

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*

<i>Compound and abbreviation</i>		<i>Cancer rating<sup>(a)</sup></i>	<i>Rings</i>	<i>Mol wt</i>
Naphthalene	Np	?	2	128
Acenaphthene	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

## 7.0 RESULTS

The concentrations of the PAH compounds measured at each site during the summer and winter sampling periods are given in Table 6. The table also gives 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, and ratio of the winter to summer geometric mean concentration for each compound.

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 Table 7.

When analysing the results it is important to remember the short duration of the measurements; two weeks (at most) at each site for each season. Furthermore, the measurement periods were not, in general, coincident at all thirteen sites. Air pollution levels are, of course, very dependent on weather conditions, and it is therefore probable that some of the differences in PAH concentrations from site-to-site (in a given season) were due to changes in weather conditions from sampling period to sampling period.

### 7.1 Concentrations - Overview

A general overview of the concentrations found is presented in Figure 1, which shows (for each site) the total PAH concentrations 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.

Points of note at this stage are the extremely high total winter concentrations at Kensington & Chelsea and Westminster,  $195.53 \text{ ng m}^{-3}$  and  $117.56 \text{ ng m}^{-3}$  respectively, and both more than 2.5 times higher than the total concentration recorded at any other site during the winter period. As mentioned in Section 6.3 problems were encountered with the sampling equipment at Kensington & Chelsea in winter and therefore these results are unlikely to accurately reflect ambient concentrations at this site.

We would expect winter PAH concentrations to be relatively high at the Westminster site, owing to the high building density in this area, and the resulting influence of space heating during winter months. However, the unusually high concentrations recorded are difficult to explain, particularly bearing in mind the rooftop location of this site, and the possibility of site specific effects associated with local combustion sources should be investigated.

Table 6 Results of Summer and Winter Sampling. PAH Concentrations at Each Site (ng m<sup>-3</sup>)

## SUMMER

Site	Borough	NP	ACE/FL	PHE	ANT	FLH	PYR	BaA/CHR	BbF	BkF	BaP	DahA	BghiP	COR	Total
1	Bexley	0.1	0.1	0.01	0.1	0.29	0.02	0.25	0.84	0.15	0.13	0.02	0.14	0.03	2.18
2	Brent	0.1	0.24	0.05	0.02	0.2	0.06	1.22	5.92	0.86	0.58	0.2	1.73	0.62	11.8
3	Ealing	0.01	0.26	0.27	0.07	0.41	0.56	1.65	4.77	0.74	0.73	0.18	1.5	0.59	11.74
4	Hammersmith	0.1	0.62	0.51	0.13	1.39	1.67	3.62	10.03	1.67	1.72	0.36	3.23	1.17	26.22
5	Harrow	0.7	1.66	0.56	0.32	1.71	2.3	2.65	6.9	1.3	1.51	0.24	2.21	0.79	22.85
6	Hounslow	0.1	0.15	0.06	0.05	0.35	0.24	0.67	3.17	0.53	0.59	0.11	1.0	0.32	7.34
7	Kingston	0.1	0.17	0.69	0.03	0.35	0.1	0.7	1.87	0.31	0.33	0.09	0.44	0.14	5.32
8	Kingston	1.05	3.37	1.31	0.17	0.34	0.3	0.74	2.87	0.55	0.45	0.08	0.64	0.17	12.04
9	Newham	0.53	2.02	0.72	0.09	0.13	0.1	0.23	1.01	0.2	0.12	0.03	0.22	0.07	5.47
10	Richmond	0.1	0.1	0.05	0.02	0.11	0.1	0.18	0.8	0.13	0.17	0.03	0.25	0.09	2.13
11	Tower Hamlets	0.1	0.25	0.05	0.02	0.2	0.02	0.29	1.24	0.2	0.14	0.04	0.29	0.12	2.96
12	Wandsworth	0.1	0.43	0.15	0.05	0.37	0.19	0.73	2.59	0.44	0.46	0.13	1.07	0.43	7.14
13	Westminster	0.1	0.36	0.09	0.04	0.18	0.03	0.3	0.91	0.15	0.11	0.03	0.17	0.05	2.52
Arithmetic Mean		0.25	0.75	0.35	0.09	0.46	0.44	1.02	3.30	0.56	0.54	0.12	0.99	0.35	9.22
Geometric Mean		0.13	0.39	0.16	0.06	0.33	0.15	0.66	2.35	0.40	0.36	0.08	0.62	0.21	6.68

## WINTER

Site	Borough	NP	ACE/FL	PHE	ANT	FLH	PYR	BaA/CHR	BbF	BkF	BaP	DahA	BghiP	COR	Total
1	Bexley	0.24	0.62	1.19	0.18	2.86	4.33	4.97	13.36	2.31	4.68	0.58	3.85	1.01	40.18
2	Brent	0.27	1.05	0.31	0.16	0.96	1.88	3.49	9.91	1.71	3.06	0.39	3.2	1.02	27.41
3	Ealing	0.1	3.39	3.11	0.1	4.67	6.94	7.02	8.65	1.43	2.5	0.57	1.24	0.54	40.26
4	Hammersmith	0.11	2.19	1.57	0.47	2.76	3.0	6.89	16.05	2.35	4.29	0.31	4.56	1.64	46.18
5	Harrow *	0.1	1.73	3.24	0.1	0.2	3.24	3.24	11.97	1.42	0.1	0.01	0.1	0.03	24.48
6	Hounslow	0.1	1.13	0.88	0.17	1.92	2.53	2.75	8.7	1.4	2.1	0.41	1.93	0.56	24.58
7	Kingston *	1.67	3.01	0.2	0.1	6.94	24.57	32.36	62.41	10.5	18.3	2.44	24.9	8.13	195.53
8	Kingston	0.1	0.81	0.2	0.1	0.51	1.61	2.18	8.37	1.45	1.77	0.31	2.23	0.68	20.32
9	Newham	0.22	1.0	0.44	0.1	1.88	4.36	6.0	14.96	2.77	5.12	0.54	4.4	1.21	42.43
10	Richmond	0.1	0.71	0.35	0.15	1.09	2.2	1.77	6.28	1.1	1.49	0.24	1.76	0.54	17.78
11	Tower Hamlets	0.22	1.15	0.91	0.33	2.0	4.36	7.13	12.61	2.04	3.49	0.28	3.24	0.92	38.68
12	Wandsworth	0.28	0.84	0.62	0.16	1.22	3.98	3.45	8.86	1.5	3.06	0.41	3.23	1.0	28.6
13	Westminster	0.42	21.4	19.94	7.37	13.71	17.03	8.71	14.93	2.44	5.18	0.4	4.71	1.33	117.56
Arithmetic Mean		0.30	3.00	2.54	0.73	3.13	6.16	6.92	15.16	2.49	4.24	0.53	4.57	1.43	51.08
Geometric Mean		0.20	1.57	0.92	0.21	1.87	4.28	4.99	12.38	2.02	2.72	0.34	2.63	0.81	38.98
Winter/Summer Ratios of Geometric Mean		1.48	4.04	5.74	3.51	5.74	28.32	7.58	5.27	5.06	7.51	4.17	4.22	3.93	5.83

\*Note: For these two sites the volume of air sampled during the winter period was considerably less than 500m<sup>3</sup> and therefore these data must be treated with some caution (see Section 6.3)

Table 7 Average Concentrations - Arithmetic Mean (ng m<sup>-3</sup>)

Site	Borough	NP	ACE/FL	PHE	ANT	FLH	PYR	BaA/CHR	BbF	BkF	BaP	DahA	BghiP	COR	Total
1	Bexley	0.17	0.36	0.6	0.14	1.575	2.175	2.61	7.1	1.23	2.405	0.3	1.995	0.52	1.63
2	Brent	0.185	0.645	0.18	0.09	0.58	0.97	2.355	7.915	1.285	1.82	0.295	2.465	0.82	1.51
3	Ealing	0.055	1.825	1.69	0.085	2.54	3.75	4.335	6.71	1.085	1.615	0.375	1.37	0.565	2.00
4	Hammersmith	0.105	1.405	1.04	0.3	2.075	2.335	5.255	13.04	2.01	3.005	0.335	3.895	1.405	2.79
5	Harrow *	0.4	1.695	1.9	0.21	0.955	2.77	2.945	9.435	1.36	0.805	0.125	1.155	0.41	1.86
6	Hounslow	0.1	0.64	0.47	0.11	1.135	1.385	1.71	5.935	0.965	1.345	0.26	1.465	0.44	1.23
7	Kensington *	0.885	1.59	0.445	0.065	3.645	12.335	16.53	32.14	5.405	9.315	1.265	12.67	4.135	7.73
8	Kingston	0.575	2.09	0.755	0.135	0.425	0.955	1.46	5.62	1	1.11	0.195	1.435	0.425	1.24
9	Newham	0.375	1.51	0.58	0.095	1.005	2.23	3.115	7.985	1.485	2.62	0.285	2.31	0.64	1.86
10	Richmond	0.1	0.405	0.2	0.085	0.6	1.15	0.975	3.54	0.615	0.83	0.135	1.005	0.315	0.77
11	Tower Hamlets	0.16	0.7	0.48	0.175	1.1	2.19	3.71	6.925	1.12	1.815	0.16	1.765	0.52	1.60
12	Wandsworth	0.19	0.635	0.385	0.105	0.795	2.085	2.09	5.725	0.97	1.76	0.27	2.15	0.715	1.38
13	Westminster	0.26	10.88	10.015	3.705	6.945	8.53	4.505	7.92	1.295	2.645	0.215	2.44	0.69	4.62
Arithmetic Mean		0.27	1.88	1.44	0.41	1.80	3.30	3.97	9.23	1.53	2.39	0.32	2.78	0.89	2.32
Geometric Mean		0.16	0.78	0.39	0.11	0.79	0.8	1.81	5.39	0.9	0.99	0.17	0.78	0.41	2.53

\*Note: For these two sites the volume of air sampled during the winter period was considerably less than 500m<sup>3</sup> and therefore these data must be treated with some caution (see Section 6.3)



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

## 7.2 *Comparison of Roadside and Background Sites*

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

The sites that can be described as 'roadside' are 2 (Brent), 3 (Ealing), 4 (Hammersmith & Fulham), 5 (Harrow), 7 (Kensington & Chelsea), 8 (Kingston-upon-Thames), 9 (Newham), 10 (Richmond), 11 (Tower Hamlets) and 12 (Wandsworth).

The Westminster site (site 13) was originally classified as 'background' owing to its rooftop location. However, in the light of the results for this site as discussed above, this site has been withdrawn from the 'roadside/background' classification and is plotted separately in Figure 2. This leaves two 'background' sites; site 1 (Bexley) and site 6 (Hounslow).

It can be seen that the roadside concentrations are consistently higher than the background ones. This result emphasises the importance of road traffic as a source of PAHs. It should be noted that concentrations at Westminster consistently exceed mean roadside concentrations, with the exception of the higher molecular weight species DahA, BghiP and COR. This is consistent with the fact that BghiP and COR have been suggested as markers for vehicle emissions.

With the exception of Kensington & Chelsea and Westminster, the highest overall total PAH concentration was recorded at site 4 (Hammersmith) followed by site 3 (Ealing). These are both sites at the facade of buildings within a few metres of busy roads.

Low overall concentrations were recorded at 'background' sites 1 and 6 (Bexley and Hounslow), but lower concentrations were recorded at some 'roadside' sites, namely site 2 (Brent), 10 (Richmond), 11 (Tower Hamlets) and site 12 (Wandsworth). The relatively low concentrations recorded at Brent and Wandsworth may be attributable to the fact that at these sites the sampler was located at the rear of buildings adjoining the

road, rather than at the building facade. The relatively low concentrations at Richmond and Tower Hamlets are more difficult to explain, but may be attributable to factors such as volume of traffic and distance from the kerb.

### 7.3 *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. However some mention must be made of the high winter/summer ratio for PYR. This appears to be due to winter concentrations of this compound being consistently higher but to some extent is driven by extremely high concentrations at two sites, Kensington & Chelsea and Westminster.

Benzo (ghi) perylene (BghiP) is one of the PAHs most often associated with vehicle emissions, and most often suggested as a marker for them. One might therefore expect it to have one of the lowest winter to summer ratios. It can be seen from Figure 3 that it has, but not strikingly so, the ratios for BghiP, BbF and KkF are roughly the same.

The relatively high total summer concentrations at site 4 (Hammersmith) and site 5 (Harrow) are largely driven by relatively high concentrations of BbF (10.03 ng m<sup>-3</sup> and 6.9 ng m<sup>-3</sup> respectively). The higher ratio for BaP is to some extent driven by high winter concentration at Kensington & Chelsea, which as explained previously must be treated with some caution.

### 7.4 *Comparison with Results of the 1991/92 LWEP PAH Survey*

For a number of sites, sampling has been undertaken at the same location throughout the 1991/92 and 1992/93 LWEP PAH surveys. For these sites (1, 2, 3, 7, 8, 9, 10, 11 and 13) some comparison of levels from year to year is possible.

For each of these sites, total PAH concentrations during 1991/92 and 1992/93 are illustrated in Figures 6 (for the summer period) and 7 (for the winter period). Note that the site at Richmond (site 10) was relocated during the 1992/93 survey and therefore no comparison can be made for the winter sampling period. Also, no summer measurements

were made at Tower Hamlets (site 11) in 1991/92 and therefore no comparison can be made for this site for this sampling period.

As Figures 6 and 7 illustrate, there is no clear annual trend. Summer concentrations were higher in 1992/93 at 3 sites, but lower at 5 sites. Winter concentrations appeared to be generally higher in 1992/93; being higher at 7 sites and lower at only 1 (Ealing). However, as mentioned previously winter data for 1992/93 for Kensington & Chelsea must be treated with some caution and 1992/93 winter data for Westminster requires further investigation regarding potential effects of local sources.

### 7.5 *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 importance of the different sources contributing to the sample.

For example, as was mentioned above, BghiP has been suggested as a marker for vehicle emissions. Coronene is also reported to be predominantly from vehicle emissions, whereas benz (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 results of atmospheric transport, and 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 shows a relatively clear patterned structure across all sites, including Kensington & Chelsea and Harrow, which perhaps relieves some of the concern regarding data for these sites. Concentrations of BbF are consistently highest at all sites and concentrations of DahA are consistently lowest.



### 7.6 BaP Concentration as a Percentage of all the 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:

$$\text{BaP conc.} \times 100 \div \text{sum of conc. (BaA/CHR + BbF + BkF + BaP + DahA + BghiP)}$$

This percentage has been calculated for the estimated annual average concentrations and the values are given in Table 8.

**Table 8: 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	15.4
2	Brent	11.3
3	Ealing	10.4
4	Hammersmith & Fulham	10.9
5	Harrow	5.1
6	Hounslow	11.5
7	Kensington & Chelsea	12.0
8	Kingston upon Thames	10.3
9	Newham	14.7
10	Richmond	11.7
11	Tower Hamlets	11.7
12	Wandsworth	13.6
13	Westminster	13.9
Arithmetic mean		11.7

Apart from the low value at site 5 (Harrow), which may be explained by sampling problems at this site during the winter period, the percentages are fairly consistent, varying between 10.3 and 15.4 %, with a mean of 11.7%.

### 7.7 *Comparison of Results with Guidelines for BaP*

If BaP is used as an index of PAH carcinogenicity, then some comparison of these BaP 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 our survey mean that any comparison can only be approximate.

The overall mean concentration of BaP varies between 0.81 ng m<sup>-3</sup> at Harrow and 9.32 ng m<sup>-3</sup> at Kensington and Chelsea. These are the 2 sites at which sampling problems were encountered during the winter period. If we remove these extremes from the data set the overall mean of the remaining data is 1.91 ng m<sup>-3</sup>, and BaP concentrations vary between 0.83 ng m<sup>-3</sup> at Richmond and 3.0 ng m<sup>-3</sup> at Hammersmith.

Across all sites (but excluding Kensington & Chelsea and Harrow from the calculations) the mean BaP concentration is considerably lower in summer (0.54 ng m<sup>-3</sup>) than winter (3.34 ng m<sup>-3</sup>). Winter concentrations were highest at Westminster (5.18 ng m<sup>-3</sup>), Newham (5.12 ng m<sup>-3</sup>), Bexley (4.68 ng m<sup>-3</sup>) and Hammersmith (4.29 ng m<sup>-3</sup>).

The survey results indicate that mean BaP concentrations in London are generally below European guidelines, but that the Dutch goal was estimated to have been exceeded or approached at 3 sites (Westminster, Newham and Bexley). The fact that Bexley is a 'background' site makes this a somewhat notable result.

In the context of current views on what might be considered an acceptable risk from environmental pollutants, an overall mean BaP concentration of 1.91 ng m<sup>-3</sup> can not be considered negligible. It exceeds the guideline value for BaP of 1 ng m<sup>-3</sup>, derived in Section 3.0 from USEPA estimates of 'acceptable risk'. Further, this figure is an average across sites and sampling periods, and recorded BaP concentrations were considerably higher on occasions, as described above.

### 7.8 *Comparisons with the Results of Other Surveys*

Because of the limited sampling periods used in our survey, and variation in sampling technique, regime and so forth, it is not appropriate to make detailed comparisons between ours and other surveys. However, bearing in mind all the limitations of the measurements, some comparison can be made between PAH values for our survey and those presented in Table 2 of this report.

Other urban surveys (i.e. those undertaken in South Kensington, Birmingham and Manchester) are of most relevance to the LWEP survey; rural values recorded at Folkestone and Ashford are, as would be expected, much lower than any of the urban series. Values of PAH species common to all these urban surveys are tabulated below to facilitate comparison between survey results.

It would appear that the results of all 4 urban surveys are broadly similar. There is some evidence to suggest that levels of the lower molecular weight species (PHE to PYR) are higher in the LWEP survey.

*Table 9: Comparison of the Results of the 1992/93 LWEP PAH Survey with the Results of Other Surveys in Urban Areas of the UK*

Compound and abbreviation		Average Particulate PAH Concentration (ng m <sup>-3</sup> )			
		LWEP Survey	South Kensington	Birmingham	Manchester
Phenanthrene	PHE	1.44	0.11	1.1	0.4
Anthracene	ANT	0.41	0.18	0.4	0.05
Fluoranthene	FLH	1.80	0.81	1.2	0.63
Pyrene	PYR	3.30	0.79	2.4	0.8
Benzo (k) fluoranthene	BkF	1.53	0.68	1.1	2.4
Benzo (a) pyrene	BaP	2.39	1.44	0.73	1.6
Benzo (ghi) perylene	BghiP	2.78	3.30	1.9	3.1
Coronene	COR	0.89	1.67	1.0	1.4

## 8.0 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 of course permit a detailed analysis of all the intersite differences.

However, despite some sampling problems at two sites it is possible to identify some general trends in the data set, the key findings of the 1992/93 survey being:

- 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' concentrations were consistently higher than 'background' ones, emphasising the importance of road traffic as a source of PAH;
- unusually high PAH concentrations were recorded at the Westminster site, and for most PAH species measured, concentrations were higher at this site than at 'roadside' sites, despite the rooftop location of the Westminster site;
- comparison of the results with last years survey reveals no clear annual trend, but some evidence of winter concentrations being higher in 1992/93 than the previous year;
- the PAH profile for the six most carcinogenic compounds monitored indicates a relatively clear patterned structure across all sites, with concentrations of BbF 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 are generally below European guidelines, but that the Dutch goal of 5 ng m<sup>-3</sup> was exceeded or approached at 3 sites. Furthermore, the overall mean BaP concentration recorded is estimated to be approximately twice the guideline value of 1 ng m<sup>-3</sup>, derived from the USEPA estimate of 'acceptable risk' for BaP;
- comparison of the results of the 1992/93 LWEPAH survey with other surveys in South Kensington, Birmingham and Manchester indicates that the results are broadly similar across all four surveys.

The short sampling periods used in this survey do limit data analysis and it would be difficult to make progress on source apportionment, and hence on methods of reducing PAH levels in London, without more extensive data. For this reason we intend to carry out continuous measurement of PAH throughout the year at one site during the 1993/94 LWEP PAH survey, in order to increase our knowledge in this area. Furthermore, as the results from the Westminster site indicate, it may be useful to investigate individual site locations in more detail, in order to identify any local combustion sources which may affect winter and/or summer PAH concentrations.

With regard to likely future trends in PAH concentrations in London, legislation relating to future control of diesel emissions from vehicles is of relevance, since diesel emissions are thought to be the primary source of PAH in urban areas.

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 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 is planned for 1 October 1995 (new models) and 1 October 1996 (all new vehicles) and matches 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 in unit emissions of controlled pollutants, these being nitrogen oxides, carbon monoxide and hydrocarbons, from both cars and goods vehicles. However, the effect these reductions will have on ambient PAH concentrations in urban air is not yet clear, particularly in light of the fact that sales of diesel engine cars have increasing significantly in recent years.

The London wide PAH surveys provide a valuable data base of information on hydrocarbon levels in London, particularly at the roadside, and their continuation will enable the impact of recent legislation on London's air quality to be monitored.



## 9.0 SUMMARY

- 9.1 The 1991/92 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. 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.
- 9.2 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  $10^{-4}$  per  $\text{ng m}^{-3}$ . 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.
- 9.3 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  $5 \text{ ng m}^{-3}$  and a guideline for the annual average BaP concentration proposed by the German Environmental Agency is  $10 \text{ ng m}^{-3}$ . The World Health Organisation has not recommended any guidelines for carcinogenic air pollutants, but 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. When considering environmental pollutants the US 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  $\text{ng m}^{-3}$ , the guideline value for BaP would be  $1 \text{ ng m}^{-3}$ .
- 9.4 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.
- 9.5 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. However, the analysis of PAH is included in the recently established UK TOMPS (Toxic Organic Micropollutants) monitoring programme and this should in the

future provide a valuable basis for data analysis and source reconciliation for these compounds.

- 9.6 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). 15 PAH compounds were selected for measurement, based upon US EPA recommendations with respect to air monitoring programmes.
- 9.7 Thirteen measurement sites were chosen, one in each of the Boroughs participating in the 1992/93 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. Sites were classified as 'roadside' and 'background'. All sites with the exception of three, were 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 were 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).
- 9.8 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. Each sample consisted of the particulate material in a volume of about 500 m<sup>3</sup> of air, however, 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<sup>3</sup>. For this reason these data must be treated with some caution.
- 9.9 The clean-up of extracted samples was carried out by standard methods, and the final extracts analysed for the 15 PAHs by high performance liquid chromatography with fluorescence detected. Adequate separation was not usually achieved for two pairs of isomers (acenaphthene/fluorene and benz (a) anthracene/chrysene) and these are therefore reported together. A result at or below the detection limit has been recorded as equal to the detection limit.
- 9.10 Survey results are tabulated in terms of total and individual PAH concentrations recorded at each site, summer, winter and overall mean concentrations and winter/summer ratios. The data set was manipulated so as to investigate intersite differences (particularly 'roadside' versus 'background'), winter/summer ratios, annual

trends, the PAH profile, percentage BaP and overall mean BaP concentration (for comparison with guidelines and standards) and comparison with the results of other surveys in urban areas.

9.11 The short sampling periods used in this survey do not of course permit a detailed analysis of all the intersite differences. However, despite some sampling problems at two sites (Harrow and Kensington & Chelsea) it is possible to identify some general trends in the data set, the key findings of the 1992/93 survey being:

- 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' concentrations were consistently higher than 'background' ones, emphasising the importance of road traffic as a source of PAH;
- unusually high PAH concentrations were recorded at the Westminster site, and for most PAH species measured, concentrations were higher at this site than at 'roadside' sites, despite the rooftop location of the Westminster site;
- comparison of the results with last years survey reveals no clear annual trend, but some evidence of winter concentrations being higher in 1992/93 than the previous year;
- the PAH profile for the six most carcinogenic compounds monitored indicates a relatively clear patterned structure across all sites, with concentrations of BbF 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 are generally below European guidelines, but that the Dutch goal of 5 ng m<sup>-3</sup> was exceeded or approached at 3 sites. Furthermore, the overall mean BaP concentration recorded is estimated to be approximately twice the guideline value of 1 ng m<sup>-3</sup>, derived from the USEPA estimate of 'acceptable risk' for BaP;
- comparison of the results of the 1992/93 London-wide PAH survey with other surveys in South Kensington (the most complete set of PAH measurements in the UK), Birmingham (at a height of 15m at Birmingham University at a distance of approximately 300m from a major road) and Manchester (preliminary results

from the Manchester TOMPS site, a rooftop site located in the city centre) indicates that the results are broadly similar across all four surveys.

- 9.12 It would be difficult to make progress on source apportionment, and hence on methods of reducing PAH levels in London, without more extensive monitoring undertaken over longer periods. For this reason we intend to carry out continuous measurement of PAH throughout the year at one site during the 1993/94 LWEP PAH survey, in order to increase our knowledge in this area. Furthermore, as the results from the Westminster site indicate, it may be useful to investigate individual site locations in more detail, in order to identify any local combustion sources which may affect winter and/or summer PAH concentrations.
- 9.13 With regard to likely future trends in PAH concentrations in London, legislation relating to future control of diesel emissions from vehicles is of relevance, since diesel emissions are thought to be the primary source of PAH in urban areas. However, despite the fact the European legislation (namely EC Directives 91/441/EEC and 91/542/EEC) will bring about a reduction in unit emissions of hydrocarbons from both diesel cars and goods vehicles (HGVs), the effect of these reductions on ambient PAH concentrations in urban air is not yet clear, particularly in light of the fact that sales of diesel engine cars have increased significantly in recent years.
- 9.14 The London wide PAH surveys provide a valuable data base of information on hydrocarbon levels in London, particularly at the roadside, and their continuation will enable the impact of recent legislation on London's air quality to be monitored.