

# Summary

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The primary aim of the London-Wide PAH survey, which has been in operation since 1991, is to make an assessment of the exposure of the London population to PAHs. The data from this survey have been compared with guidelines for PAHs and with results of PAH surveys conducted in other urban areas in the UK, in order to increase the understanding of the scale of the pollution problem posed by PAHs in London.

There is evidence from epidemiological studies on coke-oven workers and coal-gas workers to implicate inhaled PAHs as a cause of lung cancer. It is estimated that exposure to Benzo (a) pyrene (BaP) results in a unit lifetime risk of about 10<sup>-4</sup> per ng m<sup>-3</sup>. 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.

There is currently no national guideline or standard for PAH. However, PAH's are included in the EU Ambient Air Quality Framework Directive as 'other pollutants to be taken into consideration' and it is expected that the Expert Panel on Air Quality Standards (EPAQS) will recommend a guideline for PAH's within the next year.

With respect to sources and chemical origin of PAH, estimates of atmospheric emissions of PAH by source type for Sweden and the UK indicate that 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 and diesel emissions are thought to be the primary source of urban PAH.

The measurement programme for the London-wide PAH survey was devised so as to reflect the fact that vehicle emissions are the primary source of PAH in urban areas (most of the locations chosen for sampling were therefore close to busy roads) and also that PAH levels tend to be higher during winter than summer (measurements were therefore made in both seasons). Fifteen PAH compounds were selected for measurement, based upon US EPA recommendations with respect to air monitoring programmes.

Twelve measurement sites were chosen, one in each of the Boroughs participating in the 1995/96 survey. At each site, a sample of approximately two weeks duration was taken in the summer of 1995 and another in the winter of 1995/96. Sites were classified as roadside, intermediate and background. Roadside sites are generally within 20 m of a busy road, for example at the facade of buildings adjoining the road; intermediate sites are those either between 20 m and 40 m from a busy roadside and/or at a height greater than 10 m above the kerb; background sites are classed as those located at a distance greater than 40 m from any roadside. PAH measurements were also made at a site located on Southwark Street, London SE1 for two week periods in each month between July 1995 and February 1996.

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It is possible to identify some general trends in the data set, which are supported by findings from the RPT, London, SE1 continuous survey:

- As in previous LWEP PAH surveys wide variations in concentration were found, from compound to compound, site to site and season to season. This is a general feature of PAH concentrations surveyed in urban areas.
- Concentrations measured at roadside and intermediate sites were consistently higher than at the background sites, emphasising the importance of road traffic as a source of PAH.
- Use of BaP as an index of carcinogenicity indicates that concentrations of BaP in London monitored during the 1995/96 survey were considerably below European guidelines. However, annual means exceeded the US EPA guideline of 1 ng m<sup>-3</sup> at five boroughs, these being Brent, Ealing, Harrow, Hammersmith and Fulham and Kingston.
- Comparison of the results of the 1995/96 LWEP PAH survey with other surveys indicate that measured concentrations are broadly similar to those recorded in other parts of the country.
- In view of the limited quantitative information available on the health effects of the PAH species measured, it is considered that the health risks for individuals with the highest exposure to roadside PAH levels in London are finite but very small; for smokers the risks would appear trivial compared with those associated with exposure to PAH from cigarette smoke.

Policy measures to reduce emmisions from diesel cars and heavy goods vehicles include stringent emission standards and an improvement in the quality of diesel fuel. However, the effect of these reductions will have on ambient PAH concentrations in urban air is not yet clear as the legislation will be operating against an increase in the diesel fleet.

The London wide PAH survey provides a valuable database of information on hydrocarbon levels in London, particularly at roadside locations, allowing the impact of recent legislation on London's air quality to be monitored.

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# 7 The Measurement Programme

#### 7.1 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, with the remainder being at a distance from roads, in order to provide some information on background levels.

Air pollution levels tend to be higher during winter than summer because of less favourable conditions for atmospheric dispersion during the winter months. For PAHs, this effect is likely to be enhanced by the increased use of fossil fuels for the heating of homes and offices in winter. 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 ambient air and it is clearly impracticable to measure all but a small fraction of this number.

The most authoritative recommendation with respect to the selection of a species for measurement is probably that of United States Environmental Protection Agency (US EPA), which has listed 15 PAHs as priority pollutants, due to their toxicity and common occurrence, for air monitoring programmes, and it is these that have been measured in this survey. The US EPA list contains a selection of compounds likely to occur at relatively high levels, and includes members across a wide range of molecular weights, from the volatile, 2-ring, napthalene to those of higher molecular weight, which are likely to be predominantly in the particle phase. The individual compounds are listed 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 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 (2 & 3). A rough classification based on these two commentaries is given in Table 3.

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Table 3: The PAH Compounds Measured

Compound and Abb	reviation	Cancer Rating <sup>(a)</sup>	Rings	Mol wt
Napthalene	Np	?	2	128
Acenapthene	ACE	-	3	166
Fluorine	FL	) <del></del>	3	166
Phenanthrene	PHE	?	3	178
Anthracene	ANT	i i	3	178
Fluoranthene	FLH	?	4	202
Pyrene	PYR	12	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	3 <del>=</del>	7	300

#### Note

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

# 7.2 Measurement Sites and Sampling Periods

Twelve 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 1995 and another in the winter of 1995/96. The sites, together with the dates of sampling, are listed in Table 4.

Sites were classified as "roadside", "intermediate" and "background". Generally, "roadside" sites are classed as being within 20 m of a busy road, for example at the facade of buildings adjoining the road; "intermediate sites" are those either between 20 and 40 m from a busy roadside and/or at a height greater than 10 m above the kerb; "background" sites are classed as those located at a distance greater than 40 m from the roadside. Full descriptions of all the sites are given in Appendix A.



Table 4: Sites and Sampling Periods

	Site,		Samplin	ig Period
No.	Borough	Type	Summer	Winter
1	Bexley	В	24/7/95 - 7/8/95	26/2/96 - 14/3/96
2	Brent	I	9/8/95 - 24/8/95	18/1/96 - 1/2/96
3	Greenwich	В	24/7/95 - 7/8/95	5/2/96 - 26/2/96
4	Ealing	R	10/7/95 - 21/7/95	18/1/96 - 1/2/96
5	Hammersmith + Fulham	R	7/7/95 - 21/7/95	18/1/96 - 1/2/96
6	Harrow	I	9/8/95 - 24/8/95	5/3/96 - 27/3/96
7	Kingston upon Thames	R	9/8/95 - 24/8/95	5/2/96 - 26/2/96
8	Newham	R	6/7/95 - 20/7/95	27/2/96 - 27/3/96
9	Richmond	R	27/7/95 - 10/8/95	5/2/96 - 26/2/96
10	Tower Hamlets	R	6/7/95 - 20/7/95	5/2/96 - 26/2/96
11	Wandsworth	I	27/7/95 - 10/7/95	5/3/96 - 27/3/96
12	Westminster	R	6/7/95 - 20/7/95	27/2/96 - 19/3/96

Note:

B = Background

I = Intermediate

R = Roadside

PAH concentrations were measured for approximately two week periods at each Borough. The measurement periods were not, in general coincident at all twelve sites. Air pollution levels are dependant upon weather conditions, it is possible therefore that site-to-site differences reported in previous surveys may have been due to changes in weather conditions from sampling period to sampling period. In an attempt to examine possible seasonal variations in PAH concentration was monitored at a further site located on Southwark Street, London, SE1 for two week periods in each month between July 1995 to February 1996.

# 7.3 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 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 particulate material in a volume of about 500 m<sup>3</sup> of air.



The method of sampling adopted does not 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 gas and particle phases, as reported by Baek et al (6) for a set of measurements in London, is shown in Appendix C.

# 7.4 Analytical Procedure

The extraction of PAH from the filters were carried out by standard methods, and the final extracts analysed for the 15 PAH species listed in Table 3 by High Performance Liquid Chromatography (HPLC) with fluorescence detection. Adequate separation was not usually achieved for two pairs of isomers (acenapthene/fluorene and benzo (a) anthracene/chrysene) and these are therefore reported together.

A full description of the procedures is given in Appendix D.



### 7.5 Detection Limits

With the sampling and analytical procedures described above, the smallest measurable concentration of each PAH compound is as set out in Table 5. A result at, or below the detection limit has been recorded as equal to the detection limit.

Table 5: Detection Limits

Compound and Abbi	reviation	Detection Limit (ng m <sup>-3</sup> )
Naphthalene	Np	0.025
Acenaphthene/fluorene	ACE	0.027
Fluorene	FL	0.048
Phenanthrene	PHE	0.027
Anthracene	ANT	0.011
Fluoranthene	FLH	0.080
Pyrene	PYR	0.034
Benzo [a] anthracene	BaA	0.007
Chrysene	CHR	0.006
Benzo [b] fluoranthene	BbF	0.020
Benzo [k] fluoranthene	BkF	0.004
Benzo [a] pyrene	BaP	0.008
Dibenz [ah] anthracene	DahA	0.009
Benzo [ghi] perylene	BghiP	0.011
Coronene	COR	0.020



### 8 Results

The concentrations of the PAH compounds measured at each site during the summer and winter sampling periods are given in Appendix B, Tables 1 and 2 respectively. These tables also give the total PAH concentrations (i.e. the sum of the concentrations of all 15 PAHs measured) for each site, the arithmetic and geometric means of each compound across all sites. The ratio of the winter to summer geometric mean concentration for each compound is shown in Table 2.

For each compound, at each site, the average of the summer and winter values was calculated to give an estimate of the overall mean concentration. These estimates are given in Appendix B, Table 3.

#### 8.1 Concentrations - Overview

A general overview of the concentrations found is presented in Figure 1, which shows the total PAH concentrations for each site during the summer and winter sampling periods. It is evident that both the absolute concentrations and the winter/summer ratios vary considerably from site to site.

Typically it would be expected that winter PAH concentrations would be greater than those during the summer months, which was the case at all sites with the exception of those located at Tower Hamlets and Westminster. The highest winter total PAH concentration was recorded at Brent which is located close to the North Circular Road.

The wide variations in concentrations found, from compound to compound, site to site and season to season, are a general feature of the PAH concentrations found in urban areas. Efforts to explain these variations are made below.

# 8.2 Comparison of Roadside, Intermediate and Background Sites

It is of interest to make a general comparison of the PAH concentrations at roadside, intermediate and background sites. The estimated mean concentration of each compound has been averaged across all the roadside and intermediate sites and compared with the average concentrations across the background sites, these are illustrated in Figure 2.

A classification of all sites is given in Section 7.3, Table 4.

It can be seen that the roadside and intermediate concentrations were consistently higher than the background ones, emphasising the importance of road traffic as a source of PAHs. Concentrations were, for the majority of PAH species, slightly higher at the intermediate sites than at the roadside sites.

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The highest overall total PAH concentration was recorded at Brent an intermediate site located on the roof of a superstore adjacent to the North Circular Road. The lowest overall concentration was recorded at Tower Hamlets, a roadside site located approximately 15 m from the A13.

#### 8.3 Winter/summer Ratios

The winter and summer concentrations of each compound are shown in Figures 3 and 4 (absolute values) and Figure 5 (summer/winter ratios). In view of the volatility of the lower molecular weight compounds, and the relatively large fractions in the gas phase, these two figures are most informative for the compounds from benzo (f) fluoranthene (BbF) through to coronene (COR). The comments here are therefore largely confined to these compounds.

The major PAH species present in car exhaust emissions are reported to be fluoranthene (FLH) and pyrene (PYR). Benzo (ghi) perylene (BghiP) is also reported to be one of the PAHs most often associated with vehicle emissions. During the summer monitoring levels of PYR, BaA/CHR and BghiP were consistently higher than those of the other PAH species. As with the summer monitoring, PYR and BaA/CHR were again the present in the highest concentrations in the winter monitoring, levels of FLH were also consistently elevated above those of other PAHs. Such results suggest that emissions from motor vehicles were the largest contributing source to PAH levels measured in this study.

Figure 5 illustrates winter/summer ratios of PAH concentrations. Ratios were greater than one for the majority of PAHs, as winter concentrations were higher than corresponding summer ratios. This would be expected as concentrations of many PAHs increase in winter due to a number of factors. For example, PAH emissions from heating sources are increased; the number of PAHs in the particulate phase increases in cooler weather; and seasonal climatic factors result in decreased dispersion and degradation of such pollutants.

The highest total PAH concentration was recorded during the winter period at Brent. Concentrations of FLH, PYR and BaA/CHR (indicative of vehicle emissions), were higher than concentrations of the other measured PAH species during both the winter and summer period. This may be expected as the Brent site is located on the roof of a superstore, adjacent to a comparatively elevated section of the North Circular Road. Levels at this site are also likely to be influenced by vehicles starting from cold in the superstore car park, such cold starts have been shown to be a significant source of emissions (1)

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### 8.4 Comparison with Results of Previous LWEP PAH Survey

For a number of sites, sampling has been undertaken at the same location since the start of the LWEP PAH survey in 1991 and comparisons of levels from year to year are possible. Total PAH concentrations for each site monitored during 1991/92, 1992,93, 1993/94, 1994/95 and 1995/96 surveys are illustrated in Figures 6 (for the summer period) and 7 (for the winter period). Note that the site at Richmond was relocated during the 1992/93 survey; summer measurements were not made at Tower Hamlets in 1991/92; and the Kingston upon Thames site was relocated for the winter sampling period in 1995, therefore any comparisons must be made with caution at these sites.

Figure 6 illustrates that summer PAH concentrations at all sites were higher in 1995 than the previous year. Levels at Brent, Hammersmith and Fulham, Kingston and Westminster were higher than those recorded in all previous years.

Similarly the total PAH concentrations monitored in the winter 1995/96 survey were higher at all sites, except Tower Hamlets, than in the previous year of this survey. The winter concentration at Brent was higher than those recorded in all previous years. Such temporal and spatial variation is likely to reflect differences in meteorological conditions from one winter to the next.

#### 8.5 The PAH Profile

The use of the relative proportions of the individual PAHs in a given sample or series of samples - the 'PAH profile' - has often been tried as a method of determining the relative contribution of different sources. For example, BghiP and Coronene have been suggested as markers for vehicle emissions. Benzo (a) pyrene (BaP) is readily produced by coal and coke-burning as well as being present in vehicle emissions. There is no general consensus as to the use of PAH profiles for source apportionment, and one reason for this must be that the effect of atmospheric transport, degradation and deposition processes tend to blur any initial sharp differences in the emitted PAH concentrations. However, in order to investigate the use of profiles in this study, the graph shown in Figure 8 was constructed. The PAHs chosen were the six most carcinogenic of molecular weight 228 or greater, and the average of the summer and winter concentrations was used.

Figure 8 indicates that similar PAH profiles were obtained for each of the sites. At each site concentrations of BaA/CHR, BbF and BghiP were the highest and the concentration of DahA was consistently the lowest. Such similar profiles suggest that no sites were affected significantly by a specific source, e.g. a localised industrial process, and can be attributed to a much wider source e.g. vehicle emissions.



#### 8.6 PAH Concentration at Southwark Street, London, SEI

The short sampling periods used in the LWEP PAH survey limit data analysis to some extent as they only provide a snapshot of PAH concentrations. In order to assist our understanding of the individual results for each site more extensive measurements of PAH were made at one site over the 1995/96 period. This site located on Southwark Street, London, SE1 and is a rooftop site some 30 m above ground level in an area of heavy traffic. Air at this location could be considered well mixed and away from local sources. PAH concentrations were monitored for two week periods each month between July 1995 and February 1996.

The total PAH concentration (ng m<sup>-3</sup>) for each sample period is illustrated in Figure 9. As might be expected the total PAH concentrations were highest during the winter months lowest during summer. The arithmetic mean of the total PAH concentration over the sample period was 5.32 ng m<sup>-3</sup> which compares with 6.08 ng m<sup>-3</sup> at the background sites (Bexley and Greenwich), 21.80 ng m<sup>-3</sup> at the intermediate sites and the mean value of 15.79 ng m<sup>-3</sup> from the roadside sites. The PAH profile of the mean concentration of the carcinogenic compounds for each sampling period at the Southwark Street site are shown in Figure 10. Throughout the survey BaA/CHR, BbF and BghiP were consistently the PAH species with the highest concentrations, again demonstrating the importance of vehicle emissions at this urban background site.

As Figures 9 and 10 illustrate, total PAH concentration and the concentrations of individual PAH species varied from month to month, as might be expected.

### 8.7 BaP Concentration as a Percentage of all Major Carcinogenic PAHs

Benzo (a) pyrene (BaP) is the only PAH for which there are any authoritative recommendations as to an appropriate guideline or standard. It is often stated that the BaP concentration on its own is not a satisfactory index of the total carcinogenic potential of a mixture of PAHs, so it is of interest to find the BaP concentration expressed as a percentage of all the major carcinogenic PAHs. In the context of the present measurements, this is:

BaP conc. x 100 ÷ sum of conc. (BaA/CHR + BbF + BkF + BaP + DahA + BghiP).

This percentage has been calculated for the estimated annual average concentrations and the values are given in Table 6.



Table 6: BaP concentrations as a percentage of the sum of the concentrations of (BaA/CHR + BbF + BkF + BaP + DahA + BghiP)

Site	Borough	Percent BaP
1	Bexley	8.75
2	Brent	13.67
3	Greenwich	7.41
4	Ealing	17.03
5	Hammersmith and Fulham	10.22
6	Harrow	10.93
7	Kingston upon Thames	7.92
8	Newham	4.63
9	Richmond	9.53
10	Tower Hamlets	4.48
11	Wandsworth	9.76
12	Westminster	9.19
	Arithmetic Mean	9.46

Percentages for background sites ranged between 7.41 % and 8.75 %; intermediate sites ranged between 9.76 % and 13.67 %; values at roadside sites ranged from 4.48 % to 17.03%.

## 8.8 Comparison of Results with Guidelines for BaP

If BaP is used as an index of PAH carcinogenicity, then some comparison of the LWEP PAH survey results with the Dutch and German guidelines for BaP (5 and 10 ng m<sup>-3</sup> respectively) is possible. However it must be noted that these guidelines relate to annual mean concentrations, and the short sampling periods used in this survey mean that any comparison can only be approximate.

The overall mean concentration of BaP ranged between  $0.06 \text{ ng m}^{-3}$  at Tower Hamlets to  $2.14 \text{ ng m}^{-3}$  at Brent. The overall mean for the 12 sites is  $0.08 \text{ ng m}^{-3}$  (Table 3, Appendix B).

The mean BaP concentration was lower in summer (0.57 ng m<sup>-3</sup>) than winter (1.04 ng m<sup>-3</sup>). The highest winter concentration was recorded at Brent (3.63 ng m<sup>-3</sup>).

The survey results indicate that mean BaP concentrations in London Boroughs were well below European guidelines over the sampling periods. Also the mean BaP concentration recorded during the 1995/96 survey did not exceed the guideline value of 1 ng m<sup>-3</sup>, derived in Section 5.0 from US EPA estimates of 'acceptable risk'. This result is similar to those from the 1993/94 and 1994/95 surveys, but is in contrast to the results of surveys prior to 1993 in which overall mean BaP concentrations were 1.5 ng m<sup>-3</sup> (1991/92) and 1.91 ng m<sup>-3</sup> (1992/93). However, unlike the 1994/95 survey, where



concentrations of BaP were well below the guideline at all thirteen sites, annual average BaP concentrations in 1995/96 exceeded the guideline at five of the twelve sites, these being Brent, Ealing, Harrow, Hammersmith and Fulham and Kingston. Concentrations of 2.14 ng m<sup>-3</sup>, 1.17 ng m<sup>-3</sup>, 1.33 ng m<sup>-3</sup>, 1.41 ng m<sup>-3</sup> and 1.09 ng m<sup>-3</sup> were recorded at these locations respectively.

#### 8.9 Comparisons with the Results of Other Surveys

Owing to the limited sampling periods used in the Stanger Science and Environment LWEP PAH survey, and variation in sampling technique, regime and so forth, it is not appropriate to make detailed comparisons between the results obtained from this survey with other surveys. Despite the limitations of the measurements, some tentative comparisons may be made between PAH values for our survey and those presented in Table 2 of this report.

The results from the other urban surveys (i.e. those undertaken in South Kensington, Birmingham and Manchester) are compared with results from the 1995/96 LWEP survey (Table 10). It would appear that the concentrations of the PAH species recorded at the three urban sites are largely comparable with those recorded in the 1995/96 LWEP survey.

Comparison of the Results of the 1995/96 LWEP PAH Survey with the Results of Other Surveys in Urban Areas of the UK Table 7:

Compound and Al	Abbreviation	Average	e Particulate PA	Average Particulate PAH Concentration (ng m <sup>-3</sup> )	(ng m <sup>-3</sup> )
		LWEP	South	Birmingham	Manchester
Phenanthrene	PHE	1.19	0.11	1.10	0.40
Anthracene	ANT	0.14	0.18	0.40	0.05
Fluoranthene	FLH	1.89	0.81	1.20	0.63
Pyrene	PYR	2.46	0.79	2.40	08.0
Benzo [k] fluoranthene	BKF	0.79	0.68	1 10	2.00
Benzo [a] pyrene	BaP	0.80	1.44	0.73	1.60
Benzo [ghi]perylene	BghiP	1.67	3.30	1.90	3.10
Coronene	COR	1.27	1.67	1.00	1.40



# 9 Assessment of Effects of PAH on the London Population

Any statement on the health implications of the data summarised in this report is very difficult because of the very limited quantitative information available on the health effects of the substances measured. Since several of them are established carcinogens, and since no threshold has been demonstrated for the carcinogenic effects of BaP, the most thoroughly studied and most carcinogenic PAH in ambient air, it can be assumed that some risk exists; the question is just how small this risk might be.

Condensates from vehicle exhausts have been shown to be carcinogenic in tests with laboratory animals, but this activity is concentrated in the 4-7 ring fraction. Several of the 2-3 ring compounds measured in this survey - such as Np, FLH and ANT - have little or no carcinogenic activity, and so are of less concern.

The available risk estimates come from occupational groups, and hence assume the possibility of extrapolating downwards through several orders of magnitude to estimate the risks of ambient exposures. Most of these occupational studies relate to respiratory cancer in coke-oven workers, with the most important studies conducted in the US and Germany. On the basis of such evidence up to the mid-1980's, WHO provided a risk estimate for BaP exposure of 1 cancer per 10,000 for a working lifetime exposure to 1 ng m<sup>-3</sup>.

The average concentration of BaP recorded at background sites in present survey, as an annual mean, was 0.22 ng m<sup>-3</sup>. Urban background sites have been used in this calculation as such sites are considered representative of levels to which the majority of people are exposed to for significant periods of time. Hence, for an individual living at a background location over a lifetime, the respiratory cancer risk at these sites would be 22 x 10<sup>-6</sup>. The risk would be correspondingly higher for individuals who only spend a significant length of time at roadside locations. For example, the average concentration of BaP recorded at roadside sites in the present survey was 0.77 ng m<sup>-3</sup>, resulting in respiratory cancer risk of 77 x 10<sup>-6</sup>.

Furthermore, there are other significant sources of inhaled PAH, in particular cigarette smoking. The WHO in 1987 quoted that a single 'low tar' cigarette will deliver 10 ng of BaP in the mainstream smoke. For comparison, assuming a daily inhaled volume of 20 m<sup>3</sup>, an individual spending 8 hours per day at the most polluted site in this study would inhale 20 ng - equivalent to smoking one cigarette every one and a half days.

The PAH composition of coke-oven emissions, cigarette smoke, diesel exhausts and ambient London air may be very different. Since there is only limited information on the relative carcinogenicity of different PAHs, it is uncertain to what extent it is possible to extrapolate data from exposure to one of these to the effects of other types of exposure. Given these and the many other uncertainties involved in risk assessment based on occupational exposures, the risks quoted here are very uncertain. As far as can be ascertained, the risks for individuals with the highest exposure to roadside PAH levels



in London are finite but very small; for smokers, they also appear trivial compared with those through PAH exposure from cigarette smoke.

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### 10 Discussion

This survey was designed to give a snapshot of the PAH concentrations at roadside and background sites across London, and the short sampling periods used do not, therefore permit a detailed analysis of the intersite differences. The PAH survey conducted at Southwark Street, London, SE1 aimed to provide an insight into the variation in concentration at one site over time.

Despite the limitations of the LWEP PAH survey it is possible to identify some general trends in the data set, some of which are supported by findings from the Southwark Street, London, SE1 survey:

- As in previous LWEP PAH surveys wide variations in concentration were found, from compound to compound, site to site and season to season. This is a general feature of PAH concentrations surveyed in urban areas.
- "Roadside" and "intermediate" concentrations were consistently higher than the "background" sites, emphasising the importance of road traffic as a source of PAH.
- The PAH profiles for the six most carcinogenic compounds monitored were consistent across all sites, with concentrations of BghiP, BbF and BaA/CHR being consistently highest and those of DahA being consistently lowest.
- Use of BaP as an index of carcinogenicity indicates that concentrations of BaP in London monitored during the 1995/96 survey were considerably below European guidelines.
- Comparison of the results of the 1995/96 LWEP PAH survey with other surveys in South Kensington, Birmingham and Manchester indicates that the results are broadly similar across all four surveys.
- The mean concentration of BaP monitored during the LWEP 1995/96 PAH survey was well below European guidelines and did not exceed the recommended US EPA guideline value of 1 ng m<sup>-3</sup>. However, annual average BaP concentrations measured at exceeded the US EPA guideline at Brent, Ealing, Harrow, Hammersmith and Fulham and Kingston.
- The average BaP concentrations recorded at background and roadside sites were 0.22 and 0.77 ng m<sup>-3</sup> respectively, which for an individual exposed to these concentrations over a lifetime would represent a 22 x 10<sup>-6</sup> and 77 x 10<sup>-6</sup> risk of respiratory cancer.
- In view of the limited quantitative information available on the health effects of the PAH species measured, it is considered that the health risks for individuals with the highest exposure to roadside PAH levels in London are finite but very small; for smokers the risks would appear trivial compared with those associated with exposure to PAH from cigarette smoke.



The fixed site monitoring conducted at Southwark St., London SE1 provided some valuable information concerning the ambient PAH concentration the ambient PAH concentration at one site over time. The survey indicated the importance of vehicle emissions as the major PAH source in this area and the influence that seasonal factors exert on ambient PAH concentrations.

Diesel emissions from vehicles are thought to be the primary source of PAH in urban areas. Some PAH species are emitted in higher concentrations from diesel engines including known carcinogen benzo (a) pyrene (BaP).

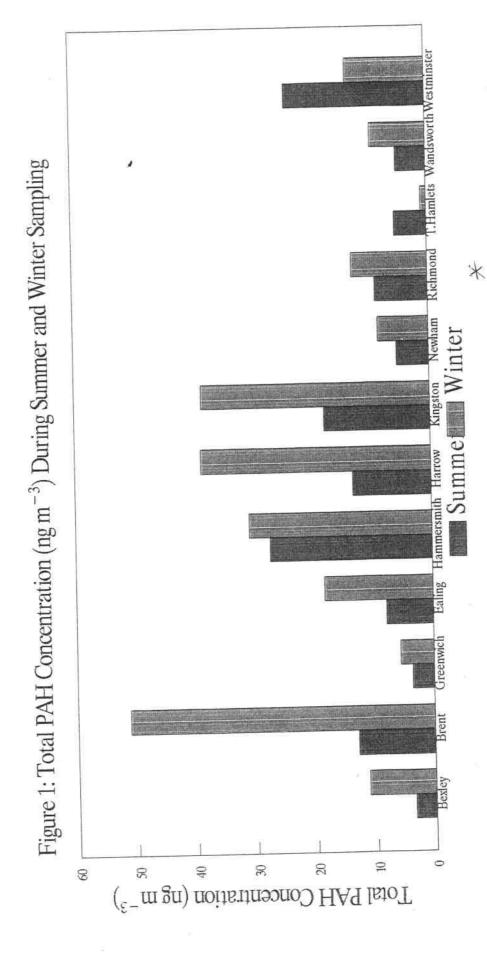
With respect to diesel emissions from cars, an amending European Community (EC) Directive (91/441/EEC) published in August 1991 consolidates European legislation on vehicle emissions and sets more stringent emission standards which are mandatory and have applied to all new cars registered from 1 January 1993, and to new models from 31 July 1992. To meet the standards diesel engine vehicles require "state-of-the-art" technology.

With respect to heavy goods vehicles (HGVs), EC Directive 91/542/EEC published in October 1991 tightened standards for gaseous emissions in two stages. The first stage reductions were planned for 1 July 1992 (new models) and 1 October 1993 (all new vehicles). The second stage controls were planned for 1 October 1995 (new models) and 1 October 1996 (all new vehicles), these match the very stringent 'US 1994' diesel standards. The new limits will require an improvement in the quality of diesel fuel.

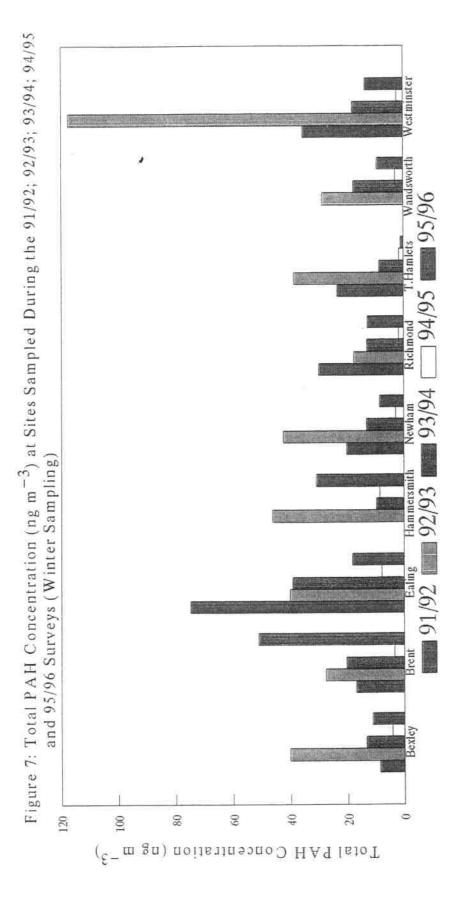
This European legislation will bring about a reduction on unit emissions of controlled pollutants, these being nitrogen oxides, carbon monoxide and hydrocarbons, from both cars and goods vehicles. A guideline for PAHs is due to be published by EPAQS in 1997.

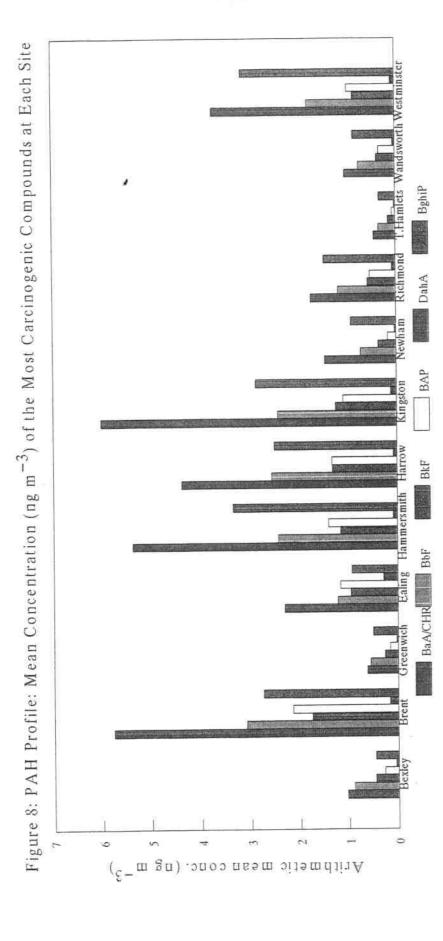
However, the effect these reductions will have on ambient PAH concentrations in urban air is not yet clear as the legislation will be operating against an increase in the diesel fleet. Currently, only 6% of the cars on the road are diesel but, if current sales are maintained it is predicted that within 10 years the diesel car population could rise to 20% (4).

The London wide PAH survey provides a valuable database of information on hydrocarbon levels in London, particularly at roadside locations, allowing the impact of recent legislation on London's air quality to be monitored.



3





Appendix B

Table 1 - Results of Summer 1995 Sampling. PAH Concentrations at Each Site (ng m<sup>-3</sup>)

FL       FL       CHR         0.29       0.29       0.31       0.01       0.32       0.47       0.44         0.61       0.75       0.99       0.12       1.27       1.50       1.89         0.52       0.21       0.34       0.01       0.40       0.58       0.39         0.74       0.53       0.07       0.75       0.17       0.89       1.10         2.01       0.38       1.07       0.52       2.13       3.51       4.89         0.70       0.40       0.71       0.15       0.67       1.99         0.74       0.34       1.07       0.04       1.82       3.50       1.99         0.44       0.34       1.07       0.04       1.82       3.50       1.99         0.60       0.18       0.49       0.01       0.46       0.67       0.54         0.60       0.18       0.49       0.01       0.93       1.33       0.94         1.15       0.21       0.56       0.05       0.52       0.99       0.67         0.05       0.05       0.01       0.40       0.72       0.58         0.77       0.30       0.44       1.69	Borough	NP	ACE/	PHE	ANT	FLH	PYR	BaA/	BbF	BkF	BaP	DahA	BghiP	COR	Total
Bexley         0.29         0.29         0.31         0.01         0.32         0.47         0.44           Brent         0.61         0.75         0.99         0.12         1.27         1.50         1.89           Greenwich         0.62         0.21         0.34         0.01         0.40         0.58         0.39           Hammersmith         0.74         0.53         0.07         0.75         0.17         0.89         1.10           Harrow         0.70         0.40         0.71         0.52         2.13         3.51         4.89           Kingston         0.70         0.40         0.71         0.04         0.75         1.99           Nwham         0.93         0.25         0.41         0.04         0.04         0.67         1.99           Richmond         0.60         0.18         0.49         0.01         0.46         0.67         0.54         0.67           Tower Hamlets         1.15         0.21         0.56         0.05         0.99         0.67         0.58           Westminster         0.77         0.24         1.07         0.44         1.69         0.31         0.49         0.71         0.69         0.71 </th <th>ű</th> <th></th> <th>FL</th> <th></th> <th></th> <th></th> <th></th> <th>CHR</th> <th></th> <th></th> <th></th> <th></th> <th></th> <th></th> <th></th>	ű		FL					CHR							
Brent         0.61         0.75         0.99         0.12         1.27         1.50         1.89           Greenwich         0.52         0.21         0.34         0.01         0.40         0.58         0.39           Hammersmith         0.74         0.53         0.07         0.75         0.17         0.89         1.10           Harrow         0.70         0.40         0.71         0.15         0.67         1.37         1.76           Kingston         0.44         0.34         1.07         0.04         1.82         3.50         1.99           Nwham         0.93         0.25         0.41         0.04         1.82         3.50         1.99           Richmond         0.60         0.18         0.49         0.01         0.93         1.33         0.94           1         Wandsworth         0.60         0.18         0.49         0.01         0.40         0.72         0.99         0.67           2         Westminster         0.79         0.24         1.07         0.44         1.69         3.37         4.80           Arithmetic Mean         0.77         0.30         0.51         0.69         1.24         1.16	xley	0.29	0.29	0.31	0.01	0.32	0.47	0.44	0.45	0.20	0.25	0.04	0.21	0.38	3.65
Greenwich         0.52         0.21         0.34         0.01         0.40         0.58         0.39           Hammersmith         0.74         0.53         0.07         0.75         0.17         0.89         1.10           Harrow         0.70         0.70         0.70         0.71         0.15         2.13         3.51         4.89           Kingston         0.70         0.40         0.71         0.15         0.67         1.37         1.76           Nwham         0.93         0.25         0.41         0.04         0.8         0.67         0.54           Nwham         0.60         0.18         0.49         0.01         0.93         1.33         0.94           I         Wandsworth         0.60         0.18         0.49         0.01         0.93         1.33         0.99         0.67           I         Westminster         0.05         0.19         0.41         0.01         0.40         0.72         0.58           Arithmetic Mean         0.77         0.30         0.51         0.69         1.54         1.16           Arithmetic Mean         0.70         0.30         0.51         0.69         1.24         1.16 </td <td>ent</td> <td>0.61</td> <td>0.75</td> <td>0.99</td> <td>0.12</td> <td>1.27</td> <td>1.50</td> <td>1.89</td> <td>1.43</td> <td>0.62</td> <td>0.64</td> <td>0.08</td> <td>1.62</td> <td>1.51</td> <td>13.04</td>	ent	0.61	0.75	0.99	0.12	1.27	1.50	1.89	1.43	0.62	0.64	0.08	1.62	1.51	13.04
Ealing         0.74         0.53         0.07         0.75         0.17         0.89         1.10           Hammersmith         2.01         0.38         1.07         0.52         2.13         3.51         4.89           Harrow         0.70         0.40         0.71         0.15         0.67         1.37         1.76           Kingston         0.44         0.34         1.07         0.04         1.82         3.50         1.99           Nwham         0.93         0.25         0.41         0.04         0.67         0.54         0.54           Richmond         0.60         0.18         0.49         0.01         0.93         1.33         0.94           0         Tower Hamlets         1.15         0.21         0.56         0.05         0.52         0.99         0.67           1         Wandsworth         0.05         0.19         0.41         0.01         0.40         0.72         0.99         0.58           Arithmetic Mean         0.77         0.33         0.63         0.18         0.90         1.58         1.67           Account Mean         0.69         0.30         0.51         0.69         1.24         1.16 </td <td>eenwich</td> <td>0.52</td> <td>0.21</td> <td>0.34</td> <td>0.01</td> <td>0.40</td> <td>0.58</td> <td>0.39</td> <td>0.37</td> <td>0.17</td> <td>0.14</td> <td>0.03</td> <td>0.41</td> <td>0.19</td> <td>3.76</td>	eenwich	0.52	0.21	0.34	0.01	0.40	0.58	0.39	0.37	0.17	0.14	0.03	0.41	0.19	3.76
Hammersmith         2.01         0.38         1.07         0.52         2.13         3.51         4.89           Harrow         0.70         0.40         0.71         0.15         0.67         1.37         1.76           Kingston         0.04         0.34         1.07         0.04         1.82         3.50         1.99           Nwham         0.93         0.25         0.41         0.04         0.46         0.67         0.54           I         Richmond         0.60         0.18         0.49         0.01         0.93         1.33         0.94           O         Tower Hamlets         1.15         0.21         0.56         0.05         0.05         0.99         0.67           Westminster         0.05         0.19         0.41         0.01         0.40         0.72         0.58           Arithmetic Mean         0.77         0.33         0.63         0.18         0.90         1.58         1.67           Arithmetic Mean         0.77         0.30         0.51         0.69         1.24         1.16	ling	0.74	0.53	0.07	0.75	0.17	68.0	1.10	0.61	0.87	1.22	0.47	0.36	0.10	7.88
Harrow         0.70         0.40         0.71         0.15         0.67         1.37         1.76           Kingston         0.44         0.34         1.07         0.04         1.82         3.50         1.99           Nwham         0.93         0.25         0.41         0.04         0.46         0.67         0.54           Richmond         0.60         0.18         0.49         0.01         0.93         1.33         0.94           1         Wandsworth         0.05         0.19         0.41         0.01         0.40         0.72         0.99         0.67           2         Westminster         0.79         0.24         1.07         0.44         1.69         3.37         4.80           Arithmetic Mean         0.77         0.33         0.63         0.18         0.90         1.58         1.67	ummersmith	2.01	0.38	1.07	0.52	2.13	3.51	4.89	2.58	1.04	1.02	0.11	4.27	3.84	27.34
Kingston         0.44         0.34         1.07         0.04         1.82         3.50         1.99           Nwham         0.93         0.25         0.41         0.04         0.46         0.67         0.54           Richmond         0.60         0.18         0.49         0.01         0.93         1.33         0.94           D         Tower Hamlets         1.15         0.21         0.56         0.05         0.05         0.99         0.67           1         Wandsworth         0.05         0.19         0.41         0.01         0.40         0.72         0.58           2         Westminster         0.79         0.24         1.07         0.44         1.69         3.37         4.80           Arithmetic Mean         0.77         0.33         0.63         0.18         0.90         1.58         1.67	urrow	0.70	0.40	0.71	0.15	0.67	1.37	1.76	1.42	0.58	0.63	90.0	2.41	2.47	13.32
Nwham         0.93         0.25         0.41         0.04         0.46         0.67         0.54           Richmond         0.60         0.18         0.49         0.01         0.93         1.33         0.94           1         Tower Hamlets         1.15         0.21         0.56         0.05         0.52         0.99         0.67           1         Wandsworth         0.05         0.19         0.41         0.01         0.40         0.72         0.58           2         Westminster         0.77         0.24         1.07         0.44         1.69         3.37         4.80           Arithmetic Mean         0.77         0.33         0.63         0.18         0.90         1.58         1.67	ngston	0.44	0.34	1.07	0.04	1.82	3.50	1.99	1.99	0.79	0.78	60.0	1.51	3.60	17.95
Richmond         0.60         0.18         0.49         0.01         0.93         1.33         0.94           0         Tower Hamlets         1.15         0.21         0.56         0.05         0.52         0.99         0.67           1         Wandsworth         0.05         0.19         0.41         0.01         0.40         0.72         0.58           2         Westminster         0.79         0.24         1.07         0.44         1.69         3.37         4.80           Arithmetic Mean         0.77         0.33         0.63         0.18         0.90         1.58         1.67           Scometric Mean         0.69         0.30         0.51         0.06         0.69         1.24         1.16	wham	0.93	0.25	0.41	0.04	0.46	0.67	0.54	0.42	0.19	0.20	0.03	89.0	0.78	2.60
Hamlets         1.15         0.21         0.56         0.05         0.52         0.99         0.67           worth         0.05         0.19         0.41         0.01         0.40         0.72         0.58           inster         0.79         0.24         1.07         0.44         1.69         3.37         4.80           0.77         0.33         0.63         0.18         0.90         1.58         1.67           0.69         0.30         0.51         0.06         0.69         1.24         1.16	chmond	09.0	0.18	0.49	0.01	0.93	1.33	0.94	0.84	0.36	0.43	0.05	1.31	1.50	96.8
worth         0.05         0.19         0.41         0.01         0.40         0.72         0.58           inster         0.79         0.24         1.07         0.44         1.69         3.37         4.80           0.77         0.33         0.63         0.18         0.90         1.58         1.67           0.69         0.30         0.51         0.06         0.69         1.24         1.16	wer Hamlets	1.15	0.21	0.56	0.05	0.52	66.0	0.67	0.55	0.23	80.0	0.03	0.54	0.03	5.61
inster 0.79 0.24 1.07 0.44 1.69 3.37 4.80 0.77 0.33 0.63 0.18 0.90 1.58 1.67 0.69 0.30 0.51 0.06 0.69 1.24 1.16	andsworth	0.05	0.19	0.41	0.01	0.40	0.72	0.58	0.48	0.20	0.17	0.03	09.0	0.88	5.17
0.77 0.33 0.63 0.18 0.90 1.58 1.67	estminster	0.79	0.24	1.07	0.44	1.69	3.37	4.80	2.34	1.00	1.22	0.09	4.64	2.18	23.86
0.69 0.30 0.51 0.06 0.69 1.24 1.16	Mean	0.77	0.33	0.63	0.18	06.0	1.58	1.67	1.12	0.52	0.57	0.09	1.55	1.46	11.35
1000	Mean	69.0	0:30	0.51	90.0	69.0	1.24	1.16	0.88	0.42	0.41	90.0	1.00	0.74	60.6

Appendix B

Table 2 - Results of Winter 1996 Sampling. PAH Concentrations at Each Site (ng m<sup>-3</sup>)

	Borough	ď	ACE/	PHE	ANT	FLH	PYR	BaA/	BbF	BkF	BaP	DahA	BghiP	COR	Total
			FL					CHR					)		
1	Bexley	0.27	0.23	1.34	0.04	2.08	2.02	1.64	1.35	0.72	0.31	90.0	0.73	0.40	11.19
2	Brent	0.37	19.0	5.02	0.35	8.02	9.37	9.64	4.75	2.88	3.63	0.26	3.87	2.22	51.07
3	Greenwich	0.20	0.90	0.55	0.03	0.82	0.73	0.87	0.75	0.37	0.19	0.02	0.61	0.50	5.73
4	Ealing	0.15	0.23	1.79	0.11	2.76	3.37	3.51	1.84	1.04	1.11	0.11	1.49	0.78	18.30
5	Hammersmith	0.35	0.26	2.37	0.24	5.18	7.32	5.85	2.26	1.29	1.81	0.07	2.43	1.35	30.78
9	Harrow	0.36	0.42	4.76	0.21	6.87	7.33	7.01	3.69	2.07	2.04	0.09	2.58	1.35	38.76
7	Kingston	1.02	0.37	2.07	90.0	3.66	3.89	10.03	2.85	1.70	1.41	0.16	4.24	2.78	38.54
8	Nwham	0.24	0.14	0.44	0.03	0.71	1.00	2.37	1.03	0.56	0.14	0.04	1.15	0.80	8.66
6	Richmond	0.42	0.17	0.97	0.04	1.54	1.62	2.54	1.52	0.78	0.63	0.08	1.64	1.03	12.99
10	Tower Hamlets	0.02	0.01	0.05	60.0	60.0	0.12	0.21	0.14	0.07	0.04	0.01	0.11	0.07	1.04
111	Wandsworth	0.54	0.12	0.84	0.05	1.24	1.28	1.47	1.02	0.55	0.48	90.0	1.09	0.71	9.46
12	Westminster	0.55	0.16	0.91	0.05	1.70	2.17	2.63	1.25	0.71	0.71	0.07	1.64	1.03	13.58
Arithm	Arithmetic Mean	0.37	0.31	1.76	0.11	2.89	3.35	3.98	1.87	1.06	1.04	80.0	1.80	1.09	20.01
Geome	Geometric Mean	0.28	0.21	1.08	0.07	1.78	2.05	2.60	1.40	0.77	0.59	90.0	1.31	0.81	13.64
Winter	Winter/Summer Ratio	0.41	69.0	2.13	1.23	2.59	1.65	2.25	1.58	1.85	1.45	0.97	1.31	1.10	1.50

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Appendix B

Table 3 - Average PAH Concentrations at Each Site - Arithmetic Mean (ng m<sup>-3</sup>)

ACE/ PHE ANT FLH PYR I FL	0.26 0.83 0.03 1.20 1.25	0.71 3.00 0.23 4.65 5.44	0.56 0.44 0.02 0.61 0.66	0.38 0.93 0.43 1.47 2.13	0.32 1.72 0.38 3.66 5.42	0.41 2.73 0.18 3.77 4.35	0.36 1.57 0.05 2.74 3.70	0.20 0.42 0.04 0.59 0.83	0.18 0.73 0.02 1.23 1.48	0.11 0.31 0.07 0.30 0.56	0.16 0.62 0.03 0.82 1.00	0.20 0.99 0.25 1.69 2.77	0.32 1.19 0.14 1.89 2.46	0.78 0.03 0.09 1.40 1.05
R BaA/ CHR	5 1.04	4 5.77	6 0.63	3 2.31	2 5.37	5 4.39	0 6.01	3 1.46	8 1.74	6 0.44	0 1.03	7 3.72	6 2.82	100
BbF BkF	0.90 0.46	3.09 1.75	0.56 0.27	1.22 0.95	2.42 1.16	2.56 1.32	2.42 1.24	0.72 0.37	1.18 0.57	0.34 0.15	0.75 0.38	1.80 0.85	1.50 0.79	100
BaP	0.28	2.14	0.16	1.17	1.41	1.33	1.09	0.17	0.53	90.0	0.33	0.97	08.0	0
DahA BghiP	0.05 0.47	0.17 2.74	0.03 0.51	0.29 0.93	0.09 3.35	0.07 2.50	0.12 2.88	0.03 0.92	0.07 1.47	0.02 0.33	0.04 0.85	0.08 3.14	0.09 1.67	
COR	0.39	1.87	0.35	0.44	2.59	1.91	3.19	0.79	1.27	0.05	0.80	1.61	1.27	, 00
Total	7.42	32.06	4.75	13.09	29.06	26.04	28.25	7.13	10.97	3.33	7.32	18.72	15.68	700