Table 1. Sites and sampling periods.

| Site no. | Name of Borough | Summer | Winter |
|---|---|---|---|
| 1 | Barking and Dagenham | Aug 91 | Jan 92 |
| 2 | Bexley | Aug 91 | Feb 92 |
| 3 | Brent | Jul 91 | Feb/Mar 92 |
| 4 | Ealing | Jun 91 | Nov/Dec 91 |
| 5 | Greenwich | Jun 91 | Nov/Dec 91 |
| 6 | Hounslow | Jun/Jul 91 | Oct 91 |
| 7 | Islington | Jun 91 | Jan/Feb 92 |
| 8 | Kensington and Chelsea | Jun 91 | Feb/Mar 92 |
| 9 | Kingston upon Thames | Jun/Jul 91 | Feb 92 |
| 10 | Newham | Aug 91 | Feb 92 |
| 11 | Richmond | Jun 91 | Feb/Mar 92 |
| 12 | Sutton | nm | Oct 91 |
| 13 | Tower Hamlets | nm | Jan/Feb 92 |
| 14 | Westminster | Jul 91 | Jan 92 |

nm: no measurements made

**The PAH compounds selected for measurement**

It is, of course, concern as to the carcinogenic effects of many of the PAHs that prompts interest in this class of compound. The carcinogenic potential of a particular compound is, however, not the only factor which influences its inclusion in a measurement programme. For example, the compound must be present in the atmosphere in sufficient concentration to permit reliable measurement with the analytical techniques and reference standards currently available. Again, in some circumstances the relative concentrations of particular compounds may give an indication of the main source of the PAHs. The USEPA list contains a selection of compounds likely to occur at relatively high levels, and includes members across a range of molecular weights - from the volatile, 2-ring, naphthalene to those of higher molecular weight, which are likely to be predominantly in the particle phase. The individual compounds are given in Table 2.

Human carcinogenicity data are available only for PAH mixtures, and our knowledge of the carcinogenicity of individual PAHs therefore comes from *in vitro* and animal studies. There is no definitive 'carcinogenicity classification' of PAH compounds, but two recent authoritative commentaries are in general accord (WHO, 1987; Sloof et al, 1989). A rough classification based on these two commentaries is given in Table 2.

Table 2: The PAH compounds measured

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

In the carcinogenic classification, a dash indicates that there is no evidence for carcinogenicity, a question mark that there is insufficient evidence, and one of more plus signs that there is sufficient evidence.
Nearly all the carcinogenic potency of the condensate from vehicle exhaust and from domestic coal fire emissions is associated with compounds of molecular weight 228 and greater.

## RESULTS

The concentrations of the PAH compounds measured at each site during the summer and winter sampling periods are given in Table 4. The table also gives the total PAH concentrations (ie the sum of the concentrations of all 15 PAHs) 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, an estimate of the annual mean concentration was made by finding the arithmetic mean of the summer and winter values. These estimates are given in Table 5.

In order to draw conclusions from such a large body of data, it is helpful to display certain features in graphical form.

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. Some of these variations are readily explicable from the nature of the sites. For example:

> The lowest overall concentrations were at sites 2 and 6, which were the two background sites most distant from roads.
>
> The third background site, site 14, showed a similar summer concentration, but a much higher winter one. This was probably a consequence of the greater building density at this site, and the resulting influence of space heating during the winter months.
>
> The highest summer concentration was at site 7, which was the site most exposed to heavy traffic.

Some of the other features of Figure 1 are less easy to explain. For example:

> Bearing in mind that site 4 was close to a busy high street, the summer concentration is relatively low, and there is no obvious reason for the very high winter concentration.

The winter and summer concentrations of each compound are shown in figure 2 (absolute values) and figure 3 (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 confined to these compounds:

> 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 BkF are roughly the same.
>
> Dibenz(ah)anthracene - one of the most carcinogenic PAH compounds -has a very low summer concentration, and this is in agreement with the values found in urban areas by other investigators. However, the high winter/summer ratio has not usually been found in other studies.

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 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 4 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 4 shows some patterned structure, but not enough to draw any confident conclusions as to source apportionment at the various sites.

It is of interest to make a general comparison of the PAH concentrations at roadside and background sites. The sites that can be most unequivocally described as 'roadside' are 1, 4, 7, 8, 9, 11, and 13; those which can be most unequivocally described as 'background' are 2 and 6. The annual concentrations of each compound, averaged across all the roadsides sites (except 13, for which there are no summer data), and averaged across both background sites, were calculated. The results are plotted in Figure 5. It can be seen that the roadside concentrations are consistently higher than the background ones. In fact, the roadside:background ratio for individual compounds ranged from 2.2 to 5.7, with an overall mean of 3. This result emphasizes the importance of road traffic as a source of 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 is intrinsically contained in Figure 4, but it is readily calculated from Tables 4 and 5. It has been calculated for the estimated annual average concentrations (Table 5), and the values are given in Table 6.

## Table 4

PAH concentrations at each site, nanograms per cubic metre

SUMMER

| Site | Borough | NP | ACE/FL | PHE | ANT | FLH | PYR | BaA/CHR | BbF | BkF | BaP | DahA | BghiP | COR | Total |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | Barking and Dagenham | 0.10 | 0.26 | 0.21 | 0.10 | 1.57 | 1.49 | 0.92 | 3.56 | 0.74 | 0.38 | 0.12 | 1.68 | 0.52 | 11.64 |
| 2 | Bexley | 0.10 | 0.10 | 0.20 | 0.10 | 0.36 | 0.67 | 0.23 | 1.24 | 0.26 | 0.14 | 0.08 | 0.70 | 0.15 | 4.33 |
| 3 | Brent | 0.15 | 0.40 | 0.20 | 0.10 | 0.20 | 0.78 | 0.11 | 0.90 | 0.42 | 0.39 | 0.02 | 0.73 | 0.09 | 4.48 |
| 4 | Ealing | 0.10 | 0.10 | 0.20 | 0.10 | 0.20 | 0.10 | 0.10 | 0.78 | 0.23 | 0.13 | 0.11 | 1.17 | 0.66 | 3.98 |
| 5 | Greenwich | 0.10 | 0.72 | 0.27 | 0.10 | 0.43 | 0.51 | 1.14 | 0.71 | 0.30 | 0.29 | 0.01 | 0.66 | 0.09 | 5.33 |
| 6 | Hounslow | 0.10 | 0.27 | 0.20 | 0.10 | 0.75 | 1.25 | 0.64 | 0.65 | 0.34 | 0.33 | 0.02 | 0.43 | 0.03 | 5.10 |
| 7 | Islington | 1.13 | 1.78 | 0.64 | 0.20 | 1.08 | 2.59 | 1.85 | 3.79 | 1.68 | 1.62 | 0.07 | 3.32 | 1.00 | 20.75 |
| 8 | Kensington and Chelsea | 0.38 | 0.88 | 0.44 | 0.15 | 0.30 | 1.49 | 0.51 | 1.88 | 0.88 | 1.03 | 0.04 | 1.74 | 0.34 | 10.04 |
| 9 | Kingston upon Thames | 0.14 | 0.10 | 0.20 | 0.10 | 0.26 | 0.49 | 0.31 | 0.63 | 0.23 | 0.23 | 0.01 | 0.34 | 0.03 | 3.07 |
| 10 | Newham | 0.10 | 0.72 | 0.50 | 0.12 | 0.20 | 1.77 | 0.27 | 1.76 | 0.84 | 0.73 | 0.03 | 1.10 | 0.29 | 8.42 |
| 11 | Richmond | 0.28 | 0.96 | 0.20 | 0.10 | 1.00 | 1.40 | 2.65 | 1.01 | 0.44 | 0.32 | 0.01 | 0.92 | 0.25 | 9.53 |
| 12 | Sutton | nm | nm | nm | nm | nm | nm | nm | nm | nm | nm | nm | nm | nm | nm |
| 13 | Tower Hamlets | nm | nm | nm | nm | nm | nm | nm | nm | nm | nm | nm | nm | nm | nm |
| 14 | Westminster | 0.12 | 0.10 | 0.20 | 0.10 | 0.20 | 0.59 | 0.56 | 0.78 | 0.33 | 0.27 | 0.01 | 0.50 | 0.03 | 3.78 |
| Arithmetic mean | | 0.23 | 0.53 | 0.29 | 0.11 | 0.55 | 1.09 | 0.77 | 1.48 | 0.56 | 0.49 | 0.04 | 1.11 | 0.29 | 7.54 |
| Geometric mean | | 0.16 | 0.34 | 0.26 | 0.11 | 0.41 | 0.85 | 0.49 | 1.20 | 0.45 | 0.37 | 0.03 | 0.90 | 0.16 | 6.40 |

WINTER

| Site | Borough | NP | ACE/FL | PHE | ANT | FLH | PYR | BaA/CHR | BbF | BkF | BaP | DahA | BghiP | COR | Total |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | Barking and Dagenham | 3.73 | 2.22 | 0.52 | 0.18 | 1.65 | 4.04 | 7.32 | 6.38 | 2.48 | 6.13 | 0.97 | 5.55 | 1.88 | 43.05 |
| 2 | Bexley | 0.10 | 0.43 | 0.28 | 0.10 | 0.55 | 1.11 | 0.90 | 1.74 | 0.70 | 0.45 | 0.12 | 1.65 | 0.55 | 8.68 |
| 3 | Brent | 0.10 | 0.57 | 0.20 | 0.10 | 0.65 | 2.01 | 2.76 | 3.59 | 1.40 | 1.48 | 0.37 | 2.78 | 1.07 | 17.08 |
| 4 | Ealing | 0.46 | 1.78 | 1.95 | 0.92 | 7.94 | 16.70 | 11.20 | 7.88 | 3.39 | 9.90 | 0.72 | 9.22 | 2.62 | 74.68 |
| 5 | Greenwich | 0.10 | 1.20 | 0.87 | 0.34 | 4.35 | 7.18 | 6.02 | 4.70 | 2.12 | 4.60 | 0.47 | 4.28 | 1.18 | 37.41 |
| 6 | Hounslow | 0.10 | 0.10 | 0.20 | 0.10 | 0.60 | 0.85 | 2.23 | 2.28 | 1.00 | 1.86 | 0.22 | 1.81 | 0.26 | 11.61 |
| 7 | Islington | 2.69 | 1.89 | 1.14 | 0.43 | 2.89 | 6.78 | 8.25 | 6.62 | 2.78 | 5.26 | 0.68 | 7.15 | 2.17 | 48.73 |
| 8 | Kensington and Chelsea | 0.87 | 0.86 | 0.91 | 0.24 | 1.37 | 1.63 | 1.97 | 3.09 | 1.27 | 1.56 | 0.36 | 2.82 | 1.11 | 18.06 |
| 9 | Kingston upon Thames | 0.10 | 2.05 | 1.34 | 0.42 | 2.51 | 2.59 | 2.12 | 3.34 | 0.98 | 0.90 | 0.22 | 2.03 | 0.58 | 19.18 |
| 10 | Newham | 0.10 | 0.78 | 0.41 | 0.10 | 1.60 | 3.08 | 3.01 | 2.97 | 1.41 | 2.72 | 0.33 | 2.86 | 0.80 | 20.17 |
| 11 | Richmond | 0.10 | 3.04 | 0.40 | 0.10 | 0.92 | 1.33 | 7.46 | 6.36 | 3.54 | 2.50 | 0.40 | 2.91 | 0.87 | 29.93 |
| 12 | Sutton | 0.20 | 0.40 | 0.20 | 0.10 | 1.41 | 0.49 | 2.72 | 3.18 | 1.51 | 2.91 | 0.26 | 3.18 | 0.64 | 17.20 |
| 13 | Tower Hamlets | 2.44 | 1.14 | 0.26 | 0.10 | 0.87 | 1.91 | 4.50 | 2.26 | 3.08 | 0.55 | 4.83 | 1.43 | 0.03 | 23.40 |
| 14 | Westminster | 3.43 | 1.88 | 0.46 | 0.16 | 1.66 | 3.60 | 5.72 | 5.28 | 2.18 | 4.64 | 0.53 | 4.51 | 1.45 | 35.50 |
| Arithmetic mean | | 1.04 | 1.31 | 0.65 | 0.24 | 2.07 | 3.81 | 4.73 | 4.26 | 1.99 | 3.25 | 0.75 | 3.73 | 1.09 | 28.91 |
| Geometric mean | | 0.36 | 0.98 | 0.50 | 0.18 | 1.52 | 2.50 | 3.83 | 3.86 | 1.77 | 2.32 | 0.45 | 3.22 | 0.77 | 24.62 |
| WINTER/SUMMER RATIO (GMs) | | 2.25 | 2.92 | 1.90 | 1.62 | 3.69 | 2.95 | 7.80 | 3.22 | 3.91 | 6.29 | 17.64 | 3.58 | 4.80 | 3.85 |

nm = no measurements made

# Table 5

PAH concentrations at each site, nanograms per cubic metre

ESTIMATED ANNUAL MEANS (arithmetic means of summer and winter concentrations)

| Site | Borough | NP | ACE/FL | PHE | ANT | FLH | PYR | BaA/CHR | BbF | BkF | BaP | DahA | BghiP | COR | Total |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | Barking and Dagenham | 1.92 | 1.24 | 0.36 | 0.14 | 1.61 | 2.76 | 4.12 | 4.97 | 1.61 | 3.26 | 0.55 | 3.61 | 1.20 | 27.35 |
| 2 | Bexley | 0.10 | 0.27 | 0.24 | 0.10 | 0.46 | 0.89 | 0.56 | 1.49 | 0.48 | 0.29 | 0.10 | 1.18 | 0.35 | 6.51 |
| 3 | Brent | 0.13 | 0.49 | 0.20 | 0.10 | 0.43 | 1.39 | 1.44 | 2.25 | 0.91 | 0.93 | 0.19 | 1.75 | 0.58 | 10.78 |
| 4 | Ealing | 0.28 | 0.94 | 1.08 | 0.51 | 4.07 | 8.40 | 5.65 | 4.33 | 1.81 | 5.02 | 0.42 | 5.20 | 1.64 | 39.33 |
| 5 | Greenwich | 0.10 | 0.96 | 0.57 | 0.22 | 2.39 | 3.85 | 3.58 | 2.71 | 1.21 | 2.45 | 0.24 | 2.47 | 0.64 | 21.37 |
| 6 | Hounslow | 0.10 | 0.18 | 0.20 | 0.10 | 0.68 | 1.05 | 1.43 | 1.47 | 0.67 | 1.09 | 0.12 | 1.12 | 0.15 | 8.36 |
| 7 | Islington | 1.91 | 1.84 | 0.89 | 0.32 | 1.99 | 4.68 | 5.05 | 5.21 | 2.23 | 3.44 | 0.37 | 5.24 | 1.59 | 34.74 |
| 8 | Kensington and Chelsea | 0.63 | 0.87 | 0.67 | 0.20 | 0.84 | 1.56 | 1.24 | 2.49 | 1.07 | 1.29 | 0.20 | 2.28 | 0.72 | 14.05 |
| 9 | Kingston upon Thames | 0.12 | 1.08 | 0.77 | 0.26 | 1.38 | 1.54 | 1.22 | 1.98 | 0.60 | 0.57 | 0.12 | 1.19 | 0.31 | 11.12 |
| 10 | Newham | 0.10 | 0.75 | 0.46 | 0.11 | 0.90 | 2.43 | 1.64 | 2.37 | 1.12 | 1.73 | 0.18 | 1.98 | 0.54 | 14.29 |
| 11 | Richmond | 0.19 | 2.00 | 0.30 | 0.10 | 0.96 | 1.36 | 5.05 | 3.69 | 1.99 | 1.41 | 0.20 | 1.92 | 0.56 | 19.73 |
| 12 | Sutton | nm | nm | nm | nm | nm | nm | nm | nm | nm | nm | nm | nm | nm | nm |
| 13 | Tower Hamlets | nm | nm | nm | nm | nm | nm | nm | nm | nm | nm | nm | nm | nm | nm |
| 14 | Westminster | 1.77 | 0.99 | 0.33 | 0.13 | 0.93 | 2.10 | 3.14 | 3.03 | 1.25 | 2.46 | 0.27 | 2.50 | 0.74 | 19.64 |
| Arithmetic mean | | 0.61 | 0.97 | 0.51 | 0.19 | 1.39 | 2.67 | 2.84 | 3.00 | 1.25 | 1.99 | 0.25 | 2.54 | 0.75 | 18.94 |
| Geometric mean | | 0.29 | 0.80 | 0.43 | 0.16 | 1.12 | 2.14 | 2.27 | 2.76 | 1.13 | 1.54 | 0.22 | 2.22 | 0.61 | 16.49 |

nm = no measurements made

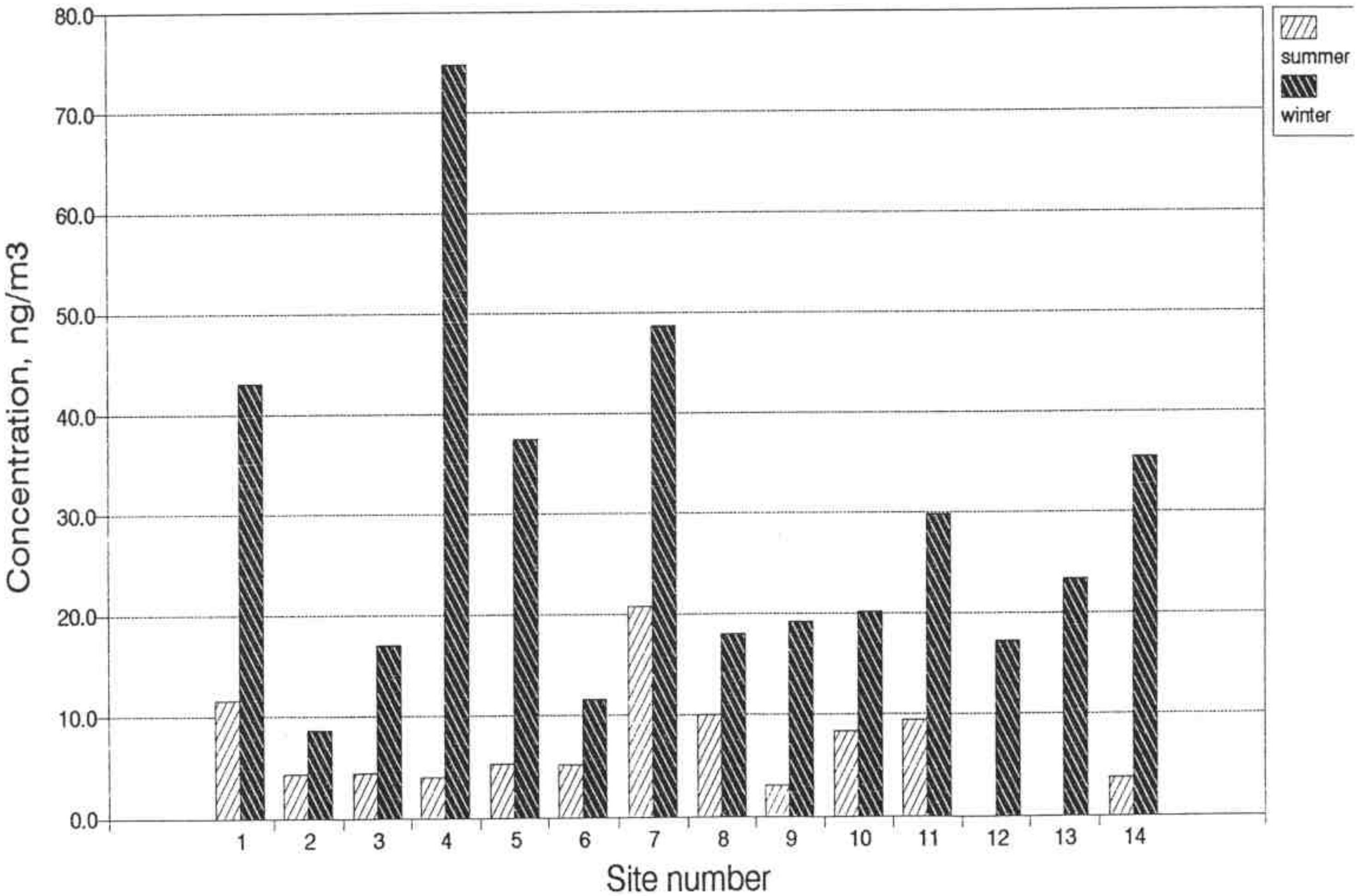
Table 6. BaP concentrations as a percentage of the sum of the concentrations of (BaA/CHR + BbF + BkF + BaP + DahA + BghiP).

| Site | Borough | percent BaP |
|---|---|---|
| 1 | Barking and Dagenham | 18 |
| 2 | Bexley | 7 |
| 3 | Brent | 13 |
| 4 | Ealing | 22 |
| 5 | Greenwich | 19 |
| 6 | Hounslow | 19 |
| 7 | Islington | 16 |
| 8 | Kensington and Chelsea | 15 |
| 9 | Kingston upon Thames | 10 |
| 10 | Newham | 19 |
| 11 | Richmond | 10 |
| 12 | Sutton | nm |
| 13 | Tower Hamlets | nm |
| 14 | Westminster | 19 |
| Arithmetic mean | | 16 |
| Geometric mean | | 15 |

Apart from the low value at site 2, the percentages are all within a factor of 1.5 of the geometric mean. Bearing in mind the considerable differences in profiles from site to site, this seems a fairly consistent result.

In all this search for rational patterns in the results, it is important to remember the short duration of the measurements - two weeks (at most) at each site for each season. Further, the measurement periods were not, in general, coincident at all fourteen 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.

Fig 1. Winter and summer concentrations
Total PAH at each site



## Fig 4. Concentrations of selected PAHs
### Averages of summer and winter values