

Affecting Factors on the Variation of Atmospheric Concentration of Polycyclic Aromatic Hydrocarbons in Central London

Sung-Ok Baek and Roger Perry*

Dept. of Environmental Engineering, Yeungnam University,
Kyungsan 713-749, Korea

* Dept. of Civil Engineering, Imperial College of Science, Technology and
Medicine, London SW7 2BU, UK

(Received 18 October 1994)

Abstract

In this study, a statistical investigation was carried out for the evaluation of any relationship between polycyclic aromatic hydrocarbons (PAHs) associated with ambient aerosols and other air quality parameters under varying meteorological conditions. Daily measurements for PAHs and air quality/meteorological parameters were selected from a data-base constructed by a comprehensive air monitoring in London during 1985-1987. Correlation coefficients were calculated to examine any significant relationship between the PAHs and other individual variables. Statistical analysis was further performed for the air quality/meteorological data set using a principal component analysis to derive important factors inherent in the interactions among the variables. A total of six components were identified, representing vehicle emission, photochemical activity/volatilization, space heating, atmospheric humidity, atmospheric stability, and wet deposition. It was found from a stepwise multiple regression analysis that the vehicle emission component is overall the most important factor contributing to the variability of PAHs concentrations at the monitoring site. The photochemical activity/volatilization component appeared to be also an important factor particularly for the lower molecular weight PAHs. In general, the space heating component was found to be next important factor, while the contributions of other three components to the variance of each PAHs did not appear to be as much important as the first three components in most cases. However, a consistency for these components in their negative correlations with PAHs data was found, indicating their roles in the depletion of PAHs concentrations in the urban atmosphere.

1. INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) and their derivatives can be formed in any combustion process involving carbonaceous fuels (Badger, 1962). The environmental concern for these compounds has been well justified since not only have many of them proven mutagenic and/or carcinogenic properties, but they are also known to be ubiquitous in the ambient air to which the general pub-

lic is exposed (International Agency for Research on Cancer, 1983; National Research Council, 1983).

The extent to which humans are exposed to these compounds is a function of several parameters including concentrations of PAHs in the ambient air, distribution between the gaseous and particulate phases in which they occur, and the size distribution of particles with which they are associated (Van Vaeck and Van Cauwenbergh, 1985; Daisey

Jet al., 1986, Baek et al., 1991a, 1991b).

These parameters are again functions not only of the strength of emissions from various sources but also of the prevailing atmospheric conditions. Thus, for complete evaluation of the significance of airborne PAHs in the ambient air, it is necessary to identify major sources of emissions in addition to evaluating the physical and chemical characteristics in the ambient air. In general, the major sources of PAHs in an urban area are emissions from motor vehicle exhausts, space heating and industrial sources, of which their relative contributions are obviously temporally and spatially variable (National Research Council, 1983).

Once PAHs are released into the atmosphere, they are subject to a variety of atmospheric processes through which their distribution, removal, transport, and degradation can occur (Baek et al., 1991b). Therefore, the amount and distribution of PAHs to which humans are exposed are dependent not only on the magnitude of emissions from various sources but also on the stability of individual PAHs in the atmosphere. However, despite of their importance in understanding the fate and behaviour of PAHs in the atmosphere, very little is known about the relationships and interactions between the atmospheric PAHs and other air quality and meteorological parameters.

In this study, a statistical investigation was performed for the evaluation of relationships between PAHs associated with ambient aerosols and other air quality parameters under varying meteorological conditions. For the statistical analysis, daily measurement data for each variable were selected from a data-base constructed by a comprehensive air monitoring in Central London during 1985-1987 (Baek et al., 1992). Correlation coefficients were calculated to examine any significant relationship between the PAHs and other individual variables. Statistical analysis was further performed with the air quality and meteorological data set using principal component analysis to derive important factors inherent in the interactions among the variables. A stepwise multiple regression was then formulated for each PAHs based on the principal components in order to determine which of the derived factors are most significant in describing the

variation of PAHs concentrations. These results may be useful for estimating the relative importance of emission sources and also to deduce information on the removal processes of PAHs in the urban atmosphere.

2. MATERIALS AND METHODS

2.1 Sampling and Monitoring of PAHs and Air Quality Parameters

A detailed description of the sampling regime and methodology is given elsewhere (Baek et al., 1991c, 1992). A total of 18 PAHs were studied in a regime incorporating 48 weeks of monitoring from October 1985 to September 1987 at Exhibition Road, South Kensington in Central London, U.K. In order to obtain sufficient data over varying meteorological and air quality conditions, the monitoring was divided into 4 periods per year: two in the summer and two in the winter. Each period consisted of 6 weeks on average. The air monitoring programme can be divided into two main categories, i.e. (i) sampling and analysis of PAHs and (ii) measurements of routine air quality/meteorological parameters.

Two different types of daily particulate samples were collected separately throughout the entire period, using 47 mm teflon and cellulose acetate filters, respectively. The teflon samples were extracted for the determination of PAHs, while the cellulose filter samples were used for the gravimetric measurement of suspended particulate matter (SPM) and then analyzed for particulate lead. In parallel with SPM sampling, a total of 9 gaseous air pollutants and 4 meteorological parameters were continuously monitored in situ using a mobile laboratory, of which details are shown in Table 1. Smoke, defined as black shade, was also measured in situ every 3 hours. In addition to these direct measurements, rainfall and sunshine hours data were obtained on a daily basis from London Weather Centre.

For this study, a subset of the data, which contains a total of 135 daily measurements of particulate PAHs and other air quality parameters, was selected from the original database. The period covered by these data is January to September

1987. For each variable, 78 data-points are correspond to the winter data (January to March), while 57 to the summer data (May to September).

2.2 Analysis of PAHs

The analytical method applied for the determination of PAHs involves a Soxhlet extraction of the particle-laden filters with dichloromethane, followed by a clean-up stage using SEP-PAK silica cartridges prior to analysis by reverse-phase HPLC with UV and wavelength programmable fluorescence detection. Details of the analytical procedure can be found elsewhere (Baek et al., 1991c).

2.3 Principal Component Analysis

The interpretation of statistical analyses of air quality data is often limited because there is usually a high degree of correlation among the variables. In order to separate such interrelationships into statistically independent variables, principal component analysis (PCA) which is a special case of factor analysis, was applied to air quality and meteorological data sets. The primary objective of applying PCA is to derive a small number of components which explain a maximum of the variance in a data set. Initially, the PCA results in as many principal components (PCs) as there are original variables. In general, however, only a limited number of these uncorrelated components are sufficient to explain virtually all of the total variance in a data set of original variables. In order for this reduction in the dimensionality to be useful, the new variables must have simple substantive interpretations. Empirically, it has been found that unrotated PCs are often not readily interpretable, since they each attempt to explain all remaining variance in the data set (Henry and Hidy, 1979). For this reason, a limited number of components are usually subjected to rotation using criteria such as Varimax, Equamax and Quartmax. After rotation, the resulting components have been found to often be more useful for interpreting the underlying nature of variation. The merits of PC rotation in analysing air pollution data have been widely discussed in the literatures (Henry and Hidy, 1979; Thurston and Spengler, 1985). Based upon the above considerations, an orthogonal rotation by the

Varimax method was carried out in this study when performing PCA. The Varimax method constitutes a maximisation of the PC loadings, which are correlations between each variable and the PCs.

2.4 Multiple Regression Analysis

To determine the relationships between each PAHs and the principal components, a stepwise multiple regression analysis was carried out using PAHs as a dependent variable and the principal components as independent variables. The forward variable selection procedure was employed. For each PAHs, the important principal components in describing the variation of PAHs were selected based on given criteria of significance level. Unless specified, all the statistical analysis were carried out using SPSS-X version 2.1, which was available from the CDC Cyber mainframe of the Imperial College Computer Centre.

3. RESULTS

A statistical summary of PAHs concentration data obtained by teflon filter samples is shown in Table 2. A list of gaseous and particulate pollutants and meteorological parameters included in the statistical analysis is presented in Table 3, together with their means and ranges of the measured levels. The implications for these variables in the physical and chemical processes of the atmosphere are given in the literature (Henry and Hidy, 1979; Wolff et al., 1986). As shown in Table 3, the standard deviation of horizontal wind direction was calculated in order to use as an indicator of atmospheric stability. This method of turbulence classification has been recommended by the U.S. Nuclear Regulatory Commission, together with the vertical temperature gradient method (Sedifian and Bennett, 1980). A computer programme for the calculation of mean and standard deviation of wind direction was made based upon the algorithm developed by Nelson (1984).

Correlations between the PAHs concentration data and measured levels of air quality and meteorological parameters are shown in Table 4. In general, the PAHs data appeared to be the best

Table 1. Instrumentation for the measurements of general air pollutants and meteorological parameters

Pollutants	Method	Instrument	Lower Limit of Detection	Sampling Frequency
Hydrocarbons	GC/FID	Beckman 6800 AQC	0.05 ppm	5 min
Carbon monoxide	GC/FID	Beckman 6800 AQC	0.05 ppm	5 min
Oxides of nitrogen	Chemiluminescence	Thermoelectron 14D	1 ppb	5 min
Sulphur dioxide	Pulsed fluorescence	Thermoelcetrytron 43	2 ppb	5 min
Ozone	UV adsorption	Dasibi 1003-AH	4 ppb	5 min
Suspended particulate matter (SPM)	Low-volume sampling/ Gravimetric measurement	47mm membrane filters in stainless steel open filter holder	2.5 $\mu\text{g}/\text{m}^3$ *	24 hr
Smoke (black shade)	Filter soiling	RAC smoke sampler	5 $\mu\text{g}/\text{m}^3$	3 hr
Particulate lead	Acid digestion/ Flameless AA	Perkinn-Elmer 603 with HGA-400 atomiser	10 ng/m^3 *	24 min
Wind speed & Wind direction	10m from ground	Cup-type anemometer and aluminum vane	0.3m/sec	5 min
Temperature	Thermistor	Testo-Term Hygrotest 55	-40°C to 80°C	5 min
Relative humidity	Thin film capacitor	Testo-Term Hygrotest 55	0-100%	5 min

* Detection limit was estimated on the basis of typical sampling volume of 40m³.

Table 2. Summary of PAHs concentration(ng/m^3) data

PAH	Abbreviation	Mean	S.D.	Min.	Max.
Phenanthrene	PHEN	0.13	0.11	0.02	0.55
Anthracene	ANTHR	0.20	0.17	0.02	0.82
Fluoranthene	FLUR	0.86	0.84	0.08	3.97
Pyrene	PYR	0.92	0.76	0.06	3.86
Benzo(c)phenanthrene	BcPH	0.94	0.89	0.10	5.53
Cyclopenta(cd)pyrene	CcdP	3.15	3.25	0.17	14.90
Benzo(a)anthracene	BaA	0.91	0.74	0.11	4.77
Chrysene	CHRY	1.35	1.41	0.10	7.66
Benzo(b)naphtho(2,1-d)thiophene	BNTH	1.21	1.53	0.06	7.44
Benzo(e)pyrene	BeP	2.18	1.33	0.61	7.88
Benzo(b)fluoranthene	BbF	1.85	1.15	0.52	6.79
Benzo(k)fluoranthene	BkF	0.80	0.53	0.29	3.32
Benzo(a)pyrene	BaP	1.66	1.11	0.39	5.98
Dibenz(a,h)anthracene	DahA	0.14	0.12	0.02	1.03
Benzo(ghi)perylene	BghiP	3.60	1.72	1.39	11.61
Indeno(1,2,3-cd)pyrene	I23P	1.76	0.92	0.55	5.97
Anthanthrene	ANTHN	0.85	0.80	0.04	4.82
Coronene	COR	1.95	0.99	0.72	6.89
18 PAH Total	Σ PAH	24.43	15.48	5.54	79.86

Table 3. Summary of air quality and meteorological data

Variable	Abbreviation	Unit	Mean	SD.	Min.	Max.
Total hydrocarbons	THC	ppm	2.2	0.3	1.5	3.0
Non-methane hydrocarbons	NMHC	ppm	0.6	0.3	0.1	1.7
Carbon monoxide	CO	ppm	1.8	0.8	0.5	5.0
Sulphur dioxide	SO ₂	ppb	13.3	7.5	2.2	36.0
Daily mean Ozone	O ₃	ppb	15.3	3.2	4.1	29.9
Hourly maximum Ozone	O ₃ X	ppb	34.8	6.4	22.0	53.0
Nitrogen oxide	NO	pphm	7.6	3.9	1.6	26.5
Nitrogen dioxide	NO ₂	pphm	3.3	1.7	1.3	6.0
Smoke	SMK	$\mu\text{g}/\text{m}^3$	35.8	12.4	14.0	78.0
Suspended particulate matter	SPM	$\mu\text{g}/\text{m}^3$	65.1	26.2	26.0	172.0
Particulate lead	PB	ng/m^3	268.5	168.4	71.0	976.0
Wind direction*	WDSD	degree	16.7	5.5	6.0	27.0
Wind speed	WSPD	m/sec	2.4	1.0	0.8	5.9
Degree days**	DGDAY	°C	9.1	5.9	-4.2	22.5
Daily maximum temperature	TMAX	°C	13.4	6.9	-2.6	29.3
Relative humidity	RH	%	63.2	14.1	30.3	97.0
Absolute humidity***	AH	g/m^3	5.8	2.2	2.0	12.1
Inverse of relative humidity****	IRH		3.5	3.1	1.4	33.2
Rainfall	RAIN	mm	32.0	4.0	0.0	24.8
Sunshine hours	SUN	hr	4.8	2.5	1.0	10.4

* Standard deviation of wind direction

** Degree Days = $18^\circ\text{C} - \text{Ambient Temperature (Daily Mean)}$

*** Absolute humidity was calculated based upon a polynomial developed by Lowe(1977)

**** $\text{IRH} = (1 - \text{RH})^{-1}$

correlated with the combustion related air pollutants such as NO and NO₂, SO₂, smoke, and hydrocarbons. Typical traffic-related pollutants such as CO and lead also exhibited significant correlations with the airborne PAHs. In contrast, very poor or no correlations were generally found between the PAHs and meteorological parameters except the ambient temperature. Significant correlations between the PAHs and the ambient temperature are reasonable, indicating the seasonal effect on the measured levels of PAHs.

Examination of Table 4 reveals that there are two distinct patterns in the results: one shows consistently positive correlations with combustion related parameters, and the other consistently negative correlations with parameters such as wind speed (WSPD), atmospheric stability (WSDS), absolute humidity (AH), rainfall (RAIN), and sunshine hours (SUN). The former factor, in accordance with the positive correlations of PAHs with degree days (DGDAY), can be related to the production sources of atmospheric PAHs, whereas the latter may be indicative of the depletion factor for atmospheric PAHs.

To further explore the relationships between PAHs and other air quality parameters given in Table 4, a principal component analysis was applied to the air quality and meteorological data in order to derive independent variables. The resulting principal component patterns are presented in Table 5, where all components with eigenvalues less than one after varimax rotation are not shown. A total of six components were derived, explaining 81.2% of the total variance of the data set.

The first component, which alone contributes 27.3% of the total variance, was undoubtedly believed to represent 'motor vehicle emissions' since it has exclusively high loadings for the traffic-related species such as NMHC, CO, NO, NO₂, smoke, and particulate Pb. The second component, accounting for 16.5% of the total variability of the data, showed very high positive loadings for ozone related variables (24 hr mean O₃ and 1 hr maximum O₃) and moderately positive loadings for daily maximum temperature, sunshine hours, and absolute humidity, which are generally known to play an important role in the atmospheric 'photochemical

activity' (Henry and Hidy, 1979).

The third component, explaining 13.0% of the total variance, was allocated as being related to 'space heating'. The high positive loading for the degree days suggests that this component is associated with lower-than-average temperature, while the moderately positive loadings for SO₂ and smoke also indicate their association with fuel consumptions for heating purposes during the winter season. The interpretation of the fourth component is much clearer, since it is well correlated with relative humidity (RH) and IRH. The IRH, as being defined in the note of Table 3, is known to be theoretically related to aerosol water content (Henry and Hidy, 1979). Thus, this component was believed to be related to the water vapour content in the ambient air, being termed as 'atmospheric humidity'.

The fifth component, which contributes 7.4% of the total variance, was interpreted as representing the degree of 'atmospheric stability'. A high positive loading for the standard deviation of wind direction and a negative loading for wind speed suggest the relationship of this component to vertically unstable atmospheric conditions with lower-than-average wind speed, which indicates the degree of atmospheric diffusion and/or transport. Finally, the sixth component, explaining 5.4% of the total variance, was simply labelled 'wet deposition', since rainfall alone indicates a high correlation with this component. In addition, although correlations appeared weak, negative loadings for particulate pollutants including smoke, SPM, and Pb further suggest the association of this component with the removal of airborne particles by precipitation or wet deposition.

The next step was to use the individual PAHs as dependent variables and regress them on the PC scores as independent variables. The results are presented in Table 6, where the regression coefficients and the percentages of the total variance of the dependent variables explained by each PC are summarized. The forward stepwise variable selection procedure was employed based on given criteria.

Examination of Table 6 indicates that overall, the greatest amount of the PAHs variance was ex-

Table 4. Correlations between PAHs and air quality/meteorological variables.

PAH	THC	NMHC	CO	SO2	O3	O3X	NO	NO2	SMK	SPM	PB	WSD	WSPD	DGDAY	TMAX	RH	AH	IRH	RAIN	SUN
PHEN	0.34	0.18	0.31	0.36	-0.30	-0.44	0.26	0.34	0.40	0.32	0.29	-0.15	-0.09	0.50	-0.50	0.21	-0.35	0.09	-0.18	-0.48
ANTHR	0.37	0.24	0.36	0.39	-0.25	-0.44	0.40	0.33	0.43	0.31	0.41	-0.01	-0.23	0.42	-0.44	0.22	-0.29	0.18	-0.21	-0.50
FLUR	0.43	0.21	0.39	0.57	-0.36	-0.52	0.27	0.35	0.60	0.51	0.43	0.08	-0.17	0.64	-0.60	0.11	-0.51	0.11	-0.21	-0.46
PYR	0.50	0.29	0.38	0.59	-0.42	-0.50	0.37	0.41	0.62	0.47	0.48	0.08	-0.16	0.64	-0.62	0.11	-0.52	0.09	-0.24	-0.52
BcPH	0.42	0.26	0.31	0.36	-0.28	-0.32	0.32	0.34	0.33	0.21	0.35	-0.16	-0.02	0.38	-0.39	0.10	-0.31	0.14	-0.19	-0.42
CcdP	0.60	0.40	0.54	0.57	-0.28	-0.33	0.67	0.50	0.55	0.34	0.62	-0.04	-0.15	0.42	-0.43	0.15	-0.31	0.17	-0.22	-0.52
BaA	0.57	0.40	0.47	0.63	-0.36	-0.36	0.60	0.42	0.63	0.41	0.62	0.02	-0.18	0.51	-0.50	0.12	-0.41	0.14	-0.22	-0.52
CHRY	0.47	0.31	0.48	0.59	-0.15	-0.36	0.44	0.39	0.60	0.34	0.60	-0.01	-0.12	0.49	-0.50	0.26	-0.34	0.45	-0.22	-0.56
BNTH	0.49	0.33	0.47	0.60	-0.12	-0.32	0.47	0.32	0.54	0.35	0.57	0.00	-0.15	0.45	-0.46	0.31	-0.26	0.41	-0.21	-0.57
BeP	0.57	0.43	0.44	0.60	-0.27	-0.32	0.59	0.40	0.68	0.53	0.60	0.03	-0.18	0.44	-0.42	0.14	-0.33	0.15	-0.21	-0.51
BbF	0.59	0.42	0.49	0.66	-0.28	-0.36	0.57	0.48	0.72	0.57	0.61	0.02	-0.18	0.55	-0.54	0.16	-0.42	0.19	-0.25	-0.55
BkF	0.62	0.45	0.55	0.67	-0.19	-0.34	0.60	0.44	0.71	0.51	0.64	0.06	-0.21	0.54	-0.53	0.25	-0.37	0.31	-0.24	-0.57
BaP	0.58	0.46	0.51	0.58	-0.32	-0.41	0.64	0.42	0.68	0.47	0.65	-0.07	-0.16	0.51	-0.51	0.23	-0.34	0.24	-0.26	-0.61
DahA	0.49	0.45	0.56	0.51	-0.18	-0.24	0.64	0.39	0.59	0.43	0.48	-0.01	-0.13	0.39	-0.38	0.19	-0.25	0.17	-0.22	-0.47
BghiP	0.52	0.55	0.58	0.35	-0.15	-0.16	0.79	0.48	0.48	0.31	0.57	-0.17	-0.11	0.18	-0.20	0.18	-0.07	0.17	-0.19	-0.37
I123P	0.55	0.49	0.54	0.55	-0.23	-0.26	0.68	0.45	0.59	0.40	0.55	-0.06	-0.09	0.41	-0.40	0.15	-0.30	0.11	-0.22	-0.47
ANTHN	0.53	0.46	0.43	0.45	-0.21	-0.26	0.59	0.38	0.58	0.52	0.51	-0.14	-0.06	0.36	-0.36	0.19	-0.21	0.09	-0.22	-0.50
COR	0.51	0.57	0.59	0.36	-0.09	-0.10	0.74	0.45	0.42	0.22	0.55	-0.14	-0.07	0.14	-0.17	0.14	-0.06	0.18	-0.18	-0.29
ΣPAH	0.63	0.50	0.58	0.64	-0.28	-0.38	0.68	0.50	0.68	0.47	0.67	-0.05	-0.16	0.51	-0.51	0.21	-0.36	0.24	-0.26	-0.59

Note: Correlation coefficients greater than | 0.14 | are significant at a level of 0.05

plained by the component representing 'motor vehicle emission'. In most cases, the contribution of the motor vehicle emission component appeared to be about 30 to 50% of the total variance. However, comparatively lower contributions of this component were found for lower molecular weight PAHs such as PHEN to BcPH. In addition, BNTH exhibited relatively poor correlation to the motor vehicle component when compared to other compounds having a similar molecular weight. The 'space heating' component appeared in general to be next in importance following the 'vehicle emission', even though there is a substantial difference between each PAHs in the amount of variance explained by this component.

The 'photochemical activity' component also explained significant amounts of the variance of some PAHs, especially lower molecular weight PAHs and BaP. Another important observation on the 'photochemical activity' component pertains to the consistently negative coefficients for all the PAHs, which revealed a statistically significant correlation with this component. Particularly, the closer association of this component with the lower molecular weight compounds than the higher ones possibly indicates the enhanced effect of volatilization of PAHs in the atmosphere when ambient temperature increases. A similar observation is also apparent for the 'wet deposition' component, although its contribution to the total variance of each PAHs was relatively small.

The fourth significant factor in describing the variations of ambient levels of PAHs was found in general to be the 'atmospheric humidity' component, while the significance of the 'atmospheric stability' component seems to be the least among the six components since it exhibited poor or no correlations with most of the PAHs, explaining only a small proportion of their variance.

4. DISCUSSION

Despite their importance in understanding the fate and behavior of PAHs in the atmosphere, very little is known about the relationships and/or interactions between the atmospheric PAHs and other air quality and meteorological parameters. Wolff et

al. (1986) observed an apparent relationship between the mutagenicity of airborne particles and the ambient concentrations of NO₂, SO₂, NMHC and particulate organic carbon. Van Houdt et al. (1987) also found strong relationships between major gaseous species and mutagenicity data. However, these findings may not be considered conclusive since only a limited number of observations were incorporated into the statistical analysis. Furthermore, such mutagenicity related information may not always be relevant to the understanding of the nature and behaviour of individual PAHs compounds in the atmosphere since the mutagenic activity was not contributed by PAHs compounds only.

In this study, in order to investigate the nature and sources of the atmospheric PAHs, a total of 135 daily measurements of 11 air quality and 9 meteorological parameters were statistically analysed in conjunction with PAHs concentration data obtained from PTFE filter samples during 1987. As shown in table 4, all major air pollutants appeared to be significantly correlated with the PAHs data in most cases, although the degree of correlation varied from one compound to another. Seasonal effects on the measured concentrations of PAHs were clearly demonstrated by the apparent negative correlations of temperature with all the 18 PAHs. Similarly, rainfall and sunshine hours also exhibited consistently negative correlations, which are considered to be an indication of their role in the depletion mechanisms of the atmospheric PAHs.

In contrast, very poor or no correlations were found between the PAHs and some of the meteorological parameters such as atmospheric stability, expressed as a standard deviation of wind direction, and average wind speed. The explanation for the poor correlation of the PAHs with such wind data is not clear, but seems to be at least in part due to the fact that the monitoring situation can be linked to a 'street canyon' morphology, which consequently makes the representativeness of the wind data questionable.

In an earlier study (Gordon and Bryan, 1973), it was reported that ambient air concentrations of coronene (COR) and lead were strongly correlated

Table 5. Result of principal component analysis for the air quality and meteorological data

Variable	PC1	PC2	PC3	PC4	PC5	PC6
THC	0.824	-0.209	0.085	0.051	0.065	-0.162
NMHC	0.867	0.027	-0.169	0.026	0.116	-0.129
CO	0.796	-0.019	0.117	0.211	0.074	0.025
SO ₂	0.457	-0.182	0.657	0.066	0.262	-0.095
O ₃	-0.097	0.857	-0.167	0.283	-0.031	-0.154
O ₃ X	-0.091	0.901	-0.097	-0.108	-0.025	0.142
NO	0.898	-0.025	-0.027	0.066	-0.01	0.014
NO ₂	0.793	-0.060	0.078	-0.153	0.055	0.084
SMK	0.697	-0.164	0.539	0.102	0.188	-0.103
SPM	0.624	-0.066	0.3644	-0.001	0.157	-0.113
LPB	0.786	-0.071	0.175	0.286	0.072	-0.131
WDSD	0.047	0.072	0.259	-0.060	0.838	0.074
WSPD	-0.364	0.035	0.241	-0.109	-0.772	0.091
DGDAY	0.059	-0.632	0.709	0.199	-0.041	-0.035
TMAX	-0.054	0.692	-0.629	-0.248	0.074	0.056
RH	0.046	-0.148	-0.060	0.93	0.020	0.174
AH	-0.007	0.517	-0.715	0.317	0.081	0.139
IRH	0.151	0.083	0.073	0.844	0.023	0.001
RAIN	-0.178	0.067	-0.135	0.147	0.007	0.927
SUN	-0.192	0.668	-0.240	-0.534	0.107	0.093
Eigenvalue	5.456	3.294	2.598	2.315	1.485	1.080
% of variance	27.3%	16.5%	13.0%	11.6%	7.4%	5.4%
Implication	Vehicle emission	Photochemical activity	Space heating	Atmospheric humidity	Atmospheric stability	Wet deposition

Table 6. Result of stepwise regression analysis for each PAHs

PAH	Principal Components														Multiple R	Σ % VAR (R ²)
	Vehicle emission		Photo-chemical		Space heating		Humidity		Atmospheric stability		Wet deposition					
	R.C.*	% VAR**	R.C.	% VAR	R.C.	% VAR	R.C.	% VAR	R.C.	% VAR	R.C.	% VAR				
PHEN	0.30	9.2%	-0.41	16.6%	0.22	4.8%	0.14	2.1%	N.S.***	-	N.S.	-	0.57	32.7%		
ANTHR	0.36	13.1%	-0.38	14.2%	0.16	2.6%	0.20	3.9%	N.S.	-	N.S.	-	0.58	33.8%		
FLUR	0.36	12.6%	-0.40	16.4%	0.45	20.3%	N.S.	-	N.S.	-	N.S.	-	0.70	49.3%		
PYR	0.42	17.9%	-0.44	19.6%	0.42	17.6%	N.S.	-	N.S.	-	N.S.	-	0.74	55.1%		
BcPH	0.39	13.0%	-0.32	10.0%	0.17	2.9%	N.S.	-	-0.19	3.6%	N.S.	-	0.54	29.5%		
CcdP	0.63	39.8%	-0.30	9.0%	0.22	4.7%	0.13	1.8%	N.S.	-	N.S.	-	0.74	55.3%		
BaA	0.56	31.5%	-0.33	11.2%	0.34	11.5%	N.S.	-	N.S.	-	N.S.	-	0.74	54.2%		
CHRY	0.46	21.0%	-0.21	4.6%	0.39	15.2%	0.37	13.4%	N.S.	-	-0.15	2.2%	0.75	56.4%		
BNTH	0.45	20.3%	-0.20	4.0%	0.33	11.0%	0.39	15.0%	N.S.	-	-0.16	2.5%	0.73	52.8%		
BeP	0.58	33.1%	-0.25	6.5%	0.33	11.0%	0.13	1.7%	N.S.	-	N.S.	-	0.72	52.3%		
BbF	0.59	34.4%	-0.28	7.9%	0.43	18.2%	0.16	2.5%	N.S.	-	-0.12	1.4%	0.80	64.4%		
BkF	0.59	35.2%	-0.23	5.3%	0.42	17.5%	0.28	7.9%	N.S.	-	-0.13	1.7%	0.82	67.6%		
BaP	0.60	36.1%	-0.35	12.2%	0.29	8.4%	0.23	5.3%	N.S.	-	-0.14	2.0%	0.80	64.0%		
DahA	0.57	32.4%	-0.19	3.5%	0.27	7.1%	0.17	3.0%	N.S.	-	N.S.	-	0.68	46.0%		
BghiP	0.69	47.8%	-0.14	2.0%	N.S.	-	0.14	2.0%	-0.23	5.2%	N.S.	-	0.75	57.0%		
I123P	0.62	38.5%	-0.22	5.0%	0.27	7.2%	N.S.	-	-0.11	4.7%	N.S.	-	0.73	53.0%		
ANTHN	0.58	33.4%	-0.22	5.1%	0.21	4.4%	N.S.	-	-0.19	3.8%	N.S.	-	0.68	46.6%		
COR	0.66	43.5%	N.S.	-	N.S.	-	0.13	1.6%	-0.23	5.4%	N.S.	-	0.71	50.5%		
ΣPAH	0.66	43.4%	-0.31	9.6%	0.32	9.9%	0.21	4.4%	-0.11	1.2%	-0.12	1.4%	0.84	69.9%		

* Regression coefficients

** Percentage of variance explained

*** Not selected as a significant variable at a level of 0.05.

for all of the four sites in the Los Angeles area where traffic was the dominant airborne particles contributor. Similar results were also obtained from four sites in New Jersey during 1979, suggesting that COR, like lead, is a good indicator of traffic density in an urban area (Greenberg et al., 1981). From this study, however, there appeared only moderate correlations between lead and COR in particular ($R = 0.55$) and PAHs in general ($R = 0.29$ to 0.65). The relatively poor relationships between the lead and the PAHs, compared to the previously reported data, might have resulted from the decreased contribution of motor vehicle sources to the atmospheric lead concentrations during this study. It was estimated that the background lead level in the air of the Greater London area was about $90\text{mg}/\text{m}^3$ during 1986, and its relative contribution to the total atmospheric lead has increased by approximately 20% as a result of the reduction in the lead content of petrol (Baek et al., 1992). In this study, the average concentration of lead included in the statistical analysis was $269\text{mg}/\text{m}^3$, which represents only less than one-fifth of that from the New Jersey area during 1979, while COR levels were comparable with each other.

Although the air quality and meteorological parameters exhibited statistically significant correlations with PAHs data in most cases, significant correlations were also apparent between these parameters. In general, the investigation of the basic relationships between air quality and other aerometric variables by statistical techniques has often been complicated by the highly intercorrelated nature of the variations in the data. The fact that many variables of interest tend to fluctuate more or less in random reveals difficulties for routine statistical analyses and interpretation of the results. It has been established that PCA can overcome such technical difficulties in air pollution studies by providing of valuable insight into the underlying chemical and physical processes of the atmosphere (Henry and Hidy, 1979; Thurston and Spengler, 1985; Wolff et al., 1986).

Application of PCA to the air quality and meteorological data set demonstrated that the 20 intercorrelated variables could be summarized by only 6 uncorrelated variables, which explain more

than 8% of the total variance of the original data set. The 6 principal components were considered to represent 'vehicle emission', 'photochemical activity', 'space heating', 'atmospheric humidity', 'atmospheric stability', and 'wet deposition'. From a viewpoint of the atmospheric evolution of PAHs, these 6 independent variables seem to be well associated with two main factors, i.e. the production and depletion of the PAHs in the atmosphere.

Generally, in an urban area the production sources are emissions by vehicular traffic, residential heating and industrial sources, whose relative strengths are obviously variable under particular situations. On the other hand, the depletion parameters are related to a number of factors, which can be summarised as following: (i) degradation by atmospheric reactions either by photochemical reactions, where the amounts of gaseous oxidising agents and solar intensity are involved, or by thermal reactions which can occur even in the dark and are controlled by the quantity of the pollutants and the temperature; (ii) shifting the equilibrium in the aerosol, between the gaseous and the particulate phases, which depends on the temperature and the molecular weight of each PAHs; (iii) dilution by increase in the mixing height, which depends on the meteorological conditions but is identically applicable for all the PAHs; (iv) the transport processes, which are functions of the wind speed and atmospheric stability; and (v) removal processes by wet and/or dry deposition (Daisey et al., 1986; Baek et al., 1991b).

In this study, the 'motor vehicle emission' component was demonstrated to be overall the most important source contributing to the variability of PAHs concentrations at the monitoring site, explaining about 30 to 50% of the total variance of each PAHs in most cases. However, comparatively lower contributions of the vehicle emission to the lower molecular weight compounds (from PHEN to BcPH) were also apparent. These more volatile compounds appeared to be explained to a similar extent by the 'photochemical activity' component. Since this component was also associated with higher-than-average ambient temperatures, the implication is that, under atmospheric conditions with an increased temperature, the concentrations of the

more volatile compounds decrease owing to the enhanced effects of volatilization and/or chemical reactions either in the atmosphere or during sampling. The importance of such meteorological factors to the variability of the more volatile PAHs appeared to be as much as that of motor vehicle emission, in terms of their contributions to the total variance. Poor correlation of BNTH with the vehicle emission component may indicate that this compound is related mainly to other sources such as coal combustion or diesel exhaust (Daisey et al., 1986).

The relatively small amount of variance explained by the 'photochemical activity' for the five to six rings PAHs is somewhat surprising since some PAHs have been demonstrated to be transformed by photochemically initiated reactions in laboratory studies (Korfmacher et al., 1980). A possible explanation for this apparent anomaly may be that the monitoring site was too close to local sources to allow enough time for appreciable atmospheric secondary reactions to occur. Furthermore, in discussing the role of photochemical and/or chemical reactivity of PAHs, it is important to differentiate, at least in principle, between losses occurring during sampling and atmospheric residence, since sampling losses due to volatilisation were demonstrated previously to be significant for up to 4-ring PAHs but negligible for five rings and larger PAHs (Pitts et al., 1986).

Nevertheless, it is interesting to note that there appeared to be a comparatively more significant correlation between the 'photochemical activity' component and BaP, about 12% of variance being explained, which has been known to be more reactive compared to other PAHs with a similar molecular weight or its isomers. (Daisey et al., 1986; Pitts et al., 1986). The Photochemical and/or chemical reactions of PAHs are of particular significance since they are capable of producing a variety of oxygenated or nitrated derivatives, some of which appear to be potent direct mutagens (Wolff et al., 1986). It is generally accepted that there is considerable reactivity between PAHs and atmospheric chemicals, while the adsorption medium appears to play a crucial role (Korfmacher et al., 1980).

The 'space heating' component also appeared to explain a significant part of the variance of a number of PAHs. The next important factor was found in general to be the 'atmospheric humidity', whereas the contributions of other components such as 'atmospheric stability' and 'wet deposition' to the variance of each PAHs did not appear to be as significant as the first four components in most cases. However, these components exhibited a consistency in their negative correlations with PAHs, which are indicative of their role in the depletion of PAHs concentrations in the atmosphere.

5. SUMMARY AND CONCLUSIONS

In this study, a statistical investigation was carried out for the evaluation of any relationships between PAHs associated with airborne suspended particulate matter and other air quality parameters under varying meteorological conditions. The air quality and meteorological data collected at South Kensington in central London during 1987 were subjected to Varimax rotated principal component analysis. A total of six components, explaining about 81% of the total variance, were retained and interpreted to represent vehicle emission (27%), photochemical activity/volatilization (17%), space heating (13%), atmospheric humidity (12%), atmospheric stability (7%), and wet deposition (5%), respectively. From a viewpoint of the atmospheric evolution of PAHs, these six components seem to be well associated with two main factors: the production and depletion of the PAHs in the urban atmosphere. It was found from the stepwise multiple regression analysis that the 'vehicle emission' component is overall the most important factor contributing to the variability of PAHs concentrations in the monitoring site, explaining about 30% to 50% of the variance of each PAHs in most cases. However, comparatively lower contributions of the 'vehicle emission' to the volatile and/or reactive PAHs were also apparent. These compounds were explained to a similar extent by the 'photochemical activity' component. The 'space heating' also explained a significant part of the variance of several PAHs, while the contributions of other com-

ponents such as 'humidity', 'atmospheric stability' and 'wet deposition' to the variance of each PAHs did not appear to be as important as the first three components in most cases. However, there was a consistency for these components in their negative correlations with PAHs data were found, indicating their roles in the depletion of PAHs concentrations in the atmosphere.

REFERENCES

- Badger, G.M. (1962) Mode of formation of carcinogens in human environment, *Nat. Cancer Inst. Monogr.*, No. 9, 1-16.
- Baek, S.O., Goldstone, M.E., Kirk, P.W.W., Lester J.N. and Perry, R. (1991a) Phase distribution and particle size dependency of polycyclic aromatic hydrocarbons in the urban atmosphere, *Chemosphere*, 22, 503-520.
- Baek, S.O., Field, R., Goldstone, M., Kirk, P.W., Lester J.N. and Perry, R. (1991b) A Review of atmospheric polycyclic aromatic hydrocarbons: sources, fate and behavior, *J. Water, Air and Soil Pollution*, 60, 279-300.
- Baek, S.O., Goldstone, M.E., Kirk, P.W.W., Lester, J.N. and Perry, R. (1991c) Methodological aspects of measuring polycyclic aromatic hydrocarbons in the urban atmosphere, *Environ. Tech.*, 12, 107-129.
- Baek, S.O., Goldstone, M.E., Kirk, P.W.W., Lester, J.N. and Perry, R. (1992) Concentrations of particulate and gaseous polycyclic aromatic hydrocarbons in London air following a reduction in the lead content of petrol in the United Kingdom, *Sci. Total Environ.*, 111, 169-199.
- Daisey, J.M., Cheney, J.L. and Liou, P.J. (1986) Profiles of organic particulate emissions from air pollution sources: status and needs for receptor source apportionment modeling, *JAPCA*, 36, 17-33.
- Greenberg, A., Bozzelli, J.W., Cannova, F., Forstner and Yokoyama, R. (1981) Correlations between lead and coronene concentrations at urban industrial sites in New Jersey, *Environ. Sci. Technol.*, 15, 567-570.
- Gordon, R.J. and Bryan, R.J. (1973) Patterns in airborne polynuclear hydrocarbon concentrations at four Los Angeles sites, *Environ. Sci. Technol.*, 7, 1050-1053.
- Henry, R.C. and Hidy, G.M. (1979) Multivariate analysis of particulate sulfate and other air quality variables by principal components-I, *Atmos. Environ.*, 13, 1581-1596.
- International Agency Research on Cancer (1983) IARC Monographs on the evaluation of the carcinogenic risk of chemicals to humans Vol 32, IARC, Lyon, 129-144.
- Korfmacher, W.A., Wehry, E.L., Mamantov, G. and Natusch, D.F.S. (1980) Resistance to photochemical decomposition of polycyclic aromatic hydrocarbons vapor-adsorbed on coal fly ash, *Environ. Sci. Technol.*, 14, 1094-1099.
- Lowe, P.R. (1977) An approximating polynomials for the computation of saturation vapor pressure, *J. App. Meteor.*, 16, 100-103.
- National Research Council (1983) Polycyclic aromatic hydrocarbons: evaluation of sources and effects, National Academy Press, Washington DC, 477 pp.
- Nelson, E.W. (1984) A simple and accurate method for calculation of the standard deviation of the horizontal wind direction, *JAPCA*, 34, 1139-1140.
- Pitts J.N.Jr., Paur, H.R., Zielinska, B., Arey, J., Winer and Mejia, V. (1986) Factors influencing the reactivity of polycyclic aromatic hydrocarbons adsorbed on filters and ambient POM with ozone, *Chemosphere*, 15, 675-685.
- Sedefian, L. and Bennett, E. (1980) A comparison of turbulence classification schemes, *Atmos. Environ.*, 14, 741-750.
- Thurston, G.D. and Spengler, J.D. (1985) A quantitative assessment of source contributions to inhalable particulate matter pollution in metropolitan Boston, *Atmos. Environ.*, 19, 9-25.
- Van Houdt, J., Alink, G. and Boleij, J. (1987) Mutagenicity of airborne particulates related to meteorological and air pollution parameters, *Sci. Total Environ.*, 61, 23-36.

- Van Vaeck, L. and Van Cauwenberghe, K.A. (1985)
Characteristic parameters of particle size distributions of primary organic constituents of ambient aerosols, *Environ. Sci. Tech.*, 19, 707-716.
- Wolff, G.T., Siak, J.S., Chan, T.L. and Korsog, P.E. (1986)
Multivariate statistical analysis of air quality data and bacterial mutagenicity data from ambient aerosols, *Atmos. Environ.*, 20, 2231-2241.