Perkin -Elmer LC 250 binary pump and a Perkin Elmer LS 40 fluorescence detector. A 2 μL injection of sample or standard was injected into a loop through a Rheodyne 7161 valve. Compound separation was carried out on a PhaseSep 'Spherisorb' octadecylsilane (ODS) (reverse phase) column. The mobile phase was an acetonitrile/water gradient running over 50 minutes at a flow rate of 1.5 mL min^{-1}. The gradient programme along with wavelength changes during the run time are displayed in Figure 3.5. An automated programme of wavelength changes, which optimised the sensitivity for the range of selected PAHs, was adopted. Data generated from the HPLC system was transfered by chromatography server to a VG Minichrom data handling software package (v1.60) for quantification.

Calibration standards were prepared from a stock solution containing all the PAHs made up from solids purchased from Greyhound (UK) and Promochem (UK). New standards were prepared every 2 months with standard regressions being obtained for each PAH compound over a range of relevant on-column concentrations (0.2 - 4.0 μg μL^{-1}). Sample peak areas were compared to the regression equations generated from the calibration standards.

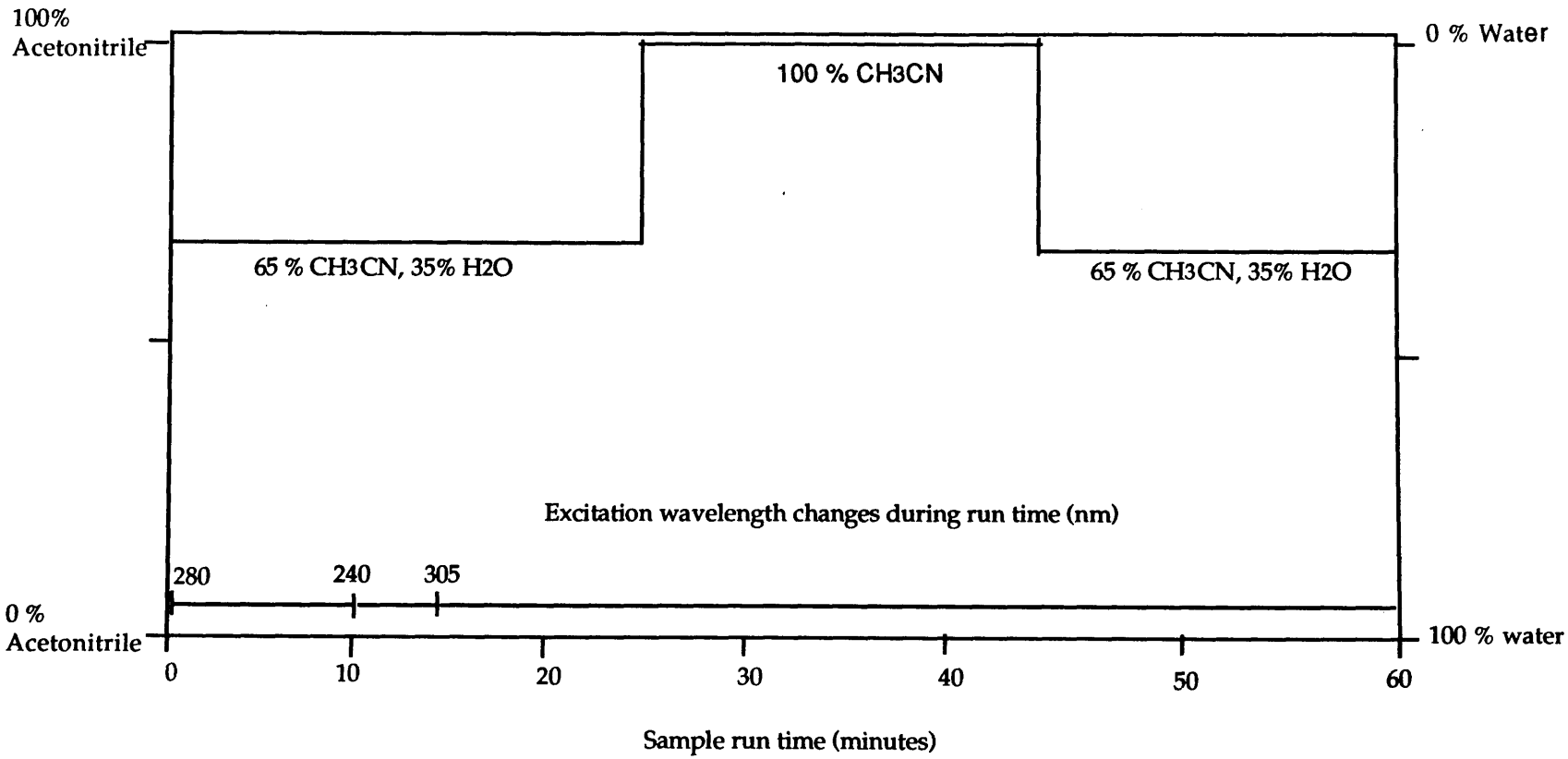

100%
Acetonitrile
0 % Water
100 % CH3CN
65 % CH3CN, 35% H2O
65 % CH3CN, 35% H2O
Excitation wavelength changes during run time (nm)
280
240
305
0 %
Acetonitrile
100 % water
0
10
20
30
40
50
60
Sample run time (minutes)

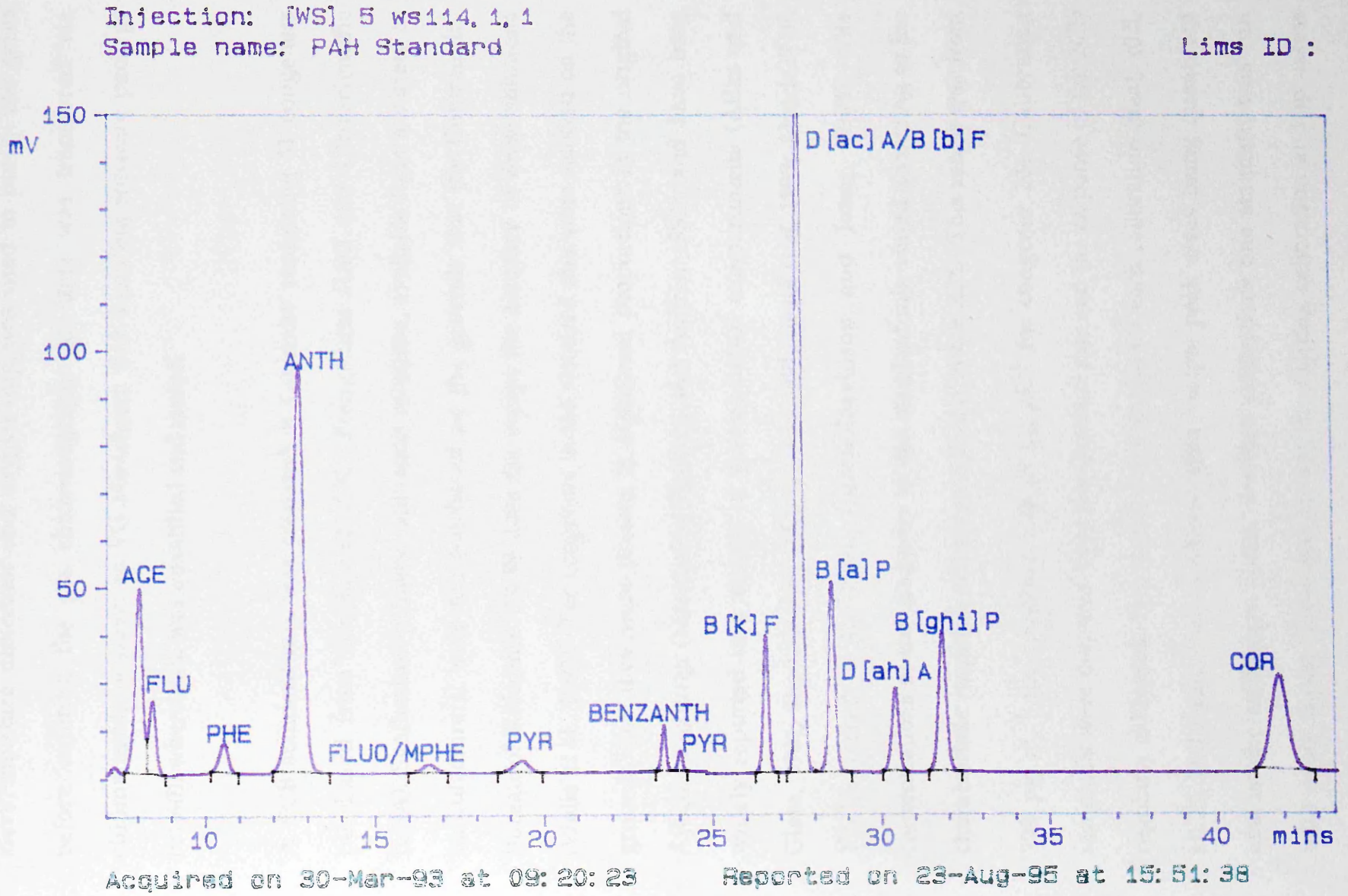
Figure 3.6 shows the chromatogram of a PAH standard (1.25 μg mL^{-1} of each PAH) with named peaks. As mentioned in Chapter 1, 15 PAHs were quantified in each sample. Co-elutions occurred between FLUO and MPHE and between D[ac]A and B[k]F and were therefore quantified together.

3.5 PCB analysis

As with all organochlorine analysis, PCB analysis is carried out using high resolution gas-chromatography (HRGC) incorporating a capillary column. PCBs are detected by either electron capture detection (ECD) or mass selective detection (MSD). The samples analysed at Lancaster were detected using ECD, with verification of several samples by MSD.

HRGC-ECD. A Hewlett Packard 5890 gas chromatograph equipped with a ^{63}Ni ECD was used for PCB analysis. Splitless injections of 1 μL were automatically injected onto a 50 m Ultra 2, 5% phenyl methyl silicone coated capillary column (i.d. 0.2 mm, film thickness 0.11 μm) via an HP 7673 auto-injector unit. The temperature programme was as follows:- 100 °C start, then 14 °C min^{-1} to 200 °C which was held for 13 min, then 14 °C min^{-1} to 280 °C and held for 8 min. The injector temperature was kept at 280 °C and the ECD at 350 °C. The carrier gas was helium maintained at a flow rate of 0.4 mL min^{-1} and the make up gas was nitrogen with a flow rate of 65 mL min^{-1}. A Chrompack (Inc.) gas filtration unit, consisting of a molecular

Figure 3.6


Injection: [WS] 5 ws114.1.1
Sample name: PAH Standard
Lims ID :
150
mV
100
50
ACE
FLU
PHE
ANTH
FLUO/MPHE
PYR
BENZANTH
PYR
B[k]F
D[ac]A/B[b]F
B[a]P
D[ah]A
B[ghi]P
COR
10
15
20
25
30
35
40
mins
Acquired on 30-Mar-93 at 09:20:23
Reported on 23-Aug-95 at 15:51:38

sieve/moisture desiccator and oxygen trap was used to purify the gases before entering the gas chromatograph. All data was transfered via chromatography server to VG Minichrom data handling software package (v1.60), where data was quantified and stored.

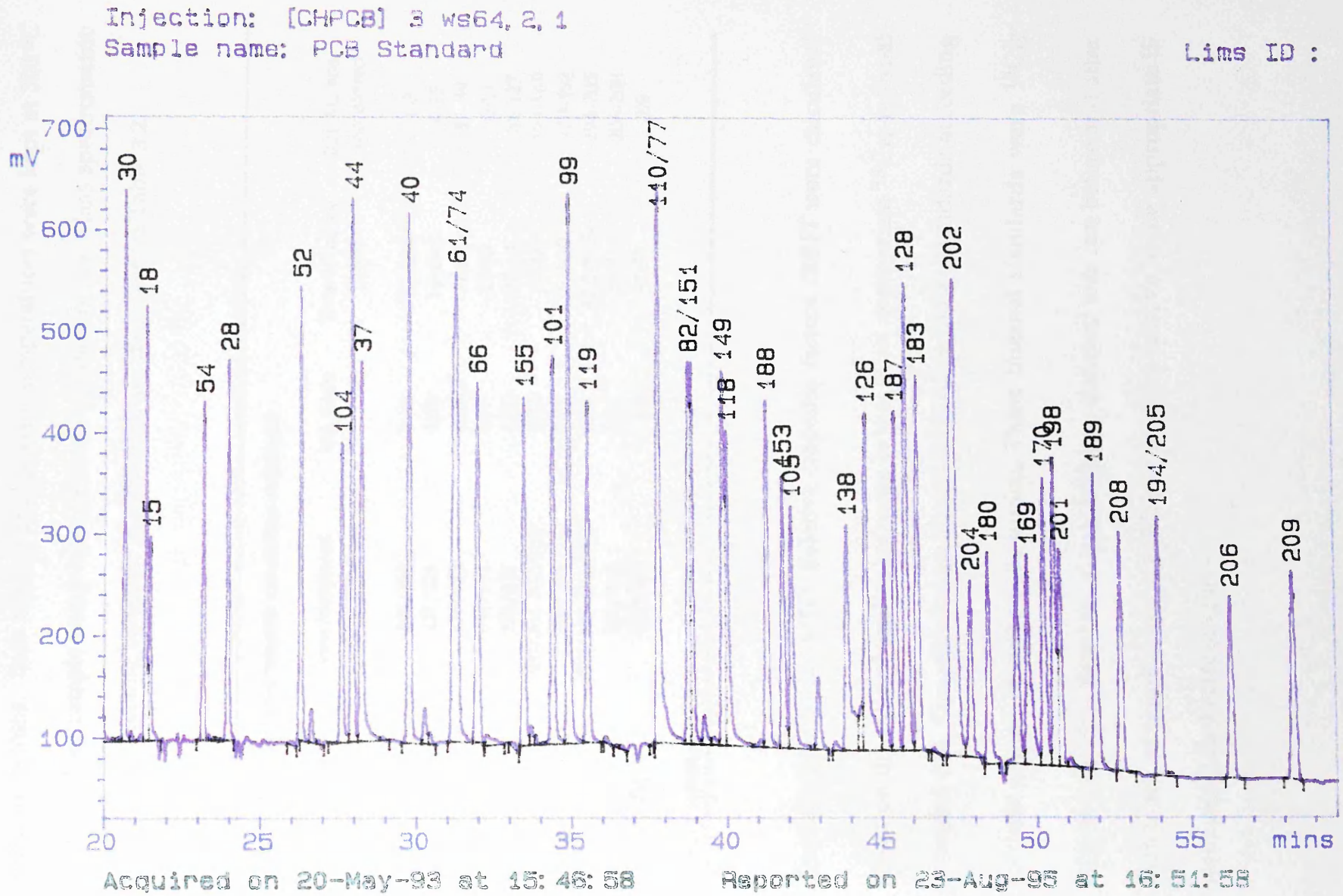
A PCB standard mix was prepared at Lancaster containing 51 congeners purchased from Greyhound (UK), Promochem (UK) and Ultrascientific (USA). Synthesised primary calibration solutions, available from a variety of manufacturers, were not purchased on the grounds that the Community Bureau of Reference (BCR) does not accept the accuracy of these solutions (Wells *et al.*, 1992). The congeners in the standard mix were selected on the grounds that they were present in significant proportions in the original Aroclor mixtures (Manchester-Neesvig and Andren 1989), and have been widely reported in a variety of environmental compartments (Atlas and Giam, 1981; Sanders *et al.* 1992; Oehme, 1991; Iwata *et al.* 1993; Alcock *et al.* 1993, Harrad *et al.* 1994, Duarte-Davidson and Jones, 1994). The concentrations of the congeners in this standard mix varied according to the characteristic response of each compound to the ECD. This range was from 598 pg μL^{-1} for congener 3 to 25 pg μL^{-1} for congener 204. Calibration standards were prepared from this standard mix and the response of the ECD regularly calibrated. Five standards were run for each calibration (neat, x0.5, x0.25, x0.10 and x0.05 dilutions) with sample peak areas being quantified against the calibration curve. Between calibrations one standard was run with every batch of samples to test the existing calibration and to assess

chromatographic response and retention time drift. Figure 3.7 displays the chromatogram of the Lancaster standard mix (neat) with peak identification.

GC-ECD analysis is a highly sensitive and precise technique. Peak area measurements have been found to be much more precise than GC-MS (Pavoni *et al.*, 1991), with the analysis of numerous samples being much easier to perform with sensitivity and precision being very good over a wide range of concentrations. However, problems can arise in peak resolution and the interferences from other halogenated compounds. Pesticides such as hexachlorobenzene (HCB) and DDT (and it's metabolites) can interfere with PCB peaks in a sample chromatogram (Pavoni *et al.*, 1991). Peak quantification is solely based on retention time using a standard, sample chromatograms therefore need to be regularly confirmed by GC-MSD.

HRGC-MSD. A high resolution gas chromatograph coupled to a mass selective detector was used to quantify the presence of PCB congeners in several samples throughout the sampling period. GC-MSD analyses were carried out on a Hewlett Packard HP5970B mass selective detector operated in selected ion mode (SIM) (unit mass resolution; EI mode, 70 eV) and interfaced to a HP5890 gas chromatograph. Congener separation was carried out on an Ultra 2, 5 % phenyl-methyl silicone coated capillary column (50 m x 0.2 mm i.d., 0.11 μm film thickness) using the following temperature programme: 100 ^{o}C for 2 min, then 20 ^{o}C min^{-1} to 140 ^{o}C, then 4 ^{o}C min^{-1} to 200 ^{o}C which was held for 13 mins. and then 4 ^{o}C min^{-1} to 280 ^{o}C , which was

Figure 3.7


Injection: [CHPCB] 3 ws64, 2, 1
Sample name: PCB Standard
Lims ID :
mV
700
600
500
400
300
200
100
30
18
15
54
28
52
104
44
37
40
61/74
66
155
101
99
119
110/77
82/151
118
149
188
105
153
138
126
187
128
183
202
204
180
169
170
198
201
189
208
194/205
206
209
20
25
30
35
40
45
50
55
mins
Acquired on 20-May-93 at 15:46:58
Reported on 23-Aug-95 at 16:51:58

held for 8 mins. Both injector and detector temperatures were kept at 300 °C with 1 μL of sample being injected in the splitless mode. Mass spectrometric conditions enabling congener qualification are displayed in Table 3.2.

Table 3.2 : Mass Spectrometric conditions employed

No. of Chlorine	Ions Monitored (m/m2+)	Ion Ratio	Time Window (min)	IUPAC nos. monitored
1	188/190	3.12	13-15.5	1-3
2	222/224	1.54	14-19.5	4-15
3	256/258	1.03	16-26	16-39
4	290/292	0.77	19-35	40-81
5	326/328	1.56	23-43	82-127
6	360/362 302/304*	1.50	27-48	128-169
7	394/396	1.03	35.5-50	170-193
8	430/432 372/374*	1.54	42.5-51.5	194-205
9	464/466	1.33	48-53	206-208
10	498/500	1.16	52-55	209

*$^{13}C_{12}$ labelled PCB

Quantification by GC-MSD. Relative response factors (RRF) were calculated based on the ratio of analyte response to that of an appropriate $^{13}C_{12}$-internal standard (IS). Congeners were quantified relative to two standards according to their degree of ortho-substitution. These internal standards were $^{13}C_{12}$ PCB 77 and $^{13}C_{12}$ PCB 169. A quantification standard was run before and after each batch of samples and the RRFs of analytes relative to the appropriate IS were calculated according to:-

$$RRF = (Anat/Ais) . (Cis/Cnat)$$

Where Anat = response of native analyte

Ais = response of IS

Cis = concentration of IS

Cnat = concentration of native analyte

The RRFs used for quantifying samples were the mean of those calculated for the two quantification standards run before and after the sample batch. Concentrations (C) of analytes in sample extracts were calculated using the following formula and adjusted for internal standard recoveries. Di- to tetra-chlorinated congeners were adjusted according to the recoveries of PCB 40 and penta- to nona- according to PCB 185.

$$C = (Anat/Ais)/RRF . (Wis/Ws)$$

Where, Wis = weight of IS added

Ws = weight of sample analysed

3.6 Quality assurance and control

"Quality assurance (QA) is a system of activities aimed at ensuring that the information provided in the environmental assessment meets the data users needs. It is designed to provide control of field and laboratory operations, results of sample collection and analytical activities" (Liabastre *et al.*, 1992).

As data for this study was collected over a long time period (ie > 1 year), it was imperative that quality assurance procedures were built into the experimental programme, to ensure the accuracy and precision of the generated data. The QA programme covered every aspect of the experimental procedure, incorporating good laboratory practice, up to date laboratory books and a series of quality controls for the air sampling procedures and analytical protocols. Separate laboratory books were kept for each sample site with dates, sample times and sample numbers logged upon each visit to a particular site.

3.6.1 Quality control

Blank samples. With every batch of air samples, blank PUF plugs and filters were extracted so that pre-sampling contamination could be subtracted to obtain true air concentrations. For deposition samples, a blank consisted of an 18.5 cm Whatman paper filter and two pre-extracted quarter PUF plugs. For the air sampling a series of field blanks were operated. This involved taking a made up sampling module to the sample site and returning it in the same manner as the real sample. Contamination from transport and on site handling could therefore be eliminated to leave a 'true' air sample. Field blanks were stored with air samples prior to analysis.

A 'rolling' system of blanks was developed for the long term sampling programme. This entailed the extraction of six replicate blanks to obtain a

mean blank value for each compound. By incorporating later blank extracts to the data set and removing the oldest ones, a running mean blank concentration for each compound was kept updated throughout the sampling duration. Mean blank concentrations are presented for the PAHs and PCBs in Tables 3.3 and 3.4 respectively.

Detection Limits. Prior to routine analysis the sensitivity of a particular analytical procedure/measurement had to be verified. This was carried out by deriving the limits of detection (LOD) for each compound. To verify the whole analytical method the method detection limits (MDL) were derived. MDL was the minimum concentration of a compound (analyte) that could be identified, measured and reported with 99% confidence that the analyte concentration was greater than zero (Liabastre *et al.* 1992). MDLs were calculated as the standard deviation of the mean blank concentration times the Student t-value at the 99% confidence limit (for six replicates the value was 3.14), thus; an individual sample had to exceed the mean blank by three standard deviations ($xs \geq xb + 3$ SD) to be considered positive. Values that fell below the LOD were considered as non-detectable (ND). LODs for PAHs and PCBs are presented in Tables 3.3 and 3.4 respectively.

Surrogate Standards. These standards are similar in both chemical composition and behaviour to the analyte of interest, but are not present in the matrix to be sampled. They are applied to the sample matrix to quantify losses of analyte in the field. An exact quantity of this standard is spiked onto

Table 3.3 PAH blank values and method detection limits for the HPLC-fluorescence method

PAH	PUF mean blank ng/PUF (SD)	LOD ng/500m3	Filt mean blank ng/Filt (SD)	LOD ng/500m3
ACE	ND	2.54	ND	2.52
FLU	ND	11.0	ND	11.0
PHE	7.10 (9.73)	36.1	ND	12.5
ANTH	14.6 (15.6)	61.4	2.67 (4.41)	15.2
FLUO/MPHE	1.63 (3.55)	12.1	ND	54.0
PYR	ND	21.0	ND	21.0
BENZANTH	1.8 (4.0)	13.8	ND	20.1
CHRY	ND	47.0	ND	47.0
B[b]F	5.41 (7.7)	28.5	5.3 (7.0)	26.3
D[ac]A/B[k]F	27.2 (12.0)	63.4	10.3 (8.0)	34.3
B[a]P	11.2 (15.1)	56.3	3.82 (5.33)	19.7
B[ghi]P	42.5 (16.0)	90.5	14.4 (10.1)	44.7
COR	34.4 (16.9)	85.1	15.4 (7.4)	37.6

LOD=Limits of detection
ND=Non detect
NA=Not analysed

Table 3.4. PCB blank values and method detection limits for the GC-ECD method

PCB	PUF mean blank pg/PUF (SD)	LOD pg/m^3	Filter mean blank pg/Filter (SD)	LOD pg/m^3
30	ND	0.40	ND	0.40
18	2.51 (1.12)	5.87	0.35 (0.40)	1.55
54	ND	0.60	ND	0.60
28*	1.85 (0.83)	4.34	0.14 (0.11)	0.47
52*	0.87 (0.77)	3.18	0.49 (0.32)	1.45
104	ND	0.40	ND	0.40
44	0.59 (0.77)	2.90	0.38 (0.22)	1.04
40	0.57 (0.43)	1.86	ND	5.00
61	0.25 (0.20)	0.85	ND	2.50
66	1.64 (1.23)	5.33	1.02 (0.12)	1.38
101*	1.06 (0.55)	2.71	0.91 (0.41)	2.14
77/110*	0.48 (0.35)	1.53	0.36 (0.41)	1.59
82/151	0.97 (0.19)	1.54	0.72 (0.14)	1.14
149	2.52 (0.29)	3.39	2.74 (0.09)	3.01
118*	0.06 (0.10)	0.36	ND	2.50
188	ND	0.40	ND	0.40
153*	1.22 (0.32)	2.18	0.81 (0.10)	1.11
105	0.44 (0.26)	1.22	0.40 (0.06)	0.58
138*	0.57 (0.32)	1.53	0.74 (0.09)	1.01
187	ND	0.48	0.36 (0.04)	0.48
183	ND	0.40	0.07 (0.11)	0.40
128	1.4 (0.58)	3.14	ND	2.50
185	ND	0.40	ND	0.40
204	1.35 (0.74)	3.57	0.60 (0.08)	0.84
180*	1.66 (0.65)	3.61	1.48 (0.03)	1.57
170	0.57 (0.40)	1.77	ND	2.50
198	ND	0.20	ND	0.20
201	0.31 (0.25)	1.06	0.11 (0.05)	0.26
208	ND	0.20	ND	0.20
194/205	0.53 (0.21)	1.16	0.29 (0.03)	0.38
206	ND	0.20	ND	0.20

* - 8 congeners analysed at all sites
LOD - Limits of detection.
ND - Non Detect.

the matrix and the recovery of this standard after sample clean up and analysis is monitored. The concentrations of the native analytes are adjusted according to the recovery of the standard. Two μg (in 5μl of hexane) of dibenz[ah]anthracene (D[ah]A) (the PAH surrogate standard) was spiked onto the GF/A filter (matrix) before module construction for air sampling, and onto a GF/A filter which was placed into the 5 L jar of the deposition apparatus. Siilarly, two PCB congeners, numbers 40 and 128, were used as surrogate spikes (100 ng of each in 10 μl of hexane) for PCBs and applied in the same manner as the PAH spike to the filter of the air sampling module and to the filter of the deposition collector. These compounds were chosen as surrogate standards on the grounds that they were not detectable in ambient air. Selection of these compounds was on the basis of previous studies indicating their absence from ambient atmospheres (Tuominen *et al.*, 1988; Manchester-Neesvig and Andren, 1989) and on preliminary samples taken in Manchester air. All 15 PAH sample concentrations were adjusted according to the recovery of D[ah]A. For the PCBs the mono- to tetra- chlorinated homologues were adjusted according to the recovery of congener 40 and the penta- to nona- chlorinated homologues according to the recovery of congener 128. Surrogate spike recoveries had to be $\geq$ 50 % and $\leq$ 120 % if a sample was to be accepted.

Matrix spikes. Before samples could be run through the extraction and clean up procedure it was necessary to quantify any analyte loss from the method. This was achieved by spiking six blank PUF plugs and six blank filters

(matrices) with a neat PAH and PCB calibration standard (matrix spike) containing exact concentrations of each analyte. Mean method recoveries were determined for each analyte from the six PUFs and the six filters. These are displayed in Tables 3.5 and 3.6(a+b) for the PAHs and PCBs respectively. Sample analytes were corrected according to the method recovery.

3.6.2 Accuracy

Accuracy indicates the degree to which the analytical measurement reflects the true value of the analyte in the sample. Accuracy was determined in two ways, firstly from the recovery of the surrogate standards and secondly from the recovery of the matrix spikes. The mean matrix spike recovery indicates the analytical performance of the extraction and clean up procedure, with sample analytes being automatically corrected against this recovery. Surrogate standard recoveries varied from sample to sample and gave an indication of analyte loss from within the field. These had to be $\geq$ 50 % and $\leq$ 120 % if a sample was to be accepted.

3.6.3 Precision

The precision of any analytical procedure is determined by running duplicate samples. This quantifies the variability in the analytical method by running replicates of the same sample. As each air sample comprised of two PUF plugs and one filter it was not possible to split a sample. A solvent

Table 3.5 PAH method recoveries from spiked PUF plugs and filters.
Data for six replicates, together with means and ranges.

PUF plugs

PAH	%rec	%rec	%rec	%rec	%rec	%rec	range	Mean %rec
ACE	35	46	49	46	44	40	35-49	43
FLU	45	52	48	49	53	43	43-53	48
PHE	60	65	69	62	64	68	60-69	65
ANTH	62	75	81	71	73	71	62-80	72
FLUO/MPHE	79	85	84	82	80	85	79-85	82
PYR	83	73	69	73	81	72	69-83	75
BENZANTH	96	88	90	91	90	94	88-96	91
CHRY	96	91	102	97	94	98	91-102	96
B[b]F	99	104	96	101	97	100	96-104	100
D[ac]A/B[k]F	98	81	83	87	86	89	81-98	87
B[a]P	98	83	79	86	89	86	79-98	87
D[ah]A	82	85	83	85	84	85	82-85	84
B[ghi]P	114	86	92	99	96	97	86-114	97
COR	105	85	86	90	90	94	85-105	92

Filters

PAH	%rec	%rec	%rec	%rec	%rec	%rec	range	Mean %rec
ACE	22	15	19	19	19	18	15-22	19
FLU	40	50	38	37	46	44	37-50	42
PHE	60	65	60	62	60	62	60-62	61
ANTH	71	68	69	69	68	70	68-71	69
FLUO/MPHE	79	85	84	78	79	79	79-85	81
PYR	59	63	56	60	62	61	56-63	60
BENZANTH	84	73	89	82	81	83	73-89	82
CHRY	85	101	90	91	93	93	85-101	92
B[b]F	91	99	99	99	98	93	91-99	96
D[ac]A/B[k]F	84	90	83	86	82	90	82-90	86
B[a]P	81	84	77	82	80	80	80-84	81
D[ah]A	95	95	90	95	93	92	90-95	94
B[ghi]P	83	98	96	95	91	90	83-98	92
COR	103	96	96	99	95	99	95-103	98

Table 3.6a Percentage recoveries of PCB matrix spike from 6 PUF plug replicates.

PCB	%rec	%rec	%rec	%rec	%rec	%rec	range	Ave % Rec
30	57	79	68	56	60	61	56-79	64
18	66	86	96	87	90	78	65-96.6	84
54	82	97	88	77	81	76	76-97	83
28	86	109	93	94	97	94	86-109	95
52	89	94	106	100	99	96	89-106	97
104	88	97	98	87	95	91	88-99	93
44	88	97	95	90	97	88	88-97	92
40	79	90	87	78	81	85	78-90	83
61	78	87	90	88	87	85	78-90	86
66	90	98	97	104	98	97	90-104	97
101	93	93	91	87	92	90	87-93	91
77/110	91	92	93	87	91	91	91-93	91
82/151	96	96	94	94	98	93	93-98	95
149	104	105	93	108	103	102	93-108	102
118	104	118	92	89	103	99	89-118	101
188	100	100	100	97	100	99	97-100	99
153	102	102	104	92	100	100	93-104	100
105	101	101	104	90	98	101	90-104	99
138	108	93	113	100	104	103	93-113	104
126	69	56	51	52	57	57	51-69	57
187	106	92	97	95	99	97	92-106	98
183	95	95	100	96	99	94	94-100	96
128	93	86	97	97	92	95	86-97	93
185	82	76	93	94	84	88	76-94	86
204	92	82	94	94	91	90	82-94	91
180	82	80	97	96	90	87	80-97	89
170	107	103	96	98	100	101	96-107	101
198	104	99	93	96	99	98	93-104	98
201	103	90	96	99	95	99	90-103	97
208	95	99	93	94	95	95	93-99	95
194/205	91	100	102	97	91	92	91-100	96
206	90	92	92	93	93	91	91-93	92

Table 3.6b Percentage recoveries of PCB matrix spike from 6 filter replicates.

PCB	%rec	%rec	%rec	%rec	%rec	%rec	range	Ave % Rec
30	67	65	80	83	84	79	65-84	76
18	76	76	76	66	71	71	66-76	72
54	83	85	80	98	89	85	80-98	87
28	102	99	105	83	99	96	83-101	97
52	96	109	100	99	104	98	96-109	101
104	95	104	96	101	98	100	95-104	99
44	92	97	85	91	96	87	85-97	91
40	85	86	79	90	77	78	77-90	83
61	90	90	90	91	90	90	90-91	90
66	104	99	102	101	104	99	99.-104	102
101	92	91	90	93	89	93	89-93	91
77/110	98	98	79	76	89	82	76-98	87
82/151	100	100	94	103	99	100	94-103	99
149	105	95	85	99	93	99	85-105	96
118	103	91	86	89	96	88	86-103	92
188	102	101	86	96	99	94	94-102	96
153	99	95	90	93	97	91	90-99	94
105	101	98	80	82	92	88	80-102	90
138	101	89	90	95	96	92	89-101	94
126	65	59	65	64	65	61	59-65	63
187	102	100	100	101	101	100	100-102	101
183	99	98	86	80	88	90	86-90	90
128	103	102	114	89	93	97	93-114	99
185	99	96	90	96	93	98	90-99	95
204	101	97	93	92	97	95	93-101	96
180	103	96	90	92	95	95	90-103	95
170	102	101	100	90	98	100	90-103	98
198	100	99	96	87	100	91	87-100	95
201	102	103	96	105	103	100	96-105	101
208	99	92	95	90	95	92	90-99	94
194/205	97	96	90	95	97	93	90-97	94
206	104	97	105	91	99	100	90-105	99

extract split to form duplicate samples would have resulted in concentrations below detectable levels for many of the analytes. Instead six replicates of the US National Institute of Standards and Technology (NIST) - Standard Reference Material (SRM) 1649 - were extracted and cleaned up in exactly the same way as the air samples. PAH and PCB concentrations for the six replicates are presented in Tables 3.7 and 3.8 respectively. Precision is expressed as the percent relative standard deviation (RSD) of the replicate samples.

For analytes to be accepted for routine measurement the average RSD for each analyte must be ≤ 50 % if measured concentrations were ≥ 5 times the LOD, and $\leq 100\%$ if measured concentrations are < 5 times the LOD. These objectives could not be met for the two ringed PAH, naphthlene, and the lighter mono- and di-chlorinated biphenyls. Hence, these compounds were not quantified in the air or deposition samples.

3.6.4 Data assurance

To assure the validity and accuracy of the data generated it was necessary to check the analytical protocol by periodically extracting the NIST - SRM 1649. This material was certified for PAH concentrations only. Extractions were cross referenced with the certified values. Table 3.9 gives the certified PAH values for this material and the mean and standard deviation of six extracted batches. This material was not certified for PCBs. However PCB

Table 3.7. Precision of PAH method (% RSD) determined by replicate analysis of NIST - SRM 1649 urban reference dust.

PAH	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	range	mean (SD)	%RSD
ACE	0.23	0.27	0.19	0.26	0.18	0.10	0.29	0.55	0.10-0.55	0.26 (0.13)	50
FLU	0.32	0.37	0.39	0.34	0.51	0.41	0.27	0.28	0.12-0.51	0.36 (0.07)	19
PHE	5.07	4.71	4.58	4.17	5.09	6.78	5.30	4.38	4.17-6.78	5.01 (0.81)	16
ANTH	0.43	0.39	0.58	0.32	0.49	0.50	0.32	0.39	0.32-0.58	0.43 (0.09)	21
FLUO/MPHE*	14.6	12.1	15.4	13.7	15.3	12.8	11.7	11.0	9.24-15.4	13.3 (1.68)	13
PYR	5.86	6.67	6.65	6.62	7.03	6.22	6.66	6.30	5.27-7.03	6.56 (0.32)	5
BENZANTH	2.52	2.15	2.54	2.22	2.80	2.41	2.25	2.81	1.95-2.81	3.50 (0.22)	6
CHRY	3.83	3.80	3.71	3.36	3.38	3.49	3.89	3.40	3.36-3.83	3.61 (0.22)	6
B[b]F	6.25	4.86	5.92	5.85	6.39	5.57	5.15	5.74	4.86-6.39	5.74 (0.45)	8
D[ac]A/B[k]F*	5.01	4.01	4.83	5.20	4.92	5.14	5.26	5.33	4.83-5.33	4.96 (0.42)	8
B[a]P	2.98	3.16	3.34	3.13	3.15	3.13	3.49	3.61	2.90-3.61	3.20 (0.17)	5
D[ah]A	0.51	0.52	0.50	0.58	0.58	0.62	0.60	0.49	0.49-0.63	0.55 (0.05)	9
B[ghi]P	5.98	3.35	3.75	3.3	4.43	4.46	4.40	4.32	3.30-5.98	4.24 (0.85)	20
COR	3.54	3.61	4.04	3.74	4.95	4.27	4.09	3.38	3.10-4.95	4.08 (0.59)	14
ΣPAH µg/g	57.2	46.0	56.4	52.8	59.2	55.9	53.6	52.0	46.0-59.2	54.1 (4.07)	7

* co-elutions

† certified values obtained by GC and LC

Table 3.8. Precision of the PCB method (%RSD) by analysing replicates of urban reference dust NIST - SRM 1649.

PCB	ng/g	ng/g	ng/g	ng/g	ng/g	ng/g	Mean (SD)	%RSD
30	ND	ND	ND	ND	ND	ND		
18	18.4	19.6	11.6	10.8	12.2	15.8	14.7 (3.74)	25
28	17	14.1	12.7	18.5	10.2	15.8	14.7 (3.01)	20
52	21.1	18.1	14.6	16.4	14.8	21.7	17.8 (3.07)	17
104	10.1	9.38	7.17	9.84	11.3	12.4	10.1 (1.78)	18
44	14.1	12.8	11.84	12.9	13.8	11.4	12.8 (1.06)	12
40	1.58	1.54	3.32	3.19	2.89	3.91	2.74 (0.97)	35
61	10.9	7.8	6.37	7.24	7.4	7.41	7.85 (1.56)	20
66	42.7	30.1	33.6	39.7	36.3	43.7	37.7 (5.32)	14
101	55.6	44.2	48.2	52.9	43.6	51.8	49.4 (4.86)	10
77/110*	56	42.7	40.8	51.1	65.1	82.3	56.3 (15.5)	27
82/151*	33.9	27.9	25.2	30.2	18.9	25.8	26.9 (5.07)	19
149	81.1	65.1	61.6	77.3	66.6	68.3	70.0 (7.55)	11
118	16.6	17.1	13.3	15.4	13.2	13.3	14.8 (1.78)	8
188	17.1	12.4	15.3	17.5	10.8	11.5	14.1 (2.91)	5
153	65.6	59.9	60.6	68.6	58.9	71.3	64.1 (5.12)	13
105	4.95	9.66	4.03	9.86	5.13	6.71	6.72 (2.51)	37
138	51.4	47.1	46.8	53.8	53	51.9	50.6 (2.99)	6
187	39.9	32.4	34.3	40.2	25.1	29.9	34.4 (6.21)	18
183	18.1	19.7	19.6	17.1	12.1	15.5	17.0 (2.88)	17
128	12.7	10.9	18.8	21.3	6.16	11.6	13.6 (5.54)	41
185	11.1	10.1	8.98	5.74	7.19	9.63	8.79 (1.98)	23
204	0.52	1.51	1.76	1.39	0.67	1.76	1.27 (0.54)	43
180	118	126	118	119	88.6	101	112 (14.0)	13
170	38.3	32.4	25.6	31.8	29.7	26.4	30.7 (4.63)	16
198	1.93	1.44	0.89	2.23	1.58	1.83	1.65 (0.46)	28
201	23.8	18.6	18.1	23.4	18.2	19.4	20.2 (2.63)	13
208	6.12	3.96	3.92	6.34	3.55	2.54	4.40 (1.51)	24
194/205*	25.1	21.5	22.1	25.1	18.1	19.7	21.9 (2.82)	13
206	28.4	19.8	22.4	28.5	19.5	13.8	22.1 (5.68)	26

* co-elutions

Table 3.9. PAH concentrations in certified NIST - SRM 1649.

PAH	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	range	Cert (GC/LC)†	Cert (LC)†
ACE	0.23	0.27	0.19	0.26	0.18	0.1	0.29	0.55	0.10-0.55		
FLU	0.32	0.37	0.39	0.34	0.51	0.41	0.27	0.28	0.12-0.51		
PHE	5.07	4.71	4.58	4.17	5.09	6.78	5.30	4.38	4.17-6.78		4.2-4.8
ANTH	0.43	0.39	0.58	0.32	0.49	0.5	0.32	0.39	0.32-0.58		
FLUO/MPHE*	14.6	12.1	15.4	13.7	15.3	12.8	11.7	11.0	9.24-15.4	6.6-7.6	6.5-7.5
PYR	5.86	6.67	6.65	6.62	7.03	6.22	6.66	6.30	5.27-7.03		5.9-6.7
BENZANTH	2.52	2.15	2.54	2.22	2.8	2.41	2.25	2.81	1.95-2.81	2.3-2.9	2.4-2.8
CHRY	3.83	3.80	3.71	3.36	3.38	3.49	3.89	3.40	3.36-3.83		3.4-3.8
B[b]F	6.25	4.86	5.92	5.85	6.39	5.57	5.15	5.74	4.86-6.39		5.9-6.5
D[ac]A/B[k]F*	5.01	4.01	4.83	5.20	4.92	5.14	5.26	5.33	4.83-5.33		1.9-2.1
B[a]P	2.98	3.16	3.34	3.13	3.15	3.13	3.49	3.61	2.90-3.61	2.4-3.4	2.3-3.0
D[ah]A	0.51	0.52	0.5	0.58	0.58	0.62	0.60	0.49	0.49-0.63		0.3-0.5
B[ghi]P	5.98	3.35	3.75	3.3	4.43	4.46	4.40	4.32	3.30-5.98	3.4-5.6	4.6-5.8
COR	3.54	3.61	4.04	3.74	4.95	4.27	4.09	3.38	3.10-4.95		
ΣPAH µg/g	57.2	46.0	56.4	52.8	59.2	55.9	53.6	52.0	46.0-59.2		

* co-elutions

† certified values obtained by GC and LC

Table 3.10 Mean PCB congener concentrations in NIST - SRM 1649 from this study (mean from six replicates see Table 3.8) and from Schantz et al. (1993).

PCB	This study Mean (SD) ng/g	Schantz et al. Mean (SD)† ng/g
30	ND	
18	14.7 (3.74)	
28	14.7 (3.01)	19.8 (1.6)
52	17.8 (3.07)	24.6 (1.9)
104	10.1 (1.78)	
44	12.8 (1.06)	
40	2.74 (0.97)	
61	7.85 (1.56)	
66	37.7 (5.32)	
101	49.4 (4.86)	41.7 (2.1)
77/110*	56.3 (15.5)	
82/151*	26.9 (5.07)	
149	70.0 (7.55)	
118	14.8 (1.78)	29.8 (1.6)
188	14.1 (2.91)	
153	64.1 (5.12)	75.4 (4.1)
105	6.72 (2.51)	
138	50.6 (2.99)	77.6 (4.8)
187	34.4 (6.21)	
183	17.0 (2.88)	
128	13.6 (5.54)	
185	8.79 (1.98)	
204	1.27 (0.54)	
180	112 (14.0)	70.6 (4.6)
170	30.7 (4.63)	
198	1.65 (0.46)	
201	20.2 (2.63)	
208	4.40 (1.51)	
194/205*	21.9 (2.82)	
206	22.1 (5.68)	

* co-elutions

† mean of two replicates

analysis was carried out to establish a mean concentration for each congener (Table 3.8). If a new extract resulted in a significant deviation from this mean (± 3SD), then that sample batch was re-analysed for PCBs. Table 3.10 presents the mean concentration and standard deviation for each congener and, included for a comparison, the mean concentrations of six congeners derived by Schantz *et al.* (1993).

PCB and PAH data presented for the London and Stevenage sampling sites were generated in a different laboratory, Warren Spring Laboratory (WSL). Therefore, if data was to be comparable it was necessary to verify the performance of both laboratories by analysing a series of intercomparison samples. One such intercomparison study was the joint analysis of Fragmentiser feedstock residue (fragmented electrical appliances) conducted by GC-MSD for PCBs. A good agreement was found between Lancaster University and WSL, as shown in Table 3.11.

Table 3.11. Comparison of PCBs in a fragmentiser residue sample supplied by Warren Spring Laboratory.

PCB	WSL (µg/Kg)	Lancaster (µg/Kg)
28	439	574
52	1355	1504
101	3450	1991
77	72	3195 (inc. PCB 110)
153	1162	941
138	1694	1495
126	17	38
180	193	594 (inc. C12 labelled 180)

Chapter 4

PCBs in UK air

4.1 Introduction

Due to their persistence, toxicity and propensity for bioaccumulation, polychlorinated biphenyls (PCBs) have elicited considerable public, governmental and scientific interest since the mid-1960's. PCBs are now widely distributed being detected in soil (Alcock *et al.*, 1993), sediments (Sanders *et al.*, 1992) as well as biota such as vegetation (Reiderer, 1990), marine mammals and seabirds (Lothigius, 1991) and human tissue (Duarte-Davidson *et al.*, 1993)

Much of the previously published data on these persistent organic compounds has been obtained by reseachers studying their environmental behaviour in the Great Lakes region of North America. It is here that the greatest concern has been expressed over the adverse effects on wildlife, given PCBs persistence, propensity to be repeatedly deposited and volatilised between air and soil or air and water and their ability to be accumulated through the foodchain. PCBs have now been detected in areas far removed from their source(s) such as the polar regions (Barrie *et al.*, 1992; Wania and Mackay, 1993). They are therefore subject to transboundary migration and can be considered truly global pollutants, the atmosphere effectively acting

as a transport medium for these compounds. The movement of PCBs through the atmosphere is key to an understanding of their global cycling (Tanabe, 1988). At any one time the loading of these compounds in the air is small in proportion to the total loading in other compartments (e.g. soils) (Harrad *et al.*, 1994). However, the atmosphere acts as a highly dynamic medium, with PCBs being deposited to land or water and then repeatedly re-entering the air by volatilisation and/or re-suspension. Monitoring of PCBs in the atmosphere is therefore essential, if transport and cycling are to be followed and understood.

Industrialised nations in temperate latitudes in the northern hemisphere are commonly believed to constitute the principle global sources of PCBs. Sources of PCBs to the atmosphere have been described in Chapters 1 and 2 but, in brief, Harrad *et al.* (1994) considered the major sources to the contemporary UK atmosphere to be soil derived, with ~88 % of the atmospheric burden coming from soils (contaminated as a result of aerial deposition, landfill and spills). They estimated leaks from transformers and capacitors to contribute ~9 % to the atmospheric loading with the production of refuse derived fuel and the recovery of contaminated scrap metal contributing some 3 % to the atmospheric burden. If these are the main sources to the UK atmosphere then it is important to monitor PCB air concentrations and report them in an international/regional context. This is particularly important now that PCB manufacture has ceased, as releases to the air are predominantly from previous uses or from contaminated

matrices such as soils and sediments. In this Chapter the atmospheric behaviour of PCBs was investigated through the routine sampling of air from both urban and rural locations, sample site location and sampling methodology being previously described in Chapter 3. Annual concentration patterns at these five sites have provided an insight into the behaviour of these chemicals in the atmosphere. Seasonal variations in PCB concentrations were followed, along with the vapour-particle distribution for individual congeners. Factors affecting this distribution being discussed relative to both the urban and rural atmospheres. Spatial variations were also investigated to allow comparisons between urban and rural sites. By studying the atmospheric behaviour over annual time scales this has provided a greater understanding of the processes that will affect their transport, fate and ultimate sinks.

4.2 Congener selection

As discussed in Chapter 1, PCBs are a complex set of individual compounds (congeners) each having a unique structure and properties that control its behaviour in the environment. There are 209 posible PCB congeners (Ballschmiter and Bell, 1980), of which approximately 100 occur in the environment (Ballschmiter and Wittlinger, 1991). Manchester-Neesvig and Andren (1989) sampled air in northern Wisconsin, USA and identified a maximum of 92 congeners from one particular sample. However, on a routine basis they found an average of 30 congeners in every vapour and

particulate air sample. In this study 8 congeners were selected for analysis at each of the sites, with a further 22 being analysed in the Manchester, Cardiff and rural (Hazelrigg) locations. The 8 congeners common to all the sites were 28, 52, 101, 77/110, 118, 138, 153 and 180. Congeners 77/110 were not resolved under the analytical conditions and were therefore quantified together. Six of the congeners are commonly referred to as the indicator congeners (28, 52, 118, 138, 153 and 180) as they are routinely screened for in most environmental samples now that the advent of capillary gas chromatography has allowed congener-specific quantification (Duarte -Davidson *et al.*, 1991). These 6 congeners have been selected due to their dominance in the original commercial PCB mixtures (Manchester-Neesvig and Andren, 1989) and their persistency in both biotic and abiotic matrices (Harrad *et al.*, 1994).

In many studies, more than the 6 indicator congeners have been analysed. For example, atmospheric studies in North America and Canada have selected further congeners to provide comprehensive information on the loading and behaviour of PCBs in ambient monitoring programmes. These extra congeners are selected on the basis of: 1) relative contribution to the overall loading within the atmosphere, 2) representation of a particular homologue group, 3) persistency (atmospheric residence time) and 4) toxicity i.e. the non-ortho and mono-ortho substituted congeners which contribute significantly to the toxicity of the PCB mixtures (Safe, 1994).

Table 4.1 presents the full compliment of 30 (8 + 22) congeners analysed in this study. The percentage, by weight, of each of these congeners to four widely used Aroclor mixtures is also displayed. These 30 selected congeners contribute to ~50 % of the total congener weight in each mixture, and > 70 % in the case of Aroclor 1260. Therefore, these congeners cover a large proportion of the total environmental loading through the use of PCB technical mixtures. Furthermore, this selection covers the major PCB homologues, from the lighter trichlorobiphenyls to the heavier nonachlorobiphenyls, thereby representing a wide range of different physical-chemical properties.

4.3 UK PCB data in an international context

As described in Chapter 3, twenty six weekly samples were taken consistently over each year (every other week) at the various sites. A summary of the PCB concentrations at the four urban sites of London, Manchester, Cardiff and Stevenage for the sampling period 1991/1992 are presented in Table 4.2. London, the largest city, had the highest median (and mean) ΣPCBa (Σa = 8 congeners) concentration of 1150 (1350) pg m^{-3}, with the median (and mean) concentrations at Manchester, Cardiff and Stevenage being 404 (455), 490 (575) and 304 (370) pg m^{-3} respectively. The median (and mean) concentrations of the ΣPCBb (Σb = 30 congeners) in Manchester and Cardiff were 1050 (1160) and 1390 (1490) pg m^{-3} respectively. The median concentrations tend to be more representative of large data sets

Table 4.1 PCB congeners quantified in this study.

Congener IUPAC no.•	Name †	GC Co-elutions	Aroclor weight percentsΔ 1242	1248	1254	1260
30	2,4,6-TCB		-	-	-	-
18	2,2',5-TCB		8.35	4.54	0.15	0.15
28*	2,4,4'-TCB		23.05	20.33	0.29	0.27
52*	2,2',5,5'-TeCB		2.33	3.85	4.21	0.25
44	2,2',3,5'-TeCB		3.36	5.25	2.32	0.09
61	2,3,4,5-TeCB		-	-	-	-
74	2,4,4',5-TeCB	61/74	1.35	2.85	0.62	0.06
66	2,3',4,4'-TeCB		3.64	7.66	1.10	0.09
101*	2,2,4,5,5'-PCB		0.44	1.19	7.06	2.46
110	2,3,3',4',6-PCB		0.66	1.90	9.61	1.38
77	3,3',4,4'-TeCB	77/110	-	-	-	-
82	2,2',3,3',4-PCB		-	-	-	-
151	2,2',3,5,5',6-HCB	82/151	0.24	0.58	1.89	3.10
149	2,2',3,4',5',6-HCB		0.15	0.34	5.93	8.68
118	2,3'4,4',5-PCB		0.17	0.61	2.83	0.20
188	2,2',3,4',5,6,6'-HeCB		NR	NR	NR	NR
153*	2,2',4,4',5,5'-HCB		0.31	0.85	5.25	5.91
105	2,2'4,4',5,5'-HCB		0.30	0.85	5.25	5.91
138*	2,2',3,4,4',5-HCB		0.09	0.29	5.85	5.23
187	2,2',3,4',5,5',6-HeCB		0.11	0.13	0.41	4.88
183	2,2',3,4,4',5',6-HeCB		0.05	0.10	0.40	3.28
185	2,2',3,4,5,5',6-HeCB		0.03	0.04	0.05	0.75
204	2,2',3,4,4',5,6,6'-OCB		NR	NR	NR	NR
180*	2,2',3,4,4',5,5'-HeCB		0.17	0.44	1.24	12.07
170	2,2',3,3',4,4',5-HeCB		0.22	0.33	1.24	12.07
198	2,2',3,3',4,5,5',6-OCB		0.04	0.05	0.06	0.16
201	2,2',3,3',4',5,5',6-OCB		0.10	0.13	0.09	3.30
194	2,2',3,3',4,4',5,5'-OCB		-	-	-	-
205	2,3,3',4,4',5,5',6-OCB	194/205	0.08	0.19	0.90	2.19
206	2,2',3,3',4,4',5,5',6-NCB		0.04	0.06	0.06	0.87
			44.7	52.6	52.2	73.4

• Arranged in order of elution from the Ultra 2 (5 % phenyl methyl silicone coated) column employed in this study.

* Six indicator congeners.

† T = tri, Te = tetra, P = penta, H = hexa, He = hepta, O = octa, N = nona.

Δ Manchester-Neesvig and Andren, 1989

Table 4.2 Summary of PCB congener data for weekly samples taken every other week throughout 1991/92 at the four urban sites (pg/m^3).

	Cardiff				Manchester			
Congener	Mean	Median	Range	SD	Mean	Median	Range	SD
28	222	159	33.4-1040	206	133	115	9.74-309	67.4
52	129	125	21.2-370	73.5	101	96.5	16.7-202	43.5
77/110*	98.3	55.3	21.6-632	11.7	80.7	62.9	12.0-241	52.8
101	91.5	71.7	26.3-360	73.3	84.5	67.1	14.4-224	51.7
118	38.6	21.2	3.02-322	5.99	29.9	25.6	2.36-74.4	18.0
153	32.5	22.0	4.65-147	32.0	36.9	32.4	6.06-122	20.2
138	33.4	19.2	6.51-216	43.9	28.0	22.2	11.7-114	22.1
180	17.0	12.4	ND-100	17.8	24.0	20.7	ND-101	17.5
ΣPCBa	575	490	112-1520	352	456	404	180-844	183
30	16.5	6.04	ND-110	22.6	17.1	13.4	1.23-70.6	15.6
18	397	362	97.4-1540	278	198	188	1.66-568	101
104	10.9	9.96	6.44-36.5	10.6	8.44	5.71	ND-49.3	10.1
44	102	1.06	6.15-246	62.9	117	108	10.5-393	76.4
61	27.0	19.8	4.82-106	21.9	22.8	20.3	3.81-77.4	14.1
66	99.1	1.03	3.08-317	74.9	98.0	91.2	1.46-257	57.6
82/151	2.27	1.83	1.01-101	20.2	26.6	24.3	1.52-84.0	19.6
149	55.1	38.8	1.08-209	48.0	65.2	58.8	5.61-198	41.0
188	12.8	6.42	2.08-167	25.5	11.1	7.15	1.33-74.4	13.4
105	28.0	15.8	8.81-292	48.2	27.0	23.1	3.06-93.5	20.7
187	10.2	6.94	1.95-62.4	12.8	17.3	13.7	2.37-105	17.9
183	5.17	3.36	1.94-23.2	5.43	8.72	6.38	3.03-37.9	6.42
185	4.43	2.51	ND-18.5	5.46	6.05	4.35	1.57-23.3	6.51
204	1.66	0.25	ND-10.0	2.63	2.41	1.48	ND-15.3	3.38
170	4.61	3.05	0.75-25.8	5.47	6.63	3.91	0.62-36.0	7.30
198	1.28	0.32	ND-12.2	2.26	1.33	0.76	ND-16.3	2.87
201	1.25	0.51	0.56-9.38	1.92	3.74	2.21	ND-25.2	5.32
208	0.80	0.64	ND-6.74	1.53	1.76	0.56	0.63-9.72	2.55
194/205	2.60	1.81	ND-15.2	3.18	5.48	4.15	ND-33.6	5.80
206	1.00	0.88	ND-6.65	1.79	1.38	0.84	ND-14.7	2.97
ΣPCBb	1490	1390	415-3710	785	1160	1050	223-2360	501

Table 4.2 Continued

London					Stevenage				
Congener	Mean	Median	Range	SD	Congener	Mean	Median	Range	SD
28	557	484	190-1490	291	28	186	151	77.5-845	137
52	531	443	116-1770	352	52	109	84.3	2.91-705	118
77	16.3	15.4	4.62-60.3	11.1	77	3.42	2.83	1.35-28.3	5.24
101	117	97.5	30.7-302	69.8	101	31.1	23.2	10.8-154	27.0
118	52.9	39.0	15.3-241	42.2	118	11.9	10.5	4.72-54.5	8.91
153	26.2	21.5	10.1-58.0	13.8	153	12.9	11.6	3.65-39.6	7.56
138	23.0	19.5	6.14-56.8	11.9	138	9.20	7.91	3.14-21.6	4.32
180	12.0	9.11	1.83-58.7	10.5	180	6.15	5.85	22.6-216	4.48
ΣPCB	1350	1150	413-3850	758	ΣPCB	370	304	141-1840	299

* Note: At Manchester and Cardiff congener 77 and 110 were quantified together. 110 will account for > 90 % of this total.

ND = non detect

ΣPCBa = sum of 8 congeners analysed at all four sites.

ΣPCBb = sum of 30 congeners analysed at Cardiff and Manchester only (including the ΣPCBa congeners).

* Max summer monthly concentration / min winter concentration

as they avoid the effects of unusually high values which elevate the mean concentrations.

In order to set the UK urban PCB data in context, Table 4.3 presents PCB air concentrations from five international urban studies conducted over the last 10 years. During the 1970's and early 80's atmospheric PCB concentrations were reported in terms of the commercial Aroclor mixtures. That is the chromatographic patterns found in atmospheric samples had to be matched and quantified against those found in the commercial mixtures. With the advances of capillary GC, congener-specific information can now be obtained, resulting in more useful data which takes into the account the tendency of individual PCB congeners to disperse, volatilise, degrade and be deposited at different rates in the environment, in relation to their varying physical-chemical properties. The studies in Table 4.3 were therefore carefully chosen on the grounds that they reported individual congener information rather than just total ΣPCB concentrations. The six indicator congeners common to each of the studies were reported separately as well as the total ΣPCB concentrations. These five urban sites had mean ΣPCB concentrations ranging from 208-1590 pg m^{-3}, while the UK sites show mean concentrations varying from 370-1350 pg m^{-3}. Therefore contemporary atmospheric ΣPCB concentrations are similar for urban centres on an international basis. Interestingly, the town of Bloomington IN, USA, listed in Table 4.3 has a mean ΣPCB concentration similar to the atmospheres of Hamburg and London. Although this town is considerably smaller than

Table 4.3 Urban atmospheric PCB concentrations (vapour and particle phases) pg/m3.

	Congeners								
	28	52	101	153	138	180	ΣPCB		Sampling details
a Kiel, Germany	NR	8.90-117	8.10-85.0	3.70-35.0	3.40-32.0	0.50-5.00		range	4 samples taken
	102	63.1	51.3	6.78	20.9	2.6	493	mean	during rain events, 1989.
b Ulm, Germany	10	24	47	52	52	23	208	total	1 sample taken in winter '87
c Hamburg,	100-400	100-300	100-600	100-400	200-500	10-300		range	25 samples taken from
Germany	270	210	280	230	230	150	1400	mean	April '86-April '87.
d Brazzaville, Congo	60.5	44.0	17.9	8.25	12.4	8.25	550	mean	14 samples, August-Sept. 1989
e Bloomington, Indiana, USA.	195	98.0	78.0	20.0	20.0	10.0	1590	mean	Samples taken between April-June 1993.
London, UK.	190-1490	116-1770	30.7-302	10.1-58.0	6.14-56.8	1.83-58.7		range	This study
	557	531	117	26.2	23.0	12.0	1350	mean	
Manchester, UK.	9.74-309	16.7-202	14.4-224	6.06-122	11.7-114	ND-101		range	This study
	133	101	84.5	36.9	28.0	24.0	456	mean	

ND = non-detect
NR = not reported
a Duinker and Bouchertall, 1989.
b Ballschmiter and Wittlinger, 1991.
c Bruckmann et al., 1988.
d Ngabe and Bidleman, 1992.
e Panshin and Hites, 1994.

these two cities, the proximity of three dump sites containing PCB-contaminated waste were considered to be a major source to the atmosphere (Hermanson and Hites, 1989; Panshin and Hites, 1994).

Three of the urban sites in Table 4.3 were located in Germany, whilst the other two were situated in different continents (Africa and the United States). Even with sampling taking place in different years the ΣPCB concentrations were similar, indicating either uniform contamination in these urban environments following the cessation of PCB production, and/or similar processes that limit their presence in the ambient atmosphere. PCBs in the ambient urban atmosphere will be a composite of the various emitting sources. Now that PCB production has ceased (Barrie *et al.*, 1992), sources are likely to be similar from one urban area to another. Point sources such as metal reclamation works, chemical waste incinerators and PCB superfund dumps like those at Bloomington (IN), USA (Table 4.3) will affect a localised area, but in terms of the ambient atmosphere of a large city such as London or Manchester these sources will be diluted and simply contribute to the urban atmospheric loading.

PCB concentrations at the rural site for 1993 are displayed in Table 4.4. The median (mean) ΣPCBb concentration was 324 (348) pg m^{-3} which is approximately a factor of 3-4 times lower than the median concentrations at the Manchester and Cardiff sites for 1991/92. In comparison to London and Stevenage, where only the eight indicator congeners were monitored, the

Table 4.4 Rural atmospheric PCB concentrations (pg/m^3).

Congener	Rural site (Field Station).				Ontario Canada c	Wisconsin USA d	Kosetice Czech Rep. e
	Mean	Median	Range	SD	Mean	Mean	Mean
28	45.2	44.5	<4.34-104	24.1	16.1	115	115
52	23.4	22.1	<3.18-55.1	15.3	16.5	10.5	48.2
77/110	10.8	10.1	<1.53-42.0	11.6	4.05	NR	NR
101	10.6	4.55	<2.71-38.5	12.1	6.42	NR	61.8
118	8.44	7.14	<0.36-25.9	7.89	2.31	1.84	NR
153	6.80	3.97	<2.18-27.9	7.86	3.24	5.26	69.1
138	3.91	0.512	<1.53-24.6	6.11	2.88	3.44	68.1
180	10.2	9.27	<3.61-37.7	8.99	1.19	NR	23.0
ΣPCBa	119	102	26.5-247	60.4	53.0	136	648
30	5.51	5.06	<0.41-23.4	5.88	NR	NR	NR
18	139	218	67.5-417	79.6	6.60	NR	NR
104	1.17	1.01	<0.40-8.98	2.19	NR	NR	NR
44	15.6	18.4	<2.90-42.5	13.4	6.90	NR	NR
61	9.93	8.14	<0.85-51.5	11.3	2.34	NR	NR
66	6.43	3.57	<5.33-23.5	7.87	6.54	NR	NR
82/151	3.34	2.16	<1.54-15.4	4.04	1.37	NR	NR
149	13.1	15.3	<3.39-30.4	11.5	2.86	NR	NR
188	2.31	2.01	<0.40-10.8	2.97	NR	NR	NR
105	7.12	6.7	<1.22-24.4	6.95	0.165	NR	NR
187	5.56	2.93	<0.48-18.9	6.29	1.74	NR	NR
183	0.338	0.331	<0.40-3.82	0.881	0.748	NR	NR
185	0.133	0.285	<0.40-2.40	0.477	0.135	NR	NR
204	ND	ND	ND	-	NR	NR	NR
170	1.84	1.79	ND-9.56	2.26	0.482	NR	NR
198	0.858	0.832	<0.20-7.81	1.76	ND	NR	NR
201	1.12	0.924	<1.06-6.54	1.61	0.920	NR	NR
194/205	6.53	7.07	<1.16-17.9	4.76	0.121	NR	NR
206	ND	ND	ND	-	0.150	NR	NR
ΣPCBb	348	324	114-732	159	84.1	NR	NR

ΣPCBa = sum of 8 congeners

ΣPCBb = sum of 30 congeners (including ΣPCBa congeners)

ND = Non-detect

NR = Not reported

c Samples taken July 1988-July 1989, 15km from nearest potential source (Hoff et al., 1992a).

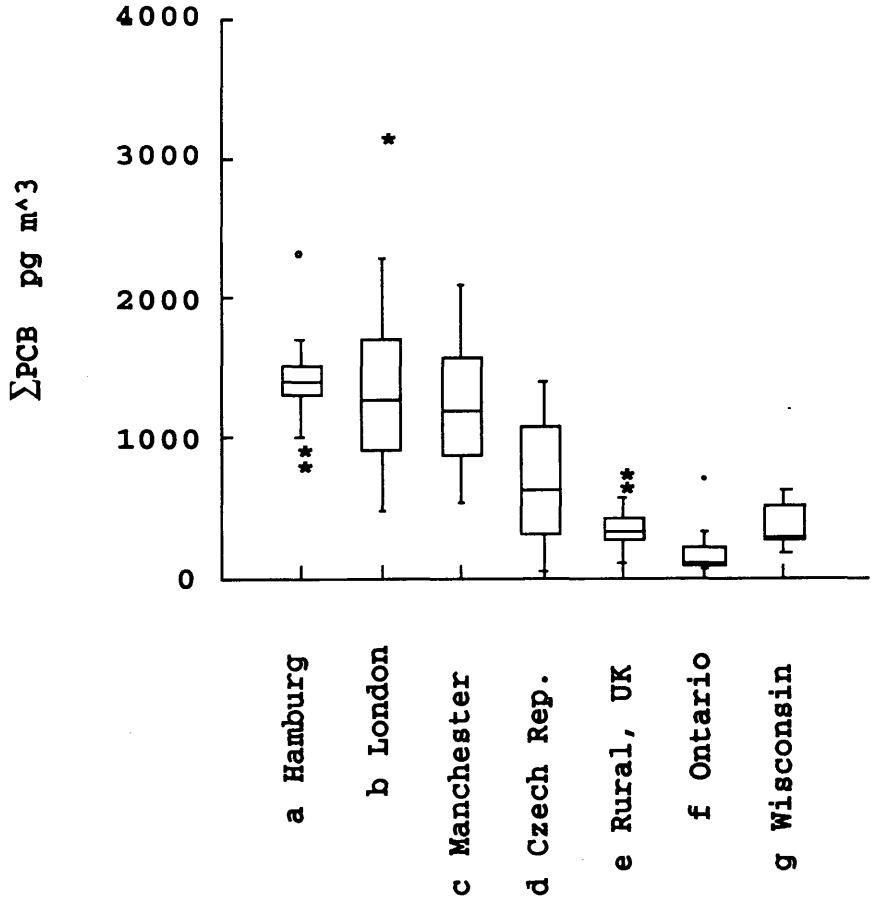
d Samples taken April1984-March 1985, remote area (Manchester-Neesvig and Andren, 1989).

e 17 samples taken March 1989-March 1991, rural area of S. Bohemia (Holoubek et al., 1992).

median ΣPCBa concentration at the rural site was 102 pg m^{-3}. This was approximately a factor of 10 lower than London and a factor of 3 lower than Stevenage. Clearly the rural location has a markedly reduced ΣPCB concentration over the urban sites indicating the reduction in PCB sources to the ambient rural atmosphere. Included in Table 4.4 are three other rural studies from Canada, USA and the Czech Republic, the ΣPCBa concentrations range from approximately 50 to 650 pg m^{-3} between these three sites, the atmospheric concentrations being the highest in the Czech study. To compare rural and urban atmospheres, Figure 4.1 displays the range and median ΣPCB concentrations from seven contemporary studies. Where possible, the selected rural studies had sampling programmes over an annual time scale, so that simple seasonal differences would not be depicted between sites. All of the rural sites had an annual median ΣPCB concentration of < 500 pg m^{-3}, apart from the study in south Bohemia in the Czech Republic, which had a median concentration of 570 pg m^{-3}. This was approximately a factor of 10 higher than the Canadian study in Ontario and a factor of 2 higher than the rural location of this work. There are several possible reasons for the elevated rural concentrations in the Czech Republic. Firstly PCB use continued in eastern Europe after many western countries had ceased (Barrie *et al.*, 1992). Secondly the Czech workers acknowledge the difficulty in selecting a true background site in a country with a high density of towns, villages and various types of industry, where continued PCB use may have resulted in increased environmental contamination.

Figure 4.1. Atmospheric total ΣPCB (vapour plus particulate phase) concentrations over annual time scales at three city and four rural locations. Results are presented as 'box and whisker' plots. The centre of the box is the median air concentration, the ends of the box are the upper and lower quartiles and the ends of the whiskers are the furthest concentration within one interquartile range (i.q.r.) either side of the box. Air concentrations out of this range are represented as outlier points.

* = concentrations ≥ ± 1.5 (i.q.r.) < ± 3 (i.q.r.); ◦ = concentrations ≥ ± 3 (i.q.r.)



a - Bruckman *et al.*, 1988. (urban)
b - This work (urban)
c - This work (urban)
d - Holoubek *et al.*, 1992. (rural)
e - This work (rural)
f - Hoff *et al.*, 1992a. (rural)
g - Manchester-Neesvig and Andren, 1989. (rural)

In contrast to these rural locations the city studies show a marked elevation in PCB air concentrations. On a national basis Harrad *et al.* (1994) estimated that ~ 12% of PCBs to the UK atmosphere were derived from activites mainly centred around urban areas, i.e. the use of transformers and capacitors and recovery of contaminated scrap metal. Furthermore, the high density of both public and domestic buildings will add to the atmospheric burden in urban areas. Indoor air concentrations have frequently been found to be an order of magnitude higher than outdoor concentrations (Balfanz *et al.*, 1993; Krieger and Hites, 1994). The ventilation of indoor air will therefore act as a source of PCBs to the 'outside' atmosphere. Sources of PCBs to indoor air have been considered to be sealant materials (Balfanz *et al*, 1993) and lighting fixtures (MacLeod, 1980). These important sources of PCBs have been largely ignored by Harrad *et al.* (1994), but it is important to acknowledge that indoor air may be a significant source of PCBs to the urban atmosphere.

The 'lines' of the box plots (extending to the furthest concentration within one interquartile range either side of the box) displayed in Figure 4.1 cover a large range of concentrations. For the London and Manchester data these lines overlap with the data from several of the rural studies. This shows that there are large fluctuations in atmospheric concentrations throughout the course of a sampling year indicating seasonal fluctuations. Several of the studies in Figure 4.1 show elevated air concentrations that fall outside the normal range of the box plot and can be considered to be anomalies or

outliers (represented as points). It is likely that specific meteorological conditions have influenced the PCB loading in the air samples represented by these outliers. Air mass transport of contaminants from a polluted source area has been shown to elevate PCB concentrations above the seasonal norm at more remote sites (Hoff *et al.*, 1992; Oehme *et al.*, 1995). These outliers generally warrant special consideration because they point to specific events or processes that have resulted in elevated concentrations. Meteorological conditions affecting contaminant loading and air mass transport of SOCs are discussed in more detail in Chapter 6.

4.4 Congener concentrations and atmospheric profile

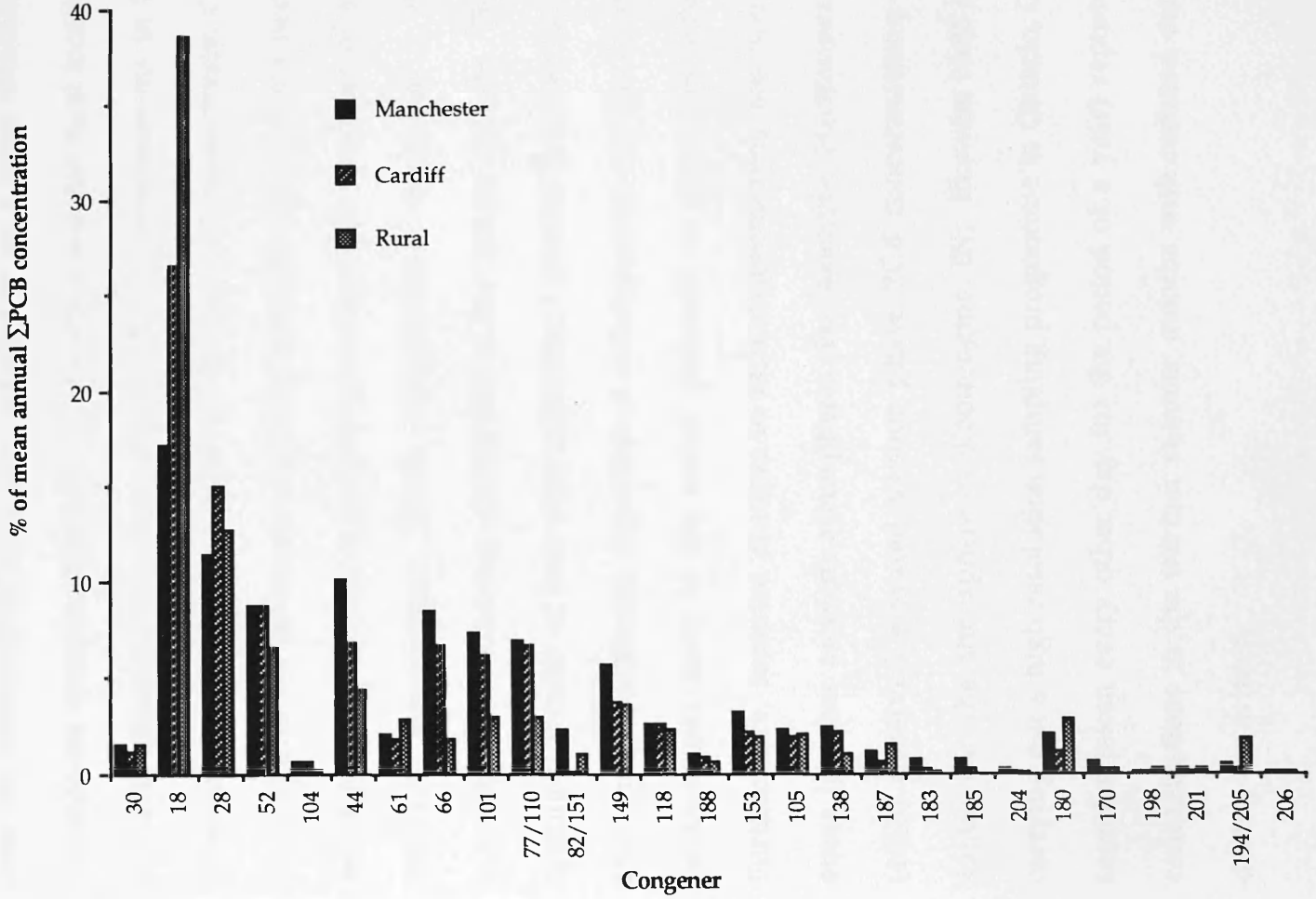
On an individual congener basis the more volatile tri- and tetrachlorinated congeners were found to predominate in the urban atmosphere of the UK. Congeners 28 and 52 constituted > 50 % of the ΣPCBa throughout each sampling year. Again, for the other urban studies in Table 4.3 these are the dominant congeners, with the exception of the city of Ulm in Germany, where only one air sample was taken during a winter period. In winter atmospheric concentrations of PCBs have been found to be at their lowest (Manchester-Neesvig and Andren, 1989). Seasonal effects on congener concentrations are discussed further in Section 4.5. At the Manchester, Cardiff and rural sites, where the full compliment of 30 congeners were analysed, the tri- and tetrachlorinated congeners dominated the mean annual ΣPCB air concentrations by > 50 %, with the three most

predominant congeners occurring in the order of 18 > 28 > 52. Figure 4.2 displays the percentage contribution each congener makes towards the ΣPCB concentrations (annual average) for Manchester, Cardiff and the rural site, respectively. This Figure shows the dominance of the lighter tri- and tetrachorobiphenyls on the congener profile in the atmosphere. The contribution towards the ΣPCB generally decreases with increasing level of chlorination. Interestingly, congeners 30 and 104, which are examples of a tri- and a pentachlorobiphenyl respectively, make only a small contribution (~1 %) to the total concentration relative to the other tri- and pentachlorobiphenyls. This is because these two congeners made only a small contribution (< 0.05 % w/w) or were absent altogether from the various Aroclor and Clophen commercial mixtures (Schulz *et al.*, 1989). At the rural location, the lower chlorinated congeners dominated the atmospheric profile, as found at the urban sites. From Table 4.4 the three congeners 18, 28 and 52 comprise ~57 % of the annual average ΣPCBb air concentration at the rural site. Similarly, congeners 28 and 52 are dominant in the rural atmospheres of the other three sites listed in this Table. Congeners are therefore prevalent in the atmosphere, depending on their abundance in the commercial PCB mixtures and on their vapour pressure.

4.5 Seasonal variations in atmospheric concentrations

From Figure 4.1, the annual ΣPCB concentrations displayed at the two UK city sites and the UK rural site, show a wide range in concentrations. That is,

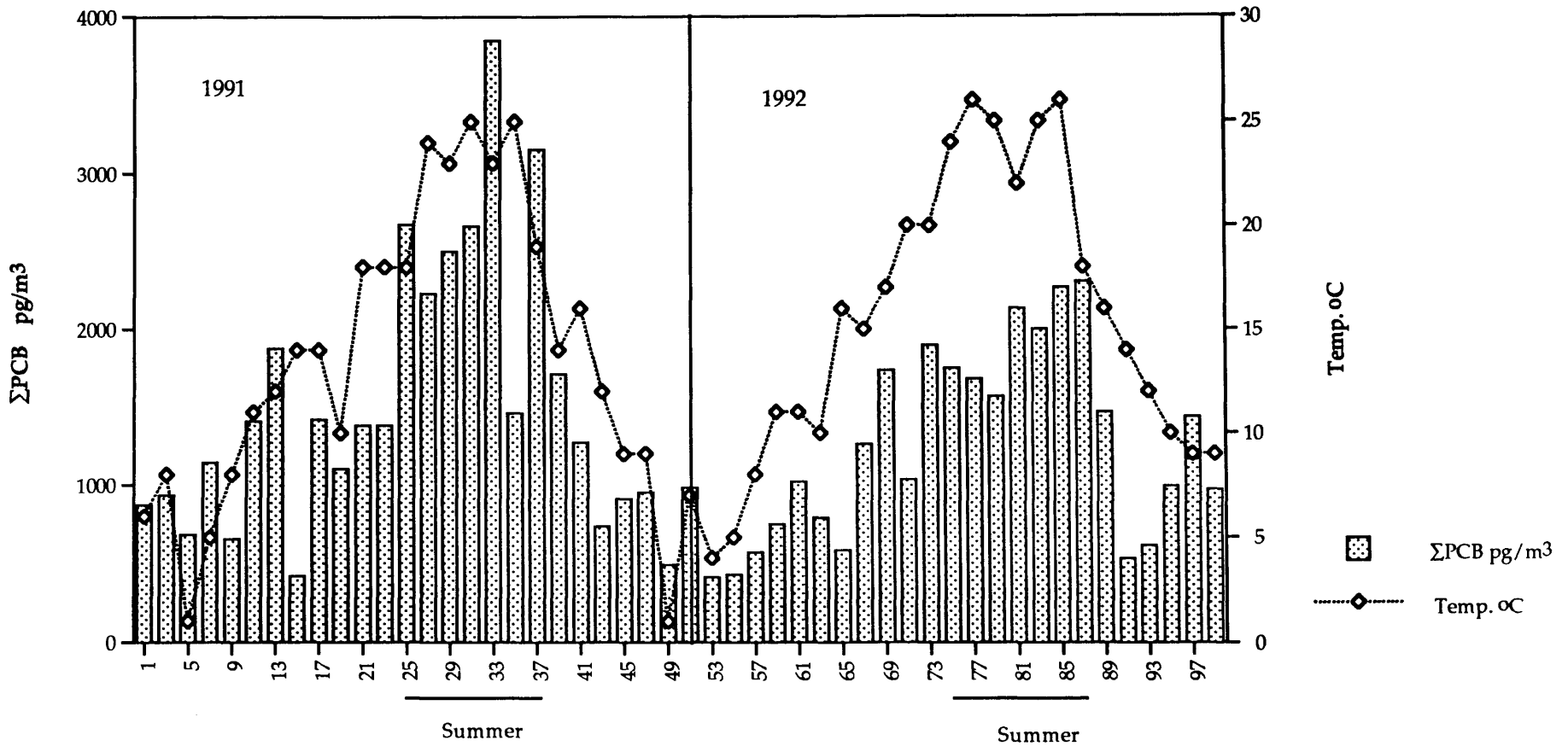
Figure 4.2. Percentage contribution made by each congener to the mean annual ΣPCBb concentration at the Manchester, Cardiff and rural (Hazelrigg) locations.



over the course of a year there appears to be a large fluctuation in the atmospheric concentrations at both the urban and the rural locations. Figure 4.3 (a+b) displays time series plots of ΣPCB concentrations in London air throughout 1991/1992 and rural air during 1993, respectively. Overlaid on these figures are the mean temperature profiles during these periods. These two figures show that as temperature rises with the onset of summer the ambient atmospheric ΣPCB concentration increases - the lowest concentrations occurring during the cooler winter months. This seasonal cycling is similar at both sites indicating a process common to both urban and rural atmospheres, regardless of anthropogenic activity, i.e. in the urban environment there is the added potential of numerous point sources. Furthermore, seasonal changes in PCB concentrations has been shown to occur in other ambient atmospheres. For example, Hermanson and Hites (1989) observed elevated vapour phase PCB concentrations during the summer in the atmosphere of Bloomington, IN; likewise Hoff *et al.* (1992a) carrying out a high resolution sampling programme in Ontario, Canada, (air samples taken every other day for the period of a year) reported elevated concentrations in the warmer summer months with reduced concentrations during the winter.

The effect of changing season (or changing air temperature) was apparent at all the sampling sites of this study. Figure 4.4 shows a correlation between ambient air temperature and total (vapour and particulate) ΣPCB concentrations for the Manchester and rural sites for 1992 and 1993

Figure 4.3a ΣPCBa concentrations in London air throughout 1991/92.



Summer nominally defined as June, July and August

Figure 4.3b ΣPCBb concentrations in rural air (Hazelrigg) throughout 1993

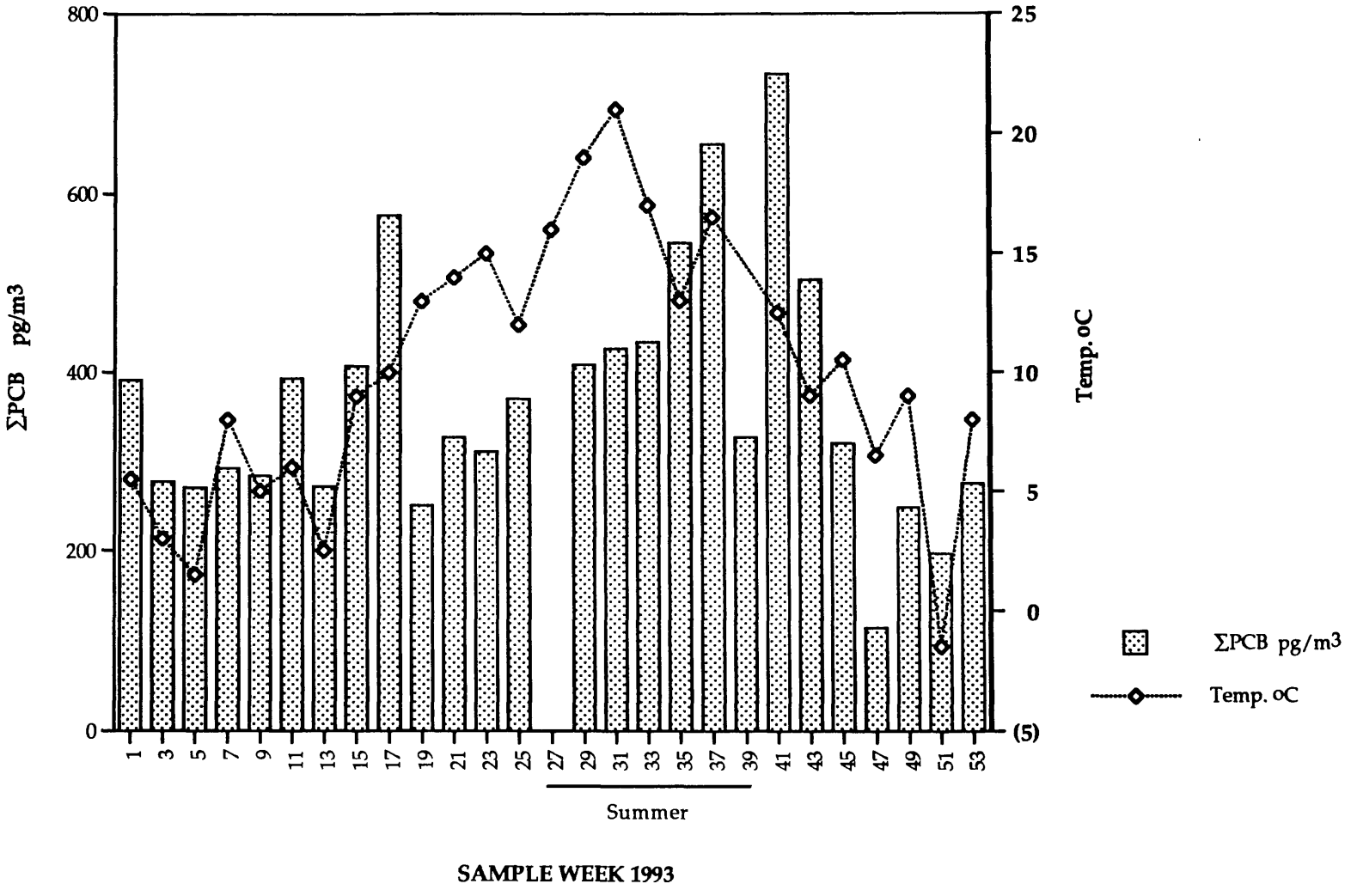
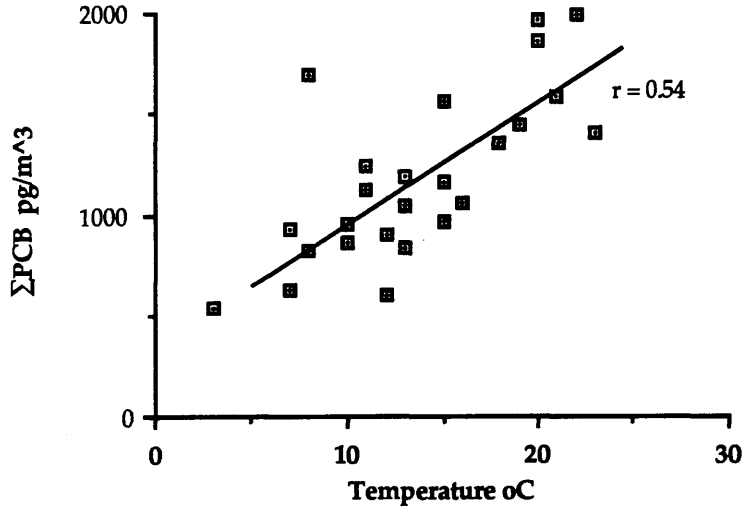
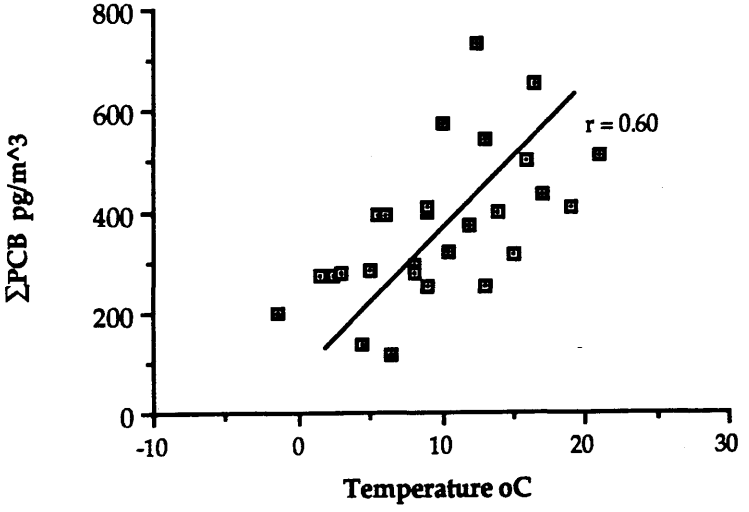


Figure 4.4 Regressions of total (vapour and particulate phase) ΣPCB concentrations against mean temperature at the Manchester and rural locations.

Manchester (1992)



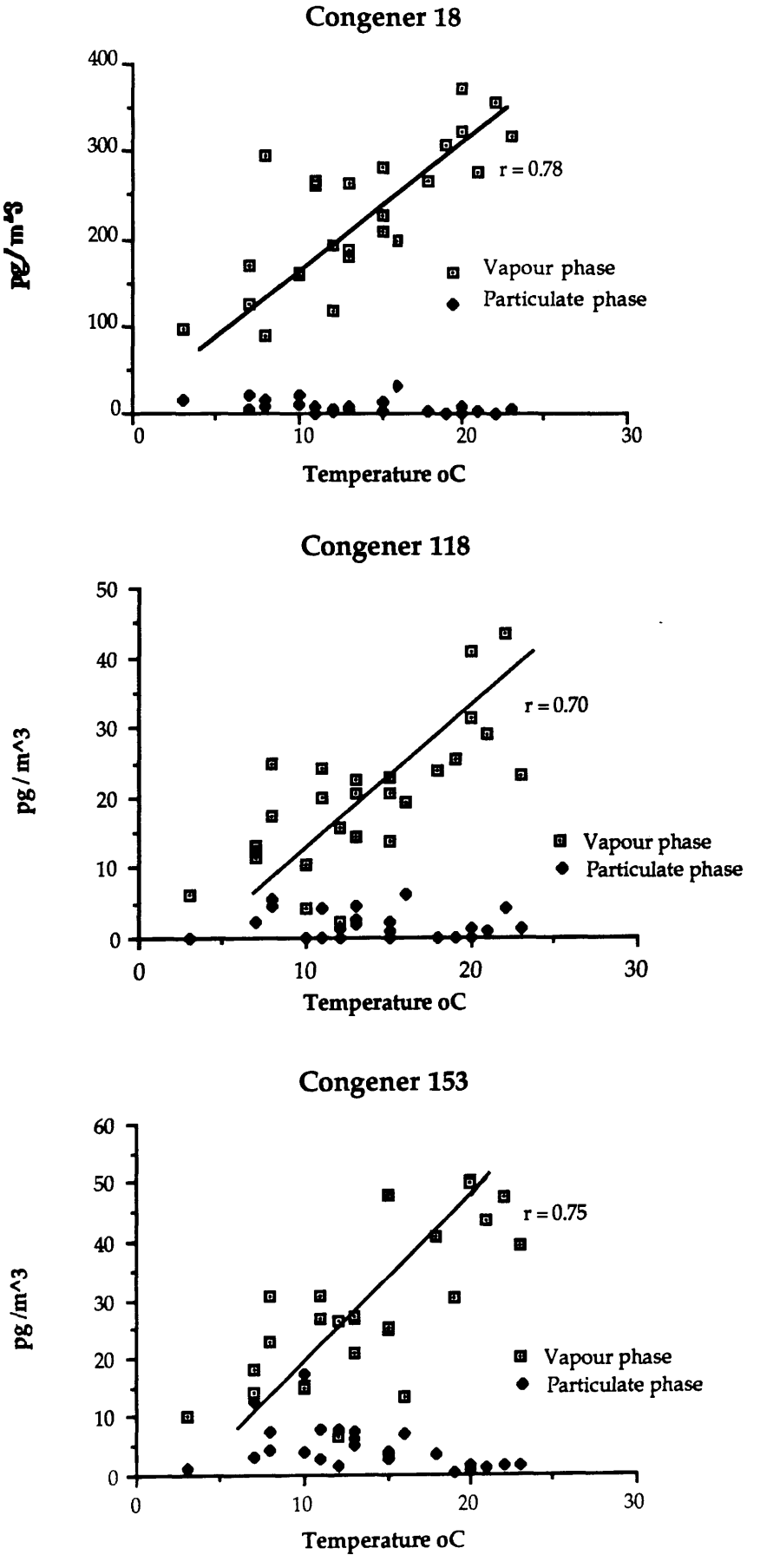
Rural (Hazelrigg) (1993)



respectively. The correlation coefficient between the air concentrations and temperature was 0.54 ($P<0.01$) for the Manchester data and 0.60 ($P<0.01$) for the rural data. These modest correlations do not reflect the strong correlations ($r \geq 0.8$) observed by both Manchester-Neesvig and Andren (1989) and Hermanson and Hites (1989) at their respective sampling sites in Wisconsin and Bloomington, IN. However, it should be noted that their sampling periods were much shorter - over a day rather than the weekly sampling used here. Their high resolution sampling over a 24 h period would result in a narrower temperature range being encountered and hence reflect more accurately the effects of temperature on atmospheric PCB concentrations.

Seasonal change can be observed in the concentrations of individual congeners at both the urban and rural sample sites. The total concentration for each congener comprises of both the vapour and particulate phases. Separate vapour phase and particulate phase concentrations of three congeners (18, 118 and 153) were plotted against temperature in Figure 4.5 for data obtained at the Manchester site. Positive correlations were evident between temperature and the vapour phase component, but not for the particulate phase component of these congeners. Vapour phase concentrations of individual congeners were strongly influenced by temperature. PCBs therefore have a tendency to volatilise from surfaces in the warmer summer months, resulting in elevated vapour phase air concentrations. The particulate phase concentrations do not show these

Figure 4.5 Separate vapour and particulate phase concentrations of 3 congeners plotted against ambient temperature in Manchester air.



correlations. Only the particulate concentrations of congener 153 showed a modest negative correlation with temperature (the correlation coefficient being -0.44, significantly different from zero at P = 0.05). That is, as temperatures decrease in the winter period the particulate PCB concentration increases, possibly by condensation of the vapour phase component onto particulate surfaces. However this is not the only process as the correlations between temperature and particulate phase concentrations were generally weak or non-existent, indicating the involvement of other possible factors such as the amount (surface area presented) and type of particulate in the atmosphere. These will play an important role in the sorption/desorption of PCB congeners in the atmosphere as suggested by Pankow and Bidleman (1992). Vapour/particle partitioning will be further examined in Section 4.6.

Seasonal cycling was therefore evident in the ΣPCB concentrations at each of the sample sites, temperature being invoked as the major controlling factor. On average, ambient summer concentrations were greater by a factor of ~2 than winter values (see Figure 4.3). Table 4.5 presents the summer and winter means for the individual congeners measured at the four urban sites of London, Manchester, Cardiff and Stevenage where summer was nominally defined as June, July and August and winter as December, January and Februrary. All the congeners show a significant increase in mean concentrations from winter to summer.

Table 4.5 Mean winter and summer concentrations at the four urban sites of this study. pg/m^3 (SD).

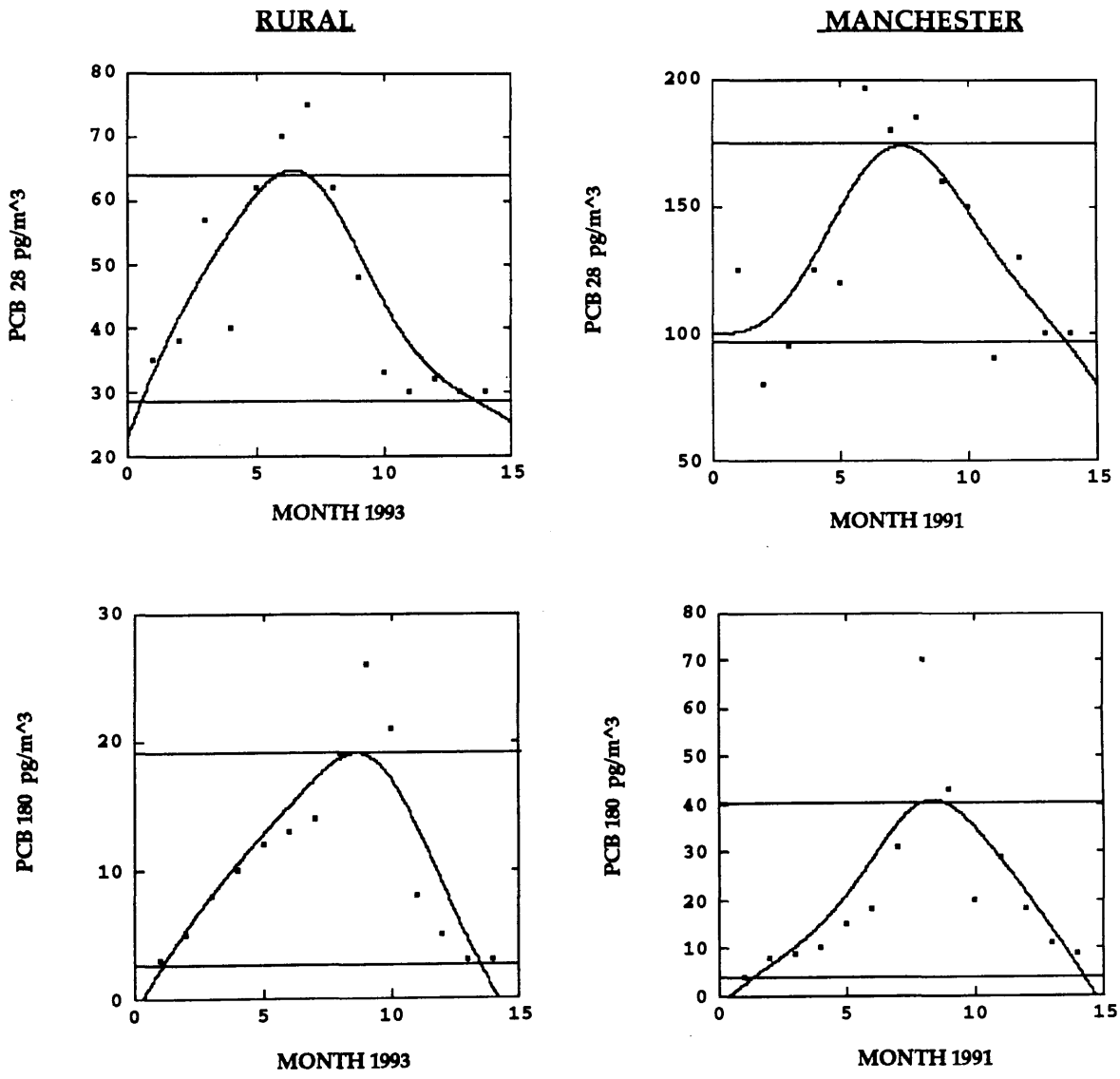
	Manchester		Cardiff		London		Stevenage†	
	Winter	Summer	Winter	Summer	Winter	Summer	Winter	Summer
Congener								
28	133 (66.3)	172 (65.3)	181 (79.4)	246 (73.6)	342 (98.4)	730 (267)	140 (88.3)	189 (42.7)
52	90.1 (37.3)	138 (40.1)	111 (98.8)	145 (33.1)	252 (104)	748 (308)	58.4 (40.6)	106 (31.2)
101	50.7 (25.1)	144 (35.9)	31.9 (31.9)	160 (83.7)	58.5 (18.7)	172 (67.4)	15.1 (7.2)	37.6 (13.3)
77	-	-	-	-	10.2 (6.99)	21.1 (7.79)	0.93 (1.24)	4.37 (1.33)
110/77*	91.6 (63.6)	133 (46.1)	20.4 (14.3)	212 (164)	-	-	-	-
118	17.9 (16.9)	40.7 (15.7)	10.7 (9.92)	81.4 (95.8)	26.5 (7.25)	88.4 (63.2)	7.40 (3.27)	13.6 (4.85)
153	22.0 (8.84)	54.4 (21.8)	13.1 (8.48)	58.8 (45.8)	15.2 (4.06)	38.0 (13.6)	8.41 (5.31)	16.4 (4.64)
138	17.0 (7.27)	50.4 (26.7)	13.3 (9.56)	66.6 (75.6)	13.9 (3.91)	33.2 (12.4)	7.24 (4.35)	10.8 (10.7)
180	16.2 (13.7)	35.2 (22.4)	9.31 (7.94)	33.0 (23.7)	8.17 (5.54)	12.2 (6.15)	4.66 (4.15)	6.42 (1.25)
ΣPCBa	438	768	391	1000	726	1840	242	384

† Sampling ceased April 1992

* co-elution GC-ECD

Interestingly, light and heavy congeners exhibit rather different behaviour in the atmosphere. In this study the range of congeners analysed have vapour pressures and molecular weights ranging from ~10^{-1} - 10^{-5} Pa and 257.5 - 462.2 g mol^{-1} (congener 18 - congener 206) respectively (Mackay *et al.*, 1992). Figure 4.6 shows the seasonal cycling in Manchester and the rural location of the tetra-CB congener 28, and the hepta-CB, 180. Distance weighted least squares (DWLS) lines have been fitted to the mean monthly concentrations for each congener (SYSTAT v5.0), data for Manchester taken for 1992 and the rural site for 1993. This has produced a smoothed curve clearly showing the increase in concentrations from winter to summer for each congener. The amplitude of this cycling is greater for the higher chlorinated congener 180. Even though congener 28 predominates in the atmosphere, greatly outweighing the contribution made by 180 to the ΣPCB concentration, the change from winter 'low' to summer 'high' is more marked for this higher chlorinated congener at both sampling sites. In other words it shows a greater 'peakedness' in curve shape, with the ratio of winter to summer concentrations being eight for 180 and yet only two for congener 28 in Manchester. Again, at the rural location the ratio of winter to summer concentrations is greater for the more chlorinated congener, five for 180 compared to two for congener 28. Maximum winter to summer ratios are presented for each congener measured at the Manchester and rural sites in Table 4.6. The increase in this ratio with increasing molecular weight agrees with the work of Hoff *et al* (1992a) who reported the amplitude (A_M) of the peak to minimum ratio of monthly averages to be largest for the higher

Figure 4.6 Distance weighted least squares (DWLS) lines fitted to monthly concentrations for congeners 28 and 180 sampled in the rural and Manchester atmospheres. Distance between horizontal lines indicate the degree of seasonal cycling for each congener.



chlorinated PCBs in rural Ontario air. It is therefore apparent that this phenomenon is not solely an urban trait, where numerous sources may influence the atmospheric loading of both the heavier and lighter congeners.

Table 4.6 Winter/Summer congener ratios* in the Manchester and rural atmospheres.

* Max summer monthly concentration / min winter concentration.

Congener IUPAC no.	Manchester 1992	Rural 1993
30	1.9	1.0
18	1.8	3.1
28	2.0	1.4
52	1.7	2.1
44	2.8	2.3
61	2.3	2.1
66	2.0	1.5
101	3.0	2.4
77/110	-	-
82/151	-	-
149	4.1	4.2
118	4.8	3.9
188	3.1	3.0
153	3.2	2.9
105	4.2	4.2
138	3.4	3.2
187	2.8	2.9
183	4.6	4.0
185	4.1	3.7
204	8.3	7.5
180	8.0	5.0
170	4.0	3.7
198	5.2	5.1
201	7.7	7.0
194/205	-	-
206	8.0	-

In this study the difference in amplitude between congeners is not as clear as that reported by Hoff *et al* (1992a) were the AM ranged from eight for trichlorinated congeners to forty for pentachlorinated congeners and above. However, their sample site was located in rural Canada, away from point sources with an annual mean ΣPCBa concentration being ~ 25 times lower

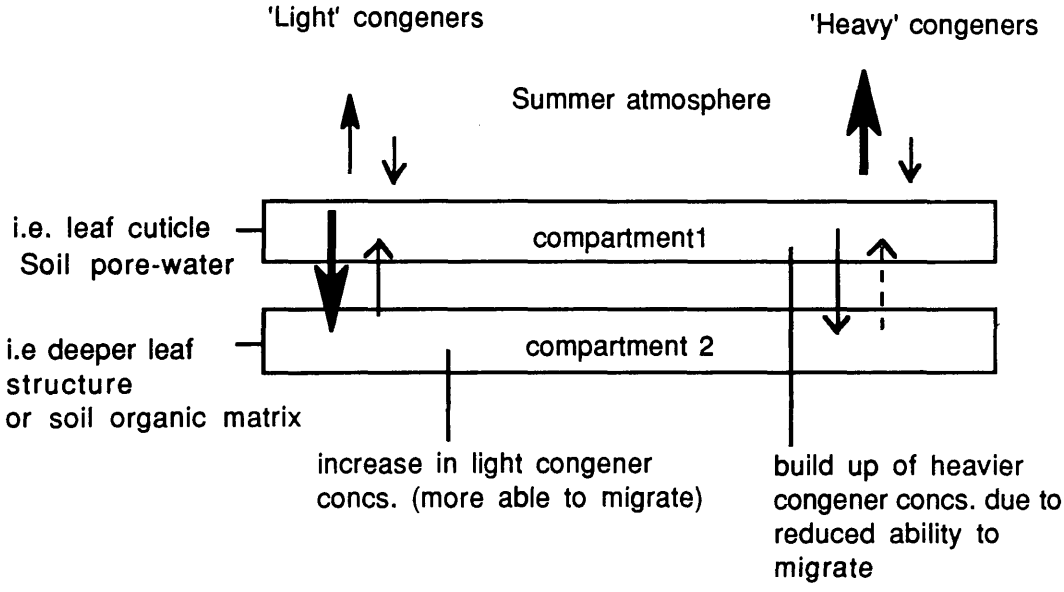
than the annual mean of London (see Table 4.2 and Table 4.4). Perhaps more importantly, the annual temperature variation is more marked in Ontario (Canada) than at any of the urban sites in this study. Temperatures in Ontario typically fluctuate between 23 and -8 °C from summer to winter; in Manchester (for example) the fluctuation was only between 19 and 4 °C. These observations may be consistent with outgassing of previously deposited PCBs constituting a significant source of PCBs to the atmosphere, especially in the summer months.

If temperature is invoked as the major controlling factor - why should the cycling amplitude be greater for the more chlorinated congeners? One possible explanation involves looking at the major sorbing compartments from which SOCs such as PCBs volatilise off with the onset of warmer temperatures. Vegetation and soil have become increasingly recognised in recent years as major compartments in the role of both sink and source, for a range of atmospheric SOCs in the terrestrial environment (Strachan *et al.*, 1994; Jones, 1994; Simonich and Hites, 1994; Welsch-Pausch *et al.*, 1995). It is postulated that from these compartments volatilisation during the warmer summer months results in the elevated PCB concentrations found in the atmosphere (Jones, 1994). For both soil and vegetation (foliage) it is considered that there are two compartments in each, the first being where the compounds reside initially and are readily exchangeable with the atmosphere. This compartment could include the waxy cuticles of leaves and the pore-water of the soil, and may also include 'accessible' soil organic

matter. From this first compartment the compounds are considered to be susceptible either to volatilisation, or to migration to a second compartment. This second compartment could be the deeper wax layer or the internal leaf structure, or in the case of soil, the organic fraction where the compounds become tightly bound. In this second compartment it is considered that the compounds are not as readily exchangeable with the atmosphere as in compartment 1. It is considered, therefore, that the more chlorinated congeners will be less mobile than the lower chlorinated congeners. This could be due to their higher molecular weight, more complicated structural configuration, higher lipophilicity and higher octanol/water partition coefficients. That is, their migration to this secondary compartment will be slower relative to the lighter congeners.

Figure 4.7 schematically represents the two sub compartments and the proposed movement of PCB congeners, 'light' congeners are nominally taken to represent tri- and tetra-chlorinated congeners and 'heavy' as hexachlorinated and above. With reduced movement from the first to the second compartment, over an annual time scale, the higher chlorinated compounds will be increasingly available for re-volatilisation with the onset of higher seasonal temperatures. This is due to their lack of mobility and hence build up in the first compartment.

Figure 4.7 Diagram showing the potential differences between the behaviour of the lighter congeners and the heavier, more chlorinated, congeners when associated with the soil/vegetation compartment. Differences in the degree of atmospheric cycling may be explained by the reduced or slower movement of the heavier congeners to a sub-compartment, making them readily available for re-volatilisation back into the atmosphere with the onset of warmer temperatures.



The lighter congeners which may migrate more easily to these 'inner' sub-compartments will not be as readily volatilised from these areas, and will therefore show a less pronounced increase in air concentrations during the warmer summer months. This theory may help to explain the increase in the seasonal cycling amplitude of the higher chlorinated congeners observed in the data collected from both an urban and rural location.

A second possible explanation is that the lighter congeners being more volatile, require colder temperatures than those experienced in a typical UK

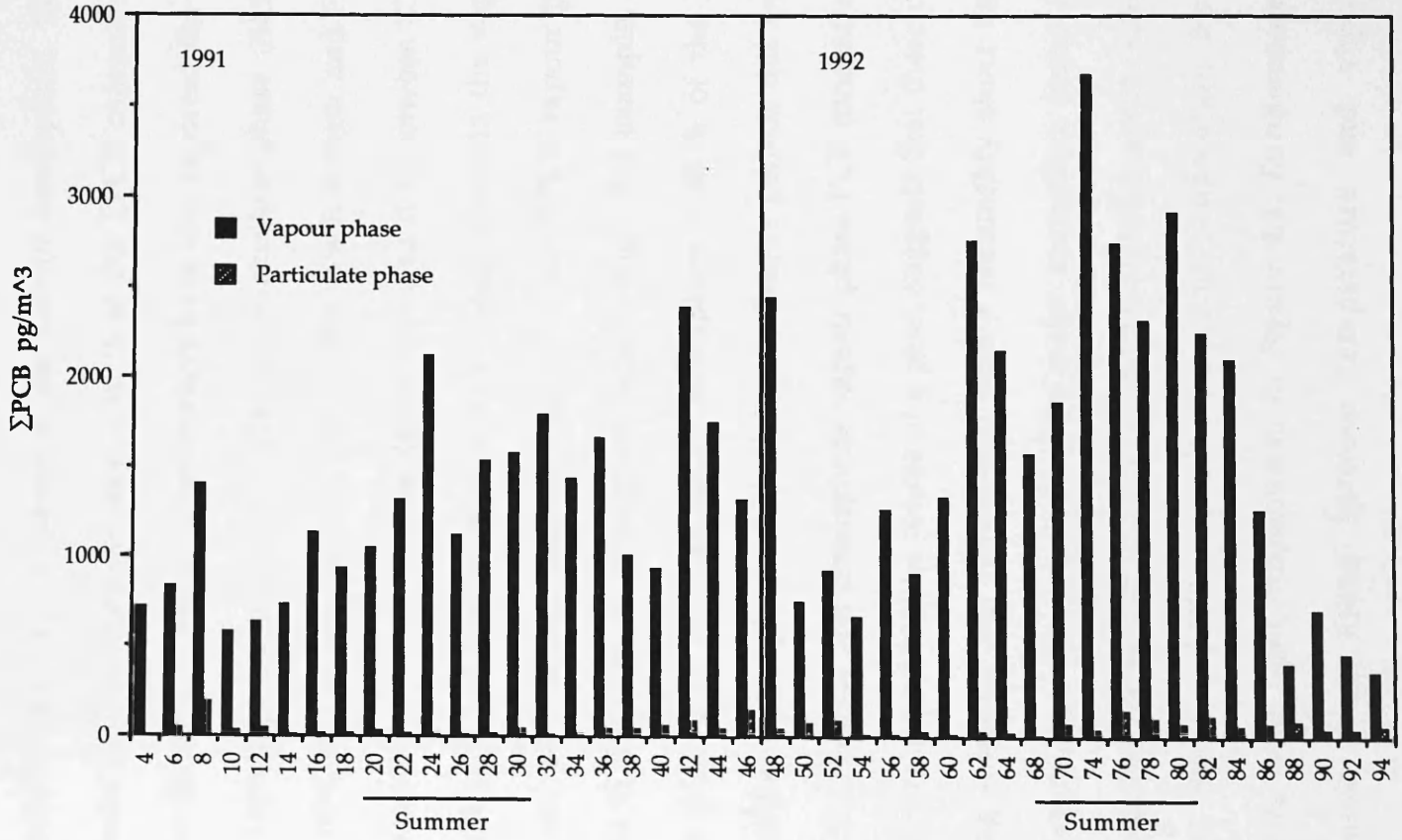
winter, before significant reduction in atmospheric concentrations occurs. The heavier, less volatile, congeners will more readily condense onto surfaces, highlighting the large seasonal change in their observed air concentrations.

4.6 Vapour/particle distribution

As described in Chapter 3 the atmospheric PCB vapour phase component was collected and analysed separately from the particulate phase for those samples collected at the Manchester, Cardiff and rural locations. The particulate phase was defined as that trapped on a glass fibre filter and the vapour phase defined as that associated with two in-line polyurethane foam (PUF) plugs. Semi-volatile organic compounds (SOCs) such as the PCBs will distribute themselves between the vapour and particulate phases primarily according to their vapour pressure, ambient temperature and the amount of surface area available for adsorption (Cotham and Bidleman, 1992). The basis of the atmospheric partitioning of SOCs was discussed in Chapter 2, Section 2.2.3. In this section both particulate and vapour phases were studied separately so that the distribution of the PCB congeners could be examined at the various sample sites.

Figure 4.8 presents the ΣPCB concentrations at Cardiff for the years 1991 and 1992. Each sample week shows the vapour and the particulate phase component. Clearly the vapour phase ΣPCB dominates over the particulate

Figure 4.8 Vapour and particulate ΣPCBb concentrations in Cardiff air throughout 1991/92.



Summer defined as June, July and August

phase throughout each sample year. On an annual basis ~ 95 % of the ΣPCB was found in the vapour phase in the Cardiff atmosphere. Similarly for Manchester and the rural location > 90 % of the ΣPCB concentrations were found in the vapour phase. Other workers have also reported the dominance of the vapour phase component over the particulate phase (Bidleman and Olney, 1974; Manchester-Neesvig and Andren, 1989; Krieger and Hites, 1994). Manchester-Neesvig and Andren (1989) reported that between 83 - 97 % of the ΣPCB sampled in rural Wisconsin air was present in the vapour phase over a one year period. Seasonal changes in the ΣPCB vapour phase were apparent in the ambient atmospheres of this study. For example, during the summer periods in the Manchester atmosphere > 98 % of the ΣPCB was found in the vapour phase while during the winter periods this was reduced to ~ 85 %. The fact that atmospheric vapour phase PCB concentrations vary in a cyclic manner over the course of a year, suggests that these compounds are being removed and replenished over a reasonably short time period. Temperature has been invoked as the major controlling factor for vapour phase concentrations (Pankow, 1993). Indeed significant correlations can be observed between ΣPCB concentrations and temperature for both the Manchester and rural atmospheres in Figure 4.4. Furthermore, stronger correlations were found between temperature and vapour phase concentrations only (see Figure 4.5).

On an individual congener basis the distribution between the vapour and particulate phases was dependent on the level of chlorination and

temperature. This is highlighted in Table 4.7 for selected congeners sampled in Manchester and rural air. In every case, the vapour phase component clearly dominates, although this dominance decreases with increasing level of chlorination (reduced vapour pressure) and during the colder winter months. This effect has also been noted previously by others in both the urban atmosphere of Denver, COL (Billings and Bidleman, 1983) and the rural atmosphere of northern Wisconsin (Manchester-Neesvig and Andren, 1989). All the congeners in Table 4.7 predominantly reside in the vapour phase during the summer (≥ 90 %) but in the winter the amount of any congener in this phase is reduced. For the lighter congeners such as 28 and 52 this is by only a few percent, but for the more chlorinated congeners there may be a fifty percent reduction in the vapour phase concentration.

Table 4.7 Percentage of selected PCB congeners associated with the PUF (nominally prescribed as the vapour phase) in Manchester air in 1991 and rural air in 1993.

	Manchester		Rural	
Congener	Summer	Winter	Summer	Winter
28	99	92	99	90
52	99	93	99	96
101	98	78	99	75
118	98	72	99	71
153	96	58	99	75
138	95	44	99	75
180	90	62	95	57

Summer - June, July, August
Winter - December, January, February

The reduction in vapour phase concentrations is not necessarily matched by a corresponding increase in particulate phase concentrations. Seasonal

cycling of particulate phase concentrations was less discernible in both urban and rural atmospheres. To show this, both the vapour and particulate concentrations of congener 153 were displayed over an annual time scale for the rural and Manchester sites in Figure 4.9. Congener 153, a hexachlorinated biphenyl, was selected as an example because as a mid-weight congener it had significant concentrations in both phases. The increase in vapour phase concentrations for this congener during the summer is evident at both sites, but the particulate concentrations do not show a clear seasonal pattern. This lack of pattern was also evident in the particulate ΣPCB concentrations. Figure 4.10 (a+b) displays the particulate ΣPCB concentrations for the Manchester and rural sites respectively. Overlaid on these figures are the total suspended particulate concentrations (TSP) determined in the atmospheres of both sites for each sample week. The TSP loading does not appear to change with season, and in fact for the Manchester atmosphere remained fairly consistent throughout the whole 2 year sampling period. Similarly in the rural atmosphere seasonal fluctuations in the TSP concentrations were not evident throughout 1993. Manchester, however, displayed the higher TSP loading with a mean (range) concentration of 47 (13 - 150) $\mu g\ m^{-3}$ compared to the rural mean (range) concentration of 31 (13 - 59) $\mu g\ m^{-3}$. This shows that a greater surface area was available for sorption in the urban atmosphere, coupled with higher atmospheric PCB concentrations led to elevated particulate phase concentrations over the rural atmosphere. On average urban ΣPCB particulate phase concentrations were a factor 2 higher than rural concentrations. It is therefore likely that changes in the

Figure 4.9 Separate vapour and particulate phase concentrations of congener 153 over an annual time frame in an urban (Manchester) and rural (Hazelrigg) atmosphere.

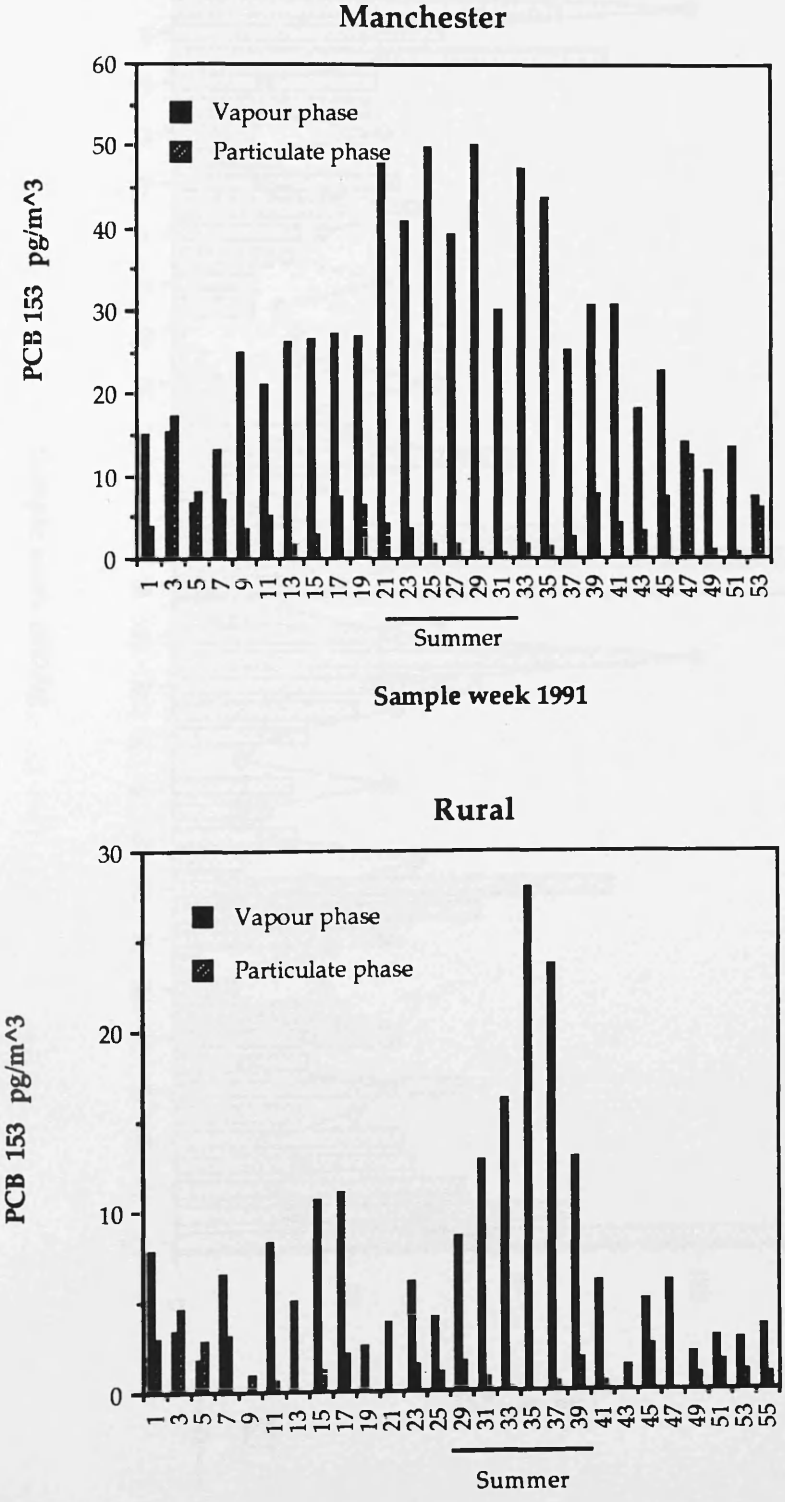


Figure 4.10a Particulate phase ΣPCB concentrations and total suspended particulate (TSP) concentrations in Manchester air.

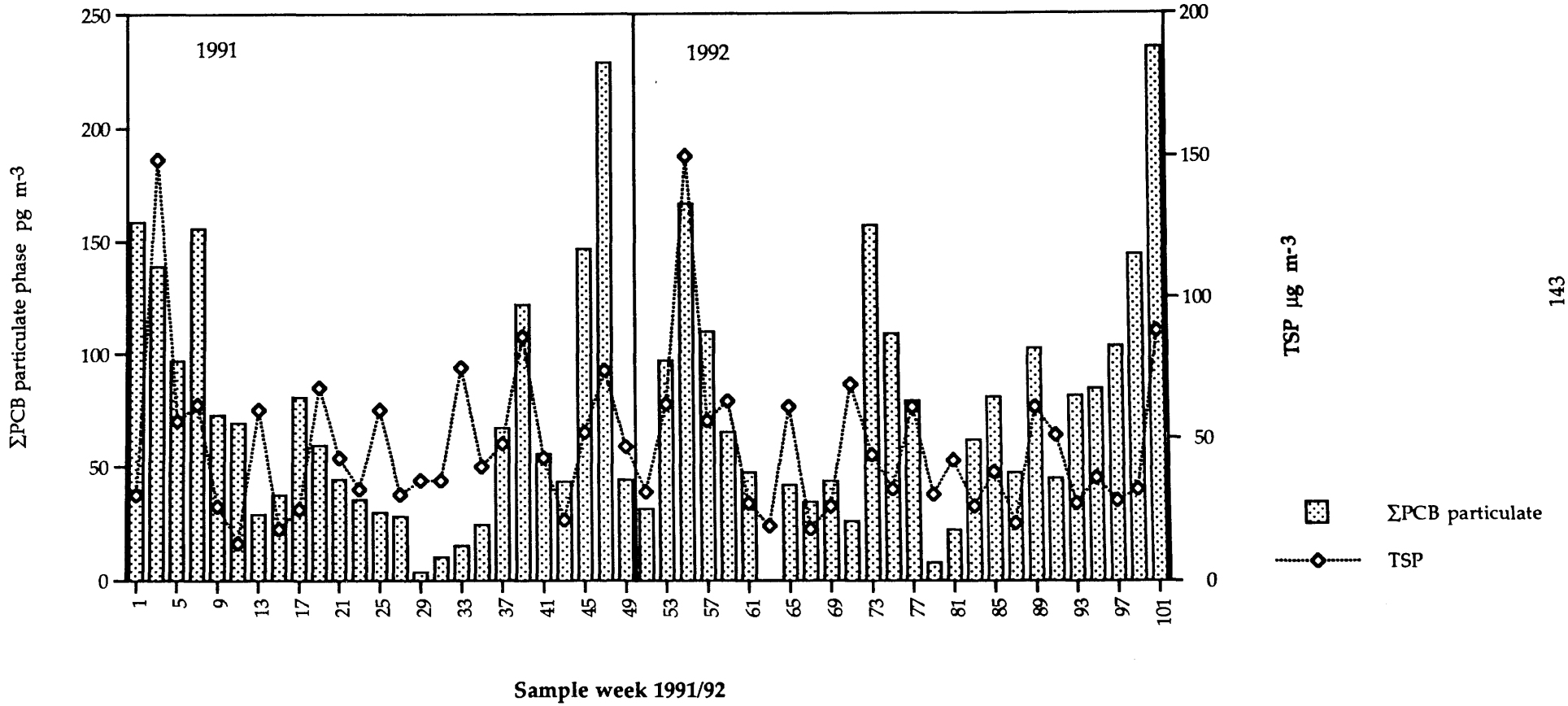
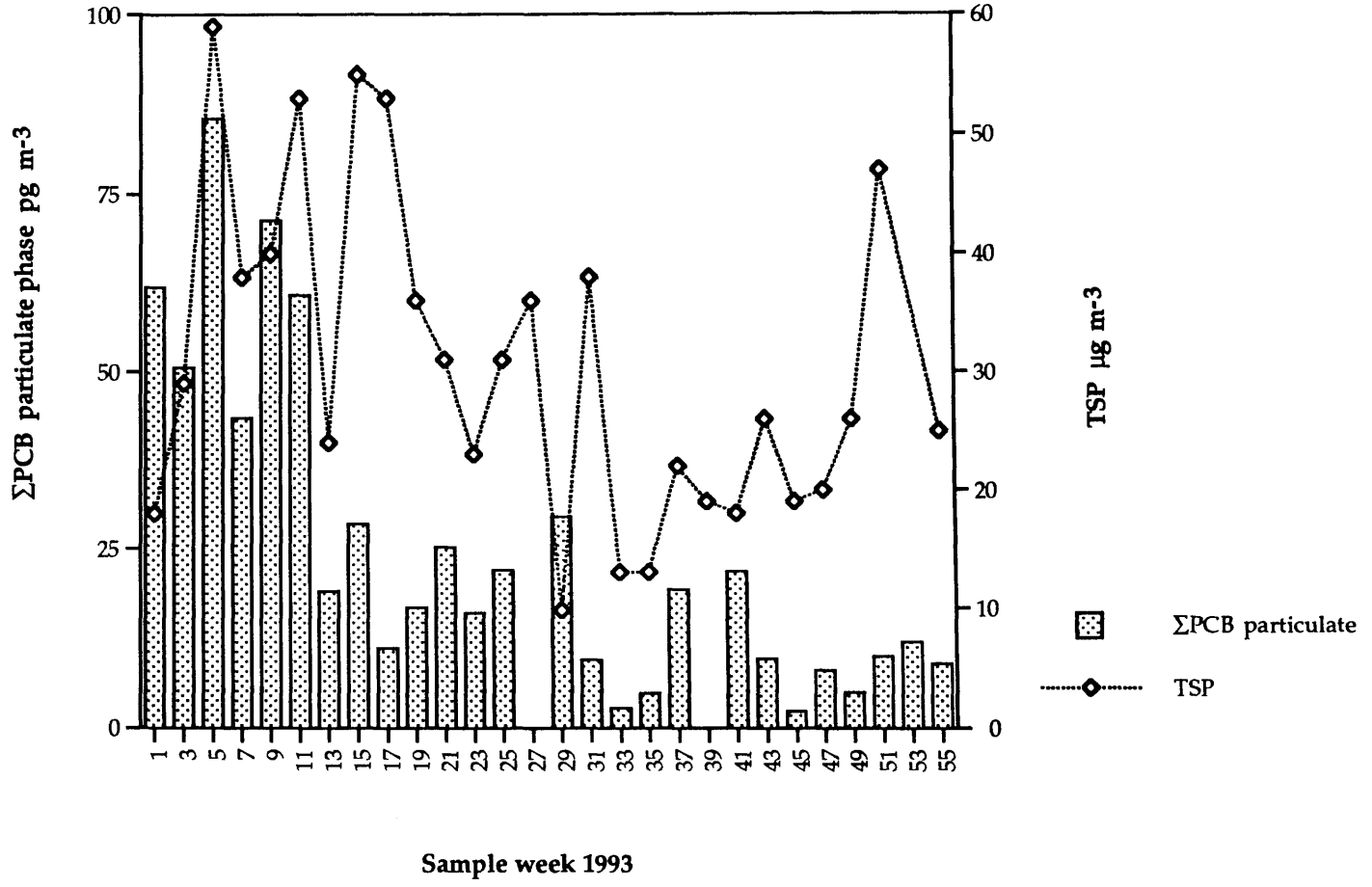


Figure 4.10b Particulate phase ΣPCB concentrations and TSP in rural air during 1993.



particulate associated PCB concentration results through changes in a combination of factors, such as temperature and atmospheric particulate. However, as mentioned in the previous section correlations between particulate associated congener concentrations and temperature were weak or non-existent. Therefore partitioning between the two phases is a more complicated picture. Factors such as the size and nature of the atmospheric particulate may play an important role. Measurement of TSP alone does not give sufficient detail on the various size fractions present within a particular air sample, as many SOCs have been found to be predominantly associated with particles of diameter < 10 μm (Katz and Chan, 1980; Kaupp *et al.*, 1994). Furthermore other factors such as humidity have also been shown to influence the partitioning behaviour of SOCs (Lee and Tsay, 1994). Water molecules compete with the surface binding sites on the particles reducing organic vapour adsorption, which would otherwise occur.

In order to examine the effects of temperature on the vapour/particle (V/F) partitioning of PCBs in this study, TSP weighted adsorbent/filter (A/F) partition coefficients were plotted against inverse temperature for the six indicator congeners (28, 52, 101, 153, 138 and 180). The A/F partitioning nominally represented the true atmospheric V/P ratio and is expresed as the TSP weighted partition coefficient [(F/TSP)/A] according to Pankow (1987). This is further described in Chapter 2, Section 2.2.3, but in effect is the ratio of the sorbed concentration of a compound (pg μg^{-1}) to its gaseous concentration (pg m^{-3}). Rural and Manchester data sets for each congener

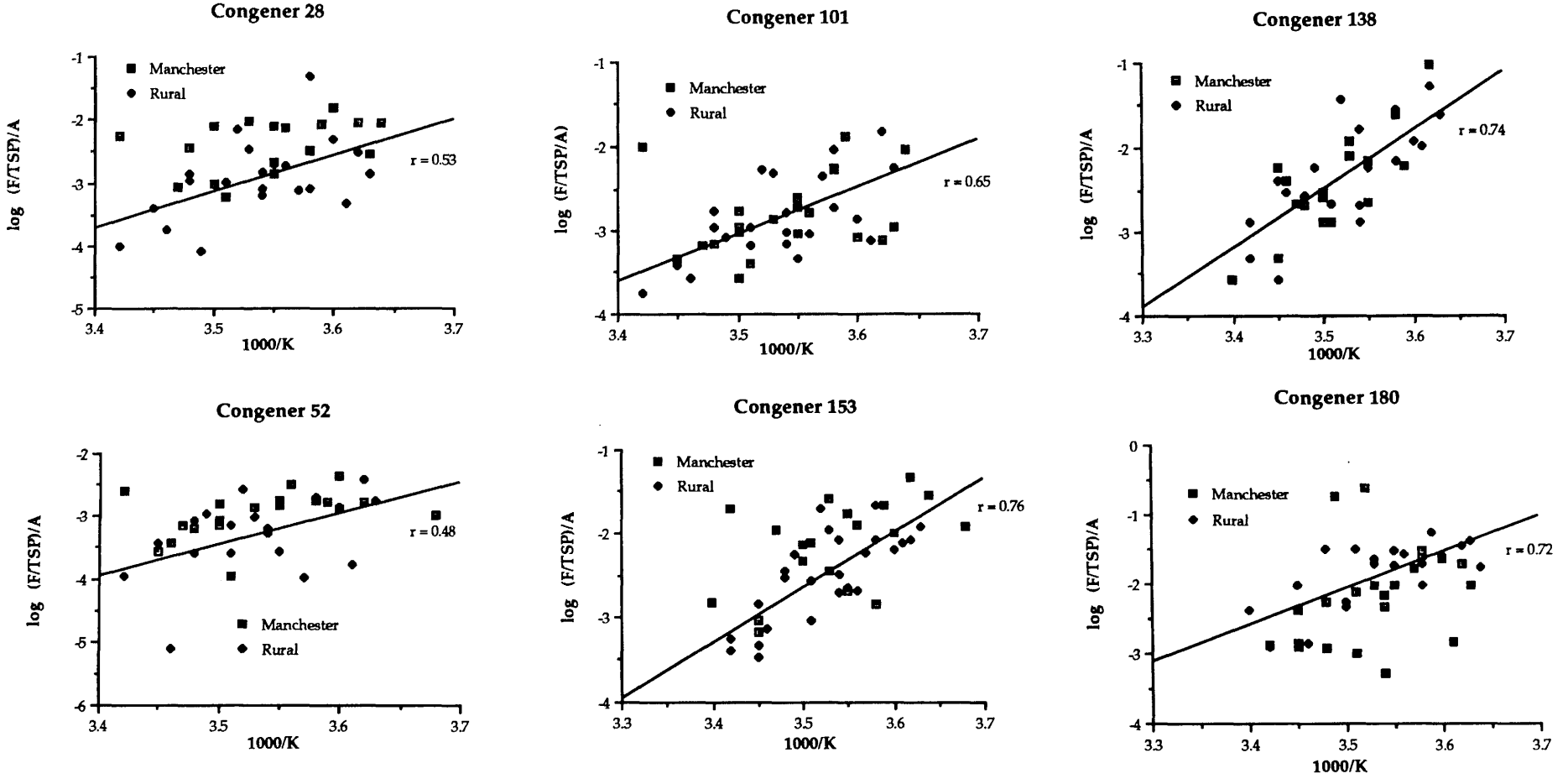
were combined in each plot so that the partitioning in these different atmospheres could be examined. The relationship between temperature and the partitioning coefficient [(F/TSP)/A] is presented in Chapter 2, Section 2.2.3 and takes the straight line form expressed as:-

$$\log[(F/TSP)/A] = m/T + b$$

Where m and b are the slope of the line and the Y-intercept respectively, and T is the mean ambient temperature (K) during a particular sampling week (Pankow, 1987).

Figure 4.11 displays the plots of log [(F/TSP)/A] against inverse temperature for the selected congeners. A positive correlation was observed for each congener, that is the partitioning coefficient increased (moving up the Y-axis) with decreasing temperature (moving away from zero on the X-axis). This denotes an increased partitioning to the solid phase with a reduction in temperature. Moreover, as seasonal patterns could not be deduced for the particulate phase PCB concentrations at either urban or rural sites (for the temperatures encountered in this study) then the increase in partition coefficents with a reduction in temperature was through a decrease in A (the vapour phase concentration). Vapour phase concentrations do show variations with season displaying significant correlations with temperature (see Figure 4.5). If particulate phase concentrations do not change with temperature, then an alternative argument is that the partitioning is

Figure 4.11. Plots of partition coefficient log[F/TSP/A] versus inverse temperature for six indicator congeners from the Manchester and rural atmospheres. 26 samples taken at the Manchester (1991) and rural sites (1993) respectively. A = Adsorbent retained (nominally the vapour phase), F = Filter retained (nominally the particulate phase) and TSP = Total suspended particulate.



All correlations statistically significant at the 99 % confidence limit ($P \leq 0.01$).

dominated not by particles in the atmosphere but by the earth's surface. This theory was put forward by Hoff *et al.* (1992b) who acknowledged the large discrepancy in surface area available for sorption between terrestrial surfaces and the particulate in the atmosphere. For example, by taking the mean rural TSP loading (this study) of 31 $\mu g\ m^{-3}$, a specific surface area of particles of 0.05 $cm^2\ \mu g^{-1}$ (Pankow, 1987) and an atmospheric mixing layer thickness of 2000 m, then a total surface area of atmospheric particulates in a 1 m^2 column up to the top of the mixed layer is approximately 0.31 m^2. The surface area of 1 m^2 of earth's surface is significantly larger than this, particularly if the surface is covered by vegetation. Simonich and Hites (1994) estimated 1 m^2 of terrestrial surface occupied by temperate vegetation has an overall surface area of 7 m^2. Thus it may be the case that terrestrial surface vapour exchange dominates over the atmospheric particulate and plays a more important role in the annual cycling of atmospheric PCBs.

For each congener in Figure 4.11 the rural data points do not form separate clusters from the urban (Manchester) points. That is the partitioning coefficients for the temperature ranges encountered do not differ between the urban and rural atmospheres. This indicates that although the TSP concentrations differed between the sites the partitioning process did not. Either the TSP substrates were similar between the urban and rural atmospheres or the partitioning process is dominated by terrestrial surfaces as suggested earlier. Rural TSP has been found to differ in composition

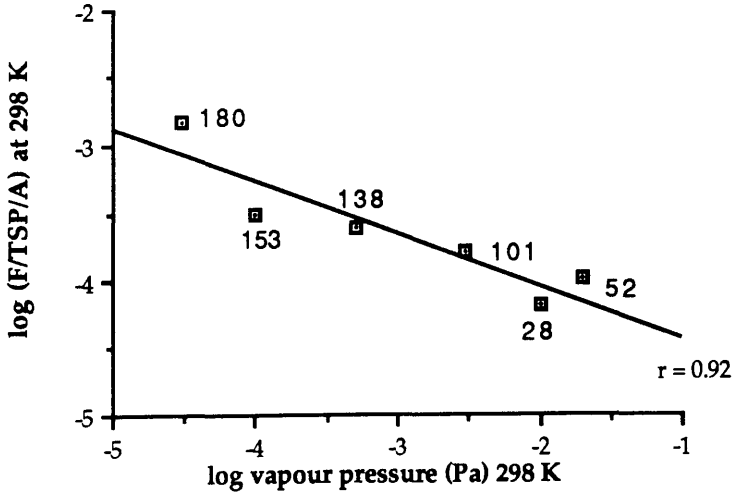
compared to urban TSP. An intensive study carried out in urban districts of New Jersey (USA) found ~ 50 % greater inhalable particulate matter (IPM) [particles of diameter ≤ 10 μm], compared to a rural control site (Lioy and Daisey, 1986). Yet it is this size fraction of atmospheric aerosol that contains > 90 % of the bound SOCs. This would indicate, therefore, that at a rural location such as the one in this study the partition coefficients for the selected congeners should be higher than those depicted in Figure 4.11, and hence differ from the urban values. This was not apparent, providing further evidence that TSP alone is not a major factor in the partitioning of atmospheric PCBs.

For the lighter congeners (28 and 52) the partition coefficients range from ~ log -4 (0.0001) at 20 °C to ~log -2 (0.01) at 2 °C. For the more chlorinated congeners of 153, 138 and 180 the change in coefficient range is much greater over these temperatures. For example congener 138 has a coefficient of 0.0003 at 20 °C and 0.1 at 2 °C. This is a change of three orders of magnitude compared to the lighter congeners which change by only two orders of magnitude. This implies that in temperate climates, such as the UK, the lighter more volatile congeners will undergo less reduction in vapour phase concentrations, compared to the more chlorinated congeners with the onset of cooler temperatures (i.e. winter) - in other words there is reduced partitioning to solid surfaces for these lighter congeners. Indeed, this is supported by the fact that the more chlorinated congeners display greater seasonal cycling with a higher amplitude change in concentrations between

winter and summer (see Table 4.6). Furthermore lower temperatures than those encountered in this study would be required to increase the partitioning coefficients for the lighter congeners.

Partitioning in both rural and urban atmospheres is therefore clearly dependent upon ambient temperature and the compound's volatility. To show this, Figure 4.12 displays the relationship between the partition coefficients at 25 °C for the six congeners represented in Figure 4.11 and their respective vapour pressures (Pa at 25 °C). A strong correlation was evident where r = -0.92 ($P < 0.01$).

Figure 4.12. Partition coefficients for six indicator congeners plotted against respective vapour pressures at 25 °C (298K).



Similarly, strong correlations have also been found for a variety of semi-volatile organochlorine contaminants such as DDT (and its metabolites), chlordane and the HCH isomers (Bidleman *et al.*, 1986; Cotham and Bidleman, 1992).

As ambient temperature and congener vapour pressure effectively govern the partitioning process both in the urban and rural atmospheres then they will have a significant effect on the transport and deposition of PCBs. As observed in Figure 4.11 the partitioning coefficients changed over two orders of magnitude for congeners 28 and 52 at the ambient temperatures encountered in this study. The change in vapour phase concentrations was not as significant as the change for the more chlorinated congeners. These heavier congeners with the lowest vapour pressures, will sorb to solid surfaces more readily than the lighter, more volatile, congeners. Therefore the lighter congeners have the potential for greater transport away from source areas, a significant increase in the partition coefficients only being brought about by much colder temperatures, resulting in a decrease in vapour phase concentrations.

This adds further evidence to the 'global fractionation' theory of Wania and Mackay (1993), where in colder climates, such as the polar regions, lower temperatures will result in increased partitioning to surfaces such as snow and ice. Lighter congeners may be transported further north in the vapour phase than the heavier congeners before finally undergoing partitioning to surfaces due to the much reduced temperatures.

4.7 Summary

Eight PCB congeners were analysed at all of the TOMPS sites, with a further 22 being analysed at Manchester, Cardiff and the rural site (Hazelrigg). London had the highest annual mean concentration of 1350 pg m^{-3} out of all the urban locations. UK urban concentrations were comparable to other urban areas on an international basis. The contemporary urban atmosphere displaying ΣPCB concentrations of ~200 - 2000 pg m^{-3}. The rural site was approximately a factor of 3 - 4 lower than the mean concentrations of Manchester and Cardiff. Internationally, rural locations displayed reduced concentrations over urban areas due to, presumably, a reduction in point sources such as the release of contaminated air from buildings.

The atmospheric PCB profile at each sampling site was dominated by the lower chlorinated, tri- and tetrachlorinated, congeners. Congeners were prevalent in the atmosphere according to their vapour pressure and abundance in the commercial PCB mixtures.

Over the course of a year seasonal fluctuations resulted in a wide range of ΣPCB concentrations at each sample site. Increases in atmospheric concentrations were observed during the warmer summer months, with correlations being apparent between temperature and total (vapour and particulate) ΣPCB concentrations. Stronger correlations occurred between the vapour phase component only and temperature, thereby showing that

temperature is the major controlling factor for vapour phase PCB concentrations.

The less volatile, more chlorinated congeners showed increased seasonal cycling with a greater amplitude change from winter to summer. These heavier congeners may be more readily exchangeable with the atmosphere, due to their reduced ability to migrate to secondary compartments, unlike the lighter congeners (i.e. to migrate from leaf cuticle/soil pore water to deeper leaf structure/soil organic matrix). In these secondary compartments congeners may be less readily available to the atmosphere. Alternatively, UK winter temperatures may not be cool enough to significantly reduce the vapour phase component of the lighter congeners, relative to the heavier PCBs.

More than 90 % of the ΣPCB concentration was found in the vapour phase. On an individual congener basis the distribution between the vapour and particle phases was dependent on the level of chlorination and temperature. For the six indicator congeners, increased partitioning to the solid phase with a reduction in temperature was observed at the Manchester and rural sites. As particulate phase concentrations did not change with temperature it is possible that partitioning is dominated not by atmospheric particulate but by the earth's surface.

Chapter 5

PAHs in UK air

5.1 Introduction

Polycyclic aromatic hydrocarbons (PAHs) produced by combustion sources are ubiquitous in urban and rural atmospheres. Due to the adverse health effects linked to PAHs, environmental monitoring is essential, as it is generally believed that long-term chronic exposure to environmental carcinogens is of greater significance than short term acute exposure (Harkov, 1982). Many studies have focused on the urban atmosphere due to the high number of PAH sources, combined with the fact that a population of high density is exposed to these contaminants. Furthermore, long term atmospheric sampling is required in both urban and rural locations to examine seasonal cycling, changes in the vapour-particle partitioning and to examine atmospheric transport and deposition. In this chapter atmospheric PAH data is presented from a 2 year sampling survey in four urban locations and a 1 year survey at a single rural location. Details of sites, sampling methods and analytical techniques are presented in Chapter 3. Briefly, the four urban sites were in London, Manchester, Cardiff and Stevenage and the rural location was near Lancaster in NW England.

5.2 Annual urban concentrations

Annual average PAH concentrations are summarised in Table 5.1 for the four urban sites for both 1991 and 1992. The weekly concentrations for each compound for the Manchester, Cardiff and Hazelrigg sites are presented in Appendix 2. The mean annual ΣPAH (Σ of 15 compounds) concentrations ranged from 59 in Cardiff (1992) to 166 ng m^{-3} in London (1991). London and Manchester had the highest mean concentrations throughout the two years, followed by Stevenage and Cardiff. Stevenage, the smallest urban site, had a mean ΣPAH concentration greater than Cardiff; Cardiff is the only urban centre to be located near the coast. The data presented in Table 5.1 and described above refers to the summed vapour and particulate phases of each PAH compound. Comparisons with other urban data can be made only with those studies that have sampled both phases i.e. a solid adsorbent has been utilised to trap the vapour phase component. Numerous PAH studies have only sampled the particulate phase (filter retained portion), neglecting the vapour phase and underestimating the total PAH loading in the atmosphere (Gordon and Bryan, 1973; Gordon, 1976; Harkov, *et al.*, 1984; Colmsjö, *et al.*, 1986; Bodzek *et al.*, 1993). Tuominen *et al.* (1988) and Baek *et al.* (1992) have shown the importance of the vapour phase in contributing to the total PAH concentration in the air. Table 5.2 presents total (vapour and particulate) ΣPAH concentrations reported from several urban areas on an international basis. Where possible individual compound concentrations have been reported. Comparison of the measurements reported in Table 5.2

Table 5.1. Mean and range of PAH air concentrations (ng/m^3) at the four urban sites for 1991 and 1992.

PAH	London		Stevenage		Manchester		Cardiff	
	1991	1992	1991	1992†	1991	1992	1991	1992
ACE	4.72 (1.34-22.6)	2.11 (0.79-5.77)	3.61 (0.81-14.1)	1.87 (0.20-4.16)	3.57 (0.08-29.9)	1.53 (0.05-7.70)	2.05 (0.6-8.54)	3.66 (0.16-31.1)
FLU	31.6 (6.31-161)	13.4 (3.44-40.2)	20.2 (5.30-85.8)	14.5 (8.43-28.2)	25.4 (0.07-111)	15.9 (0.11-71.5)	16.9 (0.28-117)	8.20 (1.70-18.6)
PHE	82.0 (9.04-396)	76.1 (23.6-492)	43.7 (8.46-196)	38.2 (17.6-57.8)	55.8 (4.88-173)	35.7 (2.25-97.7)	42.1 (2.25-174)	26.0 (5.42-81.6)
ANTH	6.7 (0.80-39.8)	5.01 (1.20-9.54)	3.52 (0.65-14.3)	3.78 (1.31-5.75)	5.37 (0.20-22.0)	2.03 (ND-9.00)	2.75 (0.61-21.9)	1.82 (ND-10.6)
FLUO	13.3 (3.12-62.4)	7.42 (2.28-16.4)	7.55 (2.03-24.1)	5.85 (2.28-12.1)				
FLUO/MPHE*					17.6 (0.93-76.4)	7.57 (2.39-21.5)	12.3 (3.23-79.8)	7.05 (0.16-37.8)
PYR	12.3 (2.18-64.4)	6.77 (2.11-15.8)	5.72 (1.42-20.5)	5.49 (3.33-10.8)	12.3 (1.69-48.7)	5.50 (1.76-24.2)	7.85 (1.00-52.4)	4.44 (0.33-22.0)
BENZANTH	1.82 (0.23-18.5)	0.80 (0.16-4.31)	1.11 (0.14-10.2)	1.11 (0.22-3.81)	2.57 (0.12-11.8)	0.79 (0.14-5.64)	1.54 (0.14-13.3)	1.02 (ND-9.15)
CHRY	3.05 (0.53-24.1)	1.48 (0.41-5.64)	2.08 (0.31-14.2)	1.67 (0.35-4.79)	3.00 (0.37-10.3)	1.35 (0.13-4.84)	2.48 (0.17-24.3)	1.69 (ND-9.19)
B[b]F	1.66 (0.31-14.8)	1.13 (0.31-3.62)	1.20 (0.20-8.99)	1.28 (0.39-3.34)	1.56 (0.31-5.46)	1.04 (0.13-7.74)	1.65 (0.13-12.6)	1.53 (ND-8.73)
D[ac]A	0.35 (ND-5.00)	0.33 (ND-1.35)	0.34 (ND-4.65)	0.44 (ND-1.35)				
D[ac]A/B[k]F*					1.99 (0.27-8.23)	1.04 (0.21-7.71)	1.75 (0.23-15.0)	1.50 (ND-10.7)
B[k]F	1.78 (0.24-16.5)	1.02 (0.23-4.15)	1.27 (0.15-10.5)	1.32 (0.34-3.76)				
B[a]P	1.06 (ND- 10.2)	0.56 (ND-3.15)	0.65 (ND-5.18)	0.63 (ND-2.36)	1.82 (0.29-8.77)	1.20 (0.18-12.5)	1.73 (0.18-13.7)	0.58 (ND-5.64)
B[ghi]P	5.33 (0.40-85.3)	4.40 (0.49-16.8)	3.26 (0.19-59.6)	4.22(0.15-12.2)	2.46 (0.52-8.49)	1.81 (0.36-16.4)	2.00 (0.36-16.4)	1.20 (ND-9.71)
COR	NA	NA	NA	NA	1.18 (0.28-3.72)	0.72 (0.17-6.92)	0.79 (0.21-6.92)	0.40 (ND-2.48)
ΣPAH	166	121	94	80	135	76	96	59

† Sample collection ceased April '92

* HPLC-method co-elution, for Manchester and Cardiff samples only

NA=Not Analysed

ND=Non Detect

Table 5.2 Urban atmospheric PAH concentrations (ng/m^3) reported by various workers (vapour and particulate phase).

PAH	Vienna, Austria	Columbia, USA	Osaka, Japan	Oslo, Norway	Kokkola, Finland	Denver, USA
	a	b	c	d	e	f
ACE	NR	NR	NR	NR	4.31	NR
FLU	NR	NR	NR	NR	9.72	NR
PHE	154	34.8	115	NR	22.2	33.0
ANTH	35.0	1.13	115	NR	0.95	3.45
FLUO	73.0	6.61	36.5	NR	6.43	7.02
PYR	75.0	11.3	27.5	NR	3.16	15.1
BENZANTH	10.5	NR	3.93	NR	ND	NR
CHRY	7.15	NR	3.90	NR	0.41	NR
B[b]F	10.0	NR	10.2	NR	0.40	NR
D[ac]A	1.40	NR	NR	NR	NR	0.49
B[k]F	10.0	0.30	NR	NR	0.40	0.49
B[a]P	9.45	0.49	4.42	NR	<0.11	1.21
B[ghi]P	14.3	1.18	2.73	NR	0.45	NR
COR	10.7	0.80	NR	NR	0.61	5.91
ΣPAH	410	56.6	319	580	49.2	66.7

a Mean concs. for 1983 and 1984 - Street level (Jaklin and Krenmayr, 1985).

b Median concs. for two sites at a height of 20-30 m, taken throughout 1981-1983 (Keller and Bidleman, 1984).

c Median concs. sampling throughout 1981, roof top height (Yamasaki et al., 1982)

d Mean concs. during Jan and Feb 1979, roof top height (Thrane and Mikalsen, 1981).

e Mean conc. of 4 samples taken in May 1985, small industrial town (Pyysalo et al., 1987).

f Mean concs. between Oct 1985-Jan 1986, at roof level (Foreman and Bidleman, 1990).

NR = Not reported

ND = Not detected

with the PAH concentrations of this study (Table 5.1) should be carried out with great prudence, since they were performed according to different procedures and conditions of sample collection. Factors such as the season when sampling took place, meteorological conditions, time of day and the characteristics of the sampling site i.e. sampling height, will all affect PAH concentrations (Menichini, 1992). An important consideration is sampler location within the urban centre itself, since Thrane and Mikalsen (1981) found a decrease of a factor of ~0.3 - 0.5 in ΣPAH concentrations from ground level to a height of 25 m in Oslo, Norway. Furthermore the various analytical techniques employed will result in discrepancies between different sampling programmes. Nevertheless from Table 5.2 it is possible to conclude that urban atmospheres have mean ΣPAH concentrations in the order of 10's-100's ng m^{-3}. This is in agreement with concentrations found at the UK urban sites in this study.

On an individual compound basis the PAH loading in the atmosphere is dominated by the lighter three ring compounds, notably PHE and FLU (MW <200) for the urban sites presented in Table 5.1. This again is consistent with other studies of urban air [Table 5.2] (Tuominen *et al.*, 1988; Baek *et al.*, 1992). Apart from FLUO and PYR, all the other PAH compounds measured had mean concentrations an order of magnitude lower than FLU and PHE at each of the four urban sample sites. B[a]P, the most carcinogenic PAH detected (IARC, 1987), ranged from ND-2.35 in Stevenage to 0.18-13.7 ng m^{-3} in Cardiff for the two sampling years. The German Federal Agency had

proposed a guideline limit of 10 ng m^{-3} for the annual mean B[a]P concentration (Baek *et al.*, 1992). None of the urban sample sites in this study had an annual mean near this limit. Manchester had the highest mean annual concentration (1991) of 1.82 ng m^{-3}.

5.2.1 B[a]P in London air

London was probably the first major city where reliable measurements of PAHs in air were made, with some data reported prior to the infamous smogs of the mid-1950's. In 1952, Waller (1952) reported the measurement of 3,4-benzopyrene (or (B[a]P) in 'town air' sampled in central London and elsewhere, using fluorescence detection. He reported the mean B[a]P concentration for air sampled at County Hall in 1947-1951 to be 4.6 μg/100 m^3 or 46 ng m^{-3}.

Further measurements by Commins and Hampton (1976) through the 1960's and 1970's elsewhere in central London led them to conclude that B[a]P concentrations had declined to "about one tenth" of Waller's values in 25 years. Concentrations detected at St. Bartholomews Hospital, for example, averaged 26 ng m^{-3} in 1962-63 and 5 ng m^{-3} in 1972-73. The TOMPS data in this study suggest this decline in B[a]P has continued still further - to an average of 0.8 ng m^{-3} in 1991/92. The highest central London value measured during our study was 10.2 ng m^{-3} compared to 3300 ng m^{-3}

reported for 'foggy days' by Waller (1952). Clearly, even allowing for improvements in analytical techniques and the inevitable spatial differences between the sites used by Waller (1952), Commins and Hampton (1976) and this study, these data provide good evidence that air quality in London has improved considerably with respect to this particular aromatic hydrocarbon over the last 45 years or so - perhaps by two orders of magnitude.

Coal burning for domestic space heating was widely practiced in London up to the 1950s. These numerous diffuse and inefficient combustion sources were likely to have generated a much greater PAH burden to the atmosphere than the contemporary gas and electric domestic heating appliances which are used most extensively in modern homes. In contrast, this general trend in improved B[a]P concentrations in inner London has occurred over a time when vehicle use (with gasoline and diesel comsumption) has increased enormously in the UK as a whole.

5.3 Rural PAH concentrations

As a comparison to the four urban sites, rural air was sampled for PAHs, a site being established near Lancaster at Hazelrigg in NW England (see Chapter 3). Table 5.3 presents the mean and range of concentrations for individual compounds sampled during 1993. Data from other studies also in rural locations where both the particulate and vapour phases were sampled

Table 5.3 PAH air concentrations (ng/m^3) at the rural location for 1993 and at rural lo from other studies. Mean concentrations (range).

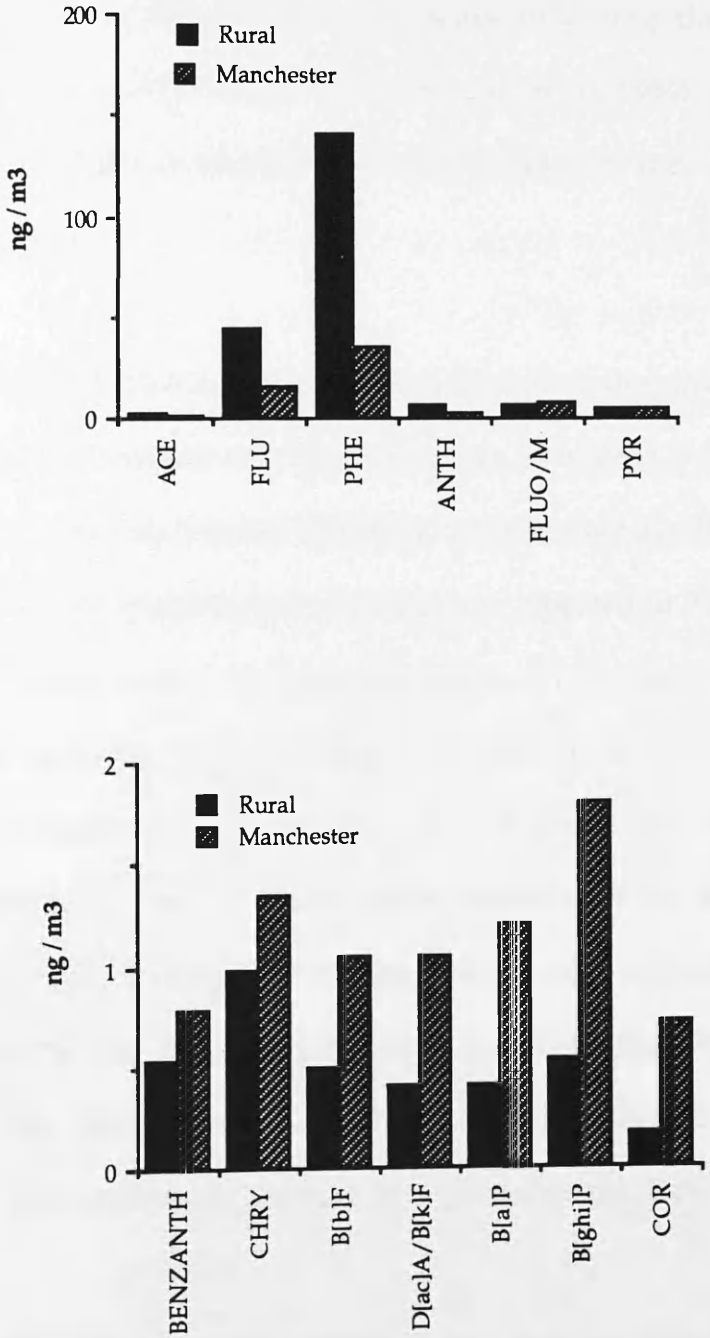
PAH	This Study (Hazelrigg)	Lake District NW England a	Birkenes South Norway b	Kosetice Czech Rep. c
ACE	2.48 (0.07 - 10.3)	*5.63 (0.08-39.3)	NR	0.99 (ND-1.80)
FLU	44.3 (1.46 - 195)	*	NR	2.13 (ND-5.20)
PHE	141 (2.91 - 686)	14.9 (2.30 - 107)	NR	2.35 (0.46-4.65)
ANTH	6.91 (ND - 16.8)	1.61 (0.16-7.49)	NR	0.42 (ND-0.64)
FLUO	-	3.83 (0.38-23.4)	NR	0.61 (ND-1.39)
FLUO/MPHE	6.26 (0.16 - 32.0)	-	NR	-
PYR	4.98 (0.14 - 15.5)	5.83 (0.26-62.5)	NR	0.88 (ND-2.50)
BENZANTH	0.54 (ND - 2.42)	†1.05 (0.04-6.16)	NR	-
CHRY	0.98 (ND - 8.41)	†	NR	1.47 (ND-2.33)
B[b]F	0.50 (0.05 - 2.99)	2.39 (0.10-16.9)	NR	ND
B[k]F	-	0.51 (0.02-3.73)	NR	0.47 (ND-4.70)
D[ac]A/B[k]F	0.41 (0.03 - 2.65)	-	NR	-
B[a]P	0.40 (0.01 - 3.35)	2.98 (ND-32.2)	NR	1.18 (ND-2.8)
B[ghi]P	0.53 (ND - 3.42)	-	NR	-
Cor	0.17 (0.03 - 0.97)	-	NR	-
ΣPAH	210 (23.9 - 987)	39.3 (5.28-254)	20 (7-40)	6.69 (0.72-10.1)

a Air samples taken over a year at Esthwaite water, Lake District (Gardner, 1993).
* co-elution for ACE/FLU
† co-elution for BENZANTH/CHRY
b Average of 10 samples, individual concentrations not reported (Thrane and Mikalsen
c 10 samples taken at a background GEMS station, South Bohemia (Holoubek et al., 19
ND = not detected

are also included. Importantly, the mean annual ΣPAH concentration at the Lancaster rural site (1993) was higher than at any of the urban sites (1991 and 1992). However on an individual compound basis, this was largely due to the concentrations of the lower molecular weight PAHs of FLU and PHE which had mean concentrations greatly exceeding the urban concentrations.

Figure 5.1 displays the mean individual rural PAH concentrations (1993) with the Manchester concentrations for 1992. It must be noted that the data was collected from two different years. However the sampling frequency and the number of samples collected for each year were the same for both sites. From Figure 5.1 the low molecular weight compounds of ACE through to ANTH have higher mean annual concentrations at the rural site than in Manchester. The two low molecular weight compounds of FLU and PHE dominate the profile at both sites, being substantially higher in the rural atmosphere (by a factor of 3 and 4 respectively). The middle weight, four ring compounds of PYR, BENZANTH and CHRY have similar mean concentrations at both sites and, from Tables 5.1 and 5.3, also display similar concentration ranges throughout the respective sampling years. The heavier compounds of B[b]F through to COR are significantly higher in Manchester air than in the rural air, ranging from a factor of 2 higher for B[b]F to a factor of 3 and 4 higher for B[ghi]P and COR respectively. Sources of these heavier compounds are numerous in the urban environment. Motor vehicles are considered to account for the majority of contemporary PAH emissions in the urban environment (Baek *et al.*, 1992). Indeed, Wild and Jones (1995)

Figure 5.1 Comparison of annual mean PAH concentrations for Manchester (1992)and the rural location (Hazelrigg) (1993).



estimated that vehicles had the second highest annual PAH emission to the UK environment after domestic coal combustion. With the decline of coal combustion in the urban environment following the implementation of the Clean Air Acts in the 1950's (Boubel *et al.*, 1994), traffic may therefore have the highest impact on PAH loading in the contemporary urban atmosphere.

The PHE and FLU concentrations measured at the rural location are higher than those reported at other rural sites presented in Table 5.3, including those reported by Gardner (1993) for a site in the Lake District. His data were similar to the Manchester concentrations reported in Table 5.1. In Gardner's Lake District study, samples were taken on the shore of Esthwaite Water, near to domestic sources where solid fuel combustion is used as the main form of residential heating i.e. coal and wood. The concentrations of the high molecular weight PAHs (B[k]F onwards) in the Esthwaite atmosphere were elevated compared to the other rural studies and more closely resemble urban concentrations detailed in Table 5.1. High molecular weight PAHs like B[b]F, B[a]P and B[ghi]P have been found at high concentrations where coal and wood combustion is predominant (Daisey *et al.*, 1986).

Rural atmospheric PAH concentrations are therefore variable, temporally and spatially. Global background concentrations of PAHs have been established at more remote sites such as the Canadian Arctic (Patton *et al.*, 1991), Norwegian Arctic (Pacyna and Oehme, 1988) and over the Atlantic

ocean (Marty *et al.*, 1984). Here the ambient atmospheres are less susceptible to localised sources, but may be influenced by more distant sources through long range atmospheric transport (Masclet *et al.*, 1988; Patton *et al.*, 1991). Examples of PAH concentrations measured at remote sites are presented in Table 5.4. The selected studies have sampled both the vapour and particulate phases, the ΣPAH concentrations being approximately an order of magnitude lower than the rural concentrations reported in Table 5.3. PHE is again the dominant PAH having the highest concentrations at all four sites. The most remote site is the Canadian Arctic site at Alert on Ellesmere Island, where the PAH concentrations are markedly lower than the other three sites, indicating the reduction in atmospheric PAHs through long-range transport away from source areas. Differences between the rural/urban data will be discussed in more detail below.

5.4 Seasonal variations

Figure 5.2 displays the ΣPAH concentrations (vapour and particulate) for Manchester and London over 1991 and 1992. For each year there are 26 sample weeks (sampling for PAHs occurred at a frequency of every other week throughout the two year period, running consistently throughout each year - see Chapter 3). ΣPAH concentrations did not vary significantly between seasons. There was statistically no significant difference in ΣPAH levels between seasons in London (ANOVA $P < 0.05$; $F = 1.2$ at 3, 38 df). Seasons were classified by splitting a sample year into four quarters, three

Table 5.4 PAH air concentrations (ng/m^3) at remote locations (vapour and particulate phase collected).

PAH	Coastal region Sweden a	Great Lakes USA b	Corsica Mediterranean c	Arctic Canada d
ACE	NR	NR	NR	NR
FLU	NR	NR	2.07	NR
PHE	0.74	1.91	3.35	0.08
ANTH	0.02	0.03	0.15	0.0008
FLUO	0.34	0.26	0.42	0.04
PYR	0.18	0.26	0.24	0.02
BENZANTH	0.03	0.04	0.16	0.003
CHRY	0.11	0.18	0.08	0.01
B[b]F	NR	NR	0.12	0.03
B[k]F	0.11	NR	0.05	NR
B[a]P	0.14	0.04	0.02	0.003
B[ghi]P	0.07	0.09	0.13	NR
Cor	0.09	NR	0.09	NR
ΣPAH	1.72	2.81	6.88	0.876

a Low volume sample taken over 135 days (Broman et al., 1991)
b Samples taken on Siskwit Island in Lake Superior, summer and winter 1983 (McVeety and Hites, 1988).
c Fourteen 24h samples collected on a remote site in Corsica (Masclet et al., 1988)
d 10 air samples taken between Feburary - April 1988.
Ellesmere Island (Patton et al., 1991).
NR = not reported.

Figure 5.2 Atmospheric ΣPAH concentrations in London and Manchester throughout 1991/92.

a) London

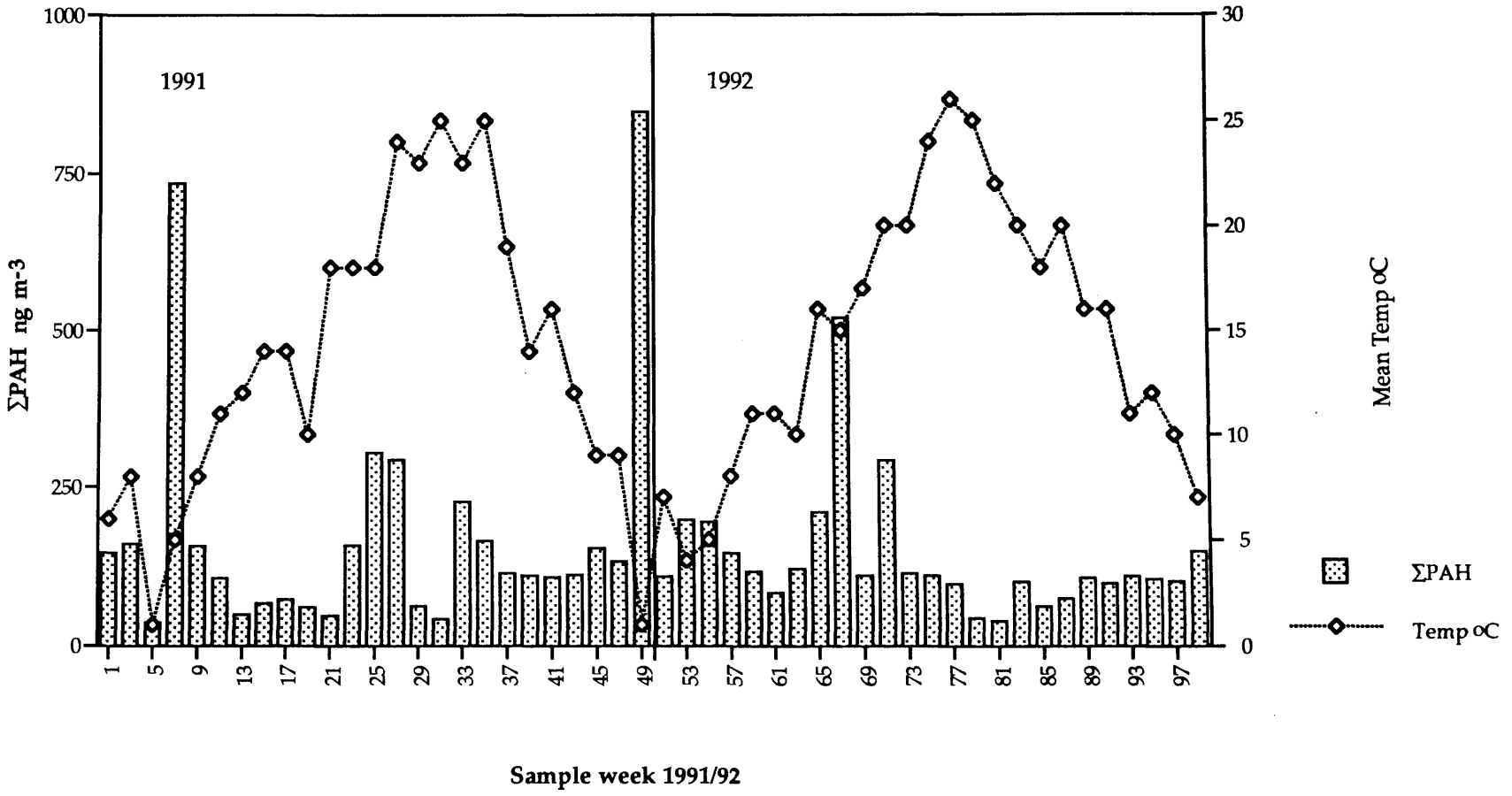
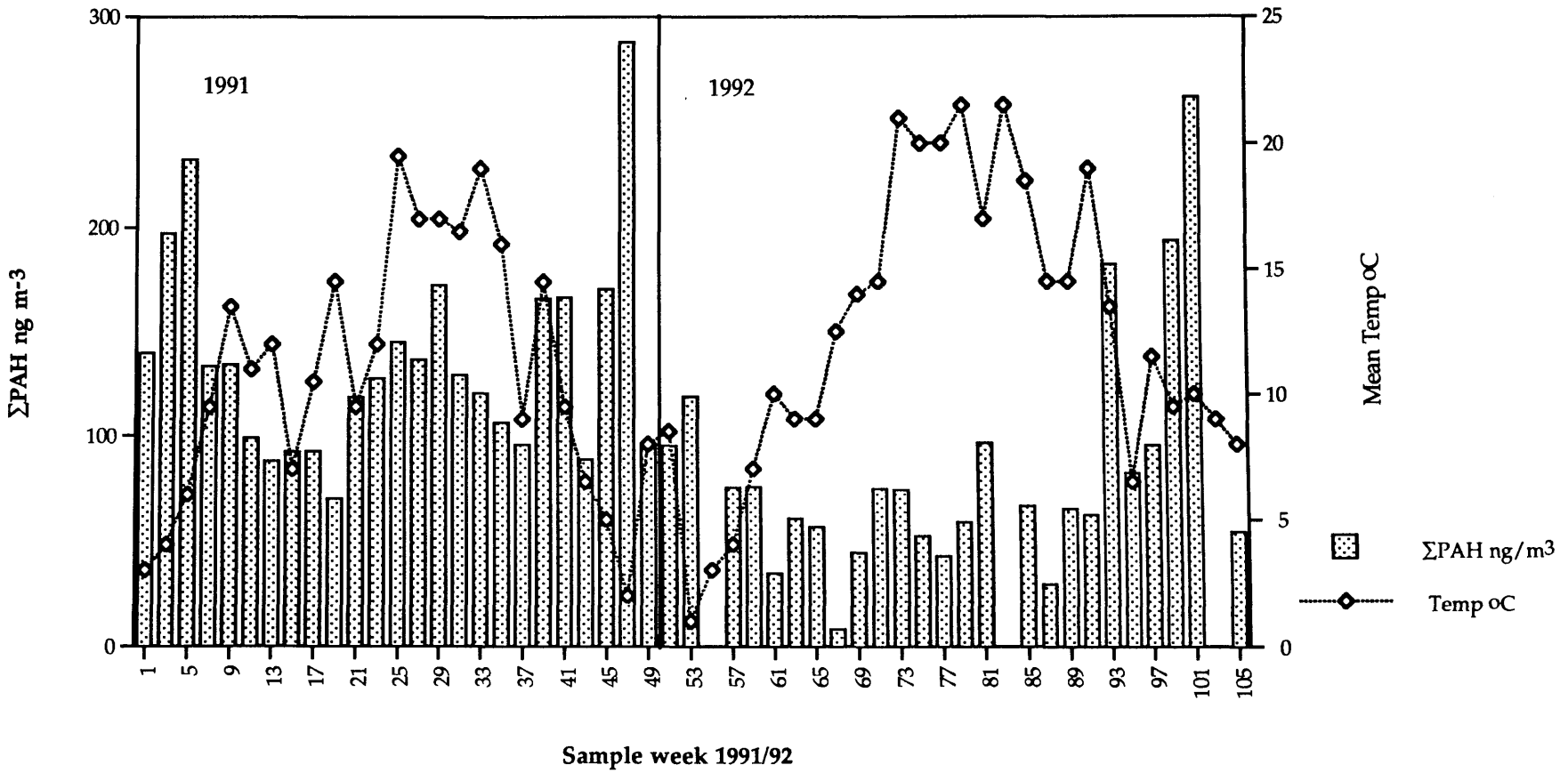


Figure 5.2b Atmospheric ΣPAH concentrations in Manchester.



months representing each season i.e. December, January and February represented winter, while June, July and August were taken as summer. Reasons for there being little seasonal differences in ΣPAH concentrations are due to the low molecular weight compounds such as FLU and PHE which dominate the PAH profile and have high concentrations throughout the year.

Seasonal cycling can be observed for the higher molecular weight multi-ringed PAH. Figure 5.3 presents the B[a]P and B[ghi]P concentrations for the London site through 1991 and 1992. Clearly, elevated concentrations can be observed during the colder winter months (weeks 1-5, 43-55 and 93-99), this phenomenon has been explained by the increased use of fuels for residential/space heating during this period (Santodonato *et al.*, 1981). The temperature profile in Figures 5.2 and 5.3 effectively mark the winter and summer periods. Reduction in the proportion of high molecular weight PAHs during the summer has been attributed to several factors, including reduced fuel combustion for residential heating (Santodonato *et al.*, 1981) and greater photolytic and thermal decomposition of analytes in the warmer summer months (Nikolaou *et al.*, 1984). In contrast concentrations of the lower molecular weight compounds, such as PHE, tend to remain more consistent throughout the year. Figure 5.4 presents PHE concentrations in Cardiff air throughout 1991/92, this lack of temporal change in the urban atmosphere may be due to the ubiquity of this compound, particularly as it is released from many different sources at significant concentrations relative

Figure 5.3 Atmospheric B[a]P and B[ghi]P concentrations in London throughout 1991/92.

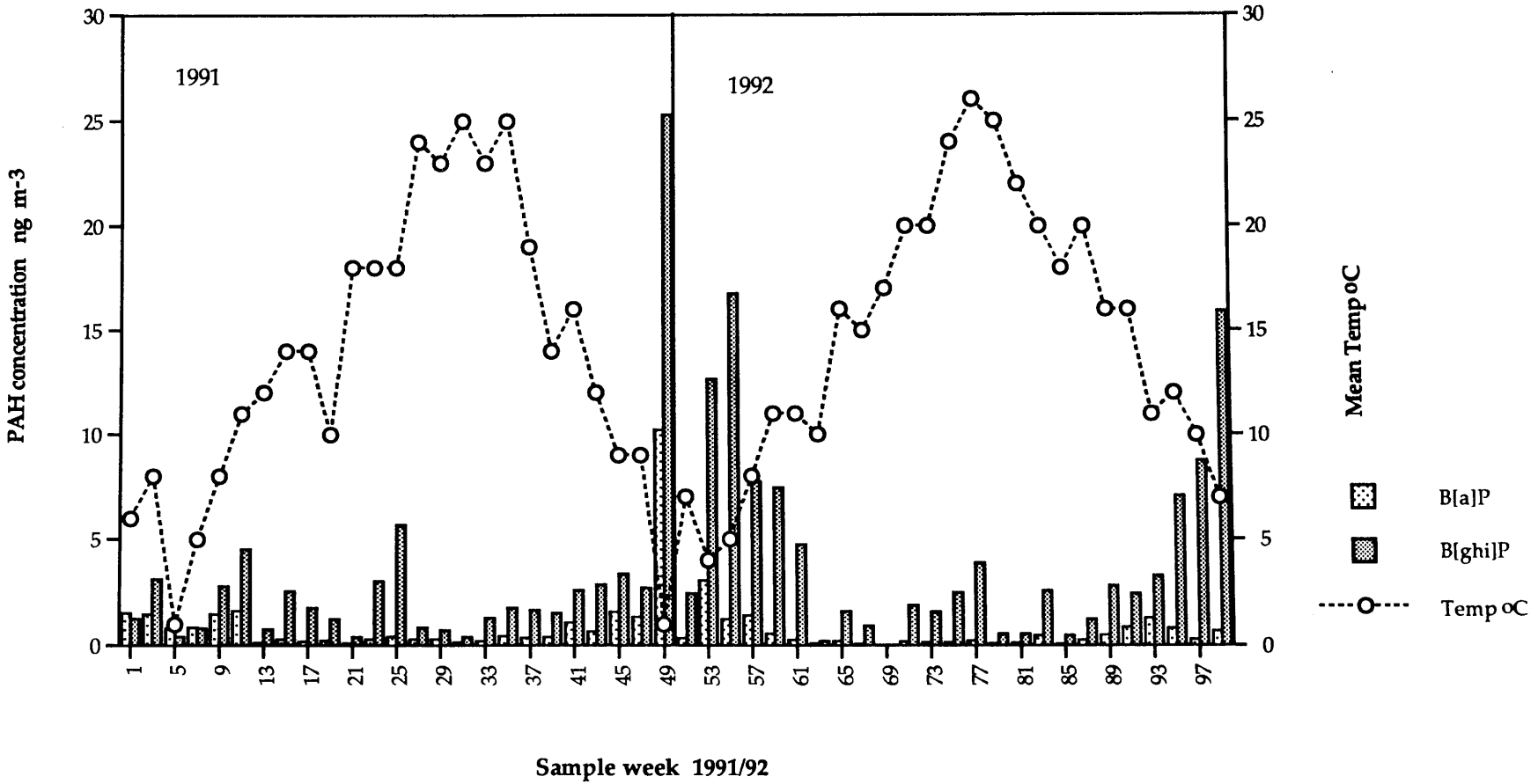
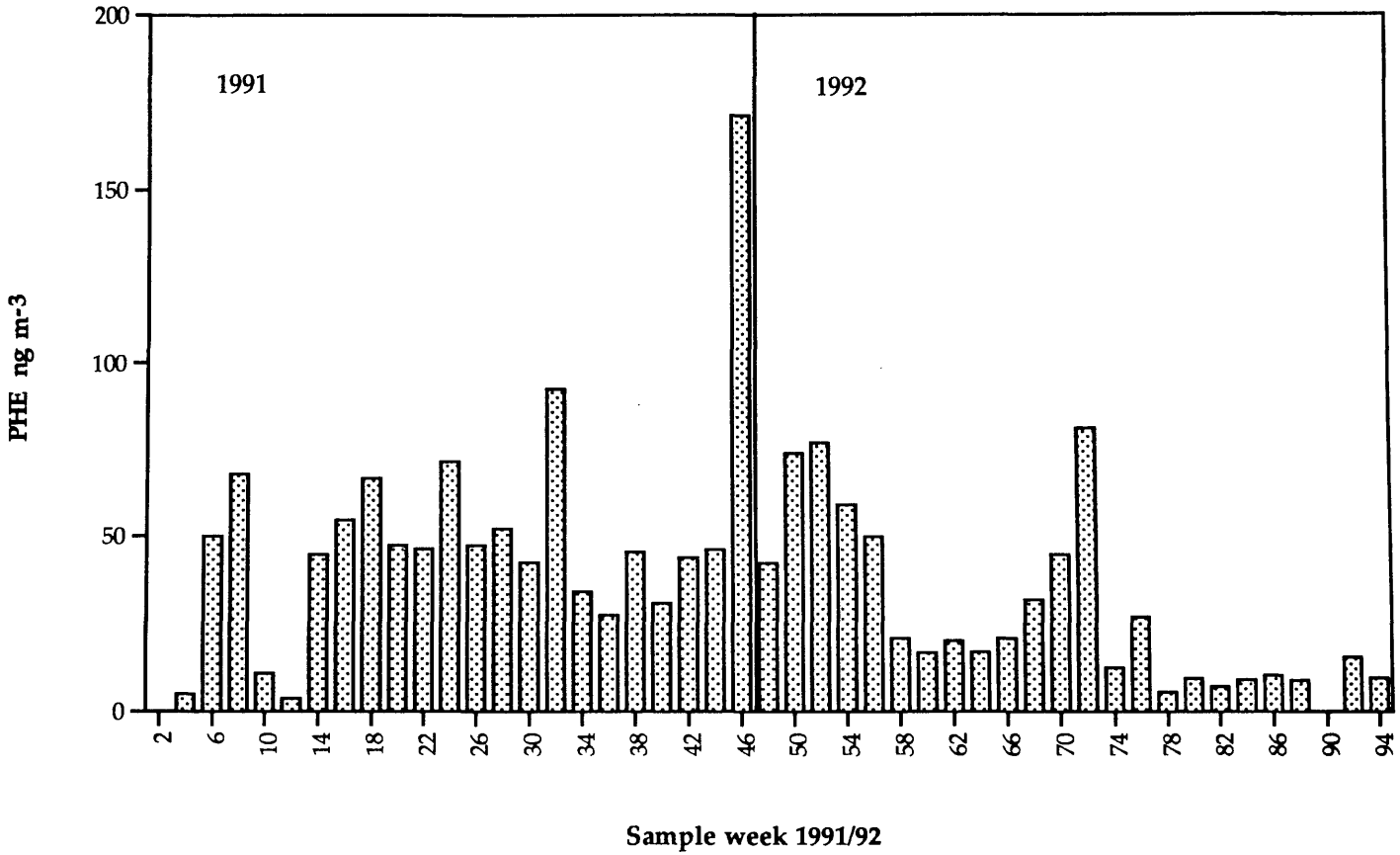


Figure 5.4 Atmospheric PHE concentrations in Cardiff* throughout 1991/92.



* temperature data not available for this site

to other PAHs. (Daisey *et al.*, 1986; Baek *et al.*, 1992). Furthermore atmospheric concentrations may be enhanced by re-volatilisation of 'old' previously deposited fractions. This phenomenon is discussed in more detail in Section 5.5.

5.5 Seasonal cycling in the rural atmosphere

Unlike the urban sites, seasonal cycling of the total ΣPAH concentrations at the rural location was apparent. However the ΣPAH was dominated by the low molecular weight compounds, more so than the urban PAH profile, and in particular by PHE. Seasonal cycling can be observed in the concentrations of PHE with higher concentrations in the warmer summer months as opposed to the winter. Figure 5.5 depicts the total PHE concentrations (vapour and particulate phases) throughout 1993. Summer is defined as sample weeks 29-39 and there was a statistically significant difference between the summer and winter mean concentrations (t-statistic = 20.1, 1df, $P<0.05$). Worthy of note is sample week 41 corresponding to Sept. 8th - 15th. The ΣPAH concentration for this sample week was 988 ng m^{-3}, with PHE comprising some 70 % of this figure, with a concentration of 685 ng m^{-3}. For this one sample week the PHE concentration was approximately a factor of 3 higher than the summer mean for this compound. Furthermore the concentrations of the other lighter PAHs (ACE - FLUO/MPHE) were elevated above their summer mean values for this week. Discussion of episodic events like this one are are detailed in Chapter

Figure 5.5 PHE concentrations in rural air throughout 1993 (Hazelrigg site).

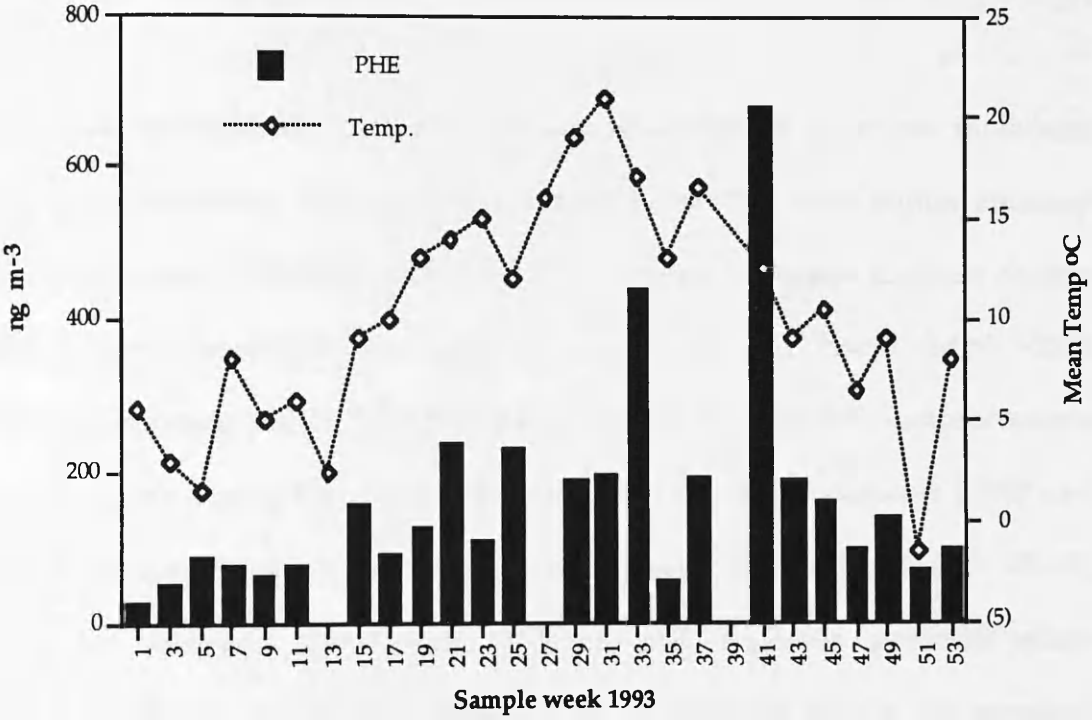
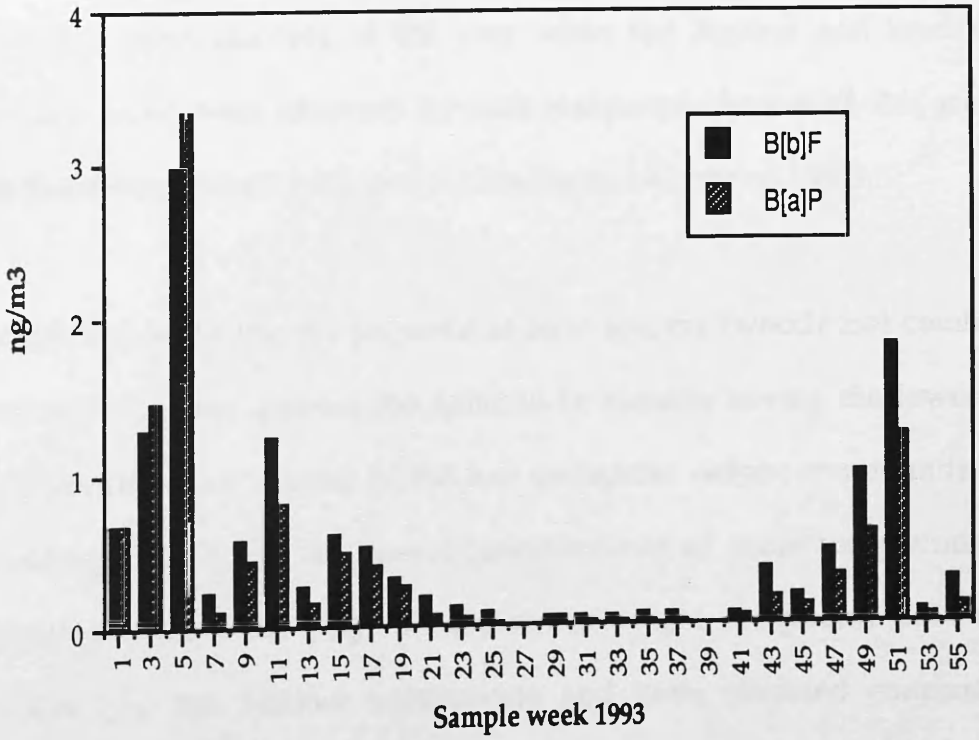


Figure 5.6 B[b]F and B[a]P concentrations in rural air (Hazelrigg) throughout 1993.



6, where meterological data is examined to explain anomalies in the data sets from the different sites.

Seasonal cycling at the rural site was also observed for other low molecular weight compounds; FLU showed a similarity to PHE with higher summer concentrations. Even the four ringed PYR showed a marked increase during the summer months. The higher molecular weight PAHs (MW >250) showed opposite trends, being similar to the urban sites with concentrations being higher during the cooler winter months. Figure 5.6 presents B[b]F and B[a]P concentrations at the rural site throughout 1993. Weeks 1, 3, 5, 47, 49, and 51 occurred during the Winter and Autumn periods when concentrations were approximately a factor of 3 higher than in the summer. Interestingly, similarities can be observed between the seasonal trends exhibited by compounds from two different rural locations. Table 5.5 presents those quarters of the year when the highest and lowest mean concentrations were observed for each compound, from both this study and the Esthwaite Water study in the Lake District (Gardner, 1993).

At the Esthwaite site the presence of local sources (wood/coal combustion) during the winter quarter has resulted in autumn having the lowest mean concentrations for several of the low molecular weight compounds, unlike Hazelrigg which has the lowest concentrations of these compounds in the winter. ANTH is the only low molecular weight compound (MW<200) to behave like the heavier compounds and have elevated concentrations

during the winter period at both sites. Why ANTH shows this pattern is unclear. ANTH is a tricyclic PAH with a molecular weight and vapour pressure very similar to PHE. However, in comparison its concentration is greatly reduced both in the urban and rural atmospheres.

Table 5.5 Summary of seasonal trends exhibited by compounds.

PAH	Esthwaite		Hazelrigg (Rural site)	
	Highest Quarter	Lowest Quarter	Highest Quarter	Lowest Quarter
ACE/FLU	Summer	Autumn	Summer	Winter
PHE	Summer	Autumn	Summer	Winter
ANTH	Winter	Autumn	Winter	Summer
FLUO/MPHE	Summer	Autumn	Summer	Winter
PYR	Summer	Autumn	Summer	Winter
BENZANTH	Winter	Autumn	Winter	Summer
CHRY	Winter	Autumn	Winter	Summer
B[b]F	Winter	Autumn	Winter	Summer
D[ac]A/B[k]F	Winter	Autumn	Winter	Summer
B[a]P	Winter	Spring	Winter	Summer
B[ghi]P	NR	NR	Winter	Summer
COR	NR	NR	Winter	Summer

NR=Not reported.

The amount of ANTH released annually from two major sources, vehicle emissions and domestic coal burning, is similar to the releases of the heavier muti-ringed PAHs (Wild and Jones, 1995). Furthermore, concentration ratios of ANTH with benz[e]pyrene (B[e]P) [a 5 ringed PAH], determined for several sources were similar to the ratios of B[e]P with the heavier multiringed compounds (Daisey *et al.*, 1986). For example, the ratio

of ANTH/B[e]P for residential coal combustion is ~ 3, for B[ghi]P/B[e]P ~ 2.5 and yet for PHE/B[e]P ~26. In this respect ANTH is produced in approximately the same quantity as the heavier PAH for this source. Therefore winter time combustion of coal and wood in rural areas may lead to a rise in ANTH concentrations, in line with the heavier PAH. Perhaps more importantly is evidence that points to the susceptibility of ANTH to photolytic decomposition. Sanders *et al.* (1993) using natural light conditions investigated the photodecomposition of selected PAHs in aqueous solution. Measured half-lives varied by a factor of 25, from < 2 h for ANTH to 50 h for FLUO. After only 6 h only 1 % of the original concentration of ANTH was present in solution compared to 79 % of PHE. Although these half-lives are only applicable to an aqueous system it is postulated that decomposition would be similar in the atmosphere. During the summer months, when the largest number of daylight hours occur, it is likely that ANTH would be most susceptible to photolytic degradation, resulting in reduced atmospheric concentrations compared to the winter.

Both rural sites have concentration ranges similar to, or greater than, the Manchester concentrations, for the low molecular weight PAHs (ACE-FLUO). In particular the FLU and PHE concentrations at the rural (Hazelrigg) site greatly exceed the urban concentrations as mentioned earlier. Why are some of the low molecular weight PAHs found at higher concentrations at the rural site than at the urban locations of this study? There are several possible explanations which are presented as follows:-

5.5.1 Local sources

The location of the rural sample site (Hazelrigg - Lancaster University Field Station) is described in Chapter 3. Briefly the sampler was positioned in an in a pasture field, approximately 20 m from the nearest building, a small wooden meteorological station. A potential source is a major motorway (M6) running in a north-south direction situated 0.5 km west of the sample site. Vehicular traffic on motorways and major roads are significant PAH sources (Tuominen *et al.*, 1988; Masclet *et al.*, 1986). However, Rasheed (1989) examined PAH deposition along a transect, perpendicular to each side of the M6 motorway, and found that within 50 meters of the hardshoulder the depositional flux of the lighter PAHs, including PHE, was similar to background levels. His background site was at a location far removed from the motorway (15 km to the east) and 1 km from the nearest metalled road. Rasheed measured the background flux of PHE as ~0.2 $\mu g\ m^{-2}\ day^{-1}$. At the rural location, used here, an annual mean flux for PHE was established at ~0.6 $\mu g\ m^{-2}\ day^{-1}$ (PAH depositional fluxes are detailed in Chapter 8). This is certainly higher than Rasheed's value indicating that the motorway may have some effect on the ambient atmosphere at Hazelrigg. However the M6 is 50 m lower than the sampler location in this study and occupies a modified channel which appears to have the effect of directing the air movement along a north/south axis away from this sample site.

5.5.2 Sea and sediments

The aspect of the field station is of a westerly nature, overlooking the coastal area of Morecambe Bay with its substantial area of tidal sands, sediments and estuarine mudflats. PAHs have been measured extensively in coastal sediments due to their accumulation within this enviroment (Hites *et al.*, 1977; Hites *et al.*, 1980, Smith *et al.*, 1985). Indeed both coastal and freshwater sediments are considered to be significant sinks for these compounds, derived from surface runoff and atmospheric deposition. Accumulation over time has resulted in sediment profiles being examined to chronicle periods of heaviest contamination and determine source type (Wickström and Tolonen, 1986; Sanders *et al.*, 1993). Recent work suggests that PAHs can be released from sediments into the water column according to their individual solubility and octanol-water partitioning constants (K_{ow}) A study by Helmstetter and Alden (1994) reported that the lighter compounds of PHE, PYR and FLUO showed the greatest efflux from the sediment (in that order), hence displaying the highest water concentrations upon equilibrium. Even at a remote ocean site (east Atlantic) Marty *et al.* (1984) found that atmospheric vapour phase PAHs were an order of magnitude higher than particulate bound PAH. Indeed, the vapour phase ΣPAH was reported as 18 ng m^{-3} with PHE dominating the profile. This concentration is higher than the values reported from remote terrestrial sites in Table 5.4, indicating the importance of the ocean as a source of PAH to the surrounding atmosphere. It is therefore reasonable to regard the Morecambe Bay area as a potential

source of the lighter, more volatile PAHs. Law (1981) reported total hydrocarbon concentrations measured around the coast of the British Isles were higher in samples containing finer sediment types and in samples from inshore areas, particularly estuaries and bays.

The tidal area of the river Lune estuary and the southern part of Morecambe Bay (directly west from Hazelrigg) is approximately 85 km^2 (OS Landranger map no. 102). Assuming the same level of PAH contamination in this sediment, with that measured in the Chesapeake Bay area of the eastern USA, then the reported flux of PHE from the sediment into the water column could be applied to the Morecambe Bay area. The sediment - water flux for PHE, measured in Chesapeake Bay, was reported as 229 $\mu g\ m^{-2}\ d^{-1}$ (Helmstetter and Alden, 1994). Therefore, over an area of 85 km^2 this would result in some 20 kg of PHE being released into the water each day. In the Great Lakes region several studies have concluded that the Lakes are significant sources of PCBs to the surrounding atmosphere, one of the primary loss mechanisms being volatilisation from the water surface into the atmosphere. PHE which has a lower molecular weight lower and a higher vapour pressure than the lightest PCBs, is assumed here to undergo a similar process once released into the water column. Assuming the tidal area of Morecambe Bay to be a source of PAHs to the atmosphere then a significant fraction of the 20 kg released into the water column may be volatilised to the atmosphere, given PHE's volatility and the shallow estuarine water. Estimating volatilisation fluxes for PAHs is extremely

difficult. Baker and Eisenreich (1990) could not calculate PAH fluxes across the air-water interface of Lake Superior due to uncertainties in PAH Henry's Law constants. Even though PHE has a lower molecular weight and a higher vapour pressure than the lightest PCBs, its Henry's Law constant is lower, indicating its increased vapour phase resistance and tendency to the liquid phase, relative to the PCBs. Therefore the volatilisation of PHE from the water surface is unlikely to be as great as that calculated for the PCBs in the Great Lakes. However, if only 1 % of the 20 kg released daily into the water column was to volatilise from the surface into the first 100 m of the atmosphere, then this would result in a coresponding atmospheric concentration of 24 ng m^{-3}. The predominant westerly wind at the Hazelrigg site could explain the observed elevated PHE concentrations.

5.5.3 Biogenic production

The biogenic production of PAHs is a poorly studied area, but there is evidence from some early studies for plant biosynthesis. Borneff *et al.* (1968, cited in Sims and Overcash, 1983) demonstrated the biosynthesis of seven PAHs by algal cells using ^{14}C-acetate as a sole carbon source, PHE was not reported in this study, the lightest compound to be detected was FLUO. For higher plants, synthesis of PAHs is questionable as Grimmer and Duvel (1970) demonstrated the absence of several high molecular weight PAHs in plants grown in chambers with filtered air. An earlier study reported that the PAH content in beech, oak and tobacco leaves increased as they matured

from green to yellow (Graf and Diehl, 1966). Edwards (1983) reviewing PAHs in the terrestrial environment noted experiments which demonstrated selected PAH uptake by both leaves and roots and subsequent translocation to different parts of the plant. However, concentrations in plants are generally less than those in soil where the plant is growing. Nevertheless, plant production may be a source of PAH to the atmosphere but it seems unlikely that it can be considered a significant source in comparison to anthropogenic production.

5.5.4 Outgassing from vegetation and soil

The abundance of FLU, PHE and ANTH in the air of the rural site (Hazelrigg) may be due to the re-volatilisation of previously deposited concentrations off plant surfaces and from the soil, particularly in the summer. The observed seasonal cycling of increased concentrations during the summer period invokes temperature as the controlling factor for the volatilisation of these lighter compounds. Plant surfaces have been considered as a significant sink for organochlorine compounds and have been utilised as biomonitors for ambient atmospheric concentrations of chlorinated pesticides (Calamari *et al.*, 1991; Strachan *et al.*, 1994) and PCBs (Umlauf *et al.*, 1994). Reiderer (1990) used a fugacity approach to model the various compartments of a leaf, and with experimental data found that >90% of the examined organochlorines were associated with the waxy cuticle on the leaf surface.

Recent work has shown that vegetation also plays an important role in the partitioning of PAHs from the atmosphere (Simonich and Hites, 1994). The PAH/vegetation partitioning process is primarily dependent upon the atmospheric vapour phase PAH concentration and the ambient temperature. At low temperatures (autumn and winter) vapour phase PAHs partition into vegetation, and at high temperatures (summer) some PAH volatilise and return to the atmosphere. The lighter more volatile compounds of FLU and PHE were found to have lower heats of vapourisation and lower vegetation binding energies than the heavier multi-ringed PAH, indicating their potential for re-volatilisation. Nakajima *et al.* (1995) found concentrations of atmospheric vapour phase PYR (4-ringed PAH) to decrease during the autumn and winter while concentrations increased in the leaves of azalea (*Rhododendron oomurasaki*). During the warmer summer months the reverse was the case, with increased atmospheric vapour phase concentrations and a decline in leaf concentrations. Furthermore, a strong correlation between log vapour-PYR/leaf-PYR and 1/T indicate that most of the PYR present in the azalea leaves was from vapour adsorption. For the high molecular weight PAHs such as B[a]P, primarily associated with suspended particulate material in the atmosphere, uptake by plant leaves is considered to be by attachment of this material to the outside of the leaf (Simonich and Hites, 1994; Nakajima *et al.*, 1995). Permeation of the leaf cuticle by the PAH from the attached particulate matter may then take place (Nakajima *et al.*, 1995).

At the Hazelrigg rural site the predominant low molecular weight PAHs (including PYR) showed seasonal cycling with higher concentrations during the summer months and reduced concentrations in the winter. A possible addition to the volatilisation off plant surfaces is the out-gassing of the lighter compounds from the soil. The soil compartment has become a significant long term sink for contaminants which come into contact with it i.e. from aerial deposition (Jones, 1991). Indeed, budget calculations for the UK show that surface soils represent the most substantial 'reservoir' of PAHs in the environment (Wild and Jones, 1995) with the low molecular weight PAHs such as PHE being the most abundant. Furthermore, the lighter compounds have higher aqueous solubilities (Mackay *et al.*, 1992) than the heavier compounds resulting in an increased potential for volatilisation from soil water. This process has been identified as a possible loss mechanism from the soil by Jones *et al.* (1989) and Wild *et al.* (1990). Therefore volatilisation from soil may add to the atmospheric loading of the lighter compounds observed during the warmer summer months. Certainly the sampler at Hazelrigg was positioned at ground level rather than at roof top height (~25 m), hence any effect of volatilisation from the soil would be exaggerated in these air samples.

Vegetation - air and soil - air exchange will be common to all rural locations, and is not peculiar to the rural site in this study. The closest study site to Hazelrigg is Esthwaite Water in the Lake District, where, apart from FLU and PHE, the other tri- and tetracyclic PAHs have similar concentration

ranges (Table 5.3). Therefore at Hazelrigg additional sources such as the volatilisation of the lighter PAHs from the Morceambe Bay area must play an important role in influencing the atmospheric concentrations at this site.

It is possible that some of the processes described above will also influence the PHE loading (and other low MW PAH) in the urban atmosphere as well. However the annual cycling depicted at the rural location could not be observed at any of the urban sites for this compound. This is probably due to the continual release of PHE from the numerous urban sources resulting in air concentrations remaining consistent throughout the year (see Figure 5.4 - PHE concentrations in Cardiff air).

5.6 Vapour-particle partitioning

PAHs may be released from combined sources either in the vapour phase or associated with particles (particulate phase) and can undergo rapid phase transfers once discharged to the atmosphere. PAH are predominantly generated in the vapour phase and are then adsorbed onto existing particles through condensation upon cooling of the emission (Van Vaeck *et al.*, 1984). The vapour pressures of the 15 PAHs examined in this study range from 6 x 10^{-1} - $2x10^{-10}$ Pa (25 ^{o}C), an enormous variation resulting in marked differences in the distribution of compounds between the vapour phase and the atmospheric particulate. This vapour-particle partitioning for a particular compound will ultimately affect it's atmospheric removal rate,

transport and atmospheric half life (Behmyer and Hites, 1988; Kwok *et al.*, 1994). For example, those compounds predominantly associated with particulate matter will undergo faster deposition than the compounds in the vapour phase. Conversely vapour phase compounds may be more susceptible to photolytic and chemical degradation. Indeed Kwok *et al.* (1994) from laboratory experiments, determined that the atmospheric lifetime of vapour phase PHE is ≤ 1 day, reaction's with the OH and NO_3 radicals being the dominant loss mechanism. Figures 5.7a and 5.7b display the chromatograms of a filter (particulate) and PUF (vapour) respectively for an air sample taken in Manchester. Clearly the later eluting high molecular weight PAHs are predominant in the particulate, while the earlier eluting, lighter compounds are predominant in the vapour phase. Partitioning of the PAHs is therefore strongly influenced by the compound's physicochemical properties.

5.6.1 Phase distribution

The contribution to the mean ΣPAH concentration by the vapour phase component exceeded the particulate phase contribution by a factor of 5.5 for Manchester and Cardiff. Taking one of the urban sites Figure 5.8 illustrates the dominance of the vapour phase component over the particulate phase in Manchester air throughout 1991 and 1992. On an individual compound basis the lighter PAH such as ACE, FLU and PHE (the most predominant PAH) exist almost exclusively in the vapour phase. Broddin *et al.*, (1980)

Figure 5.7a

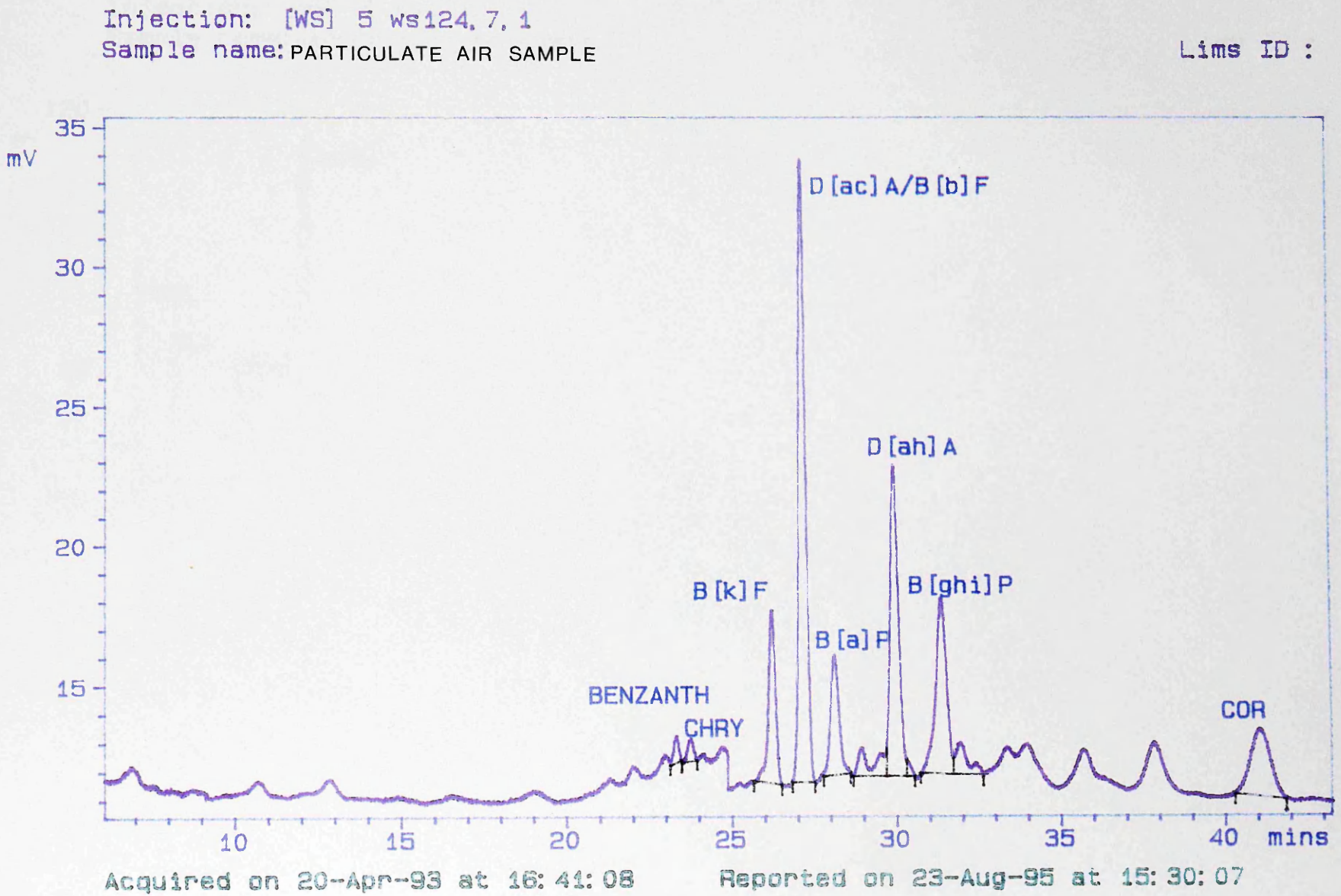

Injection: [WS] 5 ws124.7.1
Sample name: PARTICULATE AIR SAMPLE
Lims ID :
mV
35
30
25
20
15
D [ac] A/B [b] F
D [ah] A
B [k] F
B [a] P
B [ghi] P
BENZANTH
CHRY
COR
10
15
20
25
30
35
40
mins
Acquired on 20-Apr-93 at 16:41:08
Reported on 23-Aug-95 at 15:30:07

Figure 5.7b

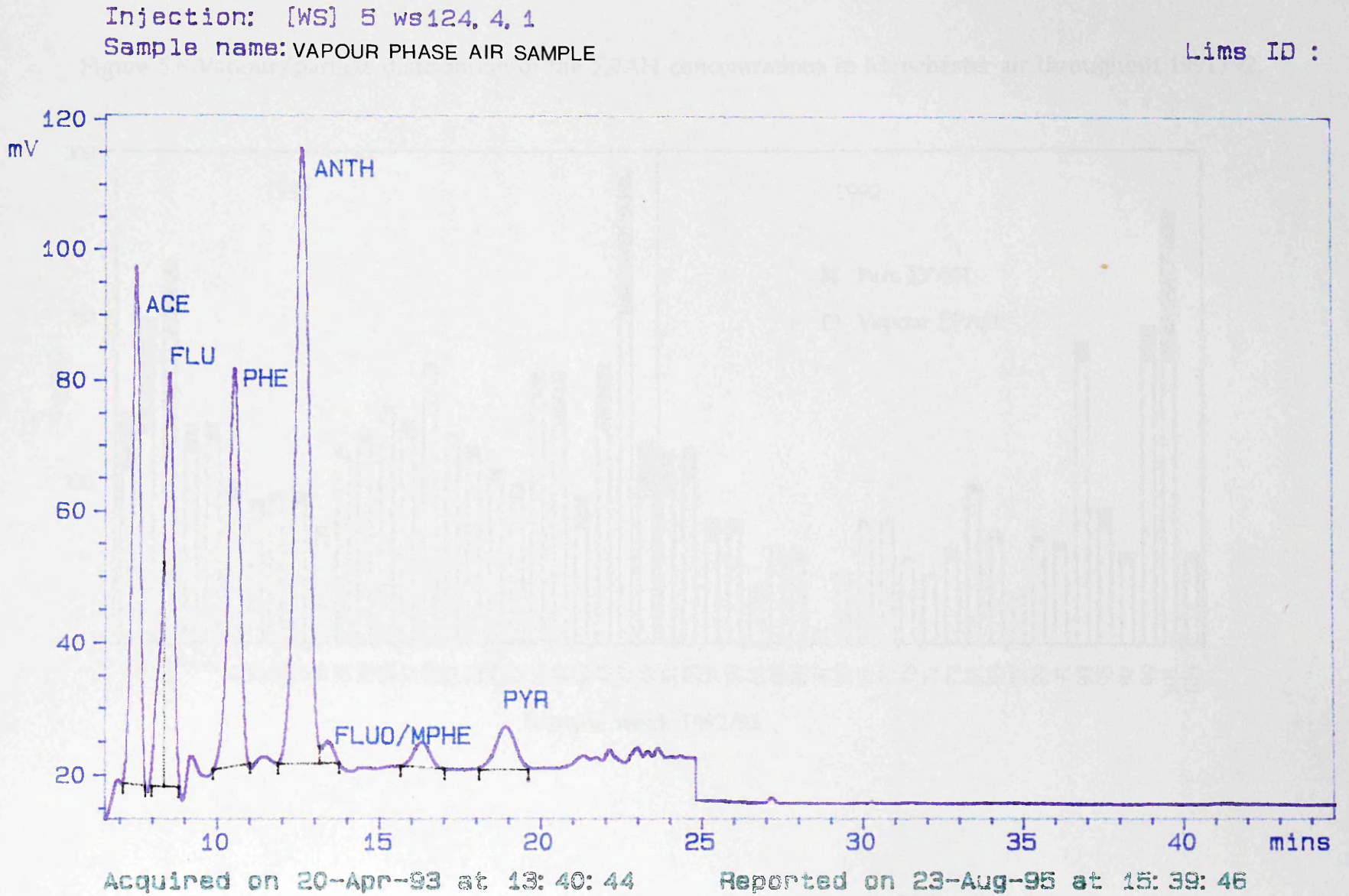
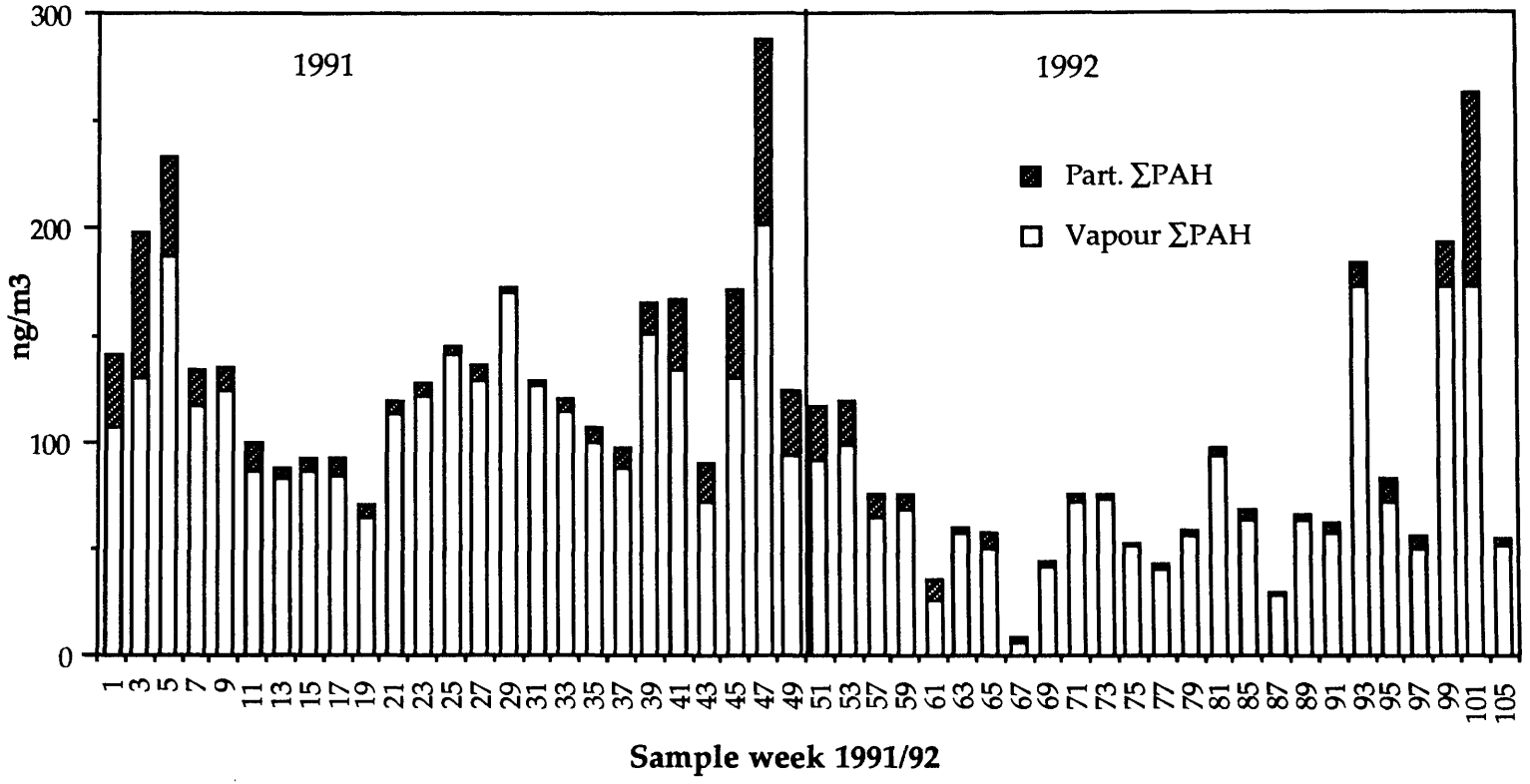

Injection: [WS] 5 ws124.4.1
Sample name: VAPOUR PHASE AIR SAMPLE
Lims ID :
120
mV
100
80
60
40
20
ACE
FLU
PHE
ANTH
FLUO/MPHE
PYR
10
15
20
25
30
35
40
mins
Acquired on 20-Apr-93 at 13:40:44
Reported on 23-Aug-95 at 15:39:46

Figure 5.8 Vapour/particle distribution of the ΣPAH concentrations in Manchester air throughout 1991/92.



reported that a considerable fraction of the more volatile PAH escape particle incorporation after their production and exist predominantly in the atmospheric vapour phase at ambient temperatures. Conversely the five-, six- and seven-ring PAHs (MW 250-300) were primarily associated with the particulate on the filter (on an annual basis >70% of B[a]P, D[ac]A, B[k]F, B[ghi]P and COR were determined on the particulate).

Table 5.6 displays the percentage of each PAH present in the vapour and particulate phases during the winter of 1991/92 and the summer of 1992 for both Manchester and Cardiff. Similarly the phase distribution of the PAHs is presented for the winter and summer seasons at the rural site for 1993. London and Stevenage were excluded as the filters and PUF plugs of each air sample were extracted together resulting in the loss of phase separation. As expected, the phase distribution follows a similar pattern for the three sites. Clearly the lighter compounds ACE, FLU, PHE and ANTH (MW <200) predominate in the vapour phase of the ambient atmospheres, changes in the phase distribution being minimal, even with a change in season. The higher molecular weight compounds of B[b]F to COR (MW 250-300) show the opposite trend being primarily associated with the particulate phase, particularly during the winter months when concentrations of these compounds were at their highest. During the summer, however, there is a significant vapour phase component for these compounds with ~10 % of COR (the heaviest compound) residing in this phase at the urban sites and 25 % at the rural site. The four-ring PAHs (MW 200-250) PYR, BENZANTH

Table 5.6 Percentage PAH phase distribution in Manchester and Cardiff.
Vap = vapour phase; Part = particulate phase

PAH	Manchester				Cardiff				Rural			
	Winter		Summer		Winter		Summer		Winter		Summer	
	% Vap	% Part	% Vap	% Part	% Vap	% Part	% Vap	% Part	% Vap	% Part	% Vap	% Part
ACE	97	3	99	1	94	6	97	3	99	1	>99	<1
FLU	95	5	99	1	87	13	>99	<1	99	1	>99	<1
PHE	98	2	99	1	97	3	>99	<1	99	1	>99	<1
ANTH	99	1	99	1	99	1	>99	<1	99	1	>99	<1
FLUO/MPHE	87	13	96	4	80	20	95	5	87	13	>99	<1
PYR	80	20	98	2	83	17	94	6	87	15	>99	<1
BENZANTH	18	82	85	15	16	84	63	37	45	55	>99	<1
CHRY	30	70	75	25	19	81	60	40	36	64	77	33
B[b]F	2	98	40	60	1	99	20	80	1	99	1	99
D[ac]A/B[k]F	<1	>99	39	61	<1	>99	15	85	1	99	13	87
B[a]P	<1	>99	12	88	<1	>99	6	94	<1	>99	11	89
B[ghi]P	<1	>99	9	91	<1	>99	17	83	<1	>99	14	86
COR	<1	>99	10	90	<1	>99	10	90	<1	>99	25	75

and CHRY showed the largest deviations between winter and summer. For example, at the urban sites approximately 17 % of BENZANTH was present in the vapour phase during the winter period while ~ 74 % resided in the vapour phase during the summer. This represents a factor of 4 increase in the vapour phase component from winter to summer. Baek *et al.* (1992) report a similar increase in London air with a factor of 4.5 increase for vapour phase BENZANTH from winter to summer. At the rural site the vapour phase fraction of ACE to BENZANTH is almost 100 % during the summer, likewise the vapour phase fraction of these compounds is higher in the winter at Hazelrigg than in Manchester and Cardiff. In the atmopshere at Hazelrigg the total suspended particulate concentrations (TSP) are, on average, lower than those in Manchester. Hence, this may have lead to a reduced surface area for vapour phase adsorption, resulting in lowered particulate concentrations in the rural atmosphere. Table 5.7 presents the monthly TSP and temperature (°C) measured at the Manchester and Hazelrigg sites.

5.6.2 Effects of temperature and TSP

If a compound's volatility largely determines it's distribution between the two phases then changes in temperature will have a marked effect on a compound's partitioning. Temporal variations in the vapour-particle partitioning can be observed in Figures 5.9a + b which display the vapour and particulate concentrations of PYR over an annual time scale in the

Table 5.7 Total suspended particulate concentrations (μg m^{-3}) and temperature (°C) at the Manchester (1992) and Hazelrigg sites (1993). *

Month	T °C		TSP	
	Manchester	Hazelrigg	Manchester	Hazelrigg
January	4	2	103	24
Feburary	7	5	45	49
March	9	5	40	47
April	11	9	39	40
May	12	10	42	45
June	15	13	33	27
July	20	18	41	23
August	14	20	35	24
September	11	14	47	13
October	10	9	42	21
November	7	6	32	22
December	6	3	60	20

* TSP and temperature data for each sample week are presented in Appendix 1 for each site.

Figure 5.9a Vapour and particulate PYR concs. in Manchester air (1991).

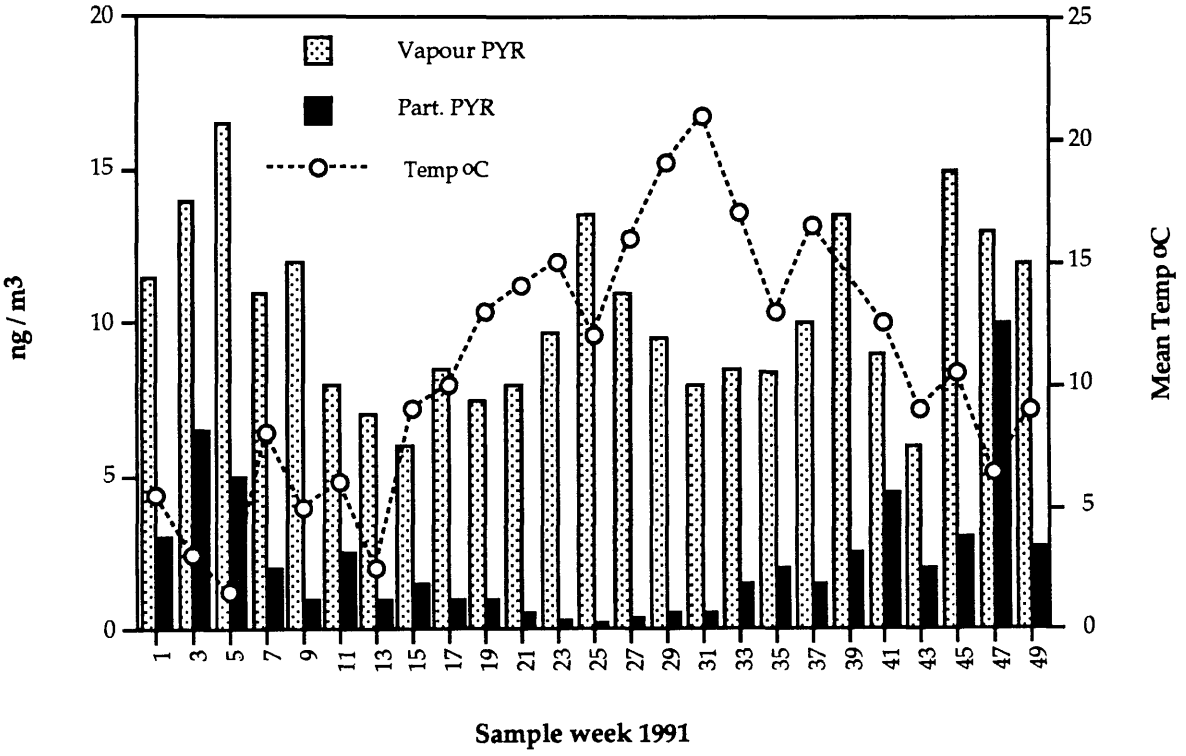
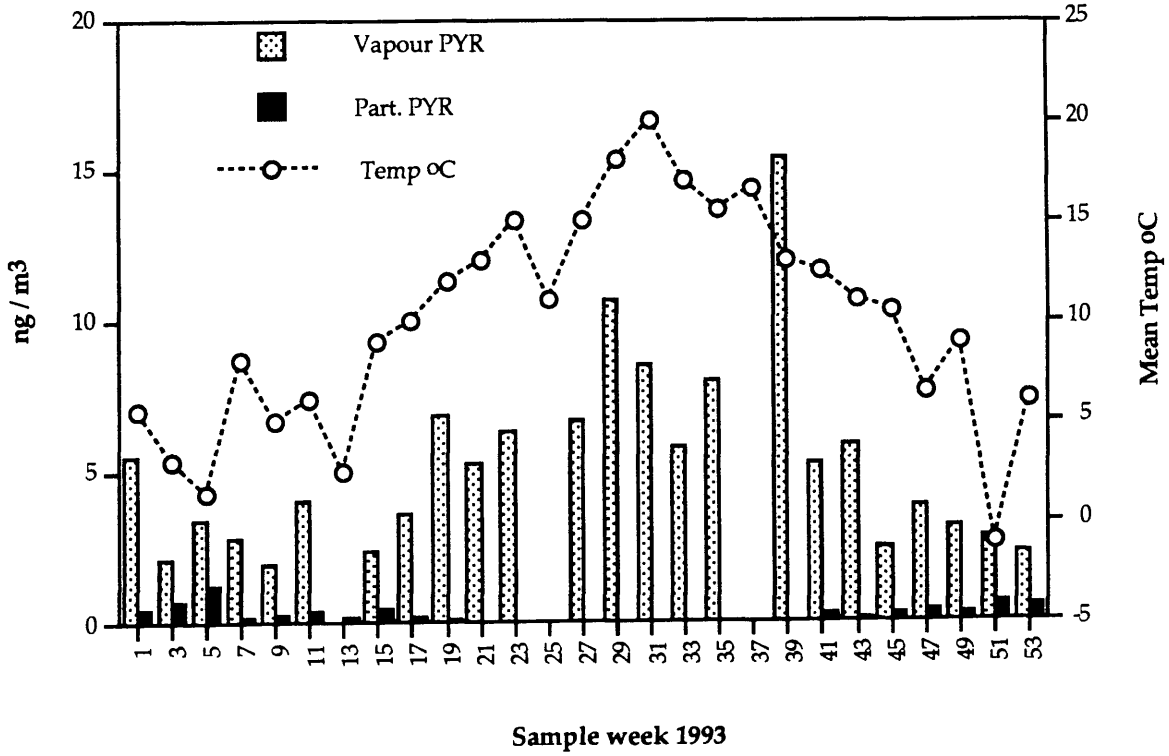


Figure 5.9b Vapour and particulate PYR concs. in rural air (Hazelrigg) (1993).



ambient atmospheres of Manchester (1991) and Hazelrigg (1993) repectively. Clearly as the temperature decreases towards winter the concentration on the particulate increases at both sites. The seasonal cycling of the vapour phase concentrations, represented by a summer maxima at Hazelrigg, is masked at the Manchester site due to the localised urban increase in PAH emissions during the winter months (see Section 5.4). Temperature appears to be the controlling factor for the partitioning of PYR. For example, the mean winter TSP concentration in Manchester (67 $\mu g\ m^{-3}$) is approximately double that found at Hazelrigg (32 $\mu g\ m^{-3}$) [Table 5.7] yet the vapour-particle ratios for PYR are the same (~3) at both sites. This indicates that TSP is playing a minor role in the partitioning of PYR. It is assumed that the surface area available for sorption will be greater in the Manchester atmosphere than in the rural atmosphere.

Correlations might be expected between ambient TSP loading and the concentrations of the higher molecular weight PAHs such as B[a]P, B[ghi]P and COR. TSP concentrations plotted against B[a]P and particulate-Σ(B[a]P, B[ghi]P, COR) concentrations for the Manchester and Cardiff data showed only weak correlations of $r = 0.37$ and 0.30 ($P \leq 0.05$), respectively. This was consistent with the work of Harkov *et al.* (1984) and Steinmetzer *et al.* (1984), who found no correlation between filter-collected PAH and TSP. Reasons for this weak correlation are probably due to the complex nature of urban aerosol. Measurement of TSP does not consider particulate composition or distribution of particle size. Size fractionation experiments (Katz and Chan,

1980; Handa *et al.*, 1980) have revealed that > 90% of particulate PAHs are associated with particles of diameter <10 μm. Furthermore, Behymer and Hites (1988) have shown that particulate bound PAH have a longer atmospheric residence time on particle substrates that are black or grey in colour i.e. they help reduce photolytic degradation of bound PAH, unlike lighter coloured particles. This association of the higher molecular weight PAHs with the smaller size particles has implications for human health. Handa *et al.* (1980) found that 94 % of the particulate-bound fraction of atmospheric B[a]P was associated with the particulate size range 0.43-2.10 μm, which has the ability to be transported deep within the bronchial region of the lungs (QUARG, 1993). B[a]P has the highest carcinogenic loading out of the 15 PAHs measured in this study (IARC, 1987).

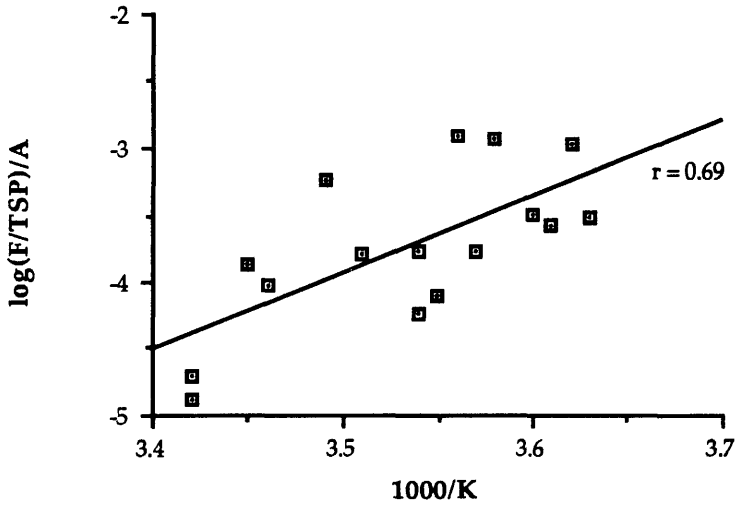
Changes with season in the phase distribution of PAHs invokes compound vapour pressure and hence temperature as the controlling factor. Indeed, Yamasaki *et al.*, (1982) and Pankow (1991) found high degrees of correlation (r = 0.70-0.90) between temperature and the phase distribution of individual PAHs. Separate vapour and particle phase measurements of PAHs in the Manchester air over an annual time scale allowed correlations to be determined between vapour/particle (V/P) ratios and temperature for a particular compound. V/P ratios or partition coefficients (K_p) were essentially adsorbent/filter (A/F) ratios of the sampling equipment and are expressed in the form (F/TSP)/A as described in Chapter 2 section 2.2.3. A and F are the adsorbent and filter retained PAH concentrations (ng m^{-3})

respectively and TSP is the total suspended particle concentration (μg m^{-3}). The use of partitioning coefficients provides some insight into the behaviour of PAHs in the atmosphere and allows the prediction of phase distribution at ambient temperatures for a particular compound. K_p is related to the average sampling temperature (T, kelvin) through log [(F/TSP)/A] = m/T + b. The units of (F/TSP)/A are (ng of PAH per μg of particle) / (ng of PAH per m^3 of air). By plotting log [(F/TSP)/A] vs. 1/T the effects of temperature can be observed on the partitioning of a compound (Yamasaki *et al.*, 1982; Pankow, 1987). The heat of desorption can be derived from the slope of the line m, where m = Hd/2.303R - T_{amb}/4.606 (see equation 2.5 (Chapter 2)). Plots of log [(F/TSP)/A] vs. 1/T for PHE and B[a]P sampled in the Manchester and Hazelrigg atmospheres are presented in Figure 5.10a and 5.10b respectively. Table 5.8 presents the constants m and b along with the correlation coefficients (r) and the heats of desorption calculated for PHE and B[a]P at both sites.

The partition co-efficient of B[a]P is over an order of magnitude higher than that of PHE, explaining it's predominance in the particulate phase. Likewise the energy required to desorb B[a]P off the particulate surface in the urban atmosphere (88.6 KJ mol^{-1}) is substantially higher than that for PHE (58.1 KJ mol^{-1}). Again in the rural atmosphere (Hazelrigg) the heat of desorption for B[a]P is greater (96.4) than that for PHE. These K_p and Hd values derived from the sampling data in Manchester air are similar to the values obtained

Figure 5.10a Plots of log (F/TSP)/A vs reciprocal temperature for PHE at the Manchester and Hazelrigg sites.

a) Manchester - 1992



b) Hazelrigg - 1993

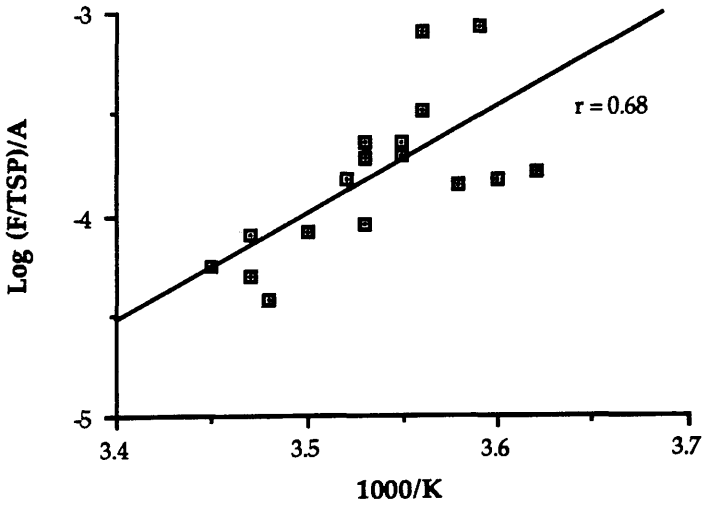
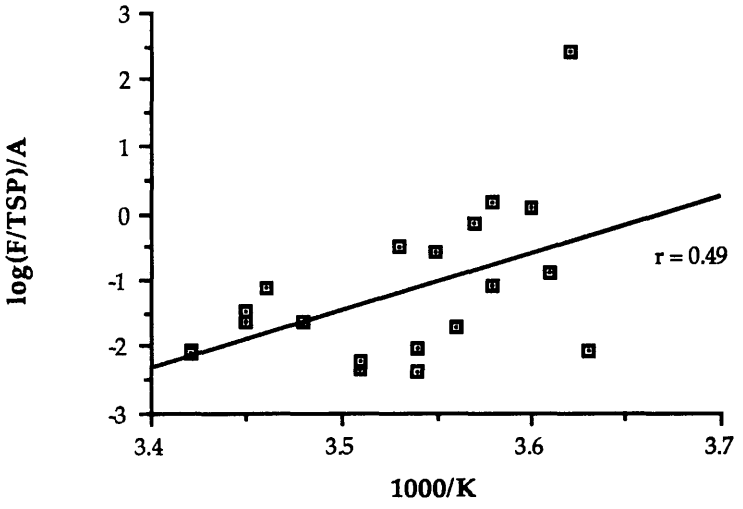


Figure 5.10b Plots of log (F/TSP)/A vs reciprocal temperature for B[a]P at the Manchester and Hazelrigg sites.

a) Manchester - 1992



b) Hazelrigg - 1993

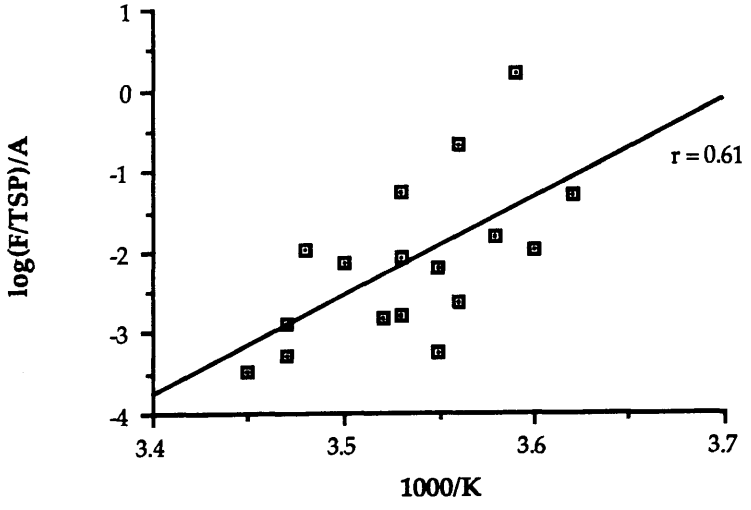


Table 5.8 Values derived for PHE and B[a]P sampled in Manchester 1992 and Hazelrigg 1993

PAH	m	b	r	Kp (20°C)	Hd (KJ mol^{-1})
Manchester					
PHE	5787	-24.2	0.69	4E-5	58.1
B[a]P	8618	-31.6	0.49	6E-3	88.6
Hazelrigg					
PHE	6120	-21.5	0.68	4E-5	63.8
B[a]P	8856	-35.2	0.61	2E-4	96.4

Constants m and b and r derived from Figs. 5.10a and b, for [F/TSP/A] = m/T + b
where m and b are constants relating to the thermodynamic properties of the compound in questi

m = slope of the line
b = the Y intercept.
r = correlation coefficient.

by Yamasaki *et al.* (1982) and Krieger and Hites (1994), who took air samples in the cities of Osaka (Japan) and Indianapolis (USA) respectively. Yamasaki *et al.* (1982) derived Hd for PHE and B[a]P as 80.2 and 103 KJ mol^{-1}, respectively, while Krieger and Hites (1994) using a low-volume diffusion denuder derived Hd for PHE as 75 and B[a]P as 96. The Hazelrigg Hd values fall within the same range of the urban values reported here. Indeed the K_P values presented in Table 5.8 are very similar between the Manchester and Hazelrigg sites indicating that the partitioning behaviour for both compounds is the same for the urban and rural atmospheres. If particulate differences occur between the two sites then the effect on partitioning is negligible, certainly the TSP concentrations are lower in the rural atmosphere (see Table 5.7) with - presumably - a reduced surface area for sorption compared to the urban site. For PHE, which has markedly higher concentrations in the Hazelrigg atmosphere, the partitioning behaviour between the two sites for this compound is similar, indicating that temperature rather than TSP is the controlling factor. B[a]P however does show a difference, with K_P being greater at the Manchester site. As B[a]P is mainly associated with the particulate, changes in TSP concentration may have a significant effect on the partitioning behaviour. In this study the correlations between log K_P and temperature for PHE and B[a]P are weaker than those of Yamasaki *et al.* (1982) who reported correlation coefficients of r = 0.88 and 0.83 for PHE and B[a]P respectively. Samples in Osaka were collected over a 24 h period instead of seven days like the Manchester and Hazelrigg samples. Temperature fluctuations over this 24 h period were far

less pronounced, resulting in reduced sampling artefacts that will affect the vapour-particle distribution of the compounds collected on the filter. Bidleman *et al.* (1986) stressed that the K_p partition coefficients are between the vapours and *urban air particulate matter on the filter,* not airborne particles. Furthermore discrepancies between Hd values derived from different sampling locations may be due to differences in particle surface characteristics (Krieger and Hites, 1994) and the relative humidity (Lee and Tsay, 1994), peculiar to that site.

5.7 PAH profile analysis

The PAH content of a sample of urban air can be considered to be a composite of the various local sources, combined with the contribution from outside that area. It is therefore possible that the pattern or profile of the individual compounds making up the ΣPAH will differ from one urban site to another, or from an urban location to a rural one. Certainly air samples taken at different locations within one city have shown PAHs to vary both qualitatively and quantitatively. For example, Masclet *et al.* (1986) took samples from various locations around Paris; sample sites included a car park, a diesel vehicle garage, a highway at road level and ambient air at roof top height. Although only particulate phase PAHs were sampled, a difference in PAH profile was recorded from site to site, with an underground carpark and a diesel vehicle garage having the highest ΣPAH concentrations. Divergent profiles of PAH, from different sampling

locations within a city have also been demonstrated by Greenberg *et al.* (1985) and Colmsjö *et al.* (1986).

Comparisons between cities, therefore, have to be between samples taken in ambient well mixed air, away from point sources such as street canyons or stack plumes, which have their own characteristic PAH profile. Air sampled at roof level is sufficient to obtain well mixed air that has a PAH profile reflecting a composite of the emission patterns of all the urban sources (Baek *et al.*, 1992).

Broman *et al.* (1991) have shown that PAHs can change in profile composition through atmospheric transport from an urban centre to a remote coastal location. It is therefore important to determine profile differences between sites to establish possible source differences, particularly between the rural and urban atmospheres. Subtle differences in PAH profile can be distinguished between sample sites by using a statistical pattern recognition technique. Principal component analysis (PCA), a multivariate technique, has been successfully applied to distinguish profile differences between air samples for a variety of SOCs, including PCDD/Fs (Eitzer and Hites, 1989; Tysklind *et al.*, 1993) and PAHs (Broman *et al.* 1991; Baek *et al.*, 1992). PCA is particularly useful in handling large data sets by reducing the number of variables between data sets to a few factors or components. A description of PCA is presented in Appendix 2.

In brief PCA is a statistical technique used to identify relationships between groups of variables i.e PAH compounds. Variables that are interrelated amongst themselves are grouped into single composite variables or factors so that each factor (or principal component) is formed of a number of variables that are highly correlated amongst each other, whilst having low correlations with the variables grouped in other factors. This technique has the overall effect of simplifying the data to allow for easier interpretation, whilst retaining most of the information from the original data set (Munro *et al.*, 1986; Daly *et al.*, 1995). PCA is a very useful technique for the analysis of environmental data sets where there are a number of measured variables, as in the case with atmospheric PAH concentrations.

PCA in this case was used to determine any pattern distribution differences that exist between the individual PAH compounds present in the atmosphere of the different sites. In using PCA it was necessary to match sample weeks from the same season, otherwise seasonal profile differences would be highlighted rather than spatial differences. For each compound the total concentration (vapour plus particulate) was considered, seven sample weeks were selected from the summer quarter of 1992 for each of the urban sites and the summer quarter of 1993 for the rural site. Stevenage was excluded as sampling ceased at this site in April 1992. PCA has therefore been used to look for differences/similarities in the PAH summer profile between the urban sites and between the urban sites and the rural location.

In Appendix 2 the stepwise procedure for the application of PCA is detailed. Initially the individual PAH concentrations for the selected sample weeks from the various sites were standardised to ensure equal weights were given to all the compounds. This ensured that concentration differences between sites were not depicted in the final results. Although fifteen PAHs were analysed only twelve PAH variables were included in the PCA as two pairs co-eluted (FLUO/MPHE and D[ac]A/B[k]F) and hence were classed together, while COR was excluded as it was not reported at the London site. In using PCA the number of variables was reduced from 12 to 3 or 4 composite factors allowing for easier interpretation of the pattern differences that might exist from summer air samples between the different sampling locations. Hence an unrotated factor matrix was determined (see Appendix 2) to obtain the number of factors to be included in the model. All data handling was carried out on statistical software SYSTAT version 5.0.

Table 5.9 presents the eigenvalues and variance accounted for (VAF), calculated from the unrotated factor matrix of the twelve variables. An eigenvalue determines the total amount of variance which is explained by a factor and is calculated by adding the squared loadings contained in a single column in the matrix. The summed value of all the eigenvalues will equal the number of factors presented. The mean of the squared loadings in a column is obtained by dividing the eigenvalue by the number of items in that column. This mean value represents the variance accounted for by a factor (% VAF). The optimum number of factors are those that account for

at least 5 % of the variance, and which have an eigenvalue greater than one (Munro *et al.*, 1986).

Table 5.9. Characteristics of the factors obtained from the unrotated factor matrix

Factor	Eigenvalue	% VAF	Communality
1	7.96	66.3	66.3
2	1.89	15.7	82.0
3	1.14	9.4	91.4
4	0.43	3.6	95.0
5	0.32	2.6	97.6
6	0.15	1.3	98.9
7	0.07	0.6	99.5
8	0.02	0.3	99.8
9	0.01	0.1	99.9
10	0.01	0.1	100
11	0.00	0.0	100
12	0.00	0.0	100

Therefore from Table 5.9 the optimum number of factors is 3. These three factors explain 91 % of the total variance in the data set. Typically, when using PCA on 15-20 air quality variables, 3 or 4 principal components or factors can explain most of the variability in the entire data set (Wolff *et al.*, 1986). The final column in Table 5.9 is the cumulative % VAF or communality, determined by adding up the % VAF values for each factor.

The matrix of the three chosen factors was then rotated using VARIMAX rotation, this is explained in Appendix 2 but in effect produces a mathematically equivalent matrix with a simpler structure, therefore allowing for easier interpretation of the data. The resulting factor loading

matrix shows the correlations between individual PAHs and a particular factor, so that the role of a particular PAH in certain patterns of interdependence can be investigated. It is important to note that rotation does not affect the goodness of fit of the model, because although the factor loadings in the matrix changes, the communality does not. However, the proportion of variance accounted for by each factor does change as rotation redistributes the explained variance for the individual factors.

The rotated factor loadings are displayed in Table 5.10 The factor loadings represent the contribution of each variable (PAH) towards the overall factor or principal component (PC). Variables that have a high loading for a particular factor or PC are said to be highly correlated to that factor. A value of 0.50 was used as a cut off point to designate high loadings. In Table 5.10 those variables with a higher loading than 0.50 are highlighted for each factor. The VARIMAX rotation has the effect of maximising the number of variable loadings of greater magnitude for each PC, so although the 12 PAH compounds have some contribution to all the factors, this contribution is only significant towards one of the factors.

B[b]F, B[ghi]P, B[a]P, BENZANTH, D[ac]A/B[k]F, CHRY and ANTH all had high positive values for factor 1 which accounted for 55.8 % of the total variance. The rest of the compounds had negative values, in particular PHE which had a strongly negative correlation to factor 1 of -0.823.

Table 5.10 Rotated factor loadings for the variables (PAHs) in each of the three factors or principal components.Variables with high factor correlations (>0.50) have been boxed.

Variables	Factor 1	Factor 2	Factor 3
B[b]F	0.910	0.190	0.283
B[ghi]P	0.907	0.177	0.238
B[a]P	0.906	0.183	0.294
BENZANTH	0.903	0.083	0.318
D[ac]A/B[k]F	0.894	0.234	0.287
CHRY	0.894	0.095	0.321
ANTH	0.841	0.227	-0.070
PHE	-0.823	0.296	0.331
PYR	-0.027	-0.984	0.138
FLUO/MPHE	-0.325	-0.907	-0.076
FLU	-0.361	0.125	-0.910
ACE	-0.441	0.257	-0.016
Eigen values	6.70	2.11	1.47
% of VAF	55.8	17.6	12.3

Most compounds had a weak positive correlation with factor 2 except PYR and FLUO/MPHE which had highly negative correlations, 17.6 % of the variance was explained by factor 2. Factor 3 expains 12.3 % of the variance with only FLU having a strongly negative correlation. All the high molecular weight compounds having weak positive correlations with this factor.

These factors describe a pattern in the PAH compound distribution, this pattern generally being associated with the molecular weight of the compound. Factor 1 is clearly dominated by the higher molecular weight

PAHs with the lighter compounds having a strong negative correlation. Factor 1 being the dominant factor, accounting for approximately 56 % of the total variance. All the compounds are weakly correlated with factor 2, except the mid-weight compounds of FLUO/MPHE and PYR, which have strong negative correlations. The relationship between the factors is best presented by plotting the factor loadings against each other. Figure 5.11 presents the plot of factor 1 against factor 2 (both accounting for over 70 % of the variance), this gives a clear picture of the PAH pattern between these two factors. Large positive factor 1 loadings are plotted to the right hand side (e.g. B[b]F, B[a]P, D[ac]A/B[k]F, B[ghi]P, BENZANTH, ANTH and CHRY) with large negative factor 1 loadings to the left (e.g. PHE, FLU and ACE). Both these groupings have similar factor 2 loadings (weak positive), unlike FLUO/MPHE and PYR which have weak negative factor 1 loadings but strong negative factor 2 loadings, both being positioned at the bottom centre of the graph. This pattern appears to be determined by molecular weight with the lighter compounds being clearly separated from the heavier PAHs. Interestingly ANTH, a three ring low molecular weight PAH, is grouped with the heavier compounds, having a high factor 1 loading (0.841). This may indicate that ANTH is produced from a similar source(s) as the heavier compounds or behaves in a similar manner in the atmosphere. In Section 5.5 (see Table 5.5) ANTH is found to behave more like the heavier PAHs, as opposed to the lighter compounds, with atmospheric concentrations being lower in the warmer summer months.

Figure 5.11 PAH factor loadings (Factor 1 versus Factor 2).

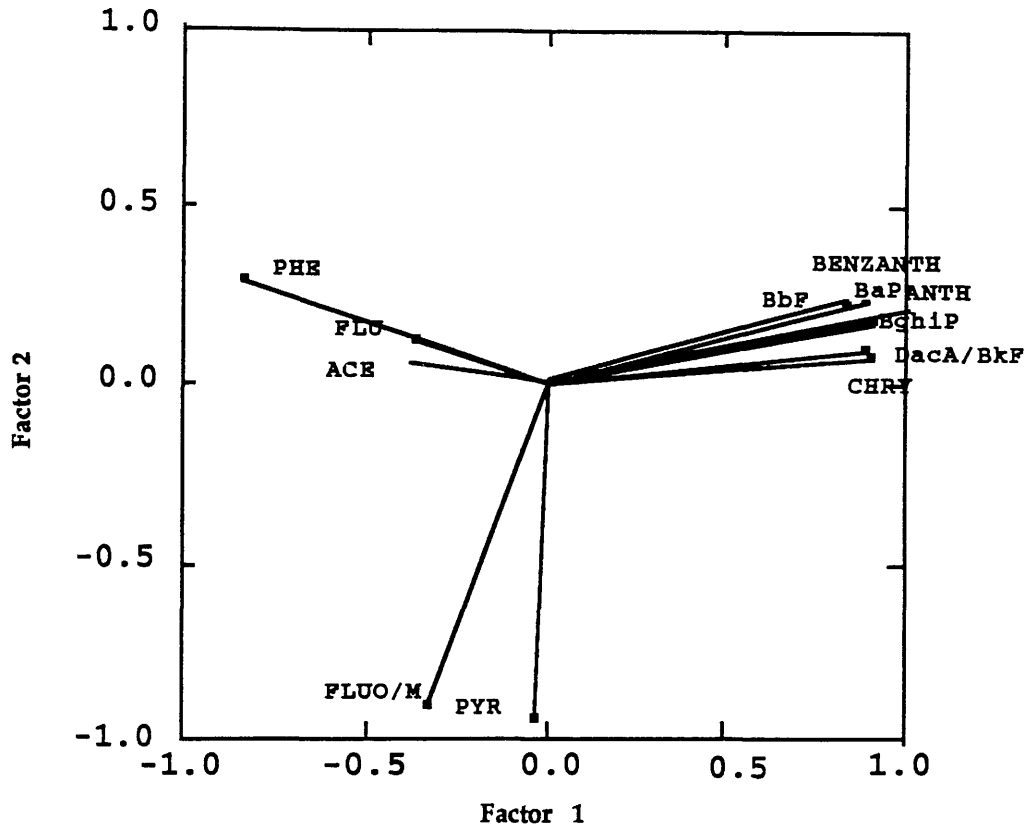
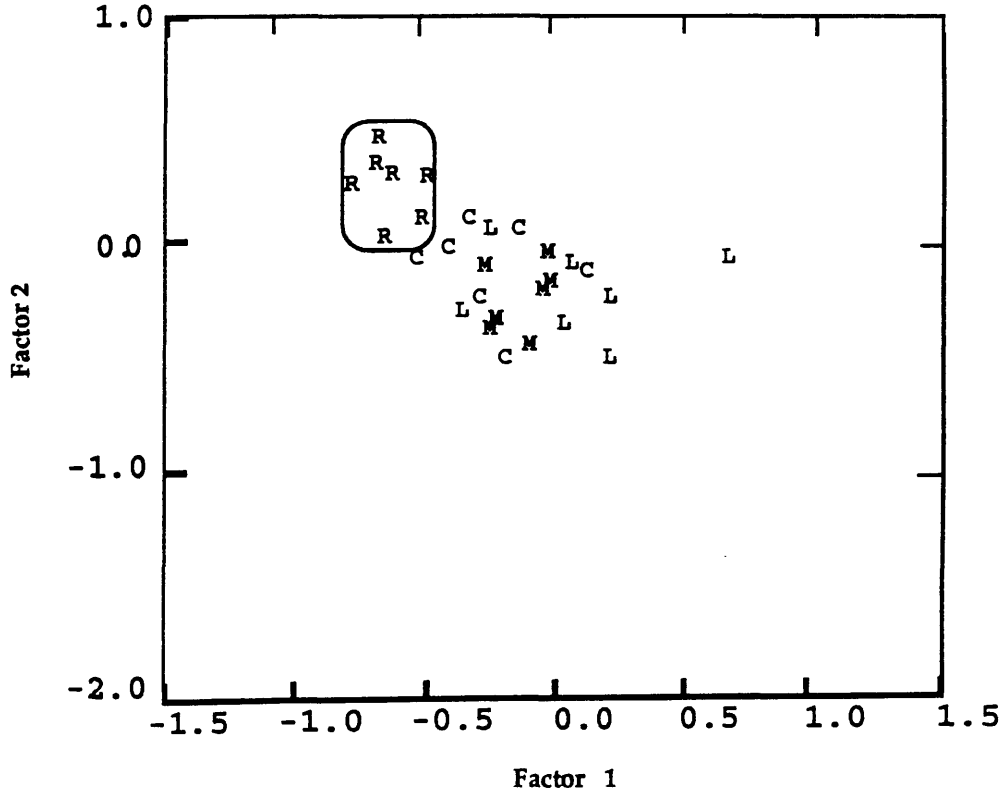


Figure 5.12 Factor 1 versus Factor 2 plot for summer city and rural samples.



Once the spatial distribution of each PAH had been determined, the factor scores for each individual sample (i.e. 7 samples from Manchester) were displayed on a factor plot, to determine whether there was any pattern distribution differences between the factors and the compounds present in the various samples from the different sites. Figure 5.12 displays a plot of factor 1 against factor 2, those samples denoted as L, M, C and R represent London, Manchester, Cardiff and Rural respectively, with 7 sample weeks for each location.

In Figure 5.12 none of the samples possess strong positive factor 1 correlations, the majority having strong negative correlations wth this factor. Compared with Figure 5.11 this shows that these samples are not influenced by the heavier PAH which have a large factor 1 loading, this would be expected as the contribution of high molecular weight compounds to the PAH profile is diminished during the summer months. Most of the summer samples at the various sites have a negative factor 1 loading indicating the dominance of the low molecular weight PHE, FLU and ACE. All of the city samples (L, M and C) are centrally clustered with no apparent grouping of any individual site samples. This indicates that the PAH profile for all the urban sites are similar during the summer months, in other words there are common sources which produce quite a uniform profile at each site. One of the city sites (London) has one sample week that deviates from this pattern. This sample has a strong positive factor 1 loading, positioned far right of centre in the graph, indicating the dominance of the

heavier compounds towards the overall profile for this sample week. Upon examination of the London data this sample week occurred in late August, where, unusually for the time of year the heavier multi-ringed PAH made a significant contribution to the PAH profile. This indicated either a localised source near the sampler or the occurrence of a meteorological episode, which influenced the atmospheric PAH loading for this week. Examination of meteorological data could not explain this anomally, as no significant weather pattern occurred during this period, such as a stable high pressure weather system which could have resulted in a build up of atmospheric contamination (Chapter 6 examines the influence of meteorological events on the SOC loading in both the urban and rural atmospheres). Therefore it is likely that the site for this sample week was under the influence of a local source with its own characteristic profile that favoured the high molecular weight PAHs. Evidence of roof tarring in the vicinity of the Hi-Vol sampler was apparent for this sample week.

The rural samples differ from the urban samples in that they are strongly clustered towards a highly negative factor 1 loading. These seven samples have been highlighted in Figure 5.12 to mark this cluster, which indicates the predominance of the lighter compounds PHE, FLU and ACE in the summer rural profile, more so than in the summer urban profile. PCA has therefore effectively separated rural air samples from the urban samples, by indicating the lighter compounds, in particular PHE, as having more influence at the rural site. This profile difference due to the lighter

compounds of PHE, FLU and ACE indicates possible source differences between the rural and urban centres. Additional sources such as volatilisation from vegetational surfaces (as discussed in Section 5.5) may be responsible for the profile difference at the rural site.

5.8 Summary

The urban atmospheres in this study displayed concentrations similar to other international studies, where both vapour and particulate phase PAHs had been sampled over an extended period i.e. > 6 months. For the urban sites the low molecular weight PAHs of FLU and PHE were the dominant compounds in the atmosphere with the heavier PAHs (B[b]F to COR) being an order of magnitude lower. Vehicular traffic with petrol and diesel combustion were considered to be the major source of PAHs to the contemporary urban atmosphere. At the rural location the mean annual ΣPAH concentration was actually higher than the urban concentrations. This was due to the predominance of the lighter compounds, in particular FLU and PHE which exceeded the 1992 Manchester concentrations by factors of 3 and 4 respectively. Comparisons with other rural studies showed marked variations in concentrations between locations. However a similar study at a rural site in the Lake District in NW England by Gardner (1993) also displayed high concentrations of FLU and PHE, comparable to the urban concentrations of this study.

Seasonal cycling of the ΣPAH concentrations was not evident at the four urban sites, due to the lack of seasonal change by the lighter PAH which dominate the PAH profile. The higher molecular weight compounds of CHRY to COR showed a seasonal pattern of high concentrations in the winter and low concentrations in the summer. At the rural site the heavier compounds showed the same pattern, conversely the lighter more volatile compounds of ACE, FLU, PHE, FLUO/MPHE and PYR displayed higher concentrations in the summer and reduced concentrations in the winter. This seasonal cycling of individual PAHs at the rural site followed a similar pattern to the Lake District study. Elevated concentrations of the lighter PAH at Hazelrigg were considered to be influenced by both local sources. These include the release from sediments in the Morecambe Bay area and the influence of a nearby motorway, however the process of re-volatilisation from soil and vegetation may also make a significant contribution to the atmospheric loading. Temperature is invoked as the controlling factor, resulting in the warmer summer months displaying the highest concentrations for the tri- and tetracyclic PAHs.

The vapour-particle distribution of individual compounds was examined at the urban sites of Manchester and Cardiff and the rural location. The % distribution for each compound was similar at each site for a particular season. Changes in the distribution were observed between the summer and winter seasons. The distribution was found to be heavily influenced by a compound's molecular weight and hence vapour pressure. The lighter

more volatile compounds of ACE, FLU, PHE and ANTH predominated in the vapour phase while the heavier PAHs of B[b]F to COR were primarily associated with the particulate phase. Changes in season and hence temperature altered this distribution, particularly for the mid-weight PAHs of FLUO/MPHE, PYR, BENZANTH and CHRY that had significant vapour phase concentrations in the summer but were found to predominate in the particulate phase during the winter. Correlations between total suspended particulate concentrations in the urban atmosphere and several of the heavier particle-associated PAH were weak, indicating the complex nature of urban aerosol. PAH partition coefficients calculated from respective adsorbent and filter fractions and ambient TSP loading, showed correlations with temperature for PHE and B[a]P selected from the Manchester and Hazelrigg studies. Temperature and TSP loading ultimately affect a compound's distribution, with calculated heats of desorption being significantly higher for the heavier multi-ringed PAH.

Principal components analysis (PCA) determined no profile differences between the city sites during the summer season, indicating similar sources to the urban atmosphere. The rural atmosphere showed a marked increase of PHE and FLU to the overall summer profile compared to the urban sites, indicating a different source of these compounds to the rural atmosphere. It is postulated that local sources and the re-volatilisation from soil and vegetation, significantly increase the concentration of the lighter more volatile PAH in the atmosphere of the rural site, during the summer.

Chapter 6

Meteorological influences on atmospheric SOC loading

6.1 Introduction

Once an organic contaminant is released into the atmosphere from source it is subject to transport. For semi-volatile organic compounds such as the PCBs and PAHs which are distributed between the vapour and particulate phases and have varying degradation rates, transport over long distances is possible. Meteorological conditions and air mass movement can result in the increase of contaminant loadings in the atmosphere and their translocation to unpolluted areas respectively. The build up of contaminants in the atmosphere over large source areas such as cities, due to prevailing meterological conditions, can result in 'episodes' such as the infamous London smog events of the 1950's (Boubel *et al.*, 1994) and the winter pollution episode in London during December 1991 (QUARG, 1993).

Transportation of contaminants on the macro scale (200 - 100,000 km) away from point sources has been recognised for many of these organic micro-pollutants. Atlas and Giam (1981) discovered PCBs, HCH isomers, DDT, dieldrin, chlordane and two phthalate esters in the atmosphere of a remote

Pacific Atoll, 1000's of km away from source areas. Importantly, the effect of air mass movement on SOC loading has been recognised as a factor influencing concentrations of these species in the Arctic atmosphere (Oehme and Manø, 1984; Hargrave *et al.*, 1988, Barrie *et al.*, 1992). Furthermore, the use of air mass back trajectories has allowed the tracking of contaminant movement and the speculation over source areas. This approach has been applied to explain elevated levels of PAHs in the atmosphere of southern Norway (Björseth *et al.*, 1979) and at a remote site on the island of Corsica in the Mediterranean (Masclet *et al.*, 1988).

In this chapter uncharacteristic, elevated concentrations of PAHs and PCBs in the urban sites of Manchester, London, Stevenage and Cardiff of the TOMPS programme, are explained in terms of pollution episodes due to prevailing meteorological conditions. In addition the importance of air mass direction, is highlighted in a high resolution sampling programme (daily samples rather than weekly) conducted at the TOMPS rural location (Hazelrigg).

6.2 Atmospheric transport and air mass tracking

An important aspect in measuring chemical species such as SOCs in the atmosphere, particularly in a rural or remote location, is to establish the source or direction of those air masses which influence contaminant loading. Alternatively, for continous sampling programmes short term

variations in the collected data may be explained by calculating a back trajectory, to deduce an air mass direction and hence determine it's passage from a potential source area.

In essence, a trajectory is the path of an imaginary air parcel as it is acted on by winds (Huschke, 1959). An application of single, forward trajectories is to follow a parcel of air from the source of a given substance and to see where the material could be transported. More likely, as Miller (1987) explained, for a chemical measurement that is made at some point, either on the ground or in the air, at a given time then a single back trajectory can be calculated, giving the path that the air mass travelled previous to the measurement.

There are various methods for calculating air mass back trajectories, all of which require regular meteorological data over the tracking period. Miller (1987) reviewed the different approaches meteorologists have developed to calculate trajectories, dividing them into two categories - dynamic and kinematic. Basically, dynamic calculations are made with such fields as pressure and temperature, to draw isobaric or isentropic trajectories, whereas kinematic calculations are made with measured wind fields. These two main categories can be broken down further into models which may have added characteristics, such as including the vertical movement in the atmosphere of the advecting air mass. In well defined meteorological phenomenon such as large anti-cyclones where air flow is simple, dynamic isentropic and kinematic models track the same paths very well. However

in more complex meteorological situations, it is assumed that the more complex isentropic calculations give more accurate trajectories. The application of the back trajectory method is therefore determined by the following factors: (1) the choice of the type of model used (dynamic, kinematic); (2) the level at which the calculation is made (whether it is a pressure surface, potential temperature field, layer in the atmsophere, etc); (3) the grid size, which determines the area of interest and the distance back a trajectory can go; (4) the number of days backward and (5) the amount of meteorological data available.

6.3 Calculation of air mass back trajectory

The trajectories calculated for this chapter are of the dynamic - isobaric type constructed from surface pressure charts (Synoptic weather summaries - Met. Office). Details of the technique, which obtains a geostrophic wind from the isobar spacing, are presented in Sykes and Hatton (1976). Basically the geostrophic wind is assumed to be parallel to the isobars, and is then used to advance the parcel of air by hand, in a horizontal plane only. Therefore, in order to construct a trajectory it was necessary to consider a series of surface pressure charts at regular intervals of 6 hours.

The geostrophic wind speed is obtained from the isobar spacing of the mean sea level pressure according to the equation:-

$$V(g) = \frac{1}{f\rho} \times \frac{dp}{dn}$$

where V(g) is the geostrophic wind speed, f is the Coriolis parameter, ρ the air density and dp/dn is the horizontal pressure gradient. For example, if the latter is equal to 4×10^{-3} mbar km^{-1} (the latitude taken as 54°N (Lancaster)), and:-

$$f = 2\Omega \sin \theta = 1.18 \times 10^{-4}\ s^{-1}$$

where Ω is the earth's angular velocity ($7.29 \times 10^{-5}\ s^{-1}$). Assuming an air density of 1.2 kg m^{-3}, then:-

$$V(g) = \frac{4 \times 10^{-4}}{1.18 \times 10^{-4} \times 1.2} = 2.8\ ms^{-1}$$

To construct a particular trajectory P_1 is selected as the position of the air parcel on chart 1 (surface pressure chart) and V_1 is the velocity vector. If there is no acceleration, and assuming strictly horizontal motion, the parcel would move a distance $D'_1 = V_1 \times 6 \times 60 \times 60$ in the six hours from chart 1 to chart 2, and arrive at a point Q'_1. In the meantime the wind speed may have changed, and D'_1 only represents a first approximation. To obtain a better approximation the wind speed V_2 at P_1, on chart 2, is used to obtain the displacement D''_1 from chart 1 to chart 2, that would have resulted if the parcel had moved with a constant velocity V_2. The vectors D'_1 and D''_1 carry

equal weight and a second approximation is obtained by the mean of the two displacements. This displacement takes the parcel to Q_1. Next, chart 2 is used to find the displacement D'_2 and the procedure outlined above is repeated from chart 2 to chart 3 etc., and a smooth curve through the points thus determined, represents the approximate trajectory.

For a particular sampling period, a pressure chart is selected which is closest to the start of the sampling time. The trajectory is worked back at six hourly intervals for 24 hours or greater. Next, a pressure chart is selected which is closest to the finish time of the sampling period, and the trajectory is worked back to the start of the sample period. This results in two lines on the map, between which is the route that the air parcel has taken.

Obviously trajectories determined in this manner can only be approximate, with the error growing the further back in time one goes. Sykes and Hatton (1976) predicted that computing a trajectory as described above would result in a ~ 40 km error when going back over 30 hours. This method does not take into account any vertical movement of the air mass and is determined from surface pressure maps (at the 1000 mbar level). Several studies measuring atmospheric SOCs have computed their trajectories at several pressure heights i.e. 1000, 925 and 850 mbar (Hoff *et al.* 1992b; Tysklind *et al.*, 1993), this allows the air movement to be assessed at varying heights with the 925 and 850 mbar trajectories being more representative of tropospheric flow - since errors may occur for surface level trajectories due to air mass

friction with the earth's surface. Because of this uncertainty air mass trajectories were calculated for this work only when clear, well defined air mass systems were apparent.

6.4 Influence of meteorological conditions on TOMPS data

Contaminant concentrations in the urban atmosphere have been found to vary considerably from one day to another (and even from hour to hour for pollutants such as CO) (QUARG, 1993). These variations have been largely determined by meteorological factors. The extent to which pollutants are dispersed and diluted depends on wind speed, turbulence, mixing depth and in the city environment, the urban topography. Atmospheric turbulence determines how rapidly a parcel of polluted air is dispersed as it moves away from source. The build up of pollutants depends on the atmospheric conditions. Dispersion is less under stable atmospheric conditions, which occur mainly at night time, than under unstable conditions, which can occur during the middle of the day, when heating of the ground causes thermal turbulence. The mixing depth is the depth of the atmosphere into which the pollutants readily mix. Temperature inversions can restrict the depth of this mixed layer, and act as a lid to the atmosphere, allowing contaminant concentrations to build up underneath. Temperature inversions occur at night time when there is rapid cooling of the ground, and also when warm air moves in over cool ground. In rural areas the inversion may lie only a few tens of metres above the ground, however, in

large urban areas the 'heat island' effect created by the additional heat sources produces inversions more typically 100 to 200 m above the ground.

The conditions that favour pollution episodes in urban areas involve low wind speeds, stable atmospheric conditions and low mixing heights. These meteorological conditions normally occur during anticyclonic weather and mainly at night time. During the day the temperature inversion is likely to break up as the sun warms the ground. However, during the winter months it is possible for inversions to persist throughout the day and they may survive for several days before breaking up. The atmospheric PCB and PAH data from the TOMPS programme presented in Chapters 4 and 5 respectively, was analysed to determine which sample weeks had uncharacteristically elevated concentrations. That is when concentrations were significantly greater than the seasonal norm (both PCBs and PAHs show seasonal cycling).

Figures 6.1a and b represent the total ΣPAH concentrations (vapour + particulate phases) for Manchester and London respectively, throughout 1991 and 1992. Although the sampling scheme was not synchronised for both sites, elevated PAH concentrations can be observed for weeks 6 and 49 at the London site and weeks 5 and 47 at the Manchester site. These weeks approximately correspond with one another between the two sites (±7 days). Weeks 5 and 6 cover the period of the 7th - 20th February 1991, while weeks 47 and 49 relate to the period from the 5th - 19th December 1991. Careful

Figure 6.1a Manchester ΣPAH concentrations.

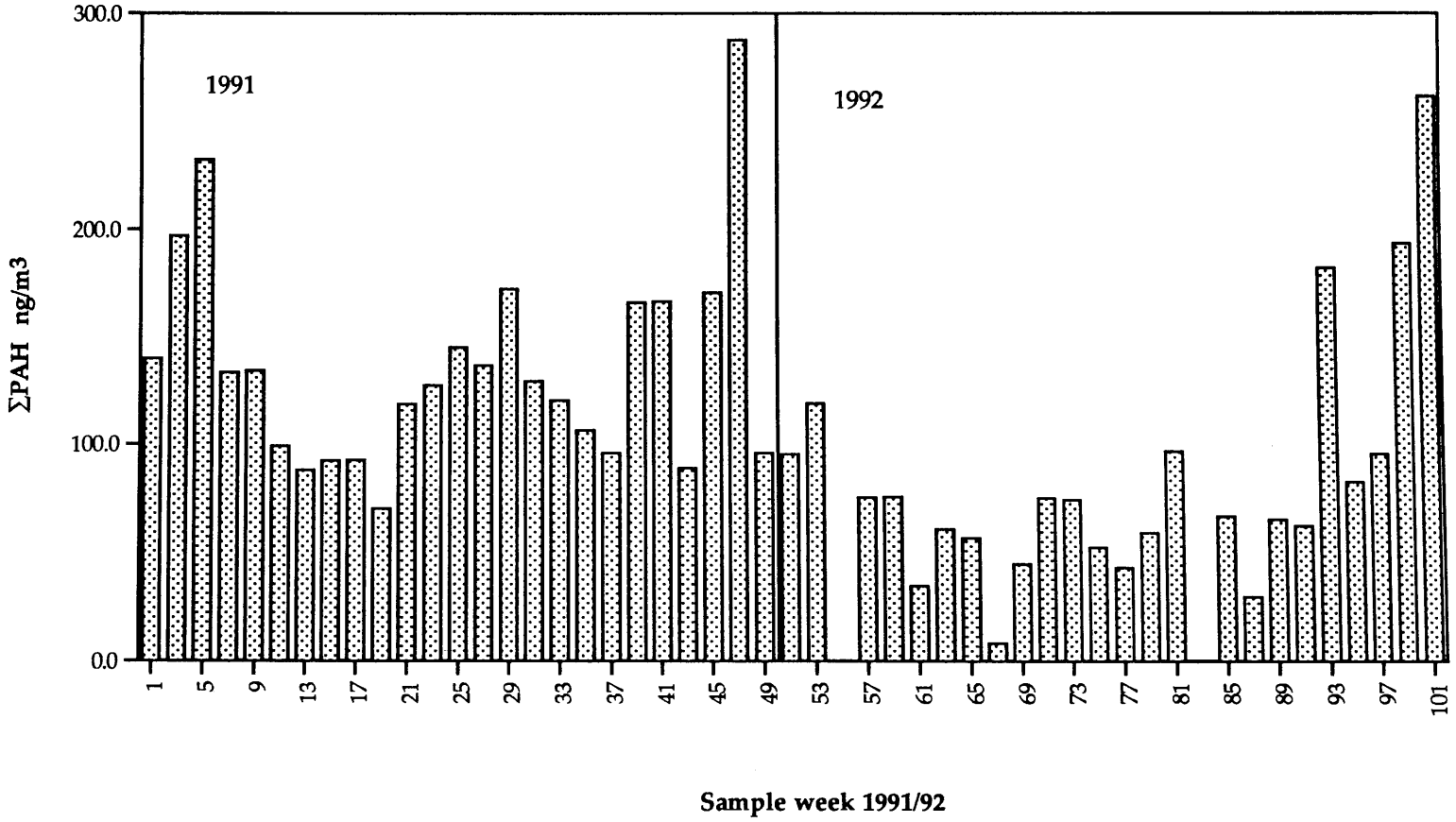
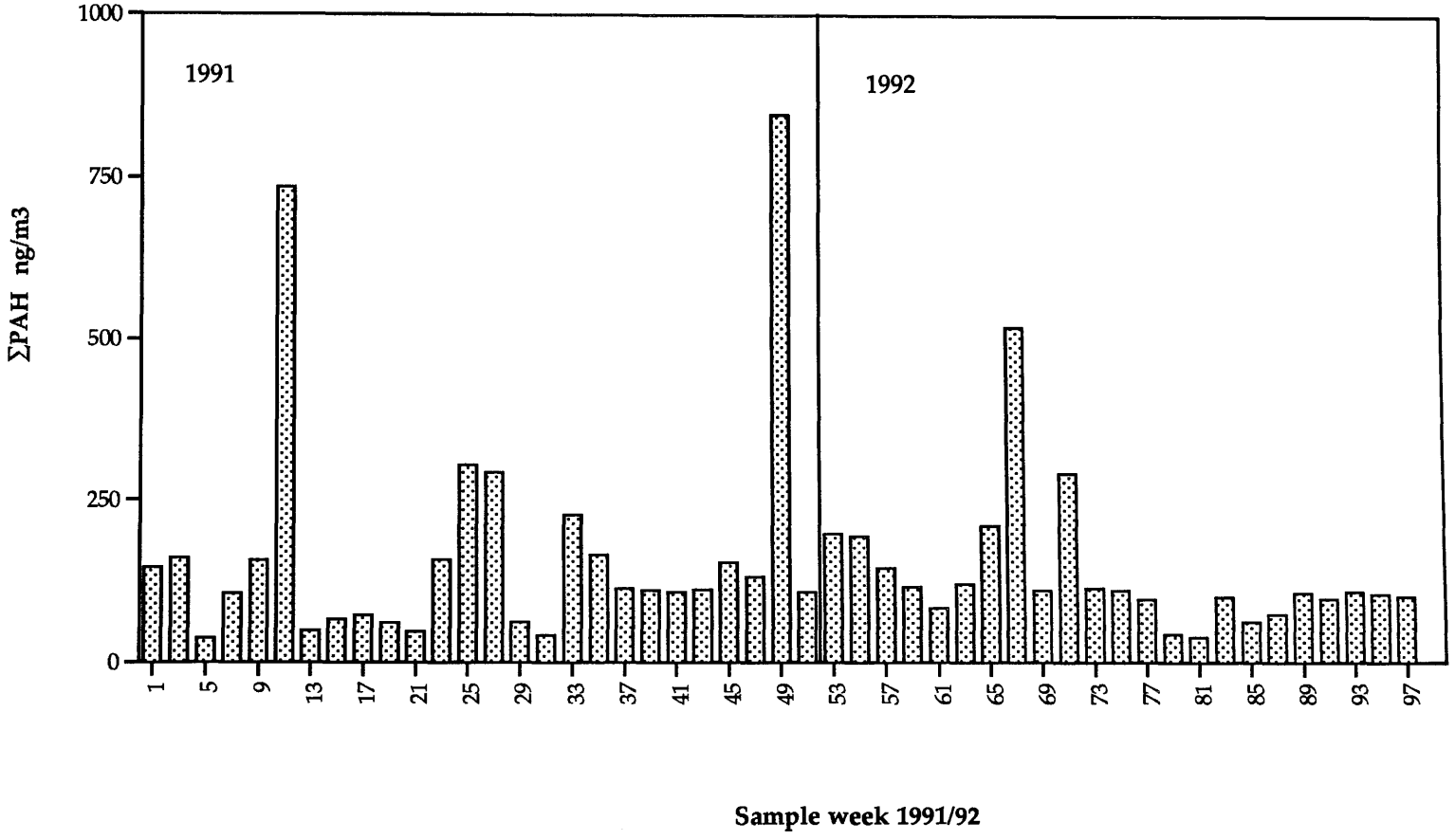


Figure 6.1b London ΣPAH concentrations.



examination of the Meteorological Office Daily Weather Summaries reveal that the weather conditions were sustained and consistent through each of the time periods, over the whole of the UK. Hence the meteorological conditions can be considered as the explanation for the build up of unusually high concentrations of PAHs at both sites during each time period. For the first period (7th-20th Feb. 1991) London and Manchester had ΣPAH concentrations of 745 ng m^{-3} and 240 ng m^{-3} respectively. Both values were significantly higher (t-statistic = 4.89, 1df , $P < 0.05$) than the mean winter value of 166 ng m^{-3} for London and 135 ng m^{-3} for Manchester. During this time the UK was under the influence of a high pressure anticyclonic system, typified by clear, calm weather with an air flow from the east. This resulted in freezing temperatures and the formation of periodic temperature inversions leading to a build up of atmospheric PAH concentrations. Similarly, the second period (5th-19th December) experienced a high pressure 'blocking' anticyclone positioned over the UK, which lasted for much of December. PAH concentrations for London and Manchester were 830 ng m^{-3} and 280 ng m^{-3} respectively, significantly higher than the mean winter concentrations (t-statistic = 6.25, 1df, $P < 0.05$). During both periods elevations of other atmospheric organic contaminants have been reported i.e. for ethane, benzene and toluene (QUARG, 1993). Other periods of elevated PAH concentrations are apparent for both cities during 1992. For London and Manchester weeks 67 (10th-16th April '92) and 101 (16th-23th Dec '92) respectively have concentrations above their seasonal mean values. Unfortunately these sample weeks do not correspond to the

opposite sample weeks in the other city, resulting that a short term meteorological condition (> 7 days) or episode will have no effect on the closest PAH sample week in the other city. Therefore, this requires a coordination of sampling events between cities, or an increase in sampling resolution i.e from a seven day period to a three day period or less.

Interestingly, the two pollution episodes described above (Feb. and Dec. 1991) occur during the winter time when the particulate phase PAH concentrations are at their highest, due to the increase in fuel consumption for domestic heating (Santodonato *et al.*, 1981). The PCBs, however, are no longer manufactured, and are not seasonally influenced by anthropogenic activity. Therefore, do they show an increase in concentrations during these pollution episodes? In Figure 6.2a Manchester's ΣPCB concentrations are presented for 1991/92 and show the seasonal cycling as highlighted in Chapter 4. The episode weeks of 5 and 47 do not show elevated concentrations and are not significantly different from the winter mean of 438 pg m^{-3} (t-statistic = 5.76, 1df, $P > 0.10$). On the other hand the particulate phase ΣPCB concentrations do show significantly higher concentrations during these meteorological episodes at all three city sites (London, Cardiff and Manchester). This is highlighted in Figure 6.2b where the Cardiff particulate phase ΣPCB concentrations are presented for 1991/92. Weeks 6 and 44 correspond to sample dates 21st-28th Feb. 1991 and the 12th-19th Dec. 1991 respectively, and are significantly higher than the winter mean concentration of 48 pg m^{-3} (t-statistic = 22.8, 1df, $P < 0.05$). The particulate

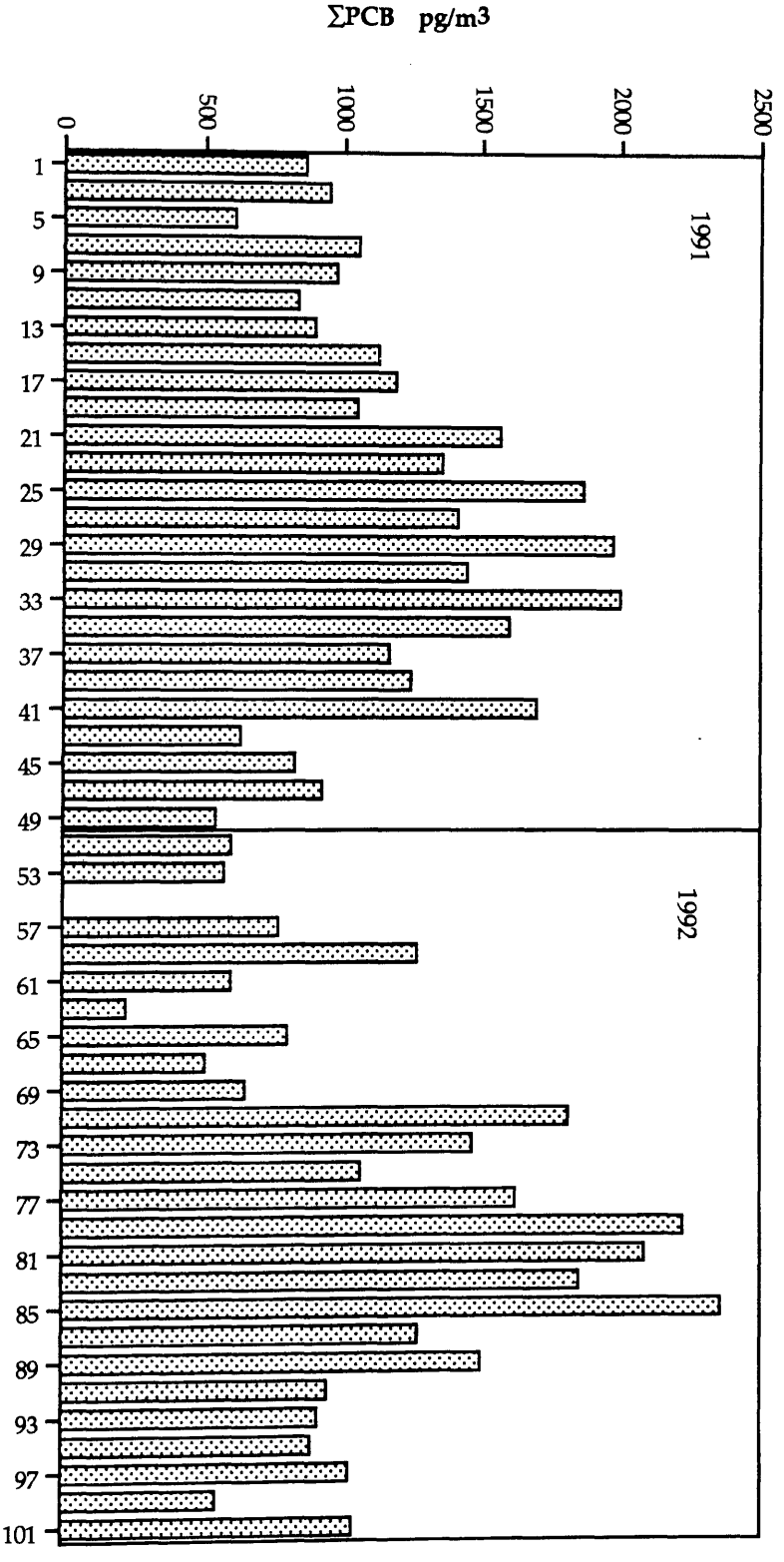


Figure 6.2a Manchester ΣPCB concentrations.

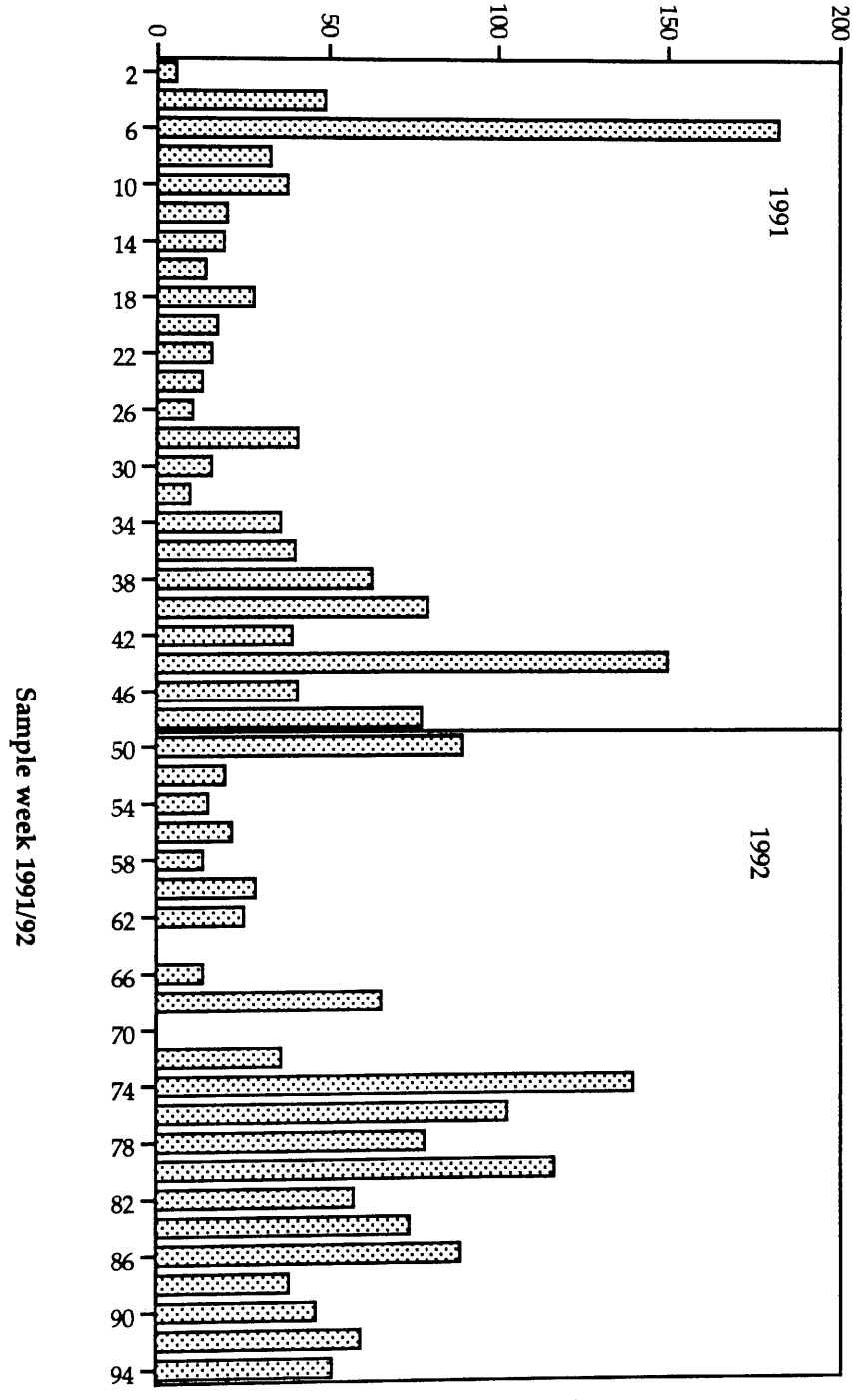


Figure 6.2b Cardiff ΣPCB (particulate phase) concentrations.

phase PCBs are therefore more influenced than the total ΣPCB concentrations, which are dominated by the vapour phase component as described in Chapter 4. This implies that the atmospheric particulate loading during these episodes increases. Certainly an increase in total suspended particulate (TSP) concentrations was evident (Appendix 1) but probably of more significance was the probable increase in PM_{10} particulate, which is the size fraction containing the majority of particulate-bound organochlorine contaminants (Kaupp *et al.* 1994).

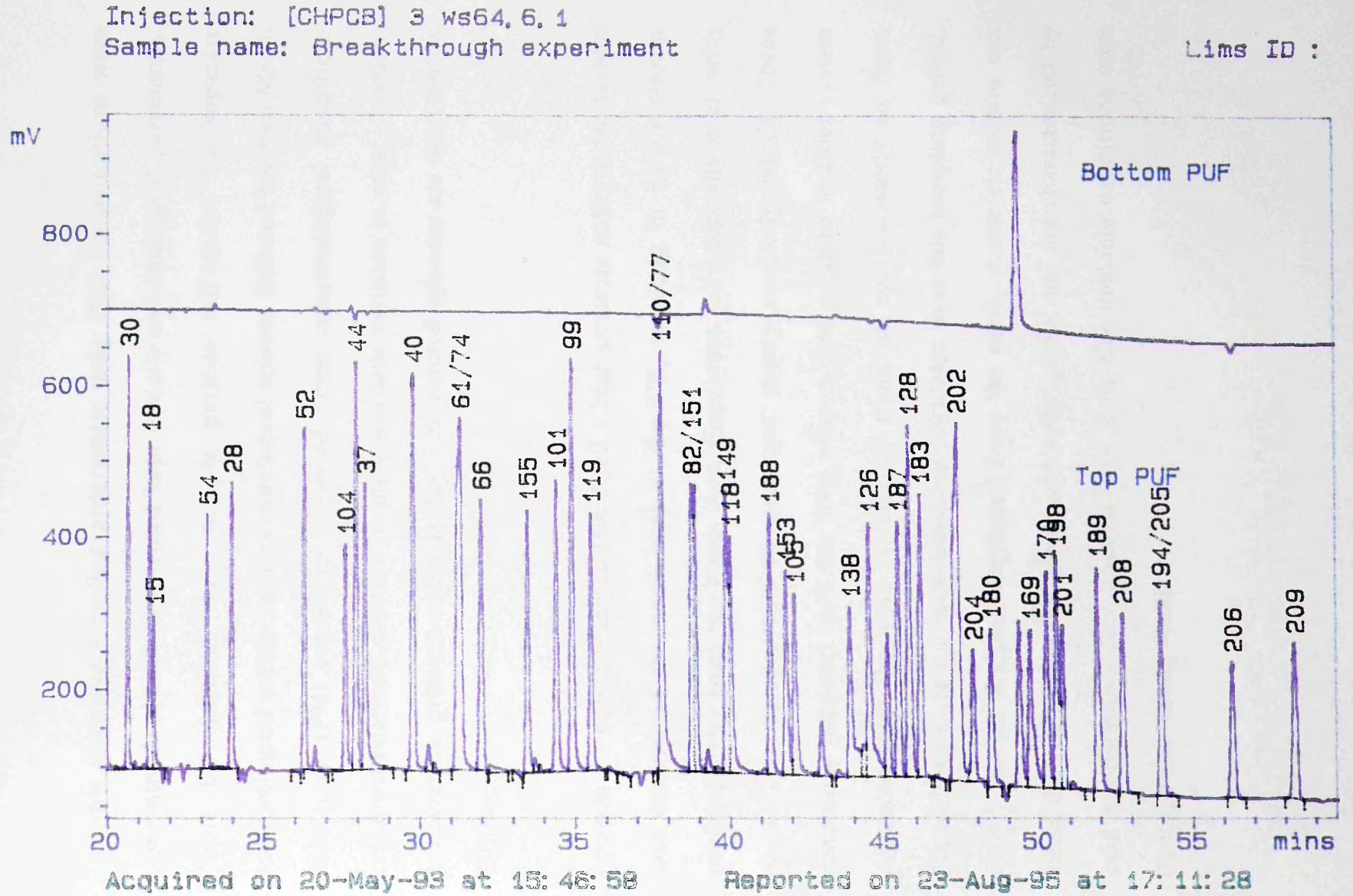
6.5 Intensive air sampling

Air samples for the TOMPs programme were taken over a period of seven days. Unless defined meteorological conditions persisted over this time short term variations in ambient conditions could not be distinguished. For any particular sample short term fluctuations (daily) in contaminant concentrations will have become blurred. To examine short term variations in atmospheric PCB concentrations a new Hi-Vol air sampler was installed at the rural TOMPs location (Hazelrigg, near Lancaster). Air samples were taken over a 24 h period with approximately 350 m^3 of air being aspirated for each sample. Sampling commenced on the 23rd March 1994 until June 1994, effectively covering the spring and early summer seasons. Due to the number of samples generated the vapour and particulate phases were not analysed separately, instead the the filters and PUFs were extracted together. The analytical protocol was identical to the TOMPs air samples which is

presented in Chapter 3.

In aspirating a large volume of air in a short period of time i.e. 24 h, there was the increased chance of analyte breakthrough - through the filter/adsorbent train (Billings and Bidleman, 1983), this is discussed in more detail in Chapter 2, Section 2.6.5. Basically, the more volatile species i.e. the tri- and tetrachlorinated biphenyls and the three ring PAH may be underestimated due to their loss from the sample train. This process has been highlighted as a significant loss mechanism for more volatile species like HCH (Pankow, 1993). Therefore as a quality assurance procedure to test for sample breakthrough 500 μL of the neat PCB standard was spiked onto the filter (980 ng ΣPCB) of a sampling module (filter and 2 PUF plugs). The module was placed in the Hi-Vol which was operated under normal sampling conditions, resulting in 500 m^3 of air being aspirated over a 24 h period. The filter and each PUF plug were analysed separately, the mass of PCBs collected from the atmosphere was considered to be negligble compared to the spiked quantity. Upon analysis ~ 90% of the ΣPCB was present on the 1st (top) PUF plug with 10% remaining on the filter. The 2nd (bottom)PUF plug showed no sign of PCB contamination, indicating that breakthrough of PCBs from the sample train was not evident. Chromatograms of the top and bottom PUFs are presented in Figure 6.3, the loading on the first PUF can be clearly observed.

Figure 6.3


Injection: [CHPCB] 3 ws64.6.1
Sample name: Breakthrough experiment
Lims ID :
mV
800
600
400
200
Bottom PUF
Top PUF
30
18
15
54
28
52
104
44
37
40
61/74
66
155
101
99
119
110/77
82/151
118
149
188
105
153
138
126
187
183
128
202
204
180
169
170
198
201
189
208
194/205
206
209
20
25
30
35
40
45
50
55
mins
Acquired on 20-May-93 at 15:46:58
Reported on 23-Aug-95 at 17:11:28

6.5.1 Meteorological factors affecting PCB concentrations

For this intensive sampling programme daily PCB concentrations were determined, as well as a record kept of daily meteorological parameters. Table 6.1 presents three sample periods influenced by separate meteorological events. Each meteorological episode (selected between March and June 1994) represents a period when meteorological conditions remained relatively constant i.e. there was little variation in wind direction, temperature, pressure and humidity. The selected episodes are described as follows:-

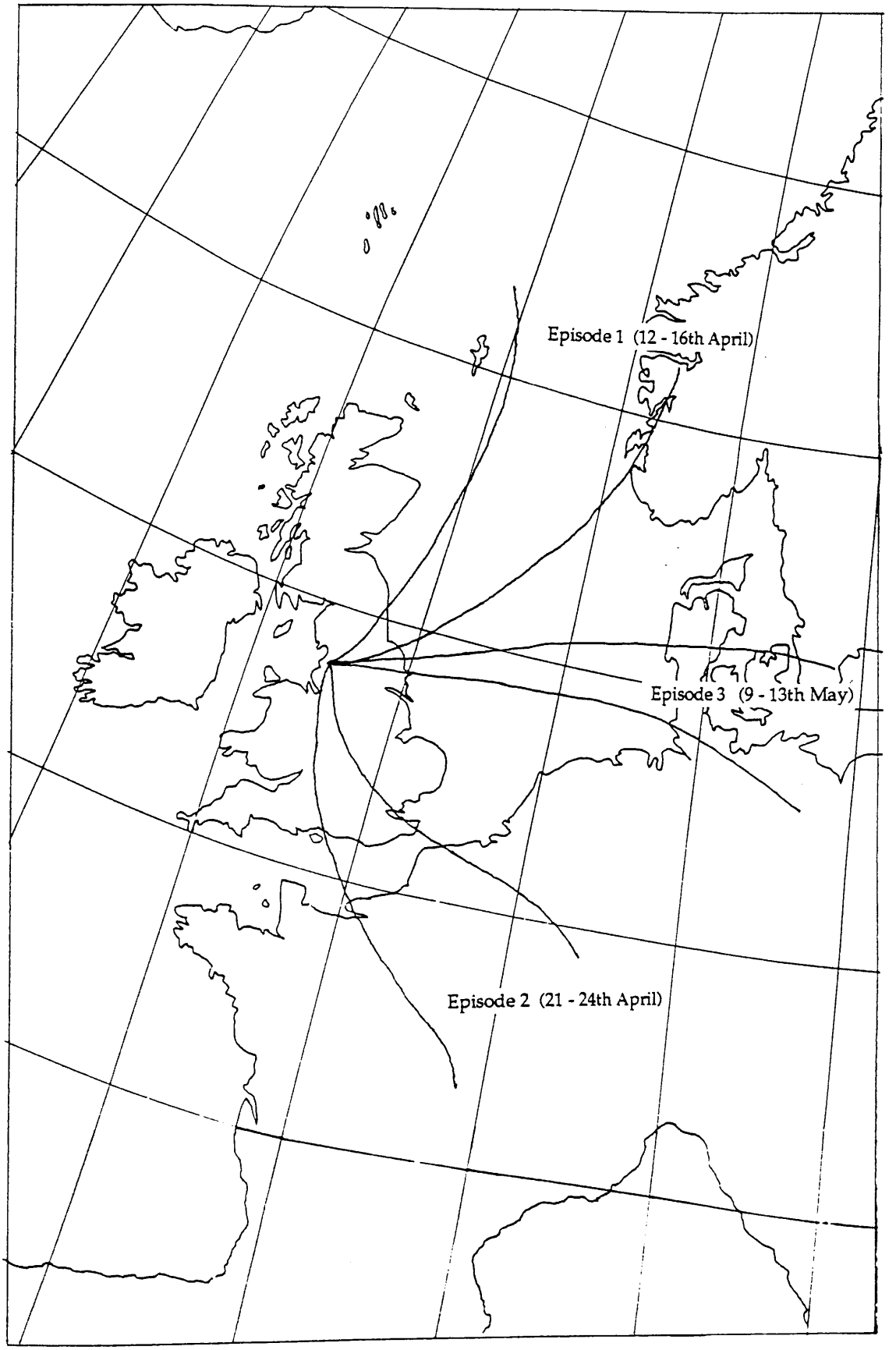
Episode 1 - Between the 12-16th April a high pressure anticyclonic system was centred to the north-west of the UK, resulting in an air stream predominantly from the North East. Conditions were typically cold, with clear skies, intermittent showers and strong northerly winds. These conditions persisted until the 17th, when a low pressure weather system advanced from the west, resulting in a milder, south-westerly air flow. Figure 6.4 shows the back trajectory calculated over this sampling period, clearly the air sampled originated from the north. Arctic air masses can affect the UK during the winter and early spring, and are characterised by cold temperatures, low humidity but generally unstable conditions once over the UK (Musk, 1988).

Table 6.1 Selected meteorological episodes influencing atmospheric conditions at a rural location in NW England.

Episode 1

Sample dates	Vol air (m3)	Temp. range °C	Wind direction and speed (m/s)	Mean pressure mbar	Relative Humidity %
12-13/4	393	2-9	N-NE 7.5	1030	68
13-14/4	389	2-11	N-NE 7.5-10	1028	62
14-15/4	340	3-10	NE 7.5-10	1027	69
15-16/4	383	2-10	NE 2.5	1030	70
Episode 2					
21-22/4	341	6-14	S-SE <2.5	1004	79
22-23/4	343	9-17	SE 2.5-5.0	1000	76
23-24/4	400	8-17	S-SE 2.5-5.0	1000	78
Episode 3					
9-10/5	350	5-16	S<2.5	1012	98
10-11/5	388	8-17	E-SE 5	1012	98
12-13/5	352	10-21	S-SE 5-7.5	1014	99

Figure 6.4 Calculated air mass back trajectories for the rural site at Hazelrigg (NW England). Three separate episodes identified between April and May 1994.



Episode 2 - Towards the end of April, from the 21-24th, the UK received air off the continent. To the south-west and north-west of the UK were two low pressure systems, their westwards progression blocked by a weak high centred over the continent. The clockwise rotation of the high pressure system located to the east of the UK, resulted in air moving from a south-easterly direction, over the British Isles. This was characterised by stable (light winds) mainly dry conditions. A calculated back trajectory displayed in Figure 6.4 reveals the path taken by the air sampled at Hazelrigg over this time period. The parcel of air originated from the continent, moving in a north-westerly direction through the Midlands to NW England.

Episode 3 - From the 10th May onwards, the northern UK was affected by a high pressure anticylonic system located to the north-east of Scotland. Air was channelled directly eastwards from Holland, northern Germany and the Baltic. Conditions were stable with light easterly winds, typified by mainly dry conditions, however, mist patches and drizzle persisted throughout the mornings. The back trajectory in Figure 6.4 confirms the air parcel movement from the east.

Table 6.2 presents the PCB concentrations for the three meteorological episodes described above. Individual PCB concentrations are displayed for the six indicator congeners as well as the homologue group concentrations. The ΣPCB concentrations ranged from 38.7 - 261 pg m^{-3} resulting in a background mean of 141 pg m^{-3} for the whole sampling period. Again,

Table 6.2 Mean PCB concentrations during three meteorological episodes at the Hazelrigg sampling site.

PCB (pg m^{-3})	Episode 1 12-16/4	Episode 2 21-24/4	Episode 3 9-13/5
28	33.6	48.5	21.6
52	13.1	19.4	13.6
101	4.94	8.15	7.00
118	1.94	3.03	2.42
153	2.96	3.78	1.62
138	1.62	1.86	2.70
180	0.940	1.80	ND
$PCB-Cl_3$	19.7	43.8	23.2
$PCB-Cl_4$	10.4	14.8	8.49
$PCB-Cl_5$	3.60	6.21	5.27
$PCB-Cl_6$	2.60	3.10	2.23
$PCB-Cl_7$	0.351	0.662	0.451
$PCB-Cl_8$	ND	ND	ND
ΣPCB	119	223	131

urban concentrations discussed in Chapter 4 are approximately a factor of 3-4 higher than the Hazelrigg values reported in this programme. At other rural locations the mean ΣPCB concentrations have been reported as 50 ng m^{-3} in Ontario, Canada (Hoff *et al.*, 1992a) and 648 ng m^{-3} in South Bohemia, Czech Republic (Holoubek *et al.*, 1992). As with the urban concentrations the atmospheric profile is dominated by the tri- and tetra -chlorinated congeners.

In episode 1 (Table 6.2) the mean ΣPCB concentration was significantly lower than the mean concentration of the whole sampling period (t-statistic = 3.19, 3df, P = 0.05 - PCB). The more volatile tri- and tetrachlorinated homologues predominated, with congeners 28 and 52 comprising of ~ 50% of the total sum. In comparison, episode 2 had a significantly greater mean ΣPCB concentration. Each homologue group also displayed higher concentrations than in episode 1. However, the congener profile stayed relatively constant, being chiefly dominated by the tri- and tetrachlorinated homologues.

Episodes 2 and 3 represent easterly air flows, however, from their trajectories in Figure 6.4, the air mass for episode 2 was from the south east while episode 3 was directly from the east. Episodes 1, 2 and 3 are all examples of deviations from the common westerly air stream, from which the background mean was derived over the whole sampling period. Episode 3 did not have elevated PCB concentrations, the episode mean ΣPCB

concentration of 131 pg m^{-3} was not statistically different from the background mean of 141 pg m^{-3} (t-statistic = 6.28, 1df, $P > 0.10$). Episode 2 had the air mass originating from the centre of continental Europe. The passage of air over the industrialised Midlands of the UK, probably resulted in the increased PCB loading. Episode 3 with the air source originating from the Baltic region, had a reduced PCB loading, being no different from the mean background concentration. During this period precipitation events were noted, with elevated humidity over the other two episodes (Table 6.1). Wet removal of organic contaminants from the atmosphere is a signifcant loss mechanism (Ligocki and Pankow, 1985a+b), with the reduction of both PAHs and PCBs being reported during rain events (McVeety and Hites, 1988; Murray and Andren, 1992; Backe *et al*, 1994). Although not measured, it is probable that precipitation events will have reduced the contaminant loading during episode 3. Masclet *et al.* (1988) undertaking an air sampling campaign in the Mediterranean, made a similar conclusion for the loss of particulate bound PAHs from an air mass originating over industrialised regions.

6.6 Summary

Meteorological conditions affect the ambient atmospheric concentrations of PCBs and PAHs. These effects are pronounced usually for a short time period (in the order of days). Longer term effects such as the winter episodes highlighted in the TOMPS city data may last for up to two weeks,

concentrations of PAHs and particulate bound PCBs greatly exceed seasonal mean concentrations, resulting in implications for human health and exposure level criteria.

Intensive sampling (daily) allows variations in ambient concentrations and compound profiles to be examined more thoroughly. In recording meteorological parameters and deriving back trajectories, episodes may be identified and the air mass paths followed. Three episodes identified at a rural site in NW England had their air masses originating from the north east, south east and east respectively. The air mass for episode 1 was of Scandinavian/Arctic origin, while the air masses of episodes 2 and 3 were from continental Europe. In various studies profile differences in separate air masses have been identified for PAHs in the Mediterranean (Masclet *et al.*, 1988), and for the PCDD/Fs in southern Sweden (Tysklind *et al.*, 1993). For the PCBs, although absolute concentrations were higher in episode 2, the profiles were similar for all three episodes, indicating that sources and transport mechanisms controlling PCB concentrations are similar. This supports the work of Panshin and Hites (1994) who found no difference in PCB profile, for various air masses sampled at Bermuda in the western Atlantic.

Chapter 7

Modelling Atmospheric PCB Concentrations

7.1 Introduction

To obtain a better understanding in the atmospheric cycling and behaviour of PCBs it is necessary to attempt to predict atmospheric concentrations over terrestrial surfaces. One way involves determining the major sources (compartments) to the atmosphere and attempting to quantify the release of PCBs from these compartments over a defined time period. In order to do this a unit surface area has to be selected and then a theoretical box created which extends up into the atmosphere. Sources within the box will be the only ones considered to make a significant input to the atmosphere.

By taking this approach the major source compartments can be defined within the box, along with an approximation of their contribution to the atmosphere for a particular compound. To enable the prediction of PCB concentrations in the atmosphere a box model developed by Pankow (1993) was utilised. This model was developed to describe the vapour phase concentrations of certain semi-volatile organic compounds (SOCs) over annual cycles that peak in the summer. This model invokes temperature as the major controlling factor of vapour phase concentrations, implying that with an increase in temperature there will be decreased partitioning to the surfaces (compartments) within the box and hence an increase in

atmospheric concentrations. It was decided that the box model would be applied to the urban area of Manchester to predict monthly congener concentrations in the urban atmosphere. The major source compartments would be defined and their contribution to the atmospheric loading evaluated for each month over a 1 year period (a full seasonal cycle). The resulting air concentrations could be compared to the actual sampled air concentrations, to investigate whether the temperature change was sufficient to explain the seasonal cycling observed in the vapour phase concentrations within this urban atmosphere.

7.2 The Simple Box Model

The basic assumption to this model is that air moving over the surface of the earth can exchange organic compounds with the surface, and so the potential exists for equilibration between the atmosphere and the surface materials. Pankow (1993) described a box that covered an area of the earth's surface of interest and extends up into the atmosphere (the height of tropospheric mixing ~ 6300 m in temperate latitudes). For PCBs which are no longer in production, then it is considered that the majority of the vapour phase component in the atmosphere is derived from desorption off solid surfaces within the box. Compartments may include soil, vegetation, and suspended particulate matter. This process is assumed to be driven by temperature only.

SOCs can have non-negligible fractions of their environmental masses in both the atmosphere and partitioned to surface materials. Temperature driven cycling of SOCs between the atmosphere and the earth's surface has been postulated by several reseachers (Manchester-Neesvig and Andren, 1989; Hoff *et al.*, 1992a; Wania and Mackay, 1993). Indeed as Pankow (1993) stated, partition coefficients depend on temperature, therefore the nature of the atmospheric/surface distribution will depend on the natural, annual cycles in the ambient temperature. This box model solely invokes temperature as the governing factor over atmospheric vapour phase concentrations for SOCs.

For the box model Pankow used two partition coefficients to describe 1) the sorption between the vapour phase and the total suspended particulate (TSP) in the atmosphere (K_p) and 2) the equilibrium sorption between the vapour phase and material at the earth's surface (K_m). Kp has been described in Chapter 2, Section 2.2.3 and takes the form (F/TSP)/A where F (ng m^{-3}) and A (ng m^{-3}) are the particulate and vapour phase concentrations for an SOC at equilibrium respectively. The units of K_p are m^3 μg^{-1}.

To derive K_m it was necessary to recognise the major sorbing compartments within the box, the mass of an SOC that is *readily exchangeable* with the atmosphere for any particular compartment can then be estimated. Note that readily exchangeable refers to that fraction of a compound that is

available to the atmosphere over an annual time basis, so the portion of a compound that is locked up in deep soil, buried in sediments or deposited within the cores of trees can therefore be discounted. K_m takes the form:-

$$K_m = \frac{S}{A} \quad (1)$$

Where S is the sorbed concentration of an SOC at the earth's surface in units of ng sorbed per μg of sorbing material and A is the atmospheric vapour phase concentration. Therefore K_m is a type of earth/atmosphere partition coefficient with units $m^3\ \mu g^{-1}$. For the numerous compartments within a selected box an overall K_m can be calculated from the different sorbing compartments by:-

$$K_m = \frac{S_1(m_1/m)}{A} + \frac{S_2(m_2/m)}{A} + \frac{S_3(m_3/m)}{A} \quad (2)$$

Where S_1, S_2 and S_3 are the sorbed concentrations (ng μg^{-1}) in the number of compartments considered within the box i.e. 1, 2, 3 etc. The parameters m_1, m_2 and m_3 are the masses in μg of sorbing material in each of the considered compartments - that is material capable of relatively rapid exchange of SOCs with the atmosphere (i.e. on a time scale of a month), and m is the total mass of sorbing material added up from all of the compartments within the box. Thus with S_1/A, S_2/A, S_3/A, ..., representing the individual sorption

constants K_{m1}, K_{m2}, K_{m3}, ..., for the different compartments, Equation (2) therefore represents a weight-average representation of K_m for all the considered compartments within the box.

By taking this approach Pankow (1993) could then estimate the total, readily exchangeable mass of a given SOC that distributes itself between the surface and the atmosphere within the box. This he represented as q (ng) and is assumed to be fixed over an annual cycle of interest. Although q might be quite large, units of ng were selected for this parameter because atmospheric measurements of organic compounds are frequently carried out at the ng m^{-3} level. A mass balance for q is represented as:-

$$q\ (ng) = VA + VK_pTSPA + K_mmA \quad (3)$$

Where V is the volume of the box. As q is fixed over an annual time frame then Equation (3) can only be applied to those compounds that have no significant inputs over a yearly period, that is there are no new emissions in the zone of interest and it is only (or at least mostly) prior released material that is cycling between the atmosphere and the earth's surface. For this reason PAHs (continually produced and emitted) and pesticides in curent use cannot be applied to this model. Equation (3) can then be re-arranged to determine A (the equilibrium vapour phase concentration) :-

$$A = \frac{q/V}{1 + K_pTSP + K_mm/V} \quad (4)$$

The term q/V is the equivalent atmospheric concentration (ng m^{-3}) of the readily exchanging fraction of a compound and m/V is the equivalent atmospheric concentration (μg m^{-3}) of sorbing surface materials. The quantity K_pTSP gives the dimensionless TSP-sorbed/gaseous ratio, while $K_m(m/V)$ is the surface-sorbed/gaseous ratio for a chosen compound (dimensionless). In order to predict changes in A with temperature Pankow then looked at the temperature dependence of the partition coefficents. Partitioning between the vapour phase and any other phase (i.e. TSP) can be expressed as a function of the heat of desorption for the compound in question and the temperature. In the case of simple physical adsorption to the solid surfaces of atmospheric particles, for a given compound Pankow predicted:-

$$Kp = \frac{A_{tsp}t_o}{275(M/T)^{1/2}} e^{H1/RT} \quad (5)$$

Where A_{tsp} is the specific surface area of the aerosol particles in the atmosphere (cm^2 μg^{-1}), t_o is a fundamental vibration time (s) of the sorbed compound on the surface of the TSP, H_1 (KJ mol^{-1}) is the compound's heat of desorption from the surface of the TSP, R is the gas constant, T is the temperature (K) and M is the molecular weight (g mol^{-1}). Based on the

nature of Equation (5) Pankow wrote a good approximation that:-

$$K_p \simeq \overline{K}_p e^{H1/RT} \quad (6)$$

where $\overline{K}p$ is a pre-exponential factor essentially independent of T and for a given compound class such as the PCBs is largely independent of any particular congener. The value of H_1 depends on the compound or congener in question. Similarly, there is reason to believe that K_m will follow an equation that is similar to Equation (6) with:-

$$K_m \simeq \overline{K}_m e^{Hm/RT} \quad (7)$$

where $\overline{K}_m$ is a pre-exponential factor independent of T and characterises the sorption of a given compound class to the materials at the earth's surface. Within a compound class, like $\overline{K}_p$, the value of $\overline{K}_m$ will be largely independent of the compound. H_m is the compound dependent heat of desorption from those materials (compartments) in the box.

Equations (6) and (7) can then be substituted into Equation (4) to give:-

$$A = \frac{q/V}{1 + \overline{K}_p e^{Q1/RT} TSP + \overline{K}_m e^{Hm/RT}(m/V)} \quad (8)$$

Therefore a change in T will alter the A value (q/V remains fixed for a particular compound in the box over an annual time scale). As TSP increases, then A will decrease because the volumetric concentration of the sorbing mass in the atmosphere is increasing. Analogously, m/V in Equation (4) is the equivalent volumetric concentration of sorbing material at the earth's surface. As with TSP, as m/V increases, for fixed q/V the value of A will decrease. For fixed q/V, TSP and m/V represented in Equation (8) increases in T during the spring and summer will increase A because the compound in question is being driven off both the TSP and m/V. The degree to which A approaches q/V will depend on $\underline{\overline{K}}_p$, H_1, TSP, $\underline{\overline{K}}_m$, H_m and m/V and, importantly, on how large T becomes. Seasonal variations in T in temperate zones can then cause significant cycling between the earth's surface and the atmosphere.

Pankow postulated that the more volatile compounds such as the lighter PCB congeners will be characterised by A being far greater than F. That is the total atmospheric concentration (i.e. A + F) will be very nearly given by A, furthermore the mass of TSP will be extremely low compared to the mass of sorbing materials at the earth's surface. Therefore the $\underline{\overline{K}}_p e^{H1/RT}$TSP term in Equation (8) will be negligible for all but the heaviest SOCs. Therefore A can be predicted by shortening Equation (8) to :-

$$A = \frac{q/V}{1 + \underline{\overline{K}}_m e^{Hm/RT}(m/V)} \quad (9)$$

Monthly A concentrations can then be predicted in the box atmosphere by simply substituting in the monthly T values. The application of this model is not without its assumptions and is important that these are clearly understood. Firstly it is assumed that near equilibrium exists for vapour phase concentrations (i.e. A values) of SOCs between the atmosphere and a mass m at the earth's surface. Secondly the temperature dependence of the earth/atmosphere partitioning causes seasonally based, annual cycles of SOC concentrations in the atmosphere. At a given point in time a mean temperature T for the box is the temperature that controls partitioning in the whole of the box. Thirdly the value of q (ng) for the readily exchanging portion of a given SOC in the box is fixed over an annual time scale. Inputs to the box over an annual type of time frame are small compared to the existing inventory in the box. Pankow also assumes that the north/south movement out of a box positioned in temperate latitudes (30-60°) is negligible. The box should also extend around the globe to avoid east/west mixing which may be extensive.

7.3 Application of the box model to the city of Manchester

For this study the box model was applied to the city of Manchester to predict monthly A concentrations of congener 52 (tetrachlorinated biphenyl) throughout 1991. The model is only suitable for those congeners which are predominantly in the vapour phase, therefore congener 52, one of the major congeners found in the atmosphere, was selected as an example. The

theoretical box was much smaller than that anticipated by Pankow - but it was believed that the potentially large source of readily exchangeable PCB 52 inside this box would negate the effects of any loss by advection. The box dimensions are presented in Table 7.1 but basically the surface area incorporated the whole of Greater Manchester (2.1×10^8 m^2). The height of the box extended up to 2000 m. The height of tropospheric mixing (6300 m) used by Pankow (1993) was considered to be too great for a box area of this size, considering the residence time of air over Manchester. Harner *et al.* (1995) used a working height of 2000 m, in an air-soil exchange fugacity model for the southern UK. It should be acknowledged, however, that there is large uncertainty over the choice of height to use. Harner *et al.* (1995) considered that treating the atmopshere as a well mixed box to 2000 m, as in their model, was a possible source of error. Most atmospheric measurements are carried out at ground level, thus ground level concentrations may be higher, with mixing to 2000 m being slow.

Within this urban box the total readily exchangeable mass of PCB 52 (q) was calculated from Equation (3). The major sorbing compartments had to be identified and m, S and K_m estimated for each; these parameters for each compartment are presented in Table 7.1. The estimation of K_m is crucial if q is to be realistic for PCB 52. The various sorbing compartments considered in the application of the box model to Manchester, are described as follows.

1) Soil The soil layer (2 cm depth) of the 'open land' fraction within the box

Table 7.1. Terms used for the three sorbing compartments (veg/soil/urban dust) applied in the Simple Box model.

Manchester, UK

Box area, a = 2.1×10^8 m^2

Box height, h = 2×10^3 m

Box volume, V = 4.2×10^{11} m^3

Open land area ~20 %

area = 4.2×10^7 m^2

Compartment 1 - Soil

Soil- top 0.02 m (soil density 1g cm^{-3}) = 8.4×10^{11} g

Soil concentration PCB-52 = 0.02 ng g^{-1} (Lead and Jones, unpub.)

Sorbing mass (soil water), m_1 = 2.1×10^{17} µg

Concentration of PCB-52 in soil water, s_1 = 8.0×10^{-12} ng μg^{-1}

K_m = 7.4×10^{-11}

Compartment 2 - Vegetation

Sorbing mass, waxy cuticle, m_2 = 8.4×10^{14} µg (Reiderer, 1990)

Herbage PCB-52 = 0.03 ng g^{-1} (Duarte-Davidson and Jones, 1994)

Concentration of PCB-52 in cuticle, s_2 = 3×10^{-8} ng μg^{-1}

K_m = 1×10^{-9}

Urbanised area ~80%

area = 1.7×10^8 m^3

Compartment 3 - Urban Dust

Urban dust = 1.8 g m^{-2} (Allot *et al.*, 1994)

PCB-52 in urban dust = 18.4 ng g^{-1} (NIST 1649 SRM - Chapter 3)

Sorbing mass (moisture), m_3 = 7.6×10^{13} µg

Concentration of PCB-52 in dust moisture, s_3 = 7.7×10^{-9} ng μg^{-1}

K_m = 2.4×10^{-11}

was considered as a potential PCB source (~20% of the surface area of the box included farmland, parkland etc.). The soil pore water was taken as the compartment which, over the period of one year would be responsible for any exchange between the atmosphere and the soil. Soil water PCB 52 concentrations were derived from average urban soil concentrations measured by Lead and Jones (unpub. data) [ng g^{-1}] using the equation developed by Hartley and Graham-Bryce (1980), which fractionates the total amount of compound present in the soil into the respective soil compartments using the distribution coefficient (K_d) and Henry's Law constant (H) for that compound/congener.

$$M_{liq}/M = V_{liq}/(V_{liq} + HV_{air} + r_b K_d) \quad (10)$$

Where, M is the total amount of PCB 52 present, V is the volume, r_b is the bulk density of the soil and the subscripts refer to the liquid and air phases. A typical soil density of 1.0 g cm^{-3} was used in the equation, along with typical percentages of the soil air volume (25 %) and soil water (25 %). K_d and H were derived for congener 52 from Mackay *et al.* (1992).

2) *Urban dust* Dust covering the mineral surfaces of the urban area (considered to be ~ 80% of the total surface area within the box) was taken as one of the primary sorbing compartments. Allot *et al.* (1994) found a loading of urban dust to be 1.8 g m^{-2} for a road surface in an industrial town located in north-west England, UK; this value was applied to the Manchester box.

PCB 52 concentrations determined in the NIST Urban Reference Dust 1649 collected in Washington D.C. were taken as representative of the congener concentrations in this material. These were presented in Chapter 3, section 3.6.4 (Table 3.8). The organic fraction of urban dust [13.5%] (Fergusson and Ryan, 1984) is significantly larger than many types of soil and could at least partially account for the higher concentrations in dust than in soil. K_m was derived by selecting a component of the dust from which PCBs (in particular congener 52) would be readily exchangeable to the atmosphere. Like soil, this was considered as the dust moisture. To determine the fraction of a congener in the dust moisture, Equation (10) of Hartley and Graham-Bryce (1980) was applied. The dust was treated in exactly the same way as the soil compartment.

3) Building air For this compartment a K_m value could not be estimated as the amount and type of PCB contaminated material was unknown. Instead building air was considered only as a significant source of PCBs, in this case the amount of congener 52 released from a percentage of building space was estimated over an annual time scale. Several studies have shown that indoor air can have significantly higher PCB concentrations than ambient outdoor air (Macleod, 1981; Balfanz *et al.*, 1993; Alcock *et al.*, 1994) suggesting that the ventilation of building air may contribute to the atmospheric PCB loading in the city environment. An average UK urban 3 storey building has a volume of 5000 m^3 with a ventilation efficiency of ~ 50 % hr^{-1} (Building Research Establishment pers. comm.). The available data on indoor air concentrations is biased towards large public buildings i.e. schools and

laboratories so these data were applied only to large non-domestic buildings. Five percent of the total urban area (Manchester city centre ~8.5 x 10^6 m^2) was considered to be covered with 3 storey buildings or greater. In the course of one month these buildings will have replaced their indoor air volumes approximately 360 times. Indoor PCB concentrations measured by Alcock *et al.* (1994) were applied to the Manchester model. A monthly release concentration of congener 52 (ng m^{-3}) was loosely derived for the building component. Therefore its contribution to the overall atmospheric loading could be assessed.

4) Vegetation The 'open land' fraction of the box consisting of parklands, farmland and gardens was assumed to be covered by vegetation. Above-ground vegetation is an important sink for some SOCs from the atmosphere (Simonich and Hites, 1994). This surface vegetational compartment is also likely to act as a contributory source to the atmosphere with the seasonal elevation of temperature. The concentrations of PCB 52 associated with root systems or inside woody plant tissue were ignored since it was assumed that they would not be readily exchangeable with the atmosphere. Reiderer (1990) found that > 90 % of HCB and PCP in leaves were associated with the waxy cuticle. It was assumed that this surface layer was the dominant sorbing/desorbing component of the vegetation, although McLachlan and co-workers have shown that plant leaves can have at least 2 'compartments' ('inner' and 'outer') where PCBs may be retained (Tolls and McLachlan, 1994; Haut *et al*, 1994). The total mass of cuticle is between 180-1500 kg ha^{-1} for temperate forests and agricultural plant communities (Reiderer, 1990). A

figure of 660 kg ha^{-1} was assumed to apply to the gardens and open parklands considered here. Congener 52 concentrations in herbage samples were taken from Duarte-Davidson and Jones (1994).

A weight-averaged K_m was determined from the individual K_m values of PCB 52 for the three different compartments of urban dust, vegetation and the soil respectively using Equation (2). This was applied to Equation (3) to obtain q (ng), this value can be divided by the volume of the box to give q/V (ng m^{-3}), which is the total atmospheric equivalent concentration of the readily exchanging fraction of the congener. Equation (9) was utilised to predict the vapour phase concentration of PCB 52 in the Manchester atmosphere for each month during 1991. Mean monthly ambient temperatures (in K) were taken as T to give mean monthly air concentrations.

Firstly the terms of H_m and $\overline{K}_m m/V$ had to be derived before Equation (9) could be solved for different T. Theoretical H_m values can be derived from measured heats of vapourisation (H_v) by regressing compounds with a known H_v against corresponding H_m (Pankow, 1993). H_m values can also be obtained using field values by plotting the log partitioning ratio for PCB-52 of the form (F/TSP)/A against 1000/T and multiplying the slope of the line by 2.303R (see Chapter 2, Section 2.2.3). Figure 7.1 displays a plot of log (F/TSP)/A vs. 1000/T (24 samples throughout 1991), the slope of the line

Figure 7.1 Plot of log partition coefficients (F/TSP/A) of PCB-52 over inverse T (1000/K). Twenty four samples taken in Manchester air throughout 1991. Correlation parameters of the form log (F/TSP)/A = m/T + b, result in m = 5002 and b = -20.9. The heat of desorption (H_m) derived from the slope of the line is 95 (± 20) KJ mol^{-1}.

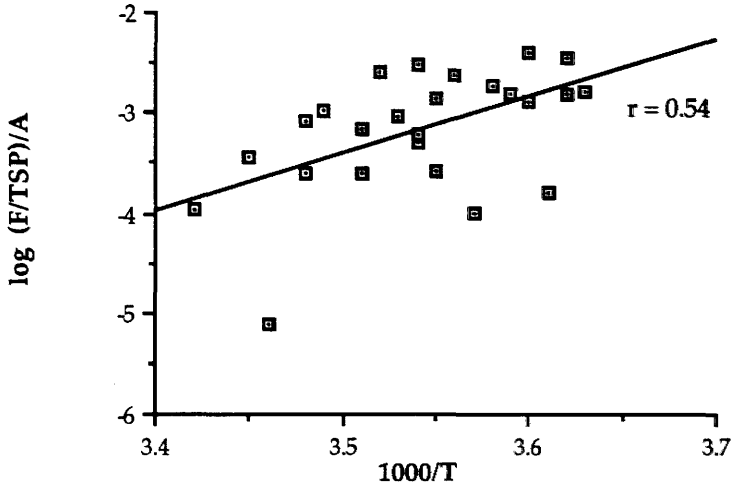
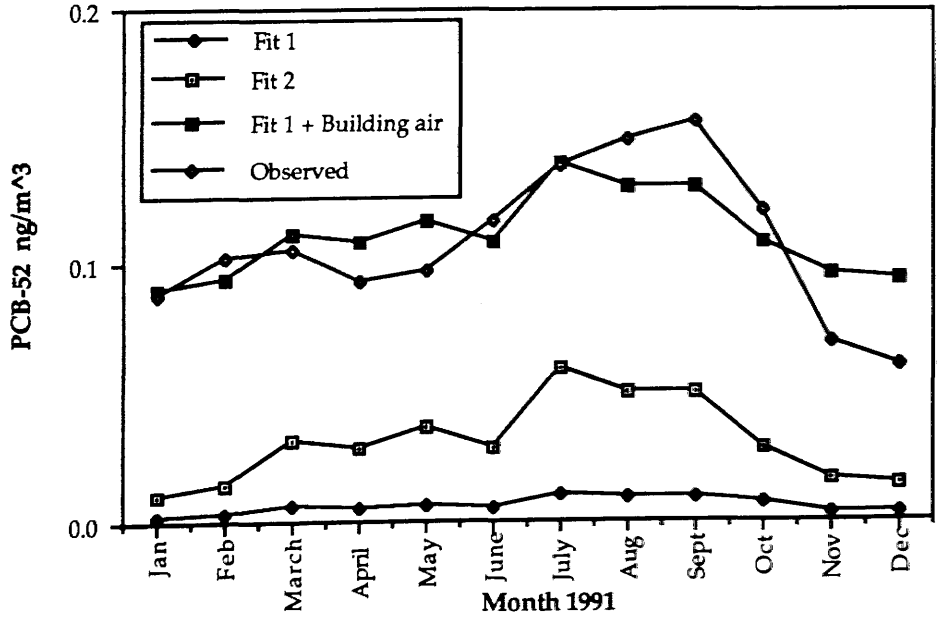


Figure 7.2 Simple box model predictions of PCB 52 vapour phase concentrations in Manchester air. Fit 1 uses H_m and $\bar{K}_m m/V$ taken from Pankow (1993), 67.0 KJ mol^{-1} and 10^{-11} respectively. Fit 2 uses H_m derived from this study as 95 KJ mol^{-1} and $\bar{K}_m m/V$ as ~10^{-19}. The building air component of 0.08 ng m^{-3} was simply added onto each monthly concentration predicted in Fit 1 to give the "Fit 1 + building air" prediction. This gives an indication of how potentially important the building compartment is, as a source to the urban atmosphere.



being 5002 and the intercept (b) -20.9. The derived value of H_m for congener 52 was 95 (± 20) KJ mol^{-1} while laboratory studies predict Hv (~ H_m) as 80.8 KJ mol^{-1} (Falconer and Bidleman, 1994). Pankow (1993) derived a H_m of 67.0 KJ mol^{-1} using the data of Hoff *et al.* (1992a) while Panshin and Hites (1994) obtained a Hv of 77 KJ mol^{-1}. The scatter observed in Figure 7.1 resulted in a weak correlation (r = 0.54). This correlation for PCB 52 was weaker than that obtained by Hoff *et al.* (1992b), hence H_m was derived with a large standard error (± 20 KJ mol^{-1}).

$\bar{K}_mm/V$ was then determined by rearranging Equation (9) to:-

$$\log \left[\frac{q/V}{A} - 1 \right] = \log \bar{K}_mm/V + H_m/2.303RT \qquad (11)$$

By applying H_m to Equation (11) $\bar{K}_mm/V$ could be calculated once q/V had been derived from Equation (3). The terms applied in the above equations for PCB 52 are displayed in Table 7.2. As the derived value of H_m was significantly higher than the value used by Pankow (1993) his estimates of $\bar{K}_mm/V$ and H_m for congener 52 were also included for comparative purposes.

Table 7.2 Terms applied to Equations (3) and (9) for the application of the box model to Manchester.

$A = 0.113$ ng m^{-3} (mean for 1991 only)	Fit 1*
$F = 0.003$ ng m^{-3} (mean)	$\overline{K}mm/V = 10^{-11}$
TSP = 40 ng m^{-3} (mean)	H_m = 67.0 KJ mol^{-1}
$K_pTSP = 2.6 \times 10^{-2}$	
Average weighted $K_m = 1 \times 10^{-9}$ m^3 μg^{-1}	Fit 2
$q = 4.8 \times 10^{10}$ ng	$\overline{K}mm/V = \sim 10^{-19}$
$q/V = 0.116$ ng m^{-3}	H_m = 95 KJ mol^{-1}

*Values for PCB 52 from Pankow (1993)

By applying the box model in this scenario it is important to clarify that the size of the box is considerably smaller than that used by Pankow (1993). For the Manchester box any volatilised PCB 52 is likely to leave the box (i.e. advective movement) particularly over a time period of 1 year. Therefore the sorbed fraction within the box had to be sufficiently large to maintain a constant q/V throughout this period. For PCB 52 it is believed that there was a sufficient sorbed quantity in the proposed compartments to maintain this, and fulfil the key assumption in Pankow's model that the mass q of exchanging compound remains constant over this time period. The parameters used to estimate the contribution of PCB-52 from buildings are presented in Table 7.3. Included in this table are the mean monthly

Table 7.3. Parameters used in the estimation of PCB-52 release from building air. Average monthly temperatures (K) and TSP ($\mu g\ m^{-3}$) used in the Simple Box Model for Manchester (1991).

Building source

Area covered by 3 storey buildings (5 % of urban area) = $8.5 \times 10^6\ m^2$

Average volume = $5000\ m^3$ •

Average height = 25 m

Total building volume = $2.1 \times 10^8\ m^3$

Indoor PCB-52 air concentration = $0.465\ ng\ m^{-3}$ ••

Building ventilation efficiency = 50 % hr^{-1} •

Total mass of PCB-52 released from buildings over one month = 3.5×10^{10} ng

Monthly contribution of building air to 'box' concentration =

mass released over 1 month/volume of box = ~ $0.08\ ng\ m^{-3}$

Monthly mean temperature and TSP concentrations

Month	K	TSP	Month	K	TSP
January	276	60	July	291	41
February	278	49	August	290	35
March	285	20	Sept.	290	47
April	284	39	Oct.	284	42
May	286	42	Nov.	279	32
June	285	33	Dec.	278	38

• Building Research Establishment (pers. comm.)

•• Alcock *et al.* (1994)

temperatures applied to the box model and the mean TSP loadings.

The model fits are presented in Figure 7.2 along with the actual monthly concentrations of PCB 52 throughout 1991. The three model fits are; one (Fit 1) using the values of H_m and $\bar{K}_m m/V$ derived by Pankow (1993) two (Fit 2) using the values of H_m and $\overline{K}_m m/V$ derived from this study (Table 7.2) and three (Fit 1 + building air) where the building air component is added to each monthly Fit 1 concentration. From Table 7.3 the contribution by building air results in an additional 0.08 ng m^{-3} per month of PCB 52 to the Manchester box. All the fits illustrate the seasonal cycling of congener 52 occurring within the atmosphere of the Manchester box. Fits 1 and 2 show the significance of the vegetation/soil/dust compartments on the atmospheric vapour phase concentrations of PCB 52. However the derivation of an accurate H_m is essential for the application of the model.

Pankow's derived H_m of 67.0 KJ mol^{-1} (Fit 1) is possibly more realistic as it closely correlates with heats of vapourisation derived from laboratory experiments. For this reason the building air component was added onto the Fit 1 monthly concentrations. The resulting fit (Fit 1 + building air), although resembling the observed concentrations, really depicts the significance of building air in urban areas as a source of PCB 52. The additional concentration to the box of 0.08 ng m^{-3} per month must only be taken as approximate. The modelled concentrations of Fit 1 and Fit 2 more closely resemble rural air discussed in Chapter 4. After the building source

the most significant compartment (greatest contributor of congener 52 to the atmosphere) was found to be the vegetation, followed by soil. These two compartments can explain the atmospheric vapour phase concentrations found at the rural location in the north west of England. As the two model fits of Fit 1 and Fit 2 (Fig. 7.2) are lower than the measured concentrations, then the city air may be subject to a source(s) of PCB such as building air or other point sources not considered here. The building air component, for example, is probably underestimated, given the number of public and domestic dwellings within the Greater Manchester area. Point sources such as emissions from landfills and incinerators (Murphy *et al.*, 1985) may also make contributions to the urban atmospheric loading. If air moves through the box by advection then outgoing air will supplement the atmospheric PCB concentration of surrounding areas, resulting in an urban area acting as a source on a regional scale.

7.4 Summary

The annual cycle which has been observed in the atmospheric concentrations of some SOCs (that demonstrate summer maxima), provides strong evidence that temperature-dependent partitioning is playing an important role in causing the observed fluctuations. The equilibrium box model applied here, provides a rough way to parameterise changes of this type, particularly for the lighter PCB congeners which are predominantly found in the vapour phase. The application of the Box Model has proved

successful in predicting the annual cycling of a tetrachlorinated congener in an urban atmosphere, invoking temperature as the controlling factor. However, the simplicity of the model has required several assumptions, primarily that the amount of readily exchangeable PCB 52 is constant throughout a twelve month period, or the amount removed by advection is adequately replaced by a substantial reservoir, counteracting this loss. Also, can the ambient air temperature (T) taken at some central, single point on the surface (roof top in Manchester) be applicable to the whole box? It is possible that microenvironments such as street canyons or wood canopies influence the atmosphere around them, and hence alter the predicted partitioning of SOCs for the whole box. Furthermore, it is assumed here that the soil and dust solution concentrations, are in equilibrium with their respective solid phases.

Therefore the use of the Box Model in this senario is one of illustration, providing a useful tool in interpreting the collected field data. The agreement between predicted values and measured values suggest that the major sorbing compartments have been recognised in the Manchester box. The contribution by each compartment to the box atmosphere has been predicted. The following order shows the importance of the considered compartments as sources of PCB 52 to the atmosphere - vegetation > urban dust > soil. Vegetation therefore plays a major role in the cycling of PCBs even in this urban box, where only 20 % of the land is considered to be 'open' and free of hard surfaces. On a national basis vegetation must,

therefore, play a large role in the partitioning and cycling of SOCs, probably acting as a source to the atmosphere during the warmer seasons and a sink during the winter. The two compartments of soil and urban dust, contain a large reservoir of PCB 52. The majority of this may not be readily exchangeable with the atmosphere over a short time period (~ 1 year), probably being strongly bound to the organic matrix within these compartments.

For the urban environment the model cannot quantify the release from the numerous point sources, perhaps the most important being the ventilation of indoor air. Although an estimate is made for the release of PCB 52 from large public buildings (represented in Figure 7.2 as Fit 1 + building air) this can only be taken as approximate. Taking the building component as a whole this is probably underestimated given the number of public and domestic dwellings within the Greater Manchester area. This indicates that numerous point sources, in the confines of the urban environment, combined with a significant building source of PCBs (indoor air concentrations are frequently amongst the the highest measured anywhere (Alcock *et al.*, 1994; Kreiger and Hites, 1994)) are likely to explain the urban atmospheric loading. Hence, on a regional scale, cities may be acting as sources to surrounding areas following outgassing of PCBs from buildings, former industrial uses, landfills and incinerators.

Chapter 8

Atmospheric Deposition

8.1 Introduction

SOCs released into the atmosphere from various processes such as industrial emissions, energy production/consumption, waste incineration and the re-volatilisation from secondary sources such as vegetation, soil and sediments will eventually be deposited to the terrestrial or marine environment. Deposition from the atmosphere may be either many kilometers away from the original source or alternatively, localised around a particular source such as an incinerator or motorway. In order to assess regional air and water quality and implement clean air legislation an understanding not only of the processes that scavenge contaminants from the atmosphere is required but also a need to quantify the amount of deposition to any one area. Atmospheric transport and deposition are important sources of many SOCs and trace elements to terrestrial and aquatic ecosystems. SOCs such as PCBs and PAHs, recognised as ubiquitous environmental contaminants, are deposited from the atmosphere by both wet and dry deposition, these processes having been discussed in Chapter 2, section 2.5.1. Aerial deposition has been found to be the primary source of these contaminants to remote areas such as the Great Lakes (Eisenreich *et al.*, 1981; Swackhamer *et al.*, 1988) and the Polar regions (Gregor and Gummer, 1989; Barrie *et al.*, 1992). It is therefore necessary to monitor

depositional fluxes in order to relate these values to known sources, and to assess the movement between the atmosphere and the earth's surface.

In this study bulk (wet + dry) deposition was collected each month at the five TOMPS sites. The deposition was analysed for PCBs and PAHs, sampling and analytical details being presented in Chapter 3. As the area of the collecting surface (Teflon coated frisbee) was known, along with the duration of exposure, depositional fluxes (mass deposited per unit area per day) could be calculated for these contaminants. Deriving deposition fluxes allows the rate of deposition to be assessed for a particular compound, allowing a mass balance to be established to determine whether releases to the atmosphere, and hence air concentrations, are related to the depositional flux.

8.2 Deposition sampling artefacts

As depicted in Chapter 2, Section 2.6.9, deposition sampling has major inherent artefacts. Firstly, are the collecting surfaces a good surrogate for natural surfaces?, secondly is sample integrity maintained throughout the exposure time?. The Teflon-coated metal frisbee (collecting surface depicted in Figure 3.1) has been shown to be an efficient collector of atmospheric aerosol (Hall and Upton, 1988), however there has been no research on its collecting abilities for SOCs in the vapour phase. Gardner (1993) has shown that significant removal of atmospheric PAHs is through vapour phase

deposition. In several studies where deposition of organics has been monitored the collecting surface has usually been larger (~1m^2) than the one used in this study (Pankow *et al.*, 1984; Ligocki *et al.*, 1985a, b).

The materials used for the collecting surfaces have also been brought into question.The collecting vessel in this study was a 5 L glass jar connected to the inverted frisbee by a 1.75 m Teflon tube. Teflon, widely recognised for its 'non-stick' properties (low sorbent capacity), has been found to sorb organochlorines to some extent and give poor reproducibility on the analysis of repeated solvent rinses (Murphy and Sweet, 1994).

Sample integrity is brought into question when the sampling equipment is left in the field for the period of a month. Many hydrophobic compounds such as the SOCs, dissolved in the collected precipitation, will migrate to the particulate or be adsorbed onto the vessel sides. Furthermore, losses from the collected sample by volatilisation cannot be ruled out, particularly during the warmer summer months. Several studies have experimented with depositional equipment which incorporates a solid adsorbent upstream from the final collecting vessel (Strachan and Huneault, 1984; Horstmann and MacLachlan, 1994). This has the effect of removing the dissolved fraction from the precipitation, effectively 'locking up' the contaminants and preventing further movement.

With these artefacts in mind, deposition samples collected using the

equipment in this study may not be accurately representing the true deposition of both PAHs and PCBs. However, the generated flux data presented in this Chapter does give an approximation, and is comparable to other studies on an international basis. Due to the above mentioned artefacts and the length of time taken to obtain a sample, no attempt was made to separate the dissolved phase from the particulate phase for any of the compounds. Instead, the generated flux data was used to compare the various sites - both urban and rural - and relate these fluxes to the measured air concentrations. Furthermore, with basic depositional information simple mass balances could be derived for the UK environment.

8.3 PAH deposition

Table 8.1 presents depositional flux data for the urban/rural sites of this study and for two other sites in the north west of England. International data on PAH fluxes is sparse and what is available is mainly centred on the Great Lakes region of North America. The fluxes monitored at these more remote sites have also been included for comparison with the UK data. London has the highest mean flux of 10.3 μg ΣPAH m^{-2} d^{-1}, displaying the greatest flux range of 0.32 - 46.0 μg m^{-2} d^{-1}. London also has the highest mean ΣPAH air concentration (discussed in Chapter 5) being ~1.4 times greater than that measured in Manchester, the mean deposition flux was also greater by a factor of ~1.4. Similarly, London's air concentration was greater than Cardiff's by a factor of 1.8, the deposition flux, again being

Table 8.1 Deposition flux rates (ΣPAH) (μg/m^2/day).

UK Urban area	Winter	Summer	Mean	Median	Range
London (1)	19	16	10	7.7	0.33 - 46
Manchester (1)	5.6	2.1	5.8	3.3	1.8 - 27
Cardiff (1)	4.1	2.9	5.1	3.9	1.0 - 18
Stevenage (1)	6.6	0.71	4.3	2.9	0.32 - 20
Castleshaw (2) (Nr. Manchester)	3.9	1.1	1.3	0.80	0.21 - 6.0
Rural area					
Hazelrigg (1)	1.7	2.5	1.9	1.7	0.95 - 2.5
Esthwaite (2)	3.9	1.0	2.6	2.3	0.20 - 8.5
USA Rural/remote area					
Chesapeake Bay (3) (Maryland)			0.54		
Siskwit Bay (4) (Lake Superior)			0.51		
Commencement Bay (5) (Puget Sound - Washington)			4.7		

* Sampling ceased April 1992
(1) This study
(2) Castleshaw, near Manchester; Esthwaite water, L. District (Gardner, 1993)
(3)Sampling over a two year period 1990 - 1991 (Leister and Baker, 1994)
(4) Sampling over a two year period 1983-1984 (McVeety and Hites, 1988)
(5) PHE and B[a]P only, 1991 [Cited in Leister and Baker (1994)]

greater by a factor of ~ 1.8 (2.0). Correlations between depositional fluxes and air concentrations were not derived, since deposition fluxes were determined from samples collected over monthly periods (to ensure detectable concentrations). The air samples, however, were collected over a much shorter time scale (1 week periods). Therefore any short term variations in deposition fluxes (possibly related to the fluctuations in air concentations) would be masked by the prolonged collection period.

The mean fluxes measured at the two UK rural sites (Hazelrigg and Esthwaite) are significantly lower than the central urban locations (by a factor of ~3), however they are comparable to Castleshaw, a semi-urban location on the NE outskirts of Manchester. This would indicate that deposition of PAHs in these rural areas is similar to suburban areas like Castleshaw, implying that greater distances away from conurbations are needed before PAH deposition is significantly reduced. Certainly studies on air mass transport has shown that urban areas act as a source of PAHs on a regional scale (Broman *et al.*, 1991). However, Windsor and Hites (1979) noted that the PAH deposition decreases dramatically with distance from urban centres. For example, they found that within a 100 km of Boston, USA, the total PAH abundance in freshwater sediments (directly related to atmospheric deposition) decreased by three orders of magnitude. These two UK rural sites are within a 100 km from urban areas, and do not show a decrease by three orders of magnitude. At the Esthwaite site local effects may also make a significant impact. For example, Gardner (1993) ascribed

increased winter depositional fluxes to the influence of local coal and wood burning for domestic heating. Given the size of the UK and the population density, many rural areas (particularly downwind of the major conurbations) will reflect semi-urban PAH deposition rates similar to those monitored at Castleshaw.

In Table 8.1 the mean winter and summer ΣPAH fluxes are presented for the UK sites. Clear seasonal trends in the monthly depositional fluxes could not be distinguished at any of the TOMPS sites. Figure 8.1 displays the monthly ΣPAH fluxes for the two urban sites of London and Manchester; no discernible seasonal patterns were observed. Furthermore, unlike the air concentrations, individual compounds such as B[a]P showed no seasonal pattern as well. However, by taking the mean ΣPAH flux of the winter and summer months respectively, the mean winter flux is greater than the summer flux at both urban and rural locations, however for the rural site at Hazelrigg there was found to be no significant difference between winter and summer ($P > 0.05$). At this particular site PHE and ACE dominate the flux profile in the summer months, corresponding to their elevated atmospheric concentrations at this time of year. Gardner (1993) monitored wet and dry deposition separately at the Esthwaite and Castleshaw sites and found that dry deposition dominated during the summer months, with wet deposition dominating in the winter.

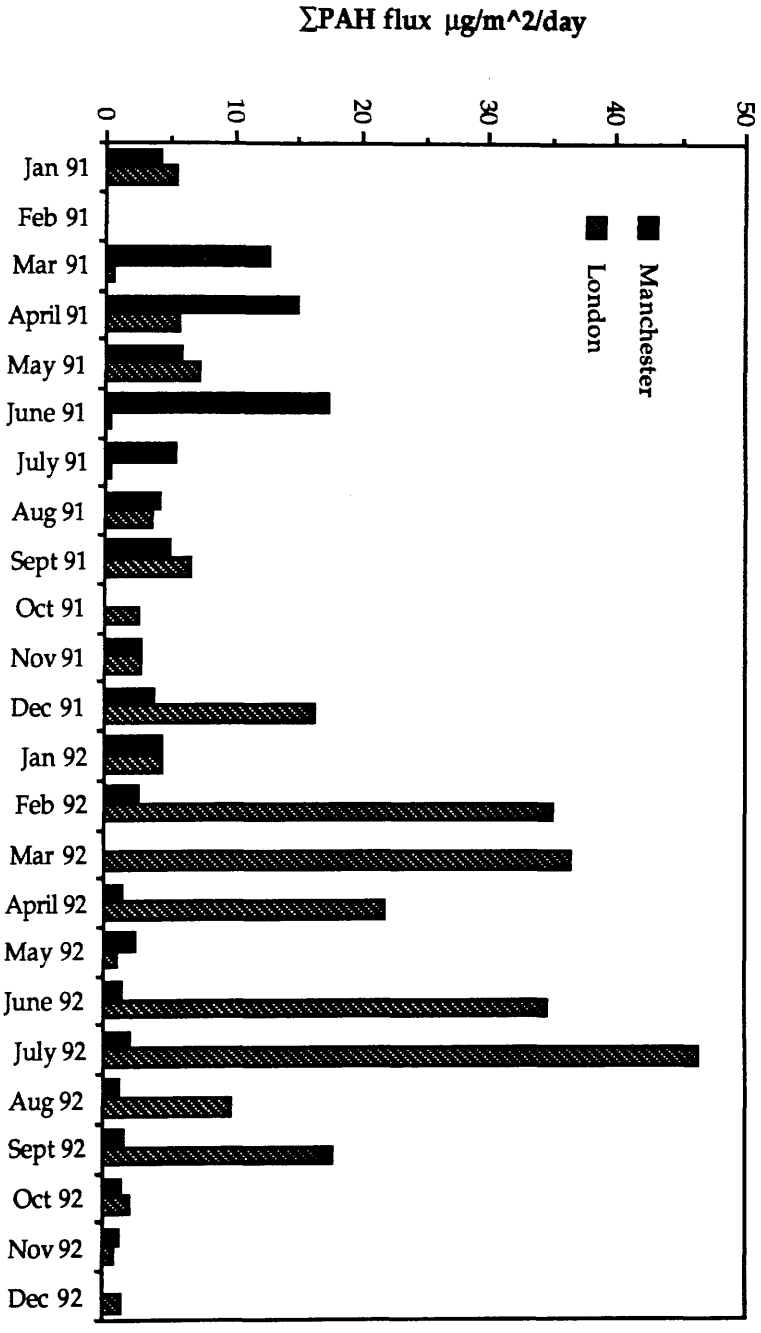


Figure 8.1 ΣPAH monthly deposition fluxes in Manchester and London throughout 1991/92.

Table 8.2 presents the percentage contribution each PAH makes to the mean ΣPAH deposition at both urban and rural locations. Similar to the air concentrations PHE is the dominant compound in the flux profile at each of the urban sites FLUO, MPHE and PYR also make a significant contribution (> 10 %) to the total deposition. Again, this follows a similar pattern to the atmospheric profile. To support this finding for the UK urban sites the deposition profile is also presented for the the city of Portland, Oregon; again PHE, FLUO and PYR are the dominant compounds in the flux profile. In this particular study wet and dry deposition were monitored separately. The two UK rural sites show a different profile from the urban locations. At Hazelrigg the lighter compounds of ACE and FLU make up a significant percentage of the mean deposition (> 12 % each), from the air data presented in Chapter 5 FLU comprises between 6 - 20% of the ΣPAH air concentration. At Esthwaite the reverse appears to be the case; the mean depositional profile (deposition samples taken over a year, July 1990 - July 1991) is dominated by the higher molecular weight compounds of B[a]P, D[ac]A, B[k]F and B[b]F. Gardner (1993) explains this phenomenon on the local effects of coal and wood combustion. These higher molecular compounds are predominantly associated with the particulate phase (Halsall *et al.*, 1994) and are therefore likely to undergo rapid deposition close to the source.

An interesting discrepancy between the heavier multiringed PAH and the lighter more volatile compounds, are the large differences observed in their respective air concentations and yet only small differences between their

Table 8.2 Percentage contribution to the mean ΣPAH deposition at a selection of urban and rural sites.

PAH	London(1)	Manchester (1)	Cardiff (1)	Portland Oregon (2)	Rural Hazelrigg (1)	Rural Esthwaite (3)
ACE	1	4	7	2	19	1
FLU	2	4	8	5	12	NR
PHEN	36	11	21	31	31	7
ANTH	4	2	1	2	>1	2
FLUO/MPHE	14	23	17	29	13	9
PYR	11	12	10	15	8	7
BENZANTH	5	5	6	2	2	14
CHRY	11	6	8	4	3	NR
B[b]F	4	7	5	2	3	20
D[ac]A/B[k]F	5	6	5	2	2	17
B[a]P	1	8	12	1	3	22
B[ghi]P	4	7	6	2	4	NR
COR	NR	2	2	1	1	NR

NR = not reported
(1) This study
(2) Wet only deposition collected over three months in 1984 (Ligocki et al., 1985)
(3) Wet and dry deposition collected separately over 1990 and 1991 (Gardner, 1993)

depositional fluxes. This can be illustrated by looking at the behaviour of PHE and B[a]P respectively at two different locations. In Table 8.3 the air concentrations and the fluxes of these two compounds are presented for two very different sites: 1) the urban site in Manchester (this study); 2) the rural site of Chesapeake Bay on the eastern seaboard of the USA (Leister and Baker, 1994). Although the sites are different, the sampling regimes in both studies covered the period of a year or greater.

Table 8.3 Mean PHE and B[a]P air concentrations and depositional fluxes measured at the urban site of Manchester, UK, and the rural site of Chesapeake Bay, USA.

	Air conc. (ng m^{-3})	Flux (ng m^{-2} d^{-1}) *
Chesapeake Bay		
PHE	1.4	57
B[a]P	0.013	16
Manchester		
PHE	45	1100
B[a]P	1.5	520

* flux reported in ng rather than μg, for comparison with air concs.

The mean air concentrations and fluxes are significantly lower, for both compounds, at the rural site in Chesapeake bay. The difference in air concentrations between PHE and B[a]P is a factor of ~100 for Chesapeake Bay and ~30 for Manchester. The deposition fluxes, however, do not show this prounounced difference. In fact, PHE deposition is only greater than B[a]P by a factor of ~3.5 at Chesapeake Bay and by only a factor of ~2 in Manchester. At both sites therefore, B[a]P deposition is more marked than for PHE

relative to their respective atmospheric concentrations. It is therefore possible that significant amounts of PHE are broken down in the atmosphere before deposition can occur. Unlike B[a]P which exists mainly in the particulate phase and hence will be deposited faster, PHE is present predominantly in the vapour phase and therefore more available for photolytic and chemical degradation (Kwok *et al.*, 1994). Alternatively, B[a]P may simply be collected more efficiently, due to its association with atmospheric particulate. However as the sampling equipment was markedly different in design between this study and the Chesapeake Bay study, then collecting efficiencies would also differ and the pattern would not be the same for the two studies. This discrepancy between air concentations and deposition fluxes is observed both in the urban and rural environment. Again at the UK rural site at Hazelrigg, the PHE air concentrations showed a summer maxima (Chapter 5), however the mean deposition flux of PHE was not elevated relative to the mean air concentration. The difference between B[a]P and PHE mean air concentrations was by a factor of ~350, whereas the deposition fluxes varied by only a factor of ~11.

8.4 A mass balance of PAHs in the UK environment

By determining fluxes in both UK urban and rural areas, the amount deposited to terrestrial surfaces annually can be estimated. Importantly, the mass deposited can be matched with emissions from known sources, and hence a potential mass balance may be determined. In recent years efforts

have been concentrated on compiling a UK source inventory for a variety of SOCs including PCBs and PAHs (Harrad *et al.*, 1993; Wild and Jones, 1995, APARG, 1995). A source inventory lists the major sources of a particular compound class, such as the PAHs, and quantifies the mass released from each considered source (i.e. waste incinerators) by extrapolation of several measurements (i.e. stack emissions). Wild and Jones (1995) quantified the primary sources of PAHs to the UK atmosphere, their summary of annual PAH emissions (tonnes) is presented in Table 8.4. Wild and Jones estimated that the annual release of ΣPAH is ~ 700 tonnes per year, further work on the UK source inventory reveals an estimated ΣPAH emission of between 560 - 1700 tonnes per year (APARG, 1995). If unregulated fires and volatilisation from secondary sources (i.e. soils and vegetation) are added to this, then it is possible that these figures could well underestimate the total ΣPAH released into the UK environment each year.

By taking the PAH air concentrations presented in Chapter 5 the total atmospheric loading can be estimated for the individual PAHs. This was done by taking an overall mean air concentration for each PAH from the urban and rural data. By calculating the volume of air over the UK this allowed a total atmospheric loading to be estimated. With the surface area of the UK being 2.5×10^{11} m^2 (Geodata, 1983) and taking the boundary layer mixing height of 2000 m (Harner *et al.*, 1995), then this gives a UK air mass volume of 5×10^{14} m^3. Table 8.5 presents the mean air concentrations for each PAH and their respective calculated atmospheric burdens. Hence the

Table 8.4 Summary of annual PAH emissions to the UK atmosphere (tonnes/year). (Wild and Jones, 1995).

PAH	Vehicles	Coal-fired power station	Coke-manufacture/ smokeless fuel production	Domestic coal com-bustion	Oil-fire power stations industrial oil users	Domestic wood com-bustion*	MSW/etc. incineration	Industrial processing	Total
ACE/FLU	13	0.13	0.32	0.70	0.32	-	0.0043	1.4	15
PHE	27	0.95	0.24	40	1.5	-	0.00014	7.7	78
ANTH	8.7	-	-	14	-	-	0.00014	-	23
FLUO	7.3	0.56	0.14	180	0.24	0.92	0.0082	2.5	190
PYR	7.8	1.2	0.30	160	0.31	1.1	0.022	4.8	180
BENZANTH/ CHRY	3.4	0.30	0.078	110	0.28	1.1	0.010	1.8	120
B[b]F	1.4	0.0054	0.0014	43	-	0.32	0.0045	0.017	45
B[a]P	2.1	0.0058	0.0015	28	0.015	0.29	0.00030	0.066	31
B[ghi]P	1.7	-	-	22	-	0.061	0.0060	-	24
ΣPAH	72	3.2	1.1	600	2.7	3.8	0.056	18	700

* Particulate phase only

defined UK air mass was estimated to have a ΣPAH burden of 53 tonnes at any one time, with the low molecular weight compounds of PHE, FLUO and PYR dominating.

From the calculated depositional fluxes it is possible to determine the annual flux in tonnes to both urban and rural surfaces. Table 8.6 presents the mean urban and rural flux for each PAH. Ten percent (2.5×10^{10} m^2) of the UK surface is considered to be urbanised, while 90% (2.25×10^{11} m^2) is considered to be rural. Using the respective urban and rural PAH fluxes the loading of each PAH to the two surfaces can be calculated. Approximately 70 tonnes of PAHs are deposited to urban surfaces while 150 tonnes are deposited to rural surfaces; therefore for the total UK surface some 220 tonnes of ΣPAH are estimated to be annually deposited. This leaves ~700 tonnes of the estimated emission of PAH unaccounted for.

Table 8.5 PAH air concentrations and estimated burden in the UK air mass.

PAH	Air concentration (ng/m^3)	UK atmospheric burden (tonnes)
ACE	2.3	1.2
FLU	19	9.5
PHE	63	32
ANTH	1.8	0.90
FLUO/MPHE	7.0	3.5
PYR	5.4	2.7
BENZANTH	0.85	0.43
CHRY	1.4	0.70
D[ac]A/B[k]F	0.98	0.49
B[b]F	0.41	0.21
B[a]P	0.67	0.34
B[ghi]P	2.4	1.2
COR	0.43	0.21
ΣPAH	110	53

Table 8.6 Annual UK PAH deposition fluxes

PAH	Urban Flux µg/m2/day	Annual Urban Flux (tonnes)	Rural flux µg/m2/day	Annual Rural Flux (tonnes)	Total Annual Flux (tonnes)
ACE	0.19	1.7	0.35	29	31
FLU	0.24	2.2	0.22	18	20
PHE	1.7	16	0.57	47	62
ANTH	0.41	3.7	0.0030	0.25	4.0
FLUO/MPHE	1.7	15	0.24	20	35
PYR	0.95	8.7	0.15	13	21
BENZANTH	0.60	5.5	0.029	2.4	7.9
CHRY	0.49	4.5	0.047	3.9	8.3
B[b]F	0.34	3.1	0.059	4.8	7.9
D[ac]A/B[k]F	0.29	2.6	0.039	3.2	5.8
B[a]P	0.25	2.3	0.049	4.0	6.3
B[ghi]P	0.37	3.3	0.070	5.7	9.1
COR	0.14	1.3	0.020	1.6	2.9
ΣPAH	7.6	70	1.9	150	220

Such a large imbalance between the amount released annually into the atmosphere and the amount deposited, requires further explanation. It is considered that there are three main processes that can explain this imbalance: (1) There are significant PAH losses in the atmosphere due to breakdown/reactions; (2) PAH are transported away from the UK with prevailing winds; and (3) there is greater PAH deposition in the vicinity of point sources.

Several studies have highlighted the susceptibility of PAH to chemical and physical transformations in the atmosphere (Nikolaou *et al.*, 1984; Baek *et al.*, 1991). As mentioned earlier in Chapter 2, section 2.2.2, the lighter, predominantly vapour phase PAHs were found to react with OH radicals, O_3 and NO_x. Kwok *et al.* (1994) under simulated laboratory conditions predicted the lifetime of atmospheric PHE to be in the order of ~1 day. Degradation of particulate-bound PAHs by O_3 and NO_x has also been observed under laboratory conditions (Lindskog *et al.*, 1985). However, photochemical transformation has generally been considered to be the most important mode of atmospheric decomposition of PAH for both particulate and vapour phases (Masclet *et al.*, 1986; Baek *et al.*, 1991). The degradation rates by photolysis of different PAH show a wide variation, but the extent of photochemical decay for particulate-bound PAH is strongly influenced by the nature of the substrate on which they are adsorbed (Behymer and Hites, 1998). Even if PAH have greater half-lives adsorbed to particulate matter such as soot and fly ash then they are more susceptible to settlement and/or

scavenging from the atmosphere than the vapour phase component.

Apart from the loss by physical-chemical processes PAHs may also be transported away from the UK by air mass movement. Masclet *et al.* (1988) investigated the long range transport of PAHs from NW Europe to the Island of Corsica in the Mediterranean. They concluded that many of the industrialised countries, such as the UK, France and Germany were an important source of PAHs. Tysklind *et al.* (1993) found evidence that PCDD/Fs, SO_2, NO_2 and soot are transported eastwards from the UK to Scandinavia. It is therefore likely that PAHs will be transported eastwards to Scandinavia and mainland Europe where they will be eventually deposited. Secondary sources such as re-volatilisation from soils and vegetation, although not quantified, could increase the atmospheric loading significantly. Evidence for this has been noted at the Hazelrigg rural site (Chapter 5), where elevated concentrations of the lighter, more volatile PAH were found during the summer months.

Another important factor leading to an imbalance between emissions and deposition is that many of the PAH, particularly the particulate-bound PAH, could be deposited within the vicinity of a source. The overall wet/dry deposition figure presented in Table 8.6 represents a national deposition away from point sources. Localised deposition around point sources has been examined by various workers. For example Hewitt and Rasheed (1990) found that up to 30 % of selected PAHs are deposited within 50 m either side

of a motorway. This particular work was described in Chapter 5, were the deposition flux of PHE at a distance of > 50 m from the motorway was equivalent to a site well removed from any roads. If PAH deposition is therefore enhanced near point sources then the overall PAH deposition loading to the total UK surface is therefore likely to be underestimated. Furthermore, the rural flux data used to estimate the annual deposition loading to ~90 % of the surface area of the UK, is based on just two sites located in NW England, the extrapolation of the deposition at these two sites to the whole of the UK may lead to errors. It must be noted, however, that these estimates of deposition and releases (emissions) are only estimates and that the source inventory is incomplete and subject to a high degree of uncertainty (APARG, 1995).

In order to assess these different factors that lead to an imbalance between amount emitted and amount deposited, then it is necessary to examine the release and deposition of the individual compounds. From Table 8.4 the compounds that dominate the emission profile are FLUO, PYR and CHRY, yet for the deposition (Table 8.6) the lighter compounds of PHE and ACE dominate. Indeed for PHE, ~80% that is released from the primary sources can be accounted for by the deposition. For the heavier compounds CHRY - B[ghi]P only between 10 and 20 % of the amount released can be accounted for. Therefore, this may indicate that deposition of these heavier compounds is greater when near the source. Certainly the urban flux of these compounds is an order of magnitude higher than the corresponding

rural flux (Table 8.6), yet the air concentrations are, on average, only a factor of 2 higher. The annual release of the lighter PAH such as PHE and ACE is probably underestimated in Table 8.4. Secondary sources such as soil and vegetation are not included and yet may account for the largest releases to the UK environment (by volatilisation). If PHE dominates the atmospheric and depositional profile, as well as being degraded rapidly in the atmosphere, then it is likely that secondary sources will play an important role in the release of this compound.

8.5 PCB deposition

The range of ΣPCB fluxes encountered at the sites of this study and internationally are presented in Table 8.7. For the UK urban sites the range of encountered fluxes cover two orders of magnitude during the two year sampling programme. Unlike the air concentrations presented in Chapter 4 where London possesses the highest mean concentration, Cardiff has the highest mean deposition flux of 2.2 $\mu g\ m^{-2}\ day^{-1}$. Although this figure is significantly higher than the mean fluxes of the other urban sites ($P < 0.01$), on an international basis the city of Chicago has a much greater flux, a value of 4.9 $\mu g\ m^{-2}\ day^{-1}$ (dry only) being reported - higher than all the UK sites. Furthermore, the median depositional fluxes for Cardiff and Manchester are 1.5 and 0.29 respectively; these fluxes are lower than the means which indicate that abnormally high values are elevating the means. At the Cardiff site between February and April 1992 the measured fluxes were $> 4\ \mu g\ m^{-2}$

Table 8.7 Deposition flux rates (ΣPCB) (ng/m^2/day).

	Winter	Summer	Mean	Median	Range
UK					
Urban					
London (1)	0.80	0.39	0.38	0.25	0.025 -3.9
Manchester (1)	0.55	0.25	0.41	0.29	0.078 - 1.4
Cardiff (1)	1.4	2.3	2.2	1.5	0.053 - 6.8
Stevenage (1)	0.15	0.45	0.33	0.18	0.035 - 2.1
Rural					
Hazelrigg (1)	0.29	0.17	0.18	0.16	0.049 - 0.33
USA					
Urban					
Chicago (2)	-	4.3	4.9		2.8 - 9.7
Bloomington, IN (3)	-	-	0.18		0.15 - 0.45
Rural/remote					
Chesapeake Bay (4)	-	-	0.009		-
L. Michigan (5)	-	-	0.021		-
Bermuda, Atlantic (6)	-	-	0.036		-
Enewetak Atoll, Pacific (7)	-	-	-		0.0005 - 0.008

1 this study ΣPCB = 8 congeners (ΣPCBa - see Chapter 4)
2 Dry deposition only ΣPCB = 109 congeners (Holsen et al., 1991).
3 Calculated flux ΣPCB = 60 congeners. (Panshin and Hites, 1994).
4 ΣPCB = 74 congeners, dry flux was calculated (Leister and Joel, 1995).
5 ΣPCB = 17 congeners, dry particulate flux was calculated (Swackhamer et al., 1988)
6 ΣPCB = 119 congeners, flux calculated from air concentrations and predicted atmospheric residence times (Panshin and Hites, 1994).
7 ΣPCB reported as Aroclor mixture (Atlas and Giam, 1981).

day^{-1}. Similarly at Manchester fluxes exceeded 1 $\mu g\ m^{-2}\ day^{-1}$ during December 1991, April 1992 and May 1992.

At Hazelrigg (rural site) the mean annual flux was significantly lower than the urban fluxes (by a factor of ~ 4), and covered a narrower range, indicating the lack of elevated months. Indeed, the median flux of 0.16 $\mu g\ m^{-2}\ day^{-1}$ is very close the mean of 0.18 due to the absence of abnormally high fluxes. The highest flux was 0.29 (December 1992), less than a factor of 2 higher than the mean flux. This would indicate, therefore, that the urban sites are prone to specific events resulting in elevated PCB deposition. At the rural site, however, the depositional flux is more consistent throughout the year. With the cessation of PCB production, point sources in the urban environment will be responsible for the elevated air concentrations, as noted, when attempting to model urban air concentrations of PCB 28 (see Chapter 7). These point sources will also presumably influence depositional fluxes. Unlike PAH deposition seasonal differences between the summer and winter were not observed. Although the PCBs exhibited markedly higher air concentrations during the summer (Hoff *et al.*, 1992a; Halsall *et al.*, 1995) a corresponding increase in the deposition was not observed. The elevation in PCB air concentrations during the summer is mainly through the increase in the vapour phase component, the net flux therefore may be one of volatilisation off surfaces rather than an increased depositional flux to surfaces. Certainly in the Great Lakes region of N. America fluxes from lake water, back into the atmosphere, are considered to be one of the

dominant processes, outweighing deposition into the lakes (Hornbuckle *et al.*, 1995). Similarly in the UK, the lack of seasonal pattern in the PCB deposition reflects on their current status. Unlike the PAHs that show increased air concentrations in the winter (due to anthropogenic input), the PCBs are not in current use and fresh inputs to the UK environment are small in comparison.

The ΣPCB fluxes at world rural/remote locations in Table 8.7 are markedly lower than the rural site in the UK. The mean depositional fluxes at these sites are, however, the same order of magnitude as the lowest monthly fluxes reported for the UK sites. Lowest reported depositional fluxes were at the remote Pacific site of Enewetak Atoll. However it must be pointed out that these are not contemporary measurements and that quantification was based on the Aroclor mixes rather than individual congeners.

Mean individual congener fluxes and air concentrations for both an urban site (Manchester) and the rural site (Hazelrigg) are presented in Table 8.8. Also included in Table 8.8 are the mean air concentrations and fluxes for several of the PCB homologue groups measured at Chesapeake Bay, USA (Leister and Baker, 1994). All three sites clearly show the predominance of the lighter tri- and tetrachlorinated congeners in both the air and in the deposition fluxes. Interestingly the ratios between air concentrations are similar to the ratios between depositional fluxes for different congeners. For example, in Manchester the ratio between the air concentrations of

Table 8.8 Mean PCB air concentrations and depositional fluxes at three different sites.

Manchester		
PCB congener	Air conc. (ng/m^3)	Flux (ng/m^2/day)*
28	0.13	210
52	0.10	78
101	0.085	28
138	0.028	22
153	0.037	27
180	0.024	27
Hazelrigg (rural site)		
28	0.045	49
52	0.023	30
101	0.011	20
138	0.0040	6.8
153	0.0070	16
180	0.0090	8.0
Chesapeake Bay (rural)		
PCB Homologue		
Tri-CBs	0.050	1.6
Tetra-CBs	0.065	3.0
Penta-CBs	0.045	2.2
Hexa-CBs	0.035	1.4
Hepta-CBs	0.020	0.55

* Fluxes in ng rather than µg, for comparison with air concs.

congeners 28 and 180 is 5.5 and between the fluxes, 7. Similarly, at the rural site the ratio between atmospheric 28 and 180 is 5 and between the fluxes, 6. Likewise at Chesapeake Bay, where only the homologue groups were reported, the ratio between the atmospheric tri-CBs and the hepta-CBs is 4.3 and between their depositional fluxes, 5.4. This similarity in the ratios between light and heavy congeners, both in atmospheric concentrations and depositional fluxes, indicates that the congeners are being deposited at a similar rate relative to their air concentrations. As discussed earlier with the PAHs, this is not the case for the low molecular weight compound PHE, the depositional flux being only slightly higher than the flux of the heavier compound, B[a]P, yet the air concentration is an order of magnitude higher. It is likely that the low molecular weight PCBs are more stable in the atmosphere than the lighter PAHs. Certainly the atmospheric residence time of the tri and tetra-CBs is estimated to be in the order of weeks (Manchester-Neesvig and Andren, 1989), whereas the residence time of PHE was determined to be in the order of ~1 day, due to rapid chemical degradation (Kwok *et al.*, 1994).

8.6 A mass balance of PCBs in the UK environment

As with the PAHs it is useful to be able to balance known releases (i.e. sources) with the deposition fluxes reported in this Chapter. Although the production of PCBs in the UK has been banned since 1976, a significant quantity of PCBs are still emitted to the atmosphere. Discarded electrical

equipment known to contain PCBs is now almost all disposed of via chemical waste incinerators, but emissions are still significant from existing components that have not been identified to contain PCBs (APARG, 1995). Harrad *et al.* (1994) compiled a source inventory list of PCBs to the UK environment and estimated that the major primary source of PCBs arises from leaks from large electrical transformers and capacitors, followed by the recovery of contaminated scrap metal. Table 8.9 presents a list of sources from Harrad *et al.* (1994) and their annual release to the atmosphere for both total ΣPCB and the six indicator congeners, their release is reported in tonnes per year. Also included in this Table are additional primary sources not considered by Harrad *et al.* (1994), namely incineration of municipal solid waste and chemical waste (APARG, 1995).

The loading of PCBs in the atmosphere at any one time can be estimated by taking the volume of air over the UK (5×10^{14} m^3) and the mean ΣPCB concentration in the atmosphere. Table 8.10 presents the mean air concentrations of the six indicator congeners and their atmospheric loading. At any one time the atmosphere contains ~ 0.06 tonnes of ΣPCB.

The total depositional loading to the UK surface can then be estimated from the measured fluxes. Table 8.11 presents the mean fluxes for both the urban and rural areas, the UK urban surface area is considered to be 2.5×10^{10} m^2 and the rural area 2.25×10^{11} m^2. Therefore in this Table the loading (tonnes/yr) of the six congeners and the ΣPCB are reported for both urban

Table 8.9 Estimated annual release from primary sources of PCBs to the UK atmosphere (tonnes/yr).

PCB	Capacitor Leaks	Transformer leaks	Scrap metal Recovery	Municipal solid waste incineration	Chemical Waste Incineration†	RDF production*	Total
28	0.27 - 0.32	0.005 - 0.007	0.026	-	-	-	0. 29
52	0.16 - 0.19	0.006 - 0.010	0.011	-	-	-	0.19
101	0.037 - 0.044	0.010 - 0.015	0.0076	-	-	-	0.06
138	0.018 - 0.022	0.007 - 0.010	0.0032	-	-	-	0.032
153	0.017 - 0.020	0.011 - 0.016	0.002	-	-	-	0.034
180	0.0015 - 0.0018	0.005 - 0.008	0.006	-	-	-	0.009
ΣPCB	3.5 - 4.2	0.20 - 0.30	0.24	0.0060 - 0.016	0.00070 - 0.0020	0.00001	3.9 - 4.8

* Refuse derived fuel
† APARG (1995)

and rural areas. For the whole of the UK the ΣPCB loading is 23 tonnes per year, with the urban surfaces receiving some 40 % of this figure.

Table 8.10 Mean UK PCB air concentrations (ng/m^3) and total atmospheric loading (tonnes).

PCB	Mean air concentration (ng/m^3)	Atmospheric loading (tonnes)
28	0.045	0.023
52	0.023	0.012
101	0.008	0.004
138	0.004	0.002
153	0.006	0.003
180	0.010	0.005
ΣPCB	0.12	0.06

The ΣPCB deposited (23 tonnes) is far greater than that released from sources (4 - 5 tonnes). At any one time the reservoir in the atmosphere (0.06 tonnes) is only a fraction of that released or deposited. Therefore either the source inventory is grossly underestimated or there are additional sources releasing PCBs into the atmosphere. Since their production PCBs have become widely distributed in the UK environment, it is now considered that soils are the major reservoir for previously released/deposited PCBs (Jones, 1994). It is increasingly likely that vegetation may also be a reservoir for PCBs and other SOCs (Simonich and Hites, unpublished). With the cessation in PCB production and the decline in air concentrations, the equilibrium has shifted so that these natural sinks have now become important secondary sources for atmospheric PCBs. Indeed, in the Great Lakes region of the USA the surrounding atmosphere is now considered to be a sink for the re-volatilisation of PCBs from surfaces (Jeremaison *et al.*,

Table 8.11 Mean depositional fluxes for both urban and rural areas, and PCB loading (tonnes) to the UK surface.

PCB	Mean urban flux (μg/m^2/day)	Urban loading Tonnes/year	Mean rural flux (μg/m^2/day)	Rural loading Tonnes/year	Total UK loading Tonnes/year
28	0.64	5.8	0.044	3.6	9.4
52	0.18	1.6	0.027	2.2	3.8
101	0.067	0.61	0.020	1.6	2.2
138	0.039	0.36	0.007	0.58	0.94
153	0.042	0.38	0.016	1.3	1.7
180	0.029	0.26	0.017	1.4	1.7
ΣPCB	0.99	9.0	0.17	14	23

1994; Hornbuckle *et al.*, 1995). Volatilisation from these secondary sources (i.e. soil and vegetation) is considered to make a significant input to the atmosphere. Therefore if releases into the atmosphere from these sources are taken into account, the discrepancy between the amount of PCBs released and the amount depositied should be reduced.

Harrad *et al.* (1994) estimated the mass of ΣPCB released through volatilisation from UK soil to be ~ 40 tonnes per year. It is important to note the author's assumptions, firstly UK soils were considered to be uniformly contaminated with the median soil concentration of 30 μg ΣPCB kg^{-1} and that secondly, only the PCB fraction in the first 1 cm of soil would be available to the atmosphere over the period of a year. Nevertheless, the mass of 40 tonnes results in a significant increase in the amount released to the atmosphere. Table 8.12 presents the yearly release, estimated by Harrad *et al.* (1994), of PCBs through volatilisation from soil and from sewage sludge-amended land.

The excess ΣPCBs which are not deposited may undergo atmospheric transport away from the UK. Long range transport of PCBs has been investigated in several studies, notably the movement away from source areas to more remote sites (Hoff *et al.*, 1992b; Panshin and Hites, 1994b). Literature on the physical/chemical degradation of PCBs in the atmosphere is sparse, but evidence of photochemical degradation has been reported for the lower chlorinated congeners in the vapour phase (Bunce *et al.*, 1989).

Manchester-Neesvig and Andren (1989) estimated that the atmospheric residence time of PCBs is in the order of weeks to months. This means that atmospheric transport may be a significant loss mechanism from the UK environment, rather than by degradation in the atmosphere.

Table 8.12 Estimated volatilisation release of PCBs from secondary sources (tonnes per year).

PCB	Soil	Land-applied sewage
28	5.1	0.0057
52	4.0	0.012
101	2.4	0.0035
138	0.84	0.0015
153	1.0	0.0013
180	0.60	0.0021
ΣPCB*	40	0.085

*Σ = 44 congeners

Although the addition of secondary sources results in the ΣPCB emissions outweighing the ΣPCB deposition (by factor of ~2), it must be clarified that Harrad *et al.* (1994), in their estimation of primary and secondary sources, used a ΣPCB where the Σ = 44 congeners. For the depositional loading (Table 8.11) the ΣPCB comprised of only the eight congeners common to all the sample sites of this study (see Chapter 4, Section 4.2). Even though these eight congeners are environmentally the most prominent, the depositional loading will still be underestimated relative to the 44 congeners used by Harrad *et al.* (1994). By including the additional 22 congeners monitored in the deposition at the Cardiff, Manchester and rural locations, the total

depositional loading is estimated to be increased to ~ 40 tonnes per year. This figure is closer to the estimated ΣPCB releases from both primary and secondary sources. Examination of the total annual release and deposition of the six indicator congeners listed in Tables 8.9 and 8.12 (for sources) and Table 8.11 (for deposition), illustrates the near balance between sources and deposition. For example, the total UK depositional loading for congeners 28 and 52 is 9.4 t/year and 3.8 t/yr respectively (Table 8.10). The release from sources for these two congeners is estimated as 5.3 and 4.2 t/yr respectively. Similarly for congener 101 the deposition is 2.2 t/yr and the release is 2.5. For these congeners, therefore, the release almost equals the deposition. In the case of 28 the deposition actually exceeds the estimated annual release.

Even with this approximate balance between the mass released and the mass deposited it is probable that the release estimates are still underestimated, particularly for the secondary sources. Atmospheric transport of PCBs away from the UK and any atmospheric degradation, will further distort this balance, reducing the amount available for deposition. Releases from vegetation as well as the volatilisation from UK water bodies may make a significant impact on the atmospheric loading. Furthermore, significant PCB volatilisation fluxes (0.82 - 2.2 $\mu g\ m^{-2}\ day^{-1}$) have been reported for the southern part of the North Sea (Thome *et al.*, 1992 - cited in Panshin and Hites, 1994b), indicating that shallow coastal regions surrounding the British Isles may also be a significant secondary source.

8.7 Summary

Monthly depositional fluxes for PAHs and PCBs are reported at four urban sites and one rural location for periods of up to, or greater than, one 1 year. Despite inherent artefacts associated with the length of sampling time and the actual sampling equipment, the generated fluxes are comparable to other studies.

PAH fluxes were higher in the urban sites than at the rural location by a factor of ~3. The rural location of this study (Hazelrigg) and a rural site in the Lake District had PAH fluxes comparable to a semi-urban location near Manchester. This indicates that greater distances away from urban areas are needed, before PAH deposition is reduced to a 'true' rural flux. No clear seasonal trends in depositional fluxes were observed, however the mean winter flux was greater than the summer flux in the urban areas. At the rural location the low molecular weight compounds of ACE and PHE dominate the summer monthly fluxes in line with their elevated atmospheric concentrations at this time of year.

Large differences in air concentrations between PHE and B[a]P were not matched by a similar difference in the deposition fluxes. For example in Manchester, PHE had an air concentration a factor of ~30 greater than B[a]P, yet its deposition flux was only a factor of 2 higher. Indeed this was found to be the case for both the rural site in this study and a rural study in the USA.

It is possible that PHE in the atmosphere is degraded more rapidly than B[a]P, resulting in reduced deposition. Likewise B[a]P, which is generally associated with the atmospheric particulate, may be more readily deposited. Furthermore, the sampling equipment may be more efficient at collecting particulate than vapour deposition, resulting in a bias towards B[a]P.

By examining the source inventory for PAHs an estimated annual release burden to the UK environment has been calculated. A discrepancy was found between this figure (~1000 tonnes) and the amount annually deposited to terrestrial surfaces (~200 tonnes). This discrepancy may be explained by five processes: 1) loss of PAHs in the atmosphere through physical-chemical transformations, 2) atmospheric transport of PAHs away from the UK environment, 3) underestimation of PAH deposition due to significant deposition occurring near the vicinity of a source, 4) uncertainties over the emission estimates or 5) a combination of these factors.

Urban PCB fluxes were approximately a factor of 4 higher than the mean rural flux. The UK rural flux at this site was higher than rural/remote fluxes measured in the USA. PCB deposition did not show any seasonal variations at any of the sites in this study, possibly reflecting their current status, which unlike the PAHs results in comparatively low inputs to the UK environment. PCB deposition is dominated by the lighter tri- and tetrachlorinated congeners. The ratio between air concentrations of the

congeners 28 and 180 was similar to their ratio in deposition. This was also the case in a rural study in N. America and suggests that PCBs, unlike the PAHs, are deposited at a similar rate relative to their air concentrations. It is postulated that PCBs are more stable in the atmosphere than the lighter PAHs, certainly their atmospheric residence time is longer, being in the order of weeks rather than days.

Using source inventory data the amount of PCB released annually into the UK environment was estimated from primary sources to be approximately 4-5 tonnes, while the release from soil (secondary source) was estimated to be approximately 40 tonnes. This annual release estimate is greater than the amount estimated to be annually deposited. This is derived from the flux data in this study as approximately 23 tonnes. If the full compliment of 30 congeners are included then the deposition loading increases to approximately 40 tonnes. Indeed the amount released is still considered to be underestimated as releases from other secondary sources such as vegetation and coastal waters have not been quantified. It is considered here that atmopsheric transport away from the UK will account for the descrepancy between the amount released and the amount deposited.

Chapter 9

Conclusions

This thesis presents a long term study of atmospheric PAHs and PCBs in both the UK urban and rural atmospheres. Attempts have been made to set this data in an international context as well as to study the spatial differences between the different study sites. Compound behaviour in the atmosphere such as seasonal fluctuations and the vapour - particle distribution have been examined. Deposition fluxes have also been monitored and simple mass balances derived. The following conclusions can be made from this work.

9.1 Atmospheric PAHs

* Mean annual ΣPAH concentrations ranged from 59 ng m^{-3} in Stevenage to 166 ng m^{-3} in London. Comparisons can only be made with those studies where the vapour phase has been sampled, and preferably in ambient air at roof top height. On an international basis contemporary urban ΣPAH concentrations range from 10's - 100's ng m^{-3}.

* The low molecular weight compounds (MW < 200) of PHE and FLU predominate in the urban atmosphere and apart from FLUO and PYR all

other compounds are an order of magnitude lower. For B[a]P, the PAH with the highest carcinogenic rating, none of the sites exceeded the German Federal Agency mean annual limit of 10 ng m^{-3}. In fact evidence here suggests that B[a]P concentrations have decreased by possibly two orders of magnitude in London air over the last 45 years.

* The mean annual ΣPAH concentration at the rural location (Hazelrigg) was greater than the urban air concentrations, specifically due to the predominance of FLU and PHE. These compounds were greater in the Hazelrigg atmosphere over Manchester by a factor of 3 and 4 respectively. However the heavier compounds of B[b]F - COR were lower in the rural atmosphere by between a factor of 2-4. It is suggested that the rural site in this study and another rural site in the Lake District (NW England) are under the influence of local sources. Deposition fluxes would suggest that greater distances away from urban areas are required before a 'true' rural atmosphere is encountered.

* Volatilisation from marine sediments, soil and vegetation may act as secondary sources for the lighter more volatile compounds.

* Seasonal variation of winter 'high' to summer 'low' was evident at all of the sites for the heavier particulate-associated PAH. In the rural atmosphere the lighter compounds showed a seasonal increase in the summer, possibly due to the volatilisation from secondary sources. This seasonal cycling for

the lighter compounds may be masked in the urban atmosphere due to the increased emissions from anthropogenic activity in the winter months, this includes the increased use of fossil fuels for residential heating.

* ACE, FLU, PHE and ANTH predominate in the vapour phase with the higher molecular weight compounds of B[b]F to COR being primarily associated with atmospheric particulate. Temperature appears to be the major controlling factor for the vapour - particle distribution with TSP playing a minor role. Heats of desorption derived from the data were greater for B[a]P than for PHE in both the rural and urban atmospheres.

* During the summer months the PAH profile is similar at all of the urban sites, indicating similar sources to the urban environment. Principal component analysis highlighted a prevalence of the lighter PAH in the rural atmosphere over the urban sites, indicating the possible effects of volatilisation from secondary sources.

* Lighter PAHs show a reduced deposition relative to their air concentrations, indicating that these compounds are rapidly degraded in the atmosphere once released. From a national source inventory ~1000 tonnes of ΣPAH are released annually into the UK atmosphere compared to ~200 tonnes deposited. PAHs may, therefore, be either degraded in the atmosphere, depositied close to source (thereby underestimating the amount actually deposited) or be transported by air mass movement away

from the UK.

9.2 Atmospheric PCBs

* London had the highest annual mean ΣPCB concentration of 1350 pg m^{-3} with Stevenage the lowest at 370 pg m^{-3}, the concentrations in the UK being similar to other urban centres on an international basis. Rural concentrations were approximately a factor of 3-4 lower than the urban values at Manchester and Cardiff. Elevated urban concentrations may be explained by numerous point sources often centred around urban areas and also the ventilation of building air into the ambient urban atmosphere.

* On an individual congener basis the more volatile tri- and tetrachlorinated biphenyls predominated at each of the sites. Congeners were prevalent in the atmosphere according to their vapour pressure and abundance in the commercial PCB mixtures.

* Seasonal variations in the ΣPCB concentrations occur in the urban and rural atmospheres with increases being observed in the warmer summer months and a reduction during the winter. This seasonal cycling of summer 'high' to winter 'low' therefore occurs in both the urban and rural atmospheres, regardless of anthropogenic activity. On an individual compound basis the more chlorinated congeners show a greater amplitude change in the cycling pattern from winter to summer. Possible explanations

for this are that the heavier congeners are more readily exchangeable from surfaces with the onset of warmer temperatures or, alternatively, the less chlorinated congeners do not condense readily onto surfaces with the mild winters experienced in the UK. In other words, colder temperatures than normally experienced in the UK, may be required to reduce vapour phase concentrations of these compounds.

* Greater than 90 % of the ΣPCB are found in the vapour phase. On an individual congener basis the vapour phase component clearly dominates, but decreases with increasing level of chlorination and during the cooler winter months. As with the PAHs the vapour-particle distribution is largely controlled by temperature. Particulate phase concentrations did not vary with season, indicating that terrestrial surface vapour exchange may play a more important role in the annual cycling of atmospheric PCBs. On average the rural TSP concentrations were a factor of 2 lower than in the Manchester atmosphere, yet the partitioning behaviour of the six indicator congeners did not differ between sites.

* Concentrations of particulate phase PAHs and PCBs were found to be elevated above the seasonal average for several winter sampling weeks at the urban sites. For these weeks, meteorological conditions were typified by high pressure stable anti-cyclonic systems, with low wind speeds, little cloud cover and low mixing heights. In a high resolution sampling programme the ΣPCB concentrations varied, depending on the source of the air mass.

Air mass back trajectories confirm that air masses over NW England originate from different areas. In an investigation of three separate episodes, the ΣPCB concentration was different, but the congener profile remained the same, indicating that PCBs are well mixed regionally, and/or processes affecting PCBs during transport, are similar.

* Urban PCB deposition fluxes are approximately a factor of 4 higher than the rural flux. PCBs are deposited at a similar rate relative to their air concentrations, indicating that PCBs may be more stable in the atmosphere than the lighter PAHs. Atmospheric transport is probably one of the dominant loss processes for PCBs from the UK environment, explaining the discrepancy between the amount released and the amount deposited annually.

9.3 Further research

1) The continuation of routine long term sampling of SOCs in urban and rural atmospheres will allow future trends in atmospheric concentrations to be assessed. For the PAHs this data can be used to set air quality guidelines, with ongoing data collection used to assess the effectiveness of emission controls, such as traffic limitation schemes in urban areas. Due to their longevity and persistence, PCB monitoring will be required to assess if atmospheric concentrations have stabilised since the post-production era. It is likely that secondary sources and numerous point sources may maintain

atmospheric concentrations for many years, resulting in continued long range transport and the contamination of remote locations.

2) Further research is required on the mobilisation of SOCs from secondary sources, notably volatilisation from soils, sediments and vegetation. As primary sources are reduced, re-cycling from secondary sources will become a major source to the atmosphere, making a significant contribution to the national inventory.

3) Insufficient is known about the atmospheric chemistry of the PAHs and the PCBs, particularly in regards to their degradation rates and atmospheric half-lives. This is important for the transport and deposition rates of these contaminants, and may at least partially explain the discrepancy between current estimates of national emissions and deposition.

4) Deposition sampling methodology needs to be improved, particularly for the collection of compounds that exist largely in the vapour phase. Deposition to plant/soil surfaces should be investigated to examine the accumulation of SOCs over an annual time scale and to investigate the compartmentalisation of the different compounds.

5) Long range transport and the influence of meteorological conditions need further work. It would be interesting to establish what conditions favour transport either to, or away from, the UK. Furthermore, a high resolution

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APPENDIX 1

London - Sampling dates

Sample Week	Start Date	Finish Date	T* ºC	TSP† µg/m^3	Sample Week	Start Date	Finish Date	T ºC	TSP µg/m^3
2	10.1.91	17.1.91	6	NA	52	2.01.92	9.01.92	5	NA
4	24.1.91	31.1.91	8		54	17.01.92	24.01.92	6	
6	7.2.91	14.2.91	2		56	31.01.92	7.02.92	8	
8	21.2.91	28.2.91	5		58	14.02.92	21.02.92	11	
10	7.3.91	14.3.91	7		60	28.02.92	6.03.92	11	
12	21.3.91	28.3.91	12		62	13.03.92	20.03.92	9	
14	4.4.91	11.4.91	14		64	27.03.92	3.04.92	16	
16	18.4.91	25.4.91	14		66	10.04.92	16.04.92	15	
18	2.5.91	9.5.91	10		68	24.04.92	1.05.92	17	
20	16.5.91	23.5.91	17		70	8.05.92	15.05.92	20	
22	30.5.91	6.5.91	18		72	21.05.92	29.05.92	20	
24	13.6.91	20.6.91	17		74	5.06.92	12.06.92	24	
26	27.6.91	4.7.91	24		76	19.06.92	26.06.92	25	
28	11.6.91	18.6.91	23		78	3.07.92	10.07.92	24	
30	25.7.91	1.8.91	26		80	17.07.92	24.07.92	23	
32	8.8.91	15.8.91	24		82	31.07.92	7.08.92	20	
34	22.8.91	29.8.91	27		84	14.08.92	21.08.92	18	
36	5.9.91	12.9.91	19		86	28.08.92	04.09.92	17	
38	19.9.91	26.9.91	15		88	11.09.92	18.09.92	18	
40	3.10.91	10.10.91	16		90	25.09.92	02.10.92	16	
42	17.10.91	24.10.91	13		92	9.10.92	16.10.92	16	
44	1.11.91	7.11.91	10		94	23.10.92	30.1092	10	
46	14.11.91	21.11.91	10		96	6.11.92	13.11.92	11	
48	28.11.91	5.12.91	2		98	20.11.92	27.11.92	9	
50	12.12.91	19.12.91	6		100	4.12.92	11.12.92	6	
					102	18.12.92	24.12.92	5	

*T = Mean temperature

†TSP = total suspended particulate

NA = Not available

Manchester - Sample dates

Sample Week	Start Date	Finish Date	T ºC	TSP µg/m^3	Sample Week	Start Date	Finish Date	T ºC	TSP µg/m^3
1	16/1/91	23/1/91	10	30	53	15/1/92	22/1/92	11	62
3	31/1/91	6/2/91	11	149	55	29/1/92	5/2/92	13	150
5	13/2/91	20/2/91	12	89	57	12/2/92	19/2/92	17	56
7	27/2/91	6/3/91	16	62	59	26/2/92	4/3/92	15	63
9	13/3/91	20/3/91	15	26	61	11/3/92	18/3/92	16	27
11	27/3/91	3/4/91	13	13	63	25/3/92	1/4/92	23	19
13	10/4/91	17/4/91	12	60	65	8/4/92	15/4/92	21	61
15	24/4/91	1/5/91	11	18	67	22/4/92	29/4/92	21	18
17	8/5/91	15/5/91	13	25	69	6/5/92	13/5/92	22	26
19	22/5/91	29/5/91	13	68	71	20/5/92	27/5/92	25	69
21	5/6/91	12/6/91	15	43	73	3/6/92	10/6/92	31	44
23	19/6/91	26/6/91	18	32	75	17/6/92	24/6/92	26	32
25	3/7/91	10/7/91	21	60	77	1/7/92	8/7/92	22	61
27	17/7/91	24/7/91	23	30	79	15/7/92	22/7/92	29	30
29	31/7/91	7/8/91	20	35	81	28/7/92	5/8/92	26	42
31	14/8/91	21/8/91	19	35	83	12/8/92	19/8/92	21	26
33	28/8/91	4/9/91	22	75	85	26/8/92	2/9/92	21	38
35	11/9/91	18/9/91	21	40	87	9/9/92	16/9/92	22	20
37	25/9/91	2/10/91	15	48	89	22/9/92	30/9/92	21	61
39	9/10/91	16/10/91	11	86	91	7/10/92	14/10/92	19	51
41	23/10/91	29/10/91	8	43	93	21/10/92	28/10/92	12	27
43	6/11/91	13/11/91	7	21	95	4/11/92	11/11/92	21	36
45	20/11/91	27/11/91	8	52	97	18/11/92	25/11/92	14	28
47	5/12/91	11/12/91	7	73	99	2/12/92	9/12/92	13	32
49	18/12/91	23/12/91	3	47	101	16/12/92	23/12/92	11	88
51	2/1/92	8/1/92	8	31	103	29/12/92	6/1/92	11	72

Cardiff - Sample dates

Sample Week	Start Date	Finish Date	T ºC	TSP µg/m^3	Sample Week	Start Date	Finish Date	T ºC	TSP µg/m^3
2	24/1/91	31/1/91	NA	48	52	30/1/92	5/2/92	NA	42
4	7/2/91	14/2/91		56	54	12/2/92	19/2/92		67
6	21/2/91	28/2/91		158	56	25/2/92	4/3/92		89
8	6/3/91	13/3/91		23	58	11/3/92	20/3/92		61
10	28/3/91	4/4/91		68	60	25/3/92	1/4/92		51
12	11/4/91	18/4/91		43	62	9/4/92	15/4/92		33
14	25/4/91	2/5/91		56	64	23/4/92	29/4/92		60
16	9/5/91	16/5/91		29	66	6/5/92	13/5/92		17
18	24/5/91	30/5/91		33	68	27/5/92	4/6/92		26
20	6/6/91	13/6/91		41	70	10/6/92	17/6/92		66
22	19/6/91	27/6/91		51	72	24/6/92	2/7/92		41
24	4/7/91	11/7/91		39	74	9/7/92	16/7/92		23
26	17/7/91	26/7/91		53	76	23/7/92	4/8/92		45
28	2/8/91	8/8/91		22	78	13/8/92	21/8/92		32
30	15/8/91	21/8/91		46	80	26/8/92	4/9/92		36
32	28/9/91	5/9/91		73	82	9/9/92	17/9/92		43
34	12/9/91	25/9/91		42	84	23/9/92	30/9/92		72
36	3/10/91	9/10/91		48	86	9/10/92	16/10/9:		40
38	19/10/91	24/10/91		35	88	22/10/92	30/10/9:		48
40	30/10/91	6/11/91		46	90	5/11/92	18/11/9:		71
42	14/11/91	21/11/91		66	92	26/11/92	4/12/92		45
44	28/11/91	5/12/91		95	94	11/12/92	17/12/9:		21
46	12/12/91	19/12/91		41	96	23/12/92	6/1/93		51
48	2/1/92	9/1/92		25					
50	16/1/92	24/1/92		61					

NA - Not available

Stevenage - Sample dates					Hazelrigg (rural) - Sample dates				
Sample Week	Start date	Finish date	T ºC	TSP µg/m^3	Sample Week	Start date	Finish date	T ºC	TSP µg/m^3
2	10.1.91	17.1.91	NA	NA	1	2/12/92	8/12/92	6	18
4	24.1.91	31.1.91			3	16/12/92	23/12/92	5	32
6	7.2.91	14.2.91			5	29/12/92	6/1/93	4	59
8	21.2.91	28.2.91			7	13/1/93	20/1/93	9	38
10	7.3.91	14.3.91			9	27/1/93	3/2/93	7	40
12	21.3.91	28.3.91			11	10/2/93	17/2/93	8	53
14	4.4.91	11.4.91			13	24/2/93	3/3/93	5	24
16	18.4.91	25.4.91			15	10/3/93	17/3/93	9	55
18	2.5.91	9.5.91			17	24/3/93	31/3/93	10	53
20	16.5.91	23.5.91			19	7/4/93	14/4/93	12	36
22	30.5.91	6.6.91			21	21/4/93	28/4/93	13	31
24	13.6.91	20.6.91			23	5/5/93	12/5/93	14	23
26	27.6.91	4.7.91			25	19/5/93	26/5/93	12	31
28	11.7.91	18.7.91			27	2/6/93	9/6/93	13	36
30	25.7.91	1.8.91			29	16/6/93	23/6/93	15	10
32	8.8.91	15.8.91			31	30/6/93	7/7/93	19	38
34	22.8.91	29.8.91			33	14/7/93	21/7/93	17	13
36	5.9.91	12.9.91			35	28/7/93	4/8/93	21	13
38	19.9.91	26.9.91			37	11/8/93	18/8/93	18	22
40	3.10.91	10.10.91			39	25/8/93	1/9/93	16	19
42	17.10.91	24.10.91			41	8/9/93	15/9/93	15	18
44	1.11.91	7.11.91			43	22/9/93	29/9/93	13	26
46	14.11.91	21.11.91			45	6/10/93	13/10/93	10	19
48	28.11.91	5.12.91			47	20/10/93	27/10/93	8	20
50	12.12.91	19.12.91			49	3/11/93	10/11/93	9	26
52	2.1.92	9.1.92			51	17/11/93	24/11/93	4	47
54	17.1.92	24.1.92			53	30/11/93	8/11/93	-1	25
56	31.1.92	7.2.92			55	15/12/93	22/12/93	6	52
58	14.2.92	21.2.92							
60	28.3.92	6.3.92							
62	13.3.92	3.4.92							
64	27.3.92	3.4.92							
66	9.4.92	16.4.92							

NA = Not available

APPENDIX 2

Application of principal component analysis (PCA) for PAH data presented in Chapter 5.
(Duarte-Davidson, 1992; Daly *et al.*, 1995)

PCA reduces the measurements (air concentrations over time) on individual objects (sample locations) to single weighted averages, in such a way that these weighted averages preserve as much of the difference between the objects as possible. In effect this reduces the measured variables (PAH compounds) to several principal variables or factors, preserving as much as possible the structure of the sample, yet defining the main variables in the data set.

1) The PAH concentrations at the various sample sites were standardised by calculating z-scores. The concentrations over seven weeks for each variable (PAH) at the different sites, produced a mean value of zero and a standard deviation of one. Non-detects were replaced in the data set with the limit of detection concentration for that compound. Other workers using data sets with a high number of non-detects, have incorporated random numbers generated between zero and the detection limit (Poland, pers. comm.).

2) A correlation matrix of the z-scores, for all the variables, was computed, and variables that were not related to each other were removed from the model.

3) An unrotated factor matrix of the data was used to determine the groupings of the variables into the different factors. Initially as many factors as variables were determined, so that the first factor was formed by a combination of variables that accounted for the largest amount of variance in the sample, and the second factor accounted for the next largest amount of variance, and is uncorrelated to the first. Successive components explained progressively smaller portions of the total sample variance. Therefore, it was possible to eliminate those factors that accounted for a low proportion of the total variance in the data set. The optimum number of factors to be included were determined by the factor eigenvalues, and by the variance accounted for - by each factor. These values were calculated from the unrotated factor matrix as follows:

> The factor matrix was formed by coefficients called factor loadings which give an indication of how much weight is assigned to each factor. Factor loadings having large coefficients (i.e. near 1) for a variable that is closely related to that factor.

> Eigenvalues were calculated by adding the squared loadings, contained in a single column of the matrix. The eigenvalue for the factor in that column, determines the total amount of variance which is explained by that factor.

The variance accounted for by that factor (%VAF), represents the average of the squared loadings in a column. This is obtained by dividing the eigenvalue by the number of items in that column.

The communality (or cumulative % VAF) is determined by adding up all the % VAF values for all the factors. The optimum number of factors are those that account for at least 5% of the variance, and which have an eigenvalue greater than one.

4) The factors chosen were then rotated to orthoganol positions using Varimax rotation. A mathematically equivalent matrix was formed which had a simpler structure, and therefore allowed for the easier interpretation of the data. Orthoganol data was formed by factors which were uncorrelated with each other. A factor loading matrix was produced which represented both regression weights and correlation coefficients. Rotation effectively redistributed the explained variance for the individual factors, changing the variance accounted for, by each factor, but not affecting the communality. Furthermore, rotation simplified the structure of the matrix by maximising the number of factor loadings of greater magnitude (and also smaller magnitude), for each factor. This resulted in the creation of a distinct pattern, by which each variable is mainly associated with one factor. This also avoided the difficulties encountered when several factors have high loadings on the same variables, resulting in a lack of pattern.

5) Scores for each factor were calculated by multiplying the factor loadings for a particular variable by the location's (Manchester, Cardiff etc.) score on each variable. The factor score matrix had as many rows as sample weeks (7 at each location), with each column representing a factor. Factor scores were then plotted against one another to establish relationships between the different locations.