Table 6 Results of Summer and Winter Sampling. PAH Concentrations at Each Site (ng m^{-3})

SUMMER

Site	Borough	NP	ACE/FL	PHE	ANT	FLH	PYR	BaA/CHR	BbF	BkF	BaP	DahA	BghiP	COR	Total
1	Bexley	ND	ND	0.17	ND	0.31	0.26	0.29	0.35	0.32	0.1	0.03	0.24	0.13	2.18
2	Brent	ND	ND	0.20	< 0.1	0.30	0.1	0.35	0.39	0.35	0.14	0.05	0.45	0.24	2.53
3	Ealing *	ND	ND	0.36	0.19	0.63	0.67	0.45	0.41	0.34	0.13	0.05	0.43	0.44	4.1
4	Greenwich	ND	ND	0.16	0.1	0.26	0.1	0.14	0.27	0.24	0.1	0.03	0.25	0.16	1.66
5	Hammersmith	0.1	ND	0.33	0.1	0.90	0.57	0.89	0.75	0.64	0.26	0.07	0.89	0.59	6.06
7	Hounslow	0.17	0.1	0.31	0.1	0.73	0.53	0.80	0.77	0.75	0.29	0.07	1.0	0.62	6.22
8	Kingston *	ND	ND	0.27	0.1	0.31	0.21	0.25	0.31	0.27	0.1	0.03	0.17	0.07	1.99
9	Newham	0.1	0.19	3.2	0.1	0.45	0.24	0.19	0.23	0.24	0.1	0.02	0.22	0.20	5.39
10	Richmond	ND	ND	0.15	0.1	0.46	0.34	0.27	0.31	0.34	0.15	0.04	0.27	0.14	2.55
11	Tower Hamlets	0.25	0.1	0.19	0.1	0.42	0.15	0.24	0.31	0.27	0.1	0.03	0.26	0.20	2.61
12	Wandsworth	0.1	ND	0.25	0.1	0.46	0.35	0.36	0.38	0.32	0.1	0.05	0.46	0.32	3.21
13	Westminster	0.1	ND	ND	ND	0.20	0.14	0.30	0.27	0.23	0.1	0.03	0.19	0.09	1.6
Arithmetic Mean		0.14	0.13	0.51	0.11	0.45	0.31	0.38	0.40	0.36	0.14	0.04	0.40	0.27	3.34
Geometric Mean		0.10	0.12	0.29	0.1	0.41	0.22	0.33	0.37	0.33	0.11	0.04	0.34	0.21	1.1

*Note: Volume of air sampled during the summer period was considerably less than 500 m3 and therefore these data must be treated with some caution (see Section 7.3)

Note: No data available for Harrow - summer period.

WINTER

Site	Borough	NP	ACE/FL	PHE	ANT	FLH	PYR	BaA/CHR	BbF	BkF	BaP	DahA	BghiP	COR	Total
1	Bexley	0.27	0.17	0.2	0.1	0.42	0.57	0.55	0.49	0.21	0.23	ND	0.53	0.35	4.09
2	Brent	ND	ND	0.2	0.26	0.22	0.19	0.58	0.55	0.22	0.19	ND	0.53	0.37	3.31
3	Ealing	0.39	ND	0.2	0.1	0.63	1.35	0.63	0.98	0.47	0.43	0.03	1.75	0.88	7.84
4	Greenwich	0.25	ND	0.2	0.13	0.26	0.15	0.43	0.35	0.13	0.15	ND	0.26	0.19	2.5
5	Hammersmith	0.3	0.36	0.2	0.33	1.05	1.45	1.5	0.79	0.37	0.45	0.11	0.92	0.7	8.51
6	Harrow	ND	0.1	0.2	0.29	0.58	1.57	1.84	0.93	0.46	0.45	0.16	1.71	0.83	9.12
7	Hounslow	6.55	2.85	1.99	0.1	0.5	0.43	0.74	0.58	0.27	0.24	0.02	0.67	0.46	15.4
8	Kingston †	ND	ND	ND	ND	ND	0.1	0.17	0.21	0.05	0.1	0.05	0.15	0.15	0.98
9	Newham	ND	ND	ND	0.1	0.31	0.35	0.44	0.47	0.2	0.21	0.06	0.45	0.3	2.9
10	Richmond	ND	ND	ND	0.1	0.2	0.21	0.2	0.33	0.11	0.14	0.02	0.23	0.17	1.71
11	Tower Hamlets	ND	ND	ND	ND	0.2	0.1	0.4	0.27	0.08	0.1	0.04	0.21	0.12	1.52
12	Wandsworth	0.1	ND	ND	0.1	0.28	0.36	0.28	0.4	0.18	0.23	0.02	0.56	0.41	2.92
13	Westminster	ND	ND	ND	ND	ND	0.28	0.55	0.44	0.19	0.22	0.01	0.37	0.24	2.3
Arithmetic mean		0.6	0.27	0.25	0.12	0.36	0.55	0.64	0.52	0.23	0.24	0.04	0.64	0.4	4.85
Geometric mean		0.67	0.73	0.5	0.22	0.43	0.36	0.51	0.47	0.19	0.21	0.08	0.49	0.33	3.58
Winter/summer ratio		1.86	1.24	1.47	0.96	1.19	0.86	1.55	1.27	0.58	1.62	2.0	1.44	1.57	1.24

†Note: Site moved for winter sampling

Table 7 Average Concentrations - Arithmetic Mean (ng m^{-3})

Site	Borough	NP	ACE/FL	PHE	ANT	FLH	PYR	BaA/CHR	BbF	BkF	BaP	DahA	BghiP	COR	Total
1	Bexley	0.14	0.09	0.2	0.05	0.37	0.41	0.42	0.42	0.26	0.17	0.02	0.38	0.24	3.18
2	Brent	ND	ND	0.2	0.13	0.26	0.15	0.46	0.47	0.28	0.16	0.03	0.49	0.31	2.94
3	Ealing *	0.2	ND	0.28	0.15	0.63	1.01	0.54	0.7	0.41	0.28	0.04	1.09	0.66	5.98
4	Greenwich	0.13	ND	0.2	0.12	0.26	0.13	0.29	0.31	0.18	0.13	0.01	0.25	0.17	2.18
5	Hammersmith	0.2	0.18	0.26	0.22	0.98	1.01	1.2	0.77	0.5	0.36	0.09	0.91	0.64	7.32
7	Hounslow	3.36	1.48	1.15	0.1	0.61	0.48	0.77	0.67	0.51	0.26	0.04	0.84	0.54	10.82
8	Kingston *†	ND	ND	0.14	ND	0.16	0.16	0.21	0.26	0.16	0.1	0.04	0.16	0.11	1.5
9	Newham	0.05	0.09	1.6	0.1	0.38	0.29	0.32	0.35	0.22	0.16	0.04	0.33	0.25	4.18
10	Richmond	ND	ND	0.1	0.1	0.33	0.27	0.23	0.32	0.22	0.14	0.03	0.25	0.15	2.14
11	Tower Hamlets	0.13	0.05	0.1	0.05	0.31	0.13	0.32	0.29	0.18	0.1	0.03	0.23	0.16	2.08
12	Wandsworth	0.1	ND	0.12	0.1	0.37	0.36	0.32	0.39	0.25	0.17	0.04	0.51	0.37	3.1
13	Westminster	0.05	ND	ND	ND	0.1	0.21	0.43	0.36	0.21	0.16	0.02	0.28	0.17	1.99
Arithmetic mean		0.36	0.16	0.36	0.09	0.40	0.38	0.46	0.44	0.28	0.18	0.04	0.48	0.31	3.95
Geometric mean		0.26	0.47	0.27	0.15	0.34	0.30	0.40	0.42	0.26	0.17	0.03	0.40	0.26	3.30

* Volume of air sampled during the summer period was considerably less than 500 m^3 and therefore these data must be treated with some caution (See Section 7.3)
† Site moved for winter sampling
NB: No summer data available for Harrow site, therefore unable to estimate an average concentration.

8 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.

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 sites at Kingston (8); Newham (9); Richmond (10) and Wandsworth (12). The highest winter total PAH concentration was recorded at Hounslow (Site 7) which is adjacent to the A4 and the M4 motorway.

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, in surveys reported by other investigators. Efforts to explain these variations are made below.

8.2 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 sites and are compared with Bexley and Greenwich which are background sites, and are illustrated in Figure 2.

The sites that can be described as 'roadside' are Brent, Ealing, Hammersmith & Fulham, Harrow, Hounslow, Kingston upon Thames, Newham, Richmond, Tower Hamlets and Wandsworth.

The Westminster site was originally classified as 'background' owing to its rooftop location. However, in the light of the results obtained for this site in earlier surveys, this site has been withdrawn from the 'roadside/background' classification and is plotted separately in Figure 2.

It can be seen that the roadside concentrations were consistently higher than the background ones. The total mean PAH concentrations at the 'roadside' sites was higher than the mean recorded at both the 'background' sites and Westminster. This result emphasises the importance of road traffic as a source of PAHs.

It should be noted that concentrations of most PAH species recorded at Westminster were largely comparable with those obtained at the 'background' sites. The total mean PAH concentration at Westminster was lower than the mean recorded for the 'background' sites.

The highest overall total PAH concentration was recorded at Hounslow (site 7) followed by Hammersmith (Site 5). The Hounslow site is at the facade of a building within a few metres of the A4 and the M4 flyover. The Hammersmith site is at the facade of building within a few metres of a busy road.

The lowest overall concentration, with the exception of Kingston upon Thames (site 8) was recorded at the 'rooftop' site at Westminster (site 13). The data obtained from Kingston upon Thames is subject to some question as the sample site was relocated for the winter monitoring period. In previous years the PAH concentrations monitored at the Kingston upon Thames site have been relatively high.

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. Though it is of note that the winter/summer ratio for both NP and ACE/FL was high which reflects the high concentrations of this species monitored during the winter sampling.

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. One might expect, therefore, that FLH, PYR and BghiP would have a winter to summer ratio in the region of 1.0 which, as can be seen from Figure 5, is indeed the case for FLH and PYR. The ratios for the other PAH species in this range are comparably low with the exception of BaP. The higher winter/summer ratio for DahA is attributable to the relatively high winter concentrations recorded for this compound (Figure 4.).

The highest total PAH concentration monitored during the summer period was recorded at Hounslow (Site 7). It is of note that concentrations of BghiP, which is indicative, were the vehicle emissions, highest species of PAH recorded at Hounslow during the summer period. This may be expected as the Hounslow site is in the vicinity of the A4 and the M4.

8.4 Comparison with Results of the 1991/92, 1992/93 and 1994/95 LWEP PAH Surveys

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 and 1994/95 surveys 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; summer measurements were not made at Tower Hamlets (site 11) 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.

As Figure 6 illustrates the summer PAH concentrations at all sites was lower in 1994 compared with previous years.

Similarly the total PAH concentrations monitored in the winter 1994/95 survey were lower than in the previous years of this survey. Although it would appear that there has been a decline in PAH concentrations at the London Borough sites it should be noted that this may reflect differences in meteorological conditions from one winter to the next rather than a genuine downward annual trend.

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.

8.6 PAH Concentration at RPT, Southwark Street, London, SE1

The short sampling periods used in the LWEP PAH survey limit data analysis to some extent as they only provide a snapshot of the PAH concentration. 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 1994/95 period. This site at RPT, Southwark Street, London, SE1, is a rooftop site some 30 m above ground level in an area of heavy traffic. PAH concentrations were monitored for two week periods each month between June 1994 and February 1995.

The total PAH concentration (ng m^{-3}) for each sample period is illustrated in Figure 9. As might be expected the total PAH concentrations were highest between the months of September 1994 and January 1995 and lowest during the summer months of June, July and August. The arithmetic mean of the total PAH concentration over the sample period was 1.61 ng m^{-3} which compares with 2.61 ng m^{-3} at the 'background' sites (Bexley and Greenwich), 1.95 ng m^{-3} at Westminster and the mean value of 4.8 ng m^{-3} from the 'roadside' sites. The PAH profile of the mean concentration of the most carcinogenic compounds for each sampling period at the Southwark Street site are shown in Figure 10. Throughout the survey BbF and BghiP were consistently the PAH species with the highest concentration, 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.

However a comparison of Figure 10 with Figure 1 illustrates that the degree of seasonal variation at the fixed site in London, SE1 is considerably less than the degree of site to site variation. This suggests that the differences in PAH concentration between sites arise as a result of genuine site specific factors.

Table 8: Results of sampling survey at 61 Southwark Street. PAH concentrations (ng m^{-3}) at periods between 26.5.94 and 7.2.95

Sample Date	NP	ACE/FL	PHE	ANT	FLH	PYR	BaA/CHR	BbF	BkF	BaP	DahA	BghiP	COR	Total
26.5.94 - 9.6.94	ND	ND	ND	ND	ND	ND	ND	0.06	0.02	0.05	0.01	ND	ND	0.21
21.7.94 - 5.8.94	ND	ND	0.17	ND	0.2	0.12	0.23	0.25	0.22	0.07	0.03	0.20	0.12	1.61
18.8.94 - 1.9.94	ND	ND	ND	ND	0.2	0.09	0.18	0.2	0.18	0.03	0.01	0.14	0.1	1.13
1.9.94 - 15.9.94	ND	ND	ND	ND	0.2	0.1	0.25	0.32	0.2	0.06	0.04	0.32	0.15	1.64
3.10.94 - 17.1.0.94	ND	ND	ND	ND	0.19	0.16	0.3	0.41	ND	0.19	0.03	0.36	0.22	1.86
10.11.94 - 25.11.94	ND	ND	ND	ND	0.25	0.32	0.78	0.54	0.22	0.33	0.11	0.54	0.34	3.43
25.11.94 - 15.12.94	ND	ND	ND	ND	0.2	0.15	0.15	0.1	0.15	0.02	0.01	0.13	0.12	1.03
5.1.95 - 19.1.95	0.09	ND	0.06	ND	0.46	0.30	0.50	0.51	0.28	0.2	0.04	0.41	0.30	3.07
19.1.95 - 7.2.95	ND	ND	ND	ND	ND	0.01	0.25	0.25	0.05	0.1	ND	0.17	0.14	0.97
Arithmetic mean	0.01	ND	0.03	ND	0.19	0.14	0.33	0.29	0.14	0.12	0.03	0.25	0.19	1.66
Geometric mean	0.09	ND	0.07	ND	0.23	0.11	0.29	0.24	0.15	0.09	0.04	0.29	0.21	1.32

8.7 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:

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 9.

Table 9: 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	10.2
2	Brent	8.5
3	Ealing	9.2
4	Greenwich	11.1
5	Hammersmith & Fulham	9.4
6	Harrow	8.1*
7	Hounslow	8.4
8	Kingston upon Thames	10.8
9	Newham	11.3
10	Richmond	11.8
11	Tower Hamlets	8.7
12	Wandsworth	10.1
13	Westminster	11
Arithmetic Mean		9.9

* Based on winter results only.

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 RPT, 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 RPT, 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' concentrations were consistently higher than the 'background' sites, emphasising the importance of road traffic as a source of PAH.

- The importance of vehicle emissions as a PAH source is demonstrated by the low winter to summer ratios of vehicle emission indicator species FLH, PYR and BghiP.

- 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 1994/95 survey were considerably below European guidelines.

- Comparison of the results of the 1994/95 LWEP PAH survey with other surveys in South Kensington, Birmingham and Manchester indicates that the results are broadly similar across all four surveys.

- The concentrations of BaP monitored during the LWEP 1994/95 PAH survey were well below European guidelines and did not exceed the recommended US EPA guideline value of 1 ng m^{-3}. The highest BaP concentrations recorded were 0.36 and 0.26 ng m^{-3} which for an individual exposed to these concentrations over a working lifetime would represent a 32 x 10^{-6} and 23 x 10^{-6} risk of respiratory cancer. These data suggest that the health risk associated with exposure to typical roadside concentrations of PAHs in central London may be comparable to that associated with exposure to benzene.

- In view of the limited quantitative information available on the health effects of the PAH species measures, however, 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 RPT, Southwark St., London, SE1 provided some valuable information concerning 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 the 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 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 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).

A comparison of the results from the 1994/95 survey with the 1993/94 LWEP survey indicates that there has been a decrease in total PAH concentrations. This apparent decline in concentration is probably due to year to year variation in meteorological conditions rather than in response to legislation aimed at reducing vehicle emissions.

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

Figure 1: Total PAH Concentration (ng m^{-3}) During Summer and Winter Sampling

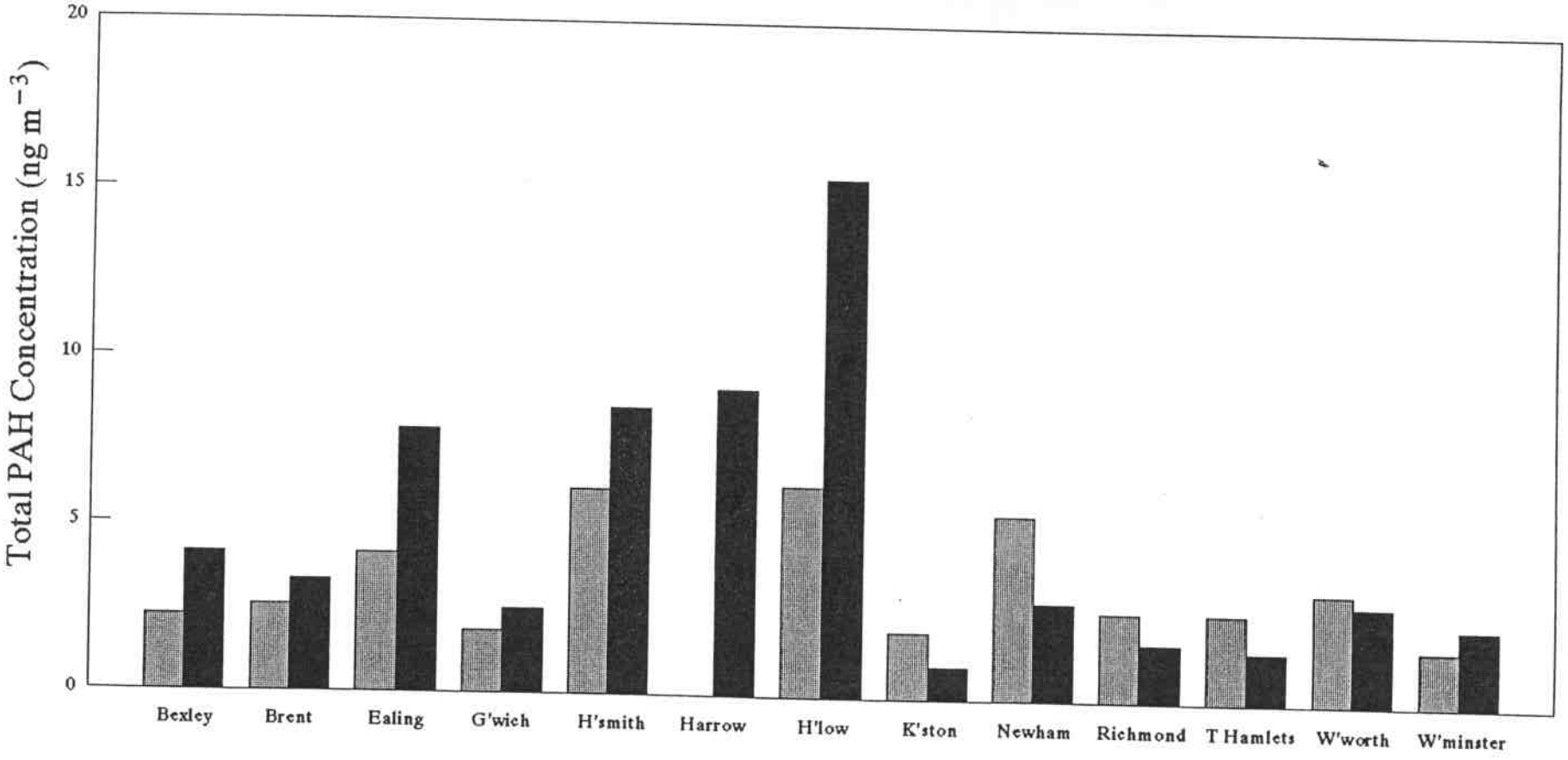

Figure 6: Total PAH Concentration (ng m^{-3}) at Sites Sampled During the 91/92; 92/93; 93/94 and 94/95 Surveys (Summer Sampling)

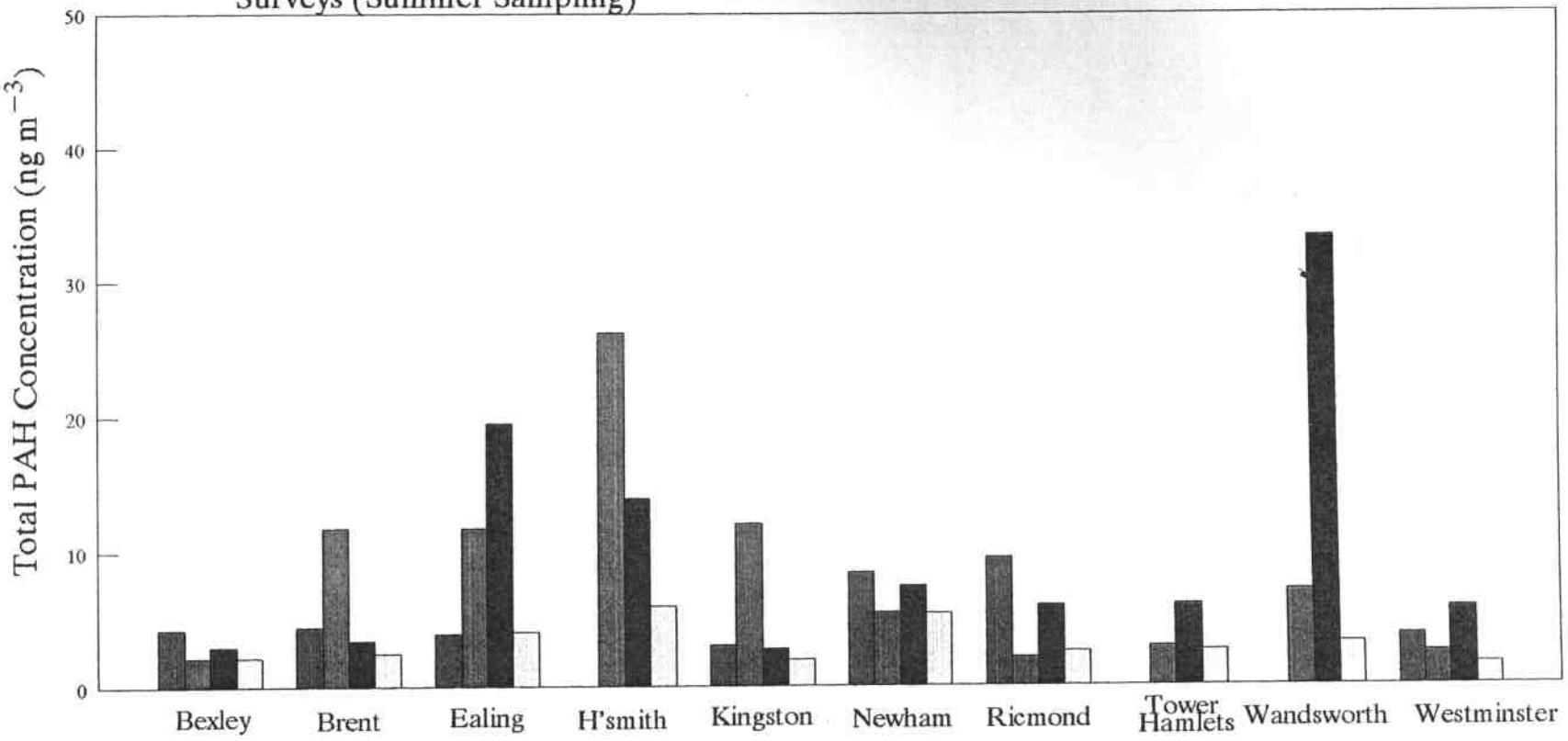

Figure 7: Total PAH Concentration (ng m^{-3}) at Sites Sampled During the 91/92; 92/93; 93/94 and 94/95 Surveys (Winter Sampling)

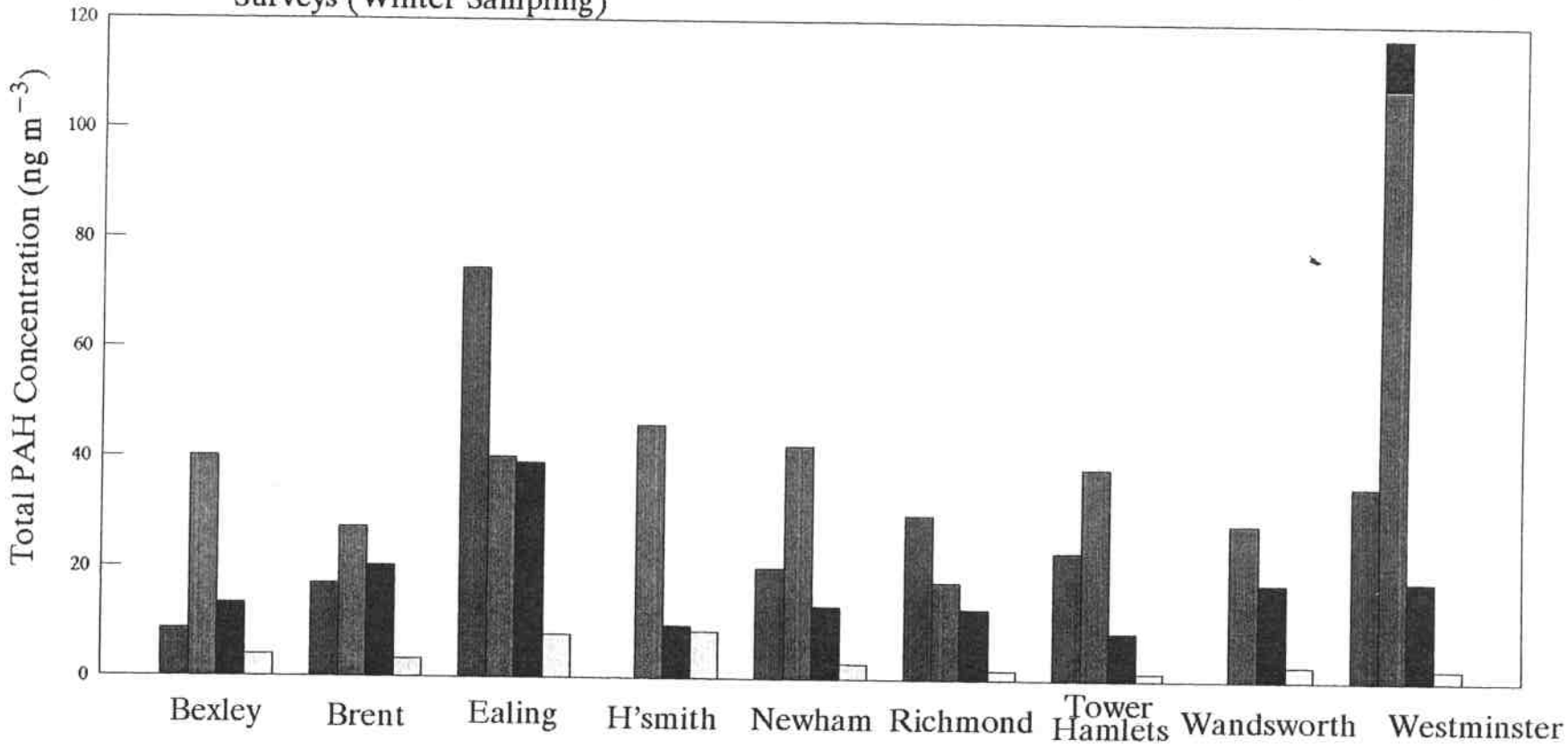

Figure 8: PAH Profile: Mean Concentration (ng m^{-3}) of Most Carcinogenic Compounds at Each Site