1.0 INTRODUCTION

Polynuclear aromatic hydrocarbons (PAHs) are a large group of organic compounds found throughout the environment. They are formed mainly by the incomplete combustion of fossil fuels and other organic material, and airborne concentrations are consequently higher in towns than in the countryside. Many PAHs, including the best known of them, benzo (a) pyrene or BaP, have been shown to be carcinogenic, and they are probably one of the several factors responsible for the higher incidence of lung cancer in urban compared with rural areas.

The 1991/2 London-wide PAH survey aimed to make an initial assessment of the exposure of Londoners to PAHs, and in particular to PAH levels near busy roads. A range of PAHs were measured at fourteen sites across London and useful data were collated relating to total PAH concentrations, relative proportions of individual compounds, and intersite differences.

The 1992/93 survey aimed to continue this process of data collection in London, and to compare the findings with guidelines for PAHs and the results of other surveys of PAH concentrations in urban areas in the UK, in order to increase our understanding of the scale of the pollution problem posed by PAHs in the capital.

2.0 HEALTH EFFECTS

There is evidence from epidemiological studies on coke-oven workers and coal-gas workers to implicate inhaled PAHs as a cause of lung cancer. The evidence is sufficient to form a quantitative estimate of the risk, and several such estimates have been published during the past decade. Two of the most authoritative are those of the World Health Organisation (WHO) (1987) and Doll and Peto (1983); these are in broad agreement, and suggest that exposure to benzo (a) pyrene (BaP) results in a unit lifetime risk of about 10^{-4} per ng m^{-3}. In other words, exposure to a concentration of 1 ng of BaP per cubic metre of air, throughout life, carries a risk of lung cancer of 1 in 10,000 or 0.01%. This is a risk over and above the already existing risk of lung cancer, which in this country is about 6% averaged over the whole population (smokers plus non-smokers); for non-smokers alone the risk is about 0.8%.

The risk has been expressed in terms of BaP rather than total PAH because BaP is the best-known carcinogen in the PAH group, and 'total PAH' is not a well-defined substance. However, it is important to remember that in deriving risk estimates for BaP in this way, a number of assumptions have been made. These include the assumption that the PAH profile is the same for coke-oven workers as for the general public.

Furthermore, with respect to the influence of smoking, it seems likely that the combined effects of smoking and BaP are much more than additive. The unit risk figure of 10^{-4} is therefore valid only for a population having the same smoking habits as the exposed worker population. The risk for non-smokers, or for any group who smoke less than did the worker group, would be expected to be less than 10^{-4}.

3.0 GUIDELINES AND STANDARDS

There is no national guideline or standard for PAH. In the Netherlands an interim goal is to reduce the annual average concentration of BaP to 5 ng m^{-3} (Tweede, Kamer 1984/5, quoted by Thrane 1987). A guideline for the annual average BaP concentration proposed by the German Environmental Agency is 10 ng m^{-3} (Undweltsbundesamt 1979, quoted by Thrane 1987).

The World Health Organisation, in its most relevant report (WHO, 1987), has not recommended any guidelines for carcinogenic air pollutants. It has instead simply given its best estimates of the unit lifetime risks, and left it to the National Authorities to decide upon an 'acceptable risk', and hence to derive numerical values for the guidelines.

There is no general consensus as to what would constitute an 'acceptable risk' in the context of urban air pollution, but a frequently quoted figure is that used by the United States Environmental Protection Agency (USEPA). When considering environmental pollutants the EPA consider a risk range of 10^{-4} to 10^{-6} to be 'protective of public health', but in fact use the upper limit of this range when making judgements. If 10^{-4} is taken as the relevant 'acceptable risk' then, with a unit risk estimate of 10^{-4} per ng m^{-3}, the guideline value for BaP would be 1 ng m^{-3}.

4.0 SOURCES AND CHEMICAL ORIGIN

Estimates of atmospheric emissions of PAH by source type for Sweden and the UK are given in Table 1. The major sources in these countries are stationary and sensitive to the type of plant and fuel. In urban areas, however, mobile sources are likely to be the major contributors to PAH emissions.

Table 1: PAH Emission to Air from Diffuse Sources in European Countries 1985 (T yr $^{-1}$)

	Sweden	***UK***
Anthracite	-	29.4
Bituminous Coal	5.8	91.0
Wood	325.0	2.5
Gasoline	3.2	17.1
Motor Diesel Oil	1.6	7.9
Coke Production	3.6	27.8
Total	***339.0***	***176.0***

Diesel emissions are the primary source of urban PAH. Recent analysis of diesel exhaust particles showed that the major PAH compounds are naphthalene, fluorene, phenanthrene and their alkyl derivatives, while carbazole and dibenzothiophene are the major N- and S- containing polycyclic aromatic compounds (PAC).

The First Report of the Department of the Environment Quality of Urban Air Review Group reports that firm evidence has been provided that the bulk of particulate PAC (including PAH) derives from unburnt fuel, with some high molecular weight (5-ring) PAH being formed in-cylinder, presumably from lower molecular weight PAH. It is also reported that the air/fuel ratio (AFR) is established as a significant determinant of PAH emissions from spark-ignition vehicles, and cold-starts were found to increase emissions substantially.

5.0 URBAN CONCENTRATIONS

Compared with other pollutants, the monitoring of speciated organic compounds in urban areas of the UK is in its infancy and long time-series data bases are not currently available.

The analysis of PAH is included in the UK TOMPS (Toxic Organic Micropollutants) monitoring programme recently established by the Warren Spring Laboratory for the Department of the Environment. Sites have been established in Westminster, Manchester, Cardiff and Stevenage to monitor PAH, polychlorinated biphenyls (PCBs) and dioxins. The TOMPS programme should in the future provide a valuable basis for data analysis and source reconciliation for these compounds.

PAHs are present as both gaseous compounds and in association with particulate matter, and techniques are available to monitor both these phases. Particulate concentrations were monitored in the LWEP PAH survey (see Section 6.3), and therefore in this section we focus on other urban measurements in this phase for comparison.

The most complete set of PAH measurements in the UK has been made in South Kensington. Annual average particulate concentrations for 1985/6 and 1987 for 18 PAH are given in Table 2 and compared with more limited measurements in Folkestone and Ashford, a rural location. Similar particulate concentrations were detected at a city centre site in Birmingham over the period 1976/8. Table 2 also shows results for particulate concentrations of 17 PAH obtained at a height of 15m at Birmingham University at a distance of approximately 300m from a major road and preliminary results from the Manchester TOMPS site (which is a rooftop site located in the city centre).

The results are broadly similar although quantitative comparisons are not very good. There is considerable variability in the results from week to week and from site to site.

Table 2 Average Particulate PAH Concentrations (ng m^{-3}) for South Kensington, Birmingham, Manchester and Folkestone and Ashford

PAH	*South Kensington*(a)	*Birmingham*(b)	*Manchester*(c)	*Folkestone & Ashford*
Naphthalene	-	0.21	-	-
Acenapthylene	-	0.61	-	-
Fluorene	-	1.10	0.50	-
Acenaphthene	-	1.60	ND	-
Phenanthrene	0.11	1.10	0.40	0.02
Anthracene	0.18	0.40	0.05	0.03
Fluoranthene	0.81	1.20	0.63	0.21
Pyrene	0.79	2.40	0.80	0.21
Benzo[c]phenanthrene	0.85	-	-	0.18
Cyclo[c,d]pyrene	2.61	-	-	0.28
Benzo[a]anthracene	0.79	1.50	1.00	0.28
Chrysene	1.22	2.20	1.80	0.16
Benzo[b]fluoranthene	0.98	-	-	0.32
Benzo[e]pyrene	2.00	-	-	0.55
Benzo[b]fluoranthene	1.61	2.00	2.40	0.52
Benzo[k]fluoranthene	0.68	1.10	2.40	0.21
Benzo[a]pyrene	1.44	0.73	1.60	0.43
Dibenzo[a,h]anthracene	0.12	0.79	-	0.05
Benzo[g,h,i]perylene	3.30	1.90	3.10	1.16
Ideno[1,2,3,c,d]pyrene	1.57	2.00	-	0.54
Anthanthrene	0.63	-	-	0.02
Coronene	1.67	1.00	1.40	0.21

(a) annual average;

(b) average of 27 daily samples, February 1992;

(c) results for week 7, Manchester TOMPS site.

6.0 THE MEASUREMENT PROGRAMME

6.1 General

Mobile sources are likely to be the major contributors to PAH emissions in urban areas and exhaust emissions from traffic have become one of the most important sources of PAHs in London and other towns. Most of the locations chosen for sampling were therefore close to busy roads, but a few were not, in order to provide some information on background levels.

Air pollution levels tend to be higher during winter than summer because of less favourable atmospheric dispersion conditions during the winter months. For PAHs, this effect is likely to be enhanced by the use of fossil fuels for the heating of homes and offices. Measurements were therefore made in both seasons.

It is generally agreed that BaP by itself is not a satisfactory index of total PAH, but there is no universally agreed selection of PAHs which does perform such a role. About 500 PAH compounds have been detected in the air and it is clearly impracticable to measure all but a small fraction of this number.

The most authoritative recommendation with respect to selection of compound for measurement is probably that of the US Environmental Protection Agency, which has listed 15 PAHs for air monitoring programmes, and it is these that have been measured in our survey. The USEPA list contains a selection of compounds likely to occur at relatively high levels, and includes members across a range of molecular weights, from the volatile, 2-ring, naphthalene to those of higher molecular weight, which are likely to be predominantly in the particle phase. The individual compounds are given in Table 3.

Factors which influence the inclusion of a particular compound in a measurement programme include its carcinogenic potential, whether the compound is present in the atmosphere in sufficient concentration to permit reliable measurement with the analytical techniques and reference standards currently available, and also whether the relative concentrations of particular compounds give an indication of the main source of the PAHs.

Human carcinogenicity data are available only for PAH mixtures, and our knowledge of the carcinogenicity of individual PAHs therefore comes from *in vitro* and animal studies. There is no definitive 'carcinogenicity classification' of PAH compounds, but two recent authoritative commentaries are in general accord (WHO, 1987; Sloof et al, 1989). A rough classification based on these two commentaries is given in Table 3.

Table 3: The PAH compounds measured

Compound and abbreviation		*Cancer rating(a)*	*Rings*	*Mol wt*
Naphthalene	Np	?	2	128
Acenapthene	ACE	-	3	166
Fluorene	FL	-	3	166
Phenanthrene	PHE	?	3	178
Anthracene	ANT	-	3	178
Fluoranthene	FLH	?	4	202
Pyrene	PYR	-	4	202
Benzo (a) anthracene	BaA	+	4	228
Chrysene	CHR	+	4	228
Benzo (b) fluoranthene	BbF	++	5	252
Benzo (k) fluoranthene	BkF	++	5	252
Benzo (a) pyrene	BaP	+++	5	252
Dibenz (ah) anthracene	DahA	+++	5	278
Benzo (ghi) perylene	BghiP	+	6	276
Coronene	COR	-	7	300

Note

(a) *Carcinogenic classification: a dash (-) indicates that there is no evidence for carcinogenicity, a question mark (?) that there is insufficient evidence, and one or more plus signs (+) that there is sufficient evidence.*

6.2 Measurement sites and sampling periods

Thirteen sites were chosen, one in each of the Boroughs participating in the survey. At each site, a sample of approximately two weeks duration was taken in the summer of 1992 and another in the winter of 1992/93. The sites, together with the dates of sampling, are listed in Table 4.

Sites are classified as 'roadside' and 'background'. All sites with the exception of three, are at the roadside. These sites are generally within 20 m of a busy road, for example at the facade of buildings adjoining the road.

The three 'background' sites are 100 m or more from the nearest busy road (in the case of sites at Bexley and Hounslow), or some distance above ground level (the site at Westminster is 30 m above ground). Note that the site at Hounslow could also be classified as 'industrial' and is 0.5 mile from the perimeter of Heathrow Airport.

Unfortunately the site at Richmond had to be relocated between the summer and winter sampling periods. Full descriptions of all the sites are given in Annex 1.

Table 4: Sites and sampling periods

Site			*Sampling Period*	
No.	***Borough***	***Type(a)***	***Summer***	***Winter***
1	Bexley	B	31.07.92 - 14.08.92	28.01.93 - 11.02.93
2	Brent	R	16.09.92 - 30.09.92	22.01.93 - 05.02.93
3	Ealing	R	04.08.92 - 18.08.92	01.03.93 - 17.03.93
4	Hammersmith Fulham	R	16.09.92 - 30.09.92	01.03.93 - 17.03.93
5	Harrow	R	26.08.92 - 09.09.92	12.02.93 - 26.02.93
6	Hounslow	B	14.09.92 - 29.09.92	01.03.93 - 17.03.93
7	Kensington & Chelsea	R	31.07.92 - 14.08.92	22.01.93 - 05.02.93
8	Kingston upon Thames	R	03.08.92 - 17.08.92	12.02.93 - 26.02.93
9	Newham	R	03.08.92 - 14.08.92	28.01.93 - 11.02.93
10	Richmond	R	24.08.92 - 07.09.92	12.02.93 - 26.02.93
11	Tower Hamlets	R	24.08.92 - 07.09.92	08.02.93 - 22.02.93
12	Wandsworth	R	26.08.92 - 09.09.92	22.01.93 - 05.02.93
13	Westminster	B	20.08.92 - 10.09.92	28.01.93 - 11.02.93

Note

(a) B = Background

R = Roadside

6.3 *Sampling procedure*

PAH samples were collected by drawing air through a filter.

Whatman GF/A glass microfibre filters (60 mm diameter), in conjunction with M-type samplers, were used throughout the survey. The filter holder was mounted with its open face horizontal and facing downwards. Prior to sampling, the filters were washed in dichloromethane, dried at 400°C, and wrapped in aluminium foil until required. After use, the filters were again wrapped in foil, and refrigerated until they were analysed. The M-type sampler operates at a flow rate of about 25 litres per minute and is fitted with a gas meter to record the total volume of air sampled. The sampling period was a nominal two weeks and each sample consisted of the participate material in a volume of about 500 m^3 of air.

Unfortunately problems were encountered during winter sampling at Harrow and Kensington & Chelsea, and the volume of air sampled at these sites was considerably less than 500 m^3. For this reason these data must be treated with some caution.

The method of sampling adopted will not, of course, collect that fraction of a PAH compound in the gas phase. The magnitude of this fraction depends principally on the molecular weight of the compound and the ambient temperature, being largest with low molecular weight compounds and high ambient temperatures. At temperatures to be expected in London during the summer months, the gaseous fraction would be the dominant one for 2 and 3 ring compounds, while for compounds having 5 rings or more, the particle phase would be dominant. The distribution of a number of PAH compounds between the gas and particle phases, as reported by Baek et al (1991) for a set of measurements in London, is shown in Annexe 2.

6.4 *Analytical procedure*

The clean-up of extracted samples was carried out by standard methods, and the final extracts analysed for the 15 PAHs given in Table 3 by high performance liquid chromatography with fluorescence detected. Adequate separation was not usually achieved for two pairs of isomers (acenapthene/fluorene and benz (a) anthracene/chrysene) and these are therefore reported together.

A full description of the procedures is given in Annexe 3.