



Inferences over the sources and processes affecting polycyclic aromatic hydrocarbons in the atmosphere derived from measured data

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ABSTRACT

Data concerning atmospheric lifetime and relative source contributions of polycyclic aromatic hydrocarbons (PAH) are fragmentary and contradictory. In this study, two datasets of measurements of atmospheric PAH (sum of particulate and gaseous phases), one from a national network, the other from a more local three-site study, were analysed and used to infer processes affecting PAH in the atmosphere, and their sources. PAH congener profiles measured at urban and rural locations were remarkably similar suggesting that atmospheric decay processes are relatively slow. This allows the use of such profiles to elucidate sources. A spatial analysis of two PAH datasets showed a clear influence of industry and road traffic upon local PAH concentrations. When Principal Component Analysis (PCA) was applied to UK national network data, it showed a clear influence of steel industry emissions and of home heating emissions from coal and oil in Northern Ireland. These sites also showed different winter/summer concentration ratios to the main group of sites. In the data from Birmingham (UK), PCA identified separate factors relating to gasoline and diesel vehicles, as well as the influence of wood combustion on “Bonfire night”, and a factor related to home heating emissions which shows up only in the cold season.

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1. Introduction

Polycyclic aromatic hydrocarbons (PAH) are a series of pollutants of concern because of the well established carcinogenicity of certain compounds (Straif et al., 2005). They are formed in combustion processes and therefore very widespread within the environment. As a result of concern over their presence in the atmosphere, the European Union has set a target concentration of 1 ng m^{-3} for benzo(a)pyrene as an annual mean concentration. The UK government has adopted a recommendation from the Expert Panel on Air Quality Standards that the annual mean concentration of benzo(a)pyrene should not exceed 0.25 ng m^{-3} . In both cases, benzo(a)pyrene is taken as a marker of the carcinogenic potency of the PAH mixture. A calculation using accepted unit risk factors for chemical carcinogens shows that PAH may make a significant contribution to the excess mortality and reduced life expectancy associated with exposure to urban air pollution (Harrison et al., 2004).

While inventories are available for PAH emissions in some countries, the level of spatial disaggregation is generally poor and knowledge of dominant sources of these pollutants derives predominantly from the analysis of airborne concentration profiles. In particular, ratios of individual PAH congeners have been considered as diagnostic of specific sources (e.g. Ravindra et al., 2008; Saarnio et al., 2008). However, on close examination the supporting literature is by no means consistent in its view as to which ratios should be taken as indicative of which sources. In fact, as the composition profile of source categories is subject to change with time and with the technology of the combustion process, it may be that diagnostic ratios are of extremely limited applicability (Galarnau, 2008).

A number of studies have used Principal Component Analysis (PCA) of PAH data either alone or in combination with simultaneously measured trace element data to identify PAH with common temporal variations, which then may be associated with the same specific sources (Lee et al., 2006; Sharma et al., 2007). One problem in the early application of such methods derives from the semi-volatility of PAH and the fact that particle–vapour partitioning is highly temperature sensitive. Consequently, methods such as PCA, when applied only to particle phase PAH, tend to show compounds of comparable volatility as associated with one another as they will vary temporally in a similar manner. This, however, simply reflects their physico-chemical properties rather than a common source. Harrison

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et al. (1996) were among the first researchers in recognising this, and therefore, in carrying out their data analyses using the sum of the vapour and particle forms of specific compounds so as to eliminate the effects of particle–vapour partitioning. This led to the recognition of PAH sources in the atmosphere of Birmingham, UK. There have been relatively few such studies reported (Tian et al., 2009; Esen et al., 2008). Consequently, the knowledge on PAH sources derived from receptor modelling is extremely limited, although some recent studies (e.g. Zhang et al., 2009; Dallarose et al., 2005) have generated useful data from particle-only measurements.

Studies in the laboratory have indicated a high reactivity for PAH both in the vapour phase and on particle surfaces (Kwok et al., 1994; Esteve et al., 2006; Nadal et al., 2006; Ananthula et al., 2007). If such reaction rates occurred in reality within the atmosphere, they would lead to very large changes in both the concentrations and congener profiles of PAH when sampled from the atmosphere as many of the reactions continue on filter substrates during PAH sampling. In their review of PAH in the atmosphere, Ravindra et al. (2008) listed half-lives of selected PAHs under simulated atmospheric conditions, showing half-lives varying from 0.15 h for anthracene to 5.38 h for benzo(e)pyrene in simulated sunlight and ozone. They reported dark reactions in the presence of 0.2 ppm of ozone as leading to half-lives from 0.62 h for benzo(a)pyrene to 52.7 h for benzo(b)fluoranthene. If such half-lives occur in the atmosphere, some compounds would decay far more rapidly than others. Changes in congener profiles between the point of emission, and the sampler, as well as those changes occurring by reactions within the sampler itself (i.e. sampling artefacts) would be significant. Consequently, the interpretation of PAH congener profiles derived from airborne measurements would be confounded by differential reactivity.

Kim et al. (2009) have determined the loss rates of individual PAH during irradiation (300–500 nm) on soot, finding a complex two phase behaviour. They review the results of other comparable studies, finding highly disparate results. They examine the implications of differential PAH decay rates for source apportionment based upon PAH ratios, showing these to be substantial, even at 24 h in the case of some ratios. Consequently there are major questions over the use of diagnostic ratios, even if unique to a source, as a means of source apportionment.

In this paper, we seek to answer questions concerning the magnitude of PAH reactivity in the atmosphere and sources contributing to measured PAH by an analysis of two PAH datasets. In particular, we address the issue of whether differential reactivity of PAH makes it impossible to conduct receptor modelling studies designed to understand PAH sources.

2. Methodology

2.1. Data sources

2.1.1. UK national network data

The PAH dataset was downloaded from the UK National Air Quality Data Archive website (www.airquality.co.uk) which is hosted by the UK Department of Environment, Food and Rural Affairs (Defra) and the devolved administrations. PAH samples were collected as both PM₁₀ particulate and gas phase fractions using modified Andersen GPS-1 pesticide samplers collecting on glass fibre and polyurethane foam filters. Data are the sum of both phases.

The dataset was made up of 178 samples collected at monitoring sites covering areas of England, Scotland, Wales and Northern Ireland. For each site, the available data corresponded to quarters (three month periods) from the third quarter of 2005 to the last quarter of 2006 in some cases, and to the last quarter of 2007 in others. Quarter 1 (Q1) covered from 01/01/ to 01/04; Quarter 2 (Q2) from 01/04 to 01/07; Quarter 3 (Q3) from 01/07 to 01/10, and Quarter 4 (Q4) from 01/10 to 01/01. In the data interpretation, Quarters 1 and 4 were considered as

“cold” while quarters 2 and 3 were regarded as “warm” periods, respectively. Samples were classified according to the sampling site and period of collection, as well as the type of location: roadside (1 site), rural (2 sites), semi-rural (1 site), urban (16 sites) and urban-industrial (4 sites).

2.1.2. Data from the Birmingham area (Pongpiachan, 2006)

Air samples were collected using a high volume sampler (Tisch Environmental Inc. Model TE-6001) fitted with a PM₁₀ inlet and QM/A quartz filter for the collection of particulate matter followed by a polyurethane foam plug to collect the vapour phase semi-volatile organic compounds. The overall efficiency exceeded 90% for all PAHs. Data are the sum of both phases. The measurement took place over consecutive 23-hour periods between 20 November 2003 and 22 December 2003 (cold period) and from 5 May 2004 to 26 May 2004 (warm period). The sampling sites were as follows:

- Bristol Road Observatory site (BROS) is on the side of the busy Bristol Road adjacent to the University of Birmingham (Birmingham, UK).
- Elms Road Observatory site (EROS), which is an urban background location in an open field located at the north-western side of the University of Birmingham campus. It is about 1 km from the BROS.
- Whitbourne, a rural site, 8 km north-west of Worcester city centre and 42 km south-west of BROS and EROS in a rural area of very low population density.

Details of the pollution climate at the BROS and EROS can be obtained from Yin and Harrison (2008), and Harrison and Yin (2008). The main sources of particulate matter are secondary sources of sulphate, nitrate and organic aerosol, and road traffic. The Whitbourne site is similar to the CPSS site reported in those papers. The quartz fibre filters and polyurethane foams were subjected separately to Soxhlet extraction with dichloromethane for 24 h. The subsequent fractionation/clean-up process followed the method of Gogou et al. (1996). The cleaned and concentrated extract was then subjected to analysis by Gas Chromatography–Mass Spectrometry (GC–MS) using deuterated internal standards and quality assurance through analysis of NIST SRM1944.

A summary of the sampling data analysed appears in Table 1.

2.2. Statistical analysis

The Levene test was used to assess the variance homogeneity, while the significance of the differences was computed by the parametric *t*-test. A probability of 0.05 was considered as significant ($p < 0.05$). All statistical analyses were performed using the SPSS 15.0 statistical package.

2.3. Principal Component Analysis (PCA)

PCA was carried out by means of the SPSS 15.0 statistical package. The objective of PCA is to derive a few new components (Principal

Table 1
Summary of the number of samples collected in each sampling site and period.

	Cold	Warm
<i>UK national network data</i>		
Urban-industrial	9	11
Urban	60	62
Roadside	3	3
Rural	10	10
Semi-rural	5	5
<i>Birmingham data</i>		
Roadside (BROS)	17	11
Urban-background (EROS)	17	11
Rural (Whitbourne)	28	22

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