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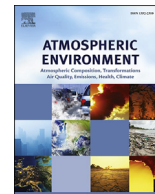
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Diurnal variability of polycyclic aromatic compound (PAC) concentrations: Relationship with meteorological conditions and inferred sources



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HIGHLIGHTS

- A wide range of PAH, oxy-PAH and nitro-PAH are analysed.
- Roadside and urban background are measured.
- Eight 3-h samples are collected each day.
- Diurnal profiles reveal compounds generated from traffic and domestic combustion.
- Isomer ratios show some influence of atmospheric chemistry.

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ABSTRACT

Polycyclic aromatic hydrocarbons (PAH) and their nitro and oxy derivatives have been sampled every three hours over one week in winter at two sites in Birmingham UK. One site is heavily influenced by road traffic and is close to residential dwellings, while the other site is a background urban location at some distance from both sources of emission. The time series of concentrations has been examined along with the ratio of concentrations between the two sampling sites. A comparison of averaged diurnal profiles has shown different patterns of behaviour which has been investigated through calculating ratios of concentration at 18:00–21:00 h relative to that at 06:00–09:00 h. This allows identification of those compounds with a strong contribution to a traffic-related maximum at 06:00–09:00 h which are predominantly the low molecular weight PAHs, together with a substantial group of quinones and nitro-PAHs. Changes in partitioning between vapour and particulate forms are unlikely to influence the ratio as the mean temperature at both times was almost identical. Most compounds show an appreciable increase in concentrations in the evening which is attributed to residential heating emissions. Compounds dominated by this source show high ratios of 18:00–21:00 concentrations relative to 06:00–09:00 concentrations and include higher molecular weight PAH and a substantial group of both quinones and nitro-PAH. The behaviour of retene, normally taken as an indicator of biomass burning, is suggestive of wood smoke only being one contributor to the evening peak in PAH and their derivatives, with coal combustion presumably being the other main contributor. Variations of PAH concentrations with wind speed show a dilution behaviour consistent with other primary pollutants, and high concentrations of a range of air pollutants were observed in an episode of low temperatures and low wind speeds towards the end of the overall sampling period consistent with poor local dispersion processes. Results from a short summer campaign give indications of the formation of some nitro-PAH by atmospheric chemical reactions.

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1. Introduction

A number of the polycyclic aromatic hydrocarbons (PAHs) which are present in the atmosphere have been identified as being carcinogenic, and the exposure to PAHs may also have other adverse health effects (WHO, 2013). One of these PAH congeners - benzo(a)pyrene – is widely used as a marker for PAHs in the atmosphere, and an EU target value of an annual average of 1 ng m^{-3} is currently in force. In the United Kingdom (UK), an air quality standard of an annual average of 0.25 ng m^{-3} for benzo(a)pyrene is included in the National Air Quality Strategy. Within the UK, a network of 34 monitoring sites collects daily samples of PM_{10} which are analysed to determine the concentration of 39 PAH congeners at each site. PAHs may be present in the atmosphere in both gaseous and particulate form, with the lower molecular weight PAH congeners being predominantly gaseous, while congeners with higher molecular weight are predominantly particulate. This partitioning is influenced by both the ambient temperature and ambient PM concentration (Yamasaki et al., 1982). PAHs are chemically reactive with atmospheric lifetimes of hours to days (Keyte et al., 2013). Consequently, while there is a long-range transport component, urban concentrations are influenced predominantly by urban emissions and processes.

Airborne PAHs are mainly combustion products or arise from the evaporation of volatile fuels. Jang et al. (2013) used Positive Matrix Factorization (PMF) and spatial distribution analysis on seven datasets to apportion PAHs measured in the UK between four source types – diesel exhausts, evaporation of vehicle fuels (although in some cases these two sources were combined), coal burning (for either domestic or industrial purposes) and wood burning. While individual PAH congeners may come from a number of source types, these authors associated low molecular weight species, especially phenanthrene, with vehicle exhaust, benz(a)anthracene and benzo(a)pyrene with coal burning, and retene and anthracene with wood burning.

Most assessments of atmospheric PAH concentrations have involved individual measurements over periods of 24 h or longer. The consequence is that information that can be extracted from diurnal changes in PAH concentrations is unavailable. Concentrations of PAH and their derivatives in the atmosphere may be subject to diurnal variations due to changes over the course of the day in source strengths, dispersion of material due to diurnal changes in meteorological factors (particularly atmospheric stability) (Williams, 2014), atmospheric reactivity (Alam et al., 2014; Keyte et al., 2013), and in the case of the particle phase, changes in temperature of the atmosphere (Yamasaki et al., 1982).

The complex nature of sample collection and analysis has limited the number and length of studies of the diurnal variability of PAH concentrations. Particulate matter has been collected by filter, over periods of less than a day, and analysed for a variety of PAH congeners and their derivatives by Souza et al. (2014) (day and night samples); Morville et al. (2011) and Delhomme and Millet (2012) (morning, midday and evening samples); Fine et al. (2004) and Reisen and Arey (2005) (four periods during day); and by Sklorz et al. (2007); Ohura et al. (2013); Tsapakis and Stephanou (2007); Pongpiachan (2013) (six periods during day). These sampling campaigns have been restricted to a limited number of days. More extensive measurement campaigns have been carried out using photo-electric aerosol sensors in which particulate matter is photo-ionised by UV radiation to which PAHs are sensitive (Chetwittayachan et al., 2002; Han et al., 2011; Cheng et al., 2012), or Aerodyne Aerosol Mass Spectrometers (Poulain et al., 2011). These instruments are limited to accessing the total PAH concentration, but are able to report concentrations on an hourly time scale.

At a site heavily influenced by road traffic (Cheng et al., 2012) concentrations of total PAH were highest throughout the working day and were correlated with the numbers of goods vehicles and buses, while Tsapakis and Stephanou (2007) found no diurnal pattern for particulate PAHs at a coastal site. The more usual diurnal pattern in urban and rural sites is for a peak in PAH concentrations in the morning, lower concentrations at midday, and a second peak in concentrations in the evening (e.g. Chetwittayachan et al., 2002; Han et al., 2011; Poulain et al., 2011; Fine et al., 2004), with these peaks generally attributed to traffic and heating respectively, in conjunction with greater atmospheric stability at these times of day.

In studies of individual congeners, Morville et al. (2011) report that in winter fluorene, phenanthrene and pyrene have similar concentrations throughout the day, while benzo(a)pyrene, benz(a)anthracene and benzo(ghi)perylene have a midday minimum concentration, with similar concentrations in the morning and evening periods. In the summer these authors found that all six congeners had a midday minimum and that the concentration was higher in the morning than in the evening. Sklorz et al. (2007) found that in summer the concentrations of benzo(ghi)perylene and coronene were greatest during the day, while those of benzo(k)fluoranthene and indeno(1,2,3-cd)pyrene were greatest at night. During the winter there was little diurnal variability of these congeners. While benzo(a)pyrene and benzo(e)pyrene concentrations did not show clear periodic variation during the summer, in winter they were higher at night (Sklorz et al., 2007).

Few studies have investigated the diurnal variation of nitro-PAH and quinone congeners. Ringuet et al. (2012) collected 12 h samples representing both diurnal and nocturnal variations at traffic and suburban sites in Paris. Although concentrations of PAH and oxy-PAH were approximately 10 times larger at the traffic site, only a small increase was observed at nighttime relative to that of daytime. 1-Nitropyrene was found to be the most abundant nitro-PAH at the traffic site suggesting a diesel source, while 2+3-nitrofluoranthene was predominantly measured at the suburban site indicative of secondary formation. Souza et al. (2014) reported significantly larger PAH, nitro-PAH and oxy-PAH concentrations during the night which was attributed to biomass burning (which occurred during night), while daytime measurements were dominated by vehicular emissions.

While a number of the studies described above were conducted in Europe, it is expected that considerable variations will be seen across the continent, reflecting the different sources and climate factors which predominate. To date, there have been many studies of PAH in the UK (e.g. Mari et al., 2010; Alam et al., 2013, 2014; Jang et al., 2013; Katsoyiannis et al., 2011), studies of PAH quinones are far fewer (Delgado-Saborit et al., 2013; Alam et al., 2013), and those of nitro-PAH are very few in number, and are now somewhat outdated (Dimashki et al., 2000). Although for PAH both airborne concentrations and source apportionment are fairly well understood, knowledge of the quinones and nitro-PAH is far less adequate.

During a one week period in January 2014, three-hourly mean concentrations of a number of particle phase PAH, quinone and nitro-PAH congeners were measured simultaneously at a roadside site and a nearby background site in southwest Birmingham. In a further short study, both particulate and vapour forms were collected during summer. We report the results and an interpretation of the influences of meteorology and sources on the measured concentrations.

2. Experimental

2.1. Measurement sites and period of measurements

The locations of the sites are presented in Table S1. The roadside

(BROS) site is located on the southern edge of the university campus, five metres from the kerb on the north side of a major arterial road, and in close proximity to a signal controlled junction with minor roads. There are two lanes of traffic in both directions, with the measurement position adjacent to the section of road where north-bound traffic queues at the traffic lights during the morning commuting period. To the south of the road there is an area of late 19th century housing which at its closest point lies some 35 m from the measurement site. The area immediately to the north of the measurement site consists of sports pitches. The background (EROS) site is some 900 m to the north of the roadside site, in an area of grassland, with a railway line and local distributor road within 100 m, respectively to the west and east. There is little housing in the close vicinity of the site.

Measurements were made at both sites over consecutive three hour periods between noon on 13th January and noon on 20th January 2014. During this winter period sunrise occurs around 08:10 h and sunset around 16:25 h, resulting in a relatively short period of solar heating.

Data for routinely measured air quality metrics is taken from the Automatic Urban and Rural Network (AURN) sites at Birmingham Tyburn and adjacent Birmingham Tyburn Roadside, approximately 10 km to the north-east of the sampling sites. A map illustrating the location of the sampling sites is shown in Fig. 1. Hourly mean values of temperature and humidity were obtained from the Winterbourne (no. 2) meteorological site which is approximately 100 m to the east of the EROS site. Hourly wind speed and direction data were obtained from the Coleshill meteorological site located in a rural area to the north east of Birmingham approximately 17 km from the PAH measurement sites. The locations of these other sites are also given in Table S1.

Three-hour PM_{2.5} samples were collected onto 150 mm diameter quartz microfiber filters simultaneously at the two locations at BROS and EROS using high volume air samplers (Digitec, DHA-80), at a typical flow rate of 500 L/min. Prior to sampling, the filters were preheated at 500 °C for 12 h in a box furnace in order to reduce organic impurities.

Samples were extracted with organic solvents and analysed for

16 PAHs, 8 quinones and 5 nitro-PAHs using similar methodologies described previously (Delgado-Saborit et al., 2013). These are based upon an earlier analytical validation study (Delgado-Saborit et al., 2010) which showed precision of 0.3%–9.7% for PAH and accuracy (defined as % deviation from reference values) of –6% to 25% in comparison with SRM 1649a. Methods for quinones and nitro-PAH were similarly validated using Standard Reference Material SRM 1649b (Delgado-Saborit et al., 2013). Briefly, filters were spiked with 1000 pg μL⁻¹ deuterated internal standards for quantification, immersed in dichloromethane (DCM) and ultra-sonicated at room temperature (25 °C) for 20 min. The extract was subsequently dried and filtered using a clean glass Pasteur pipette chromatography column filled with a small amount of glass wool and 0.5 g of fine anhydrous sodium sulphate (puriss grade for HPLC), followed by further concentration to 50 μL under a gentle N₂ flow.

Deuterated and native PAH and nitro-PAH (NPAH) standards (>98% purity in toluene or isooctane) and p-terphenyl-d14 recovery standard (>99% purity, in toluene) were obtained from Greyhound Chromatography, Merseyside, UK, as pre-prepared solutions by Chiron AS, Trondheim, Norway. Deuterated and native OPAH internal standards and 1-fluoro-7-nitrofluorene recovery standard (purity >98%) were obtained initially as solids from Sigma–Aldrich Company Ltd., Gillingham, UK and solutions prepared by dilution with hexane.

Samples were analysed for PAH compounds using Gas Chromatography (GC – 6890N Agilent Technologies) fitted with a non-polar capillary column (Agilent HP-5MS, 30 m, 0.25 mm ID, 0.25 μm film thickness – 5% phenylpolysiloxane) in tandem with a Mass Spectrometer (5973 N, Agilent Technologies) running in electronic ionisation (EI) and selective ion monitoring (SIM) mode. For quinone and nitro-PAH compounds an Agilent Technologies GC–MS (GC 6890W and 5973 MSD) equipped with a Restek Rxi-PAH column (60 m, 0.25 mm ID, 0.1 μm film thickness) was operated in negative ion chemical ionisation (NICI) and SIM mode.

A summer campaign was also conducted from August 7–9, 2012. In this campaign, both particulate and vapour forms of PAC were collected simultaneously in four daily sampling intervals, from 07.00 to 11.00, 11.00 to 15.00, 15.00 to 19.00 and 19.00 to 07.00

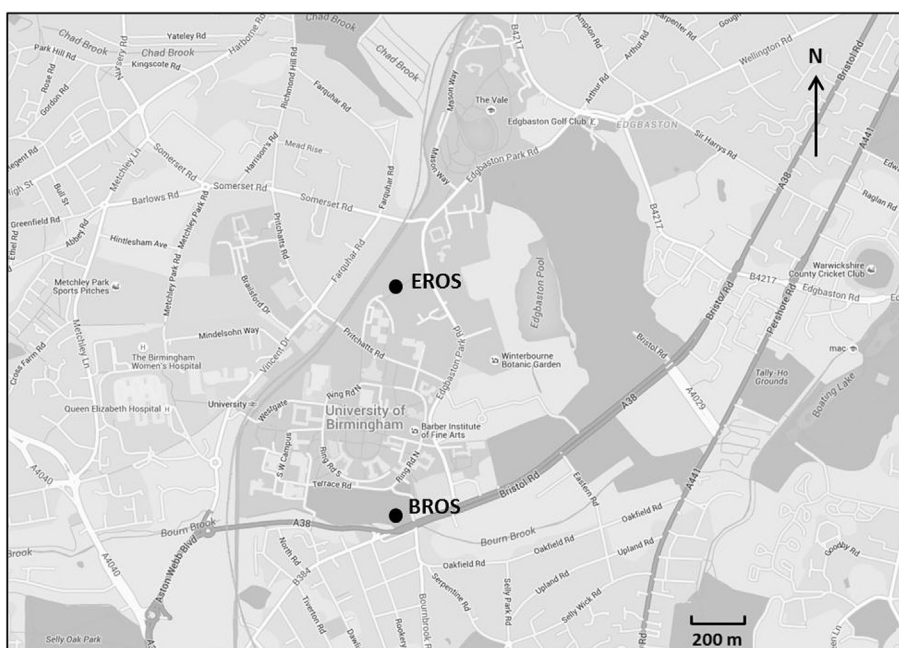


Fig. 1. Location of sampling sites.

local time (British Summer Time). The sampling methods were similar to those described in Dimashki et al. (2000) except for use of a PM₁₀ inlet in this study, and analyses were conducted using the same methods and instruments as for the winter campaign. A smaller range of compounds was however analysed.

3. Results

3.1. Measurements of meteorological and other air quality metrics during January 2014

The mean hourly values of temperature (measured at Winterbourne), and of wind speed and direction (measured at Coleshill), during the month of January 2014, are presented in Figure S1. Also shown on the graphs is the period of the campaign in which PAH concentrations were measured. Manning et al. (2000) found that, in general, when not affected by local obstacles, wind direction was consistent when measured at sites 40 km apart, although at low wind speeds this may be less true (Arciszewska and McClatchey, 2001). As Coleshill is 17 km from the PAH measurement sites, wind direction measured at Coleshill is likely to be reasonably representative of that at the measurement sites. Due to greater surface roughness, wind speed is typically lower within an urban area than at a rural location.

Measurements of NO_x and PM₁₀ made at the AURN Birmingham Tyburn background site during the month of January 2014 are presented in Fig. 2. Also shown is the period of the PAH measurement campaign. It is notable that during the final six hours of the PAH measurement campaign, there was a large increase in the concentration of the air quality metrics measured at Tyburn (Fig. 2). These high concentrations were associated with a period of low wind speed and low temperature (Figure S1), which is likely to be the cause of poor dispersal of pollutants.

During the period of the PAH measurements the wind direction was generally southerly (Figure S1) and all measurements at the BROS site are likely to be influenced by emissions both from the road and from the housing to the south. The southerly winds also probably resulted in higher air temperatures than the seasonal average. The average diurnal profiles of wind speed and temperature (Figure S2) show that both followed a diurnal cycle with maximum values during the 12:00 to 15:00 h period.

The three hourly mean concentrations of the standard air quality metrics were calculated for the Tyburn and Tyburn Roadside sites to allow comparison with the PAH results. While the Tyburn site is located at the corner of a car park to the rear of a two story office building on the south side of Tyburn Road, Birmingham, the Tyburn Roadside site is located on a narrow area of grass between the building and the road. Although during the period of the campaign the wind direction was from the building to the road, the position of the building may result in rotating eddies which transport exhaust emissions from the road to the roadside sampling

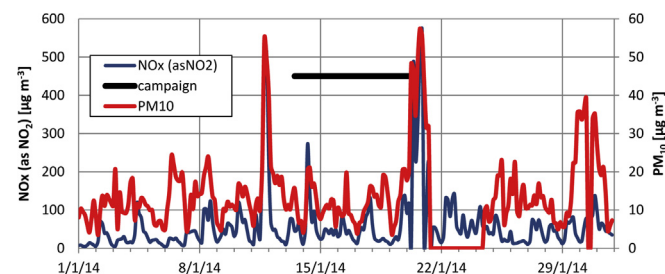


Fig. 2. NO_x and PM₁₀ concentrations measured at Birmingham Tyburn during January 2014.

position (Harrison et al., 2004). Sulphur dioxide was not measured at the roadside site, and PM_{2.5} data was not available.

3.2. Mean and median concentrations of PAH

The mean, standard deviation of the mean, and median concentrations of each of the PAHs, quinones and nitro-PAHs measured at both sites are presented in Tables 1–3 respectively. Concentrations of particle-associated PAH (Table 1) are broadly similar to those reported earlier from work at the BROS and EROS sites (Alam et al., 2013). PAH at UK urban sites typically arise from emissions from road traffic, wood combustion and coal combustion (Jang et al., 2013). Industry makes an additional contribution in locations with local sources, such as the steel industry (Jang et al., 2013), but such sources are not influential in Birmingham, where sampling took place. Concentrations of quinones were in most cases also broadly comparable with earlier measurements of the particle phase in Birmingham (Delgado-Saborit et al., 2013; Alam et al., 2014), although some appreciable differences were seen. Measurements of nitro-PAH in the Birmingham atmosphere have not been reported since collection of data in 1995/6 by Dimashki et al. (2000). That study measured only a small range of compounds and did not attempt to elucidate the sources. Concentrations in the current study appear to be substantially higher than those measured in 1995/6, possibly due to a large increase in the volume of diesel traffic. The ratios of the median concentration at BROS to that at EROS were calculated and most values of this ratio lie between 1.0 and 2.0, although some ratios are much higher (see Figure S3). Metrics with higher values of this ratio are indicated by **bold** case in Tables 1 to 3. Other expressions of the ratio, i.e. ratio of means, mean of ratios, ratio of medians and median of ratios appear in Table S2.

3.3. Variation in concentrations of PAH over the week

The concentrations of selected PAHs, quinones and nitro-PAHs at both sites are plotted over the duration of the measurement campaign in Fig. 3. Full results are given in the supplementary information (Figures S4 to S6). High concentrations of all metrics at the BROS site, and of PAHs at the EROS site, occurred during the final six hours of sampling. The concentrations of the regulated air quality metrics monitored at Tyburn (Fig. 2) show the start of a period of higher values at this time, which is likely to be a result of the meteorological conditions – low wind speed and temperature. High concentrations of some quinones and nitro-PAHs were not measured (Fig. 3, S5 and S6) at the EROS site at this time.

There is similarity in the variation of concentrations of most of the compounds over the one week period of the campaign. Higher concentrations are generally apparent during the evenings of 17 and 19 of January, while concentrations were generally low on 15 and 16 January, although to a lesser extent in the case of phenanthrene (Fig. 3d).

3.4. Diurnal variation of concentration

The mean diurnal profile of concentration (specifically excluding the last six hours of sampling so as not to bias the data) was calculated for each of the congeners, and is shown for selected examples in Fig. 4. The supplementary information contains diurnal profiles for all PAHs, quinones and nitro-PAHs (Figures S7 to S9). Each of the mean values was calculated from 6 or 7 individual values of concentration, and the error bars in these figures show the standard error in the mean for each time period. The final six hours of sampling were excluded as this period was clearly exceptional and the higher concentrations measured during this time would

Table 1
Average PAH concentrations at the roadside and background sites (winter campaign).

PAHs [ng m ⁻³]	BROS (roadside)			EROS (background)			Ratio of medians
	Mean	Std dev	Median	Mean	Std dev	Median	
Fluorene	0.0557	0.0285	0.0485	0.0362	0.0228	0.0285	1.70
Phenanthrene	0.5879	0.2904	0.5210	0.2732	0.2531	0.1930	2.70
Anthracene	0.0898	0.0540	0.0790	0.0631	0.0501	0.0493	1.60
Fluoranthene	1.0108	0.4651	0.9696	0.3686	0.5007	0.1928	5.03
Pyrene	1.0752	0.5296	0.9940	0.3472	0.5546	0.1836	5.42
Benzo(a)anthracene	0.2773	0.2427	0.1883	0.2305	0.4011	0.1109	1.70
Chrysene	0.6577	0.5277	0.4911	0.5953	0.8083	0.3212	1.53
Retene	0.4020	0.4308	0.2770	0.2083	0.2621	0.1109	2.50
Benzo(b)fluoranthene	0.3493	0.3033	0.2514	0.4282	0.4781	0.2344	1.07
Benzo(k)fluoranthene	0.3932	0.3404	0.2922	0.3836	0.4582	0.1890	1.55
Benzo(e)pyrene	0.3548	0.2903	0.2731	0.3910	0.4277	0.2144	1.27
Benzo(a)pyrene	0.3612	0.3061	0.2798	0.3155	0.4060	0.1702	1.64
Indeno(1,2,3-cd)pyrene	0.2939	0.2381	0.2343	0.3355	0.3832	0.2120	1.11
Dibenz(a,h)anthracene	0.0599	0.0534	0.0457	0.0752	0.0768	0.0430	1.05
Benzo(ghi)perylene	0.4513	0.3216	0.3691	0.4796	0.5264	0.3082	1.20
Coronene	0.1764	0.1284	0.1479	0.1817	0.2480	0.1045	1.42

Table 2
Average Quinone concentrations at the roadside and background sites (winter campaign).

Quinones [ng m ⁻³]	BROS (roadside)			EROS (background)			Ratio of medians
	Mean	Std dev	Median	Mean	Std dev	Median	
1,4-Naphthoquinone	0.0052	0.0056	0.0031	0.0150	0.0622	0.0020	1.59
2-Methyl-1,4-naphthoquinone	0.8077	1.6064	0.2597	0.5676	0.7955	0.2290	1.13
Anthraquinone	0.5431	0.5026	0.3763	0.3262	0.3089	0.2563	1.47
2-Methyl-anthraquinone	0.0478	0.0477	0.0302	0.0311	0.0483	0.0182	1.66
Phenanthraquinone	0.5150	0.4756	0.3571	0.3104	0.2940	0.2439	1.46
2,3-Dimethyl-anthraquinone	0.0243	0.0288	0.0138	0.0207	0.0448	0.0097	1.41
Benz[a]anthracenequinone-7,12-dione	0.2015	0.2641	0.0898	0.1574	0.1706	0.0781	1.15
5,12-Naphthacenequinone	0.312	0.4969	0.1322	0.1447	0.2937	0.0619	2.14

Table 3
Average Nitro-PAH concentrations at the roadside and background sites (winter campaign).

Nitro-PAHs (ng m ⁻³)	BROS (roadside)			EROS (background)			Ratio of medians
	Mean	Std dev	Median	Mean	Std dev	Median	
1-Nitronaphthalene	2.2242	2.9084	1.2704	0.5295	0.6523	0.3446	3.69
2-Nitronaphthalene	1.4719	1.7297	0.9847	0.4612	0.5420	0.2580	3.82
1,5-Dinitronaphthalene	0.2364	0.4017	0.1485	0.1451	0.3287	0.0833	1.78
2-Nitrofluorene	0.6894	1.0343	0.3832	0.2646	0.1867	0.2305	1.66
9-Nitroanthracene	0.4063	0.5953	0.2154	0.2956	0.3635	0.1523	1.41

have dominated diurnal profiles calculated from only seven days of data in certain cases. Including this six hour period would also have resulted in much larger values for the calculated error in the mean during the 06:00 to 09:00 h and 09:00 to 12:00 h periods than in the other time periods. The effect of including the last six hours of data is shown in Fig. 4 (and supplementary information, Figures S7 to S9) by dotted lines. The result in the case of some of the congeners (e. g. retene, Fig. 4c) is to introduce a peak at 09:00 to 12:00 h which dominates the diurnal profile artificially as data from after 12:00 h during this period of high concentrations was not available.

It is clear from Fig. 4 that the average diurnal profiles vary quite significantly. A comparison, for example between phenanthrene and indeno(1,2,3-cd)pyrene shows phenanthrene to have a much larger elevation at the BROS site and to have a larger concentration at 06:00–09:00 h compared to that at 18:00–21:00 h in comparison to indeno(1,2,3-cd)pyrene. Since the plot of averaged temperatures (Figure S2) shows averaged temperatures at these two time intervals to be almost identical at 5.0 °C and 5.2 °C respectively, it can be concluded that particle-vapour partitioning should

not be an appreciable influence on the comparison of ratios at these times. Consequently, the median of the concentration ratio of 18:00–21:00 to that at 06:00–09:00 at both EROS and BROS sites is tabulated in Table 4. This shows a very substantial range of ratios from below 1 at BROS for the low molecular weight PAHs to values in excess of 4 for a few compounds. The table has been shaded to distinguish different groupings of compounds. Those in Group A have typically low ratios at both sites implying that the 06:00–09:00 peak is of similar magnitude to the evening peak at 18:00–21:00 h. The large morning peak is likely to be associated with rush hour traffic and hence these compounds appear to be predominantly traffic-associated. The Group C compounds have the highest ratios, in most cases >2 showing a strong predominance in the evening and most probably associated primarily with residential heating emissions. Group B compounds lie somewhere in between and presumably there are significant contributions from both source types. One compound that does not fit well with this interpretation is retene which lies in Group B but is generally regarded as arising only as an emission from wood combustion and is certainly not from road traffic in Birmingham (unpublished data).

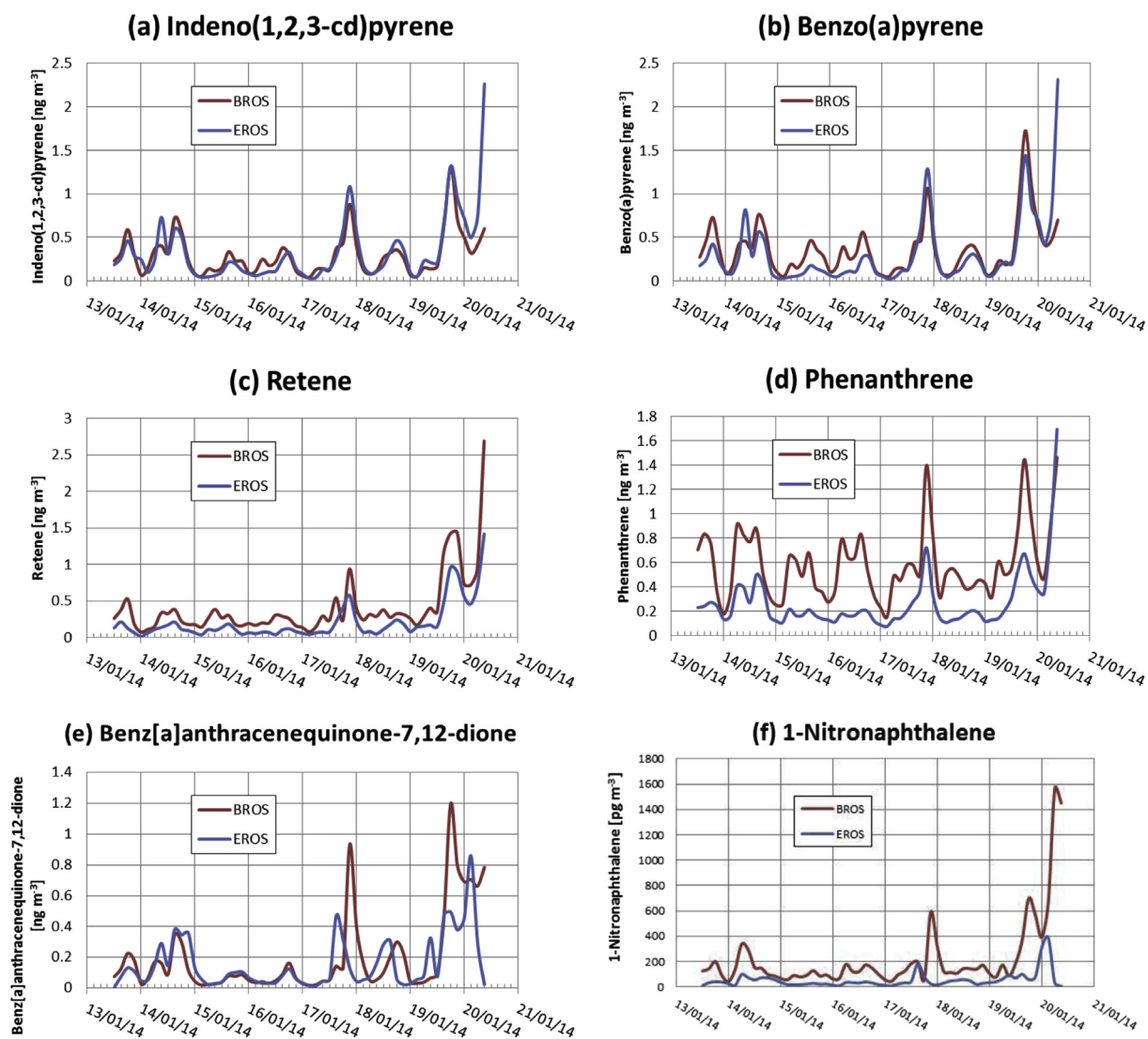


Fig. 3. Concentration of selected PAHs, quinones and nitro-PAHs over the duration of the measurement campaign: (a) Indeno(1,2,3-cd)pyrene; (b) Benzo(a)pyrene; (c) Retene; (d) Phenanthrene; (e) Benz(a)anthracenequinone-7,12-dione; (f) 1-Nitronaphthalene.

Our interpretation of this behaviour is that the evening peak is driven by residential heating using both wood and coal as fuels and the wood burning emissions are only partially responsible for the high elevation in concentrations seen in the Group C compounds for which combustion of coal is likely to make a more significant contribution.

3.5. Variation of diurnal concentration with diurnal temperature

The mean value of the concentration for each time period is plotted against the mean temperature of that time period in Fig. 5 for indeno(1,2,3-cd)pyrene, benzo(a)pyrene, retene, phenanthrene, benz(a)anthracenequinone-7,12-dione, and 1-nitronaphthalene. The equivalent graphs for all PAHs, quinones and nitro-PAHs measured are shown in the Supplementary information (Figures S10 to S12). The concentrations measured during the final six hours of sampling were again excluded from these calculations of mean values for the reasons addressed above. The direction of the diurnal cycle is shown by arrows, while the 06:00 to 09:00 h and 15:00 to 18:00 h periods – when the influence of traffic emissions is likely to be greatest – are indicated by symbols.

In the case of most metrics these profiles are similar, with an increase in concentration during daylight hours (08:00 to 16:00), and an often larger increase in concentration as temperatures fall rapidly until the 19:00 to 21:00 period, followed by a reduction in concentration until the pre-dawn period as temperature falls less rapidly. There is evidence in Fig. 5, and S10 to S12 of an elevated concentration in the 06:00 to 09:00 h period at the roadside (BROS) site, while the background (EROS) site has elevated concentrations during the 09:00 to 12:00 h period, although this effect is generally small compared to the standard errors in the means of concentration (Figures S7 to S9).

A number of distinct characteristics are apparent in the profiles (Fig. 5). The profiles of indeno(1,2,3-cd)pyrene (Fig. 5a), benzo(b) fluoranthene, benzo(e)pyrene (see Figure S10) are similar at both sites indicating that there is no dominant local source at either site and that primary emissions from road traffic or the nearby housing at BROS are not significant influences. Certain of the other profiles show higher concentrations at the roadside site where the concentration either shows a greater variation at one site (e.g. benzo(a) pyrene (Fig. 5b) and chrysene (Figure S10)), or where the concentrations at the roadside site are higher by a constant quantity (e.g.

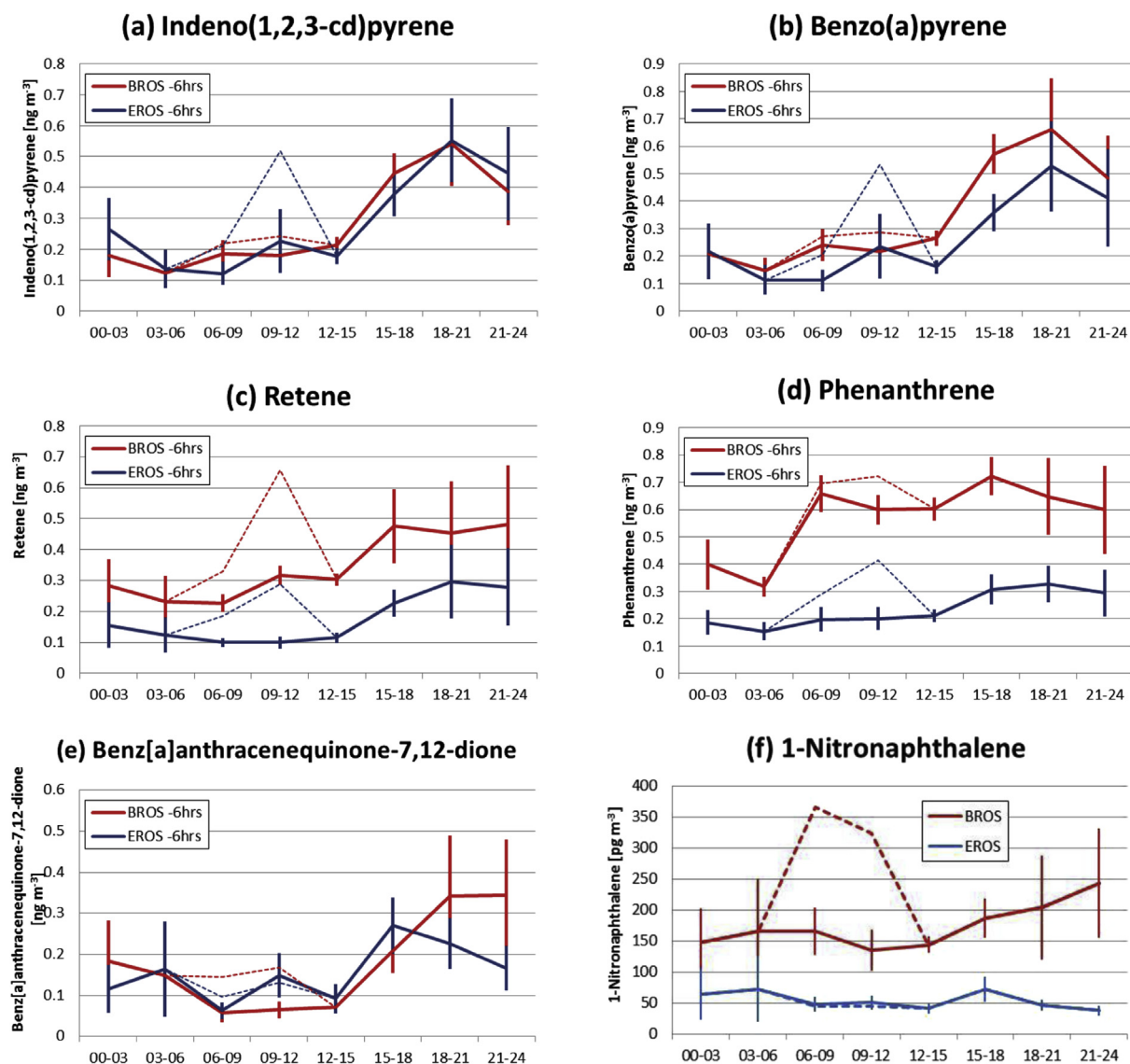


Fig. 4. Diurnal concentration profiles of selected PAHs, quinones and nitro-PAHs over the duration of the measurement campaign: (a) Indeno(1,2,3-cd)pyrene; (b) Benzo(a)pyrene; (c) Retene; (d) Phenanthrene; (e) Benz(a)anthracenequinone-7,12-dione; (f) 1-Nitronaphthalene.

retene; Fig. 5c).

In the case of some congeners such as phenanthrene (Fig. 5d), fluorene, anthracene, fluoranthene and pyrene (Figure S10) concentrations are higher at the roadside site than at the background site, increasing rapidly during the 06:00 to 09:00 h period, remaining high until the 15:00 to 18:00 h period, and then falling. This effect can be ascribed to primary road traffic emissions as a result of higher traffic flows during the working day. In contrast there are other compounds (e.g. benz(a)anthracenequinone-7,12-dione (Fig. 5e)), which have similar diurnal concentration profiles for most of the day, but where concentrations at the BROS site are elevated during the 18:00 to 21:00 h and 21:00 to 24:00 h periods. This may be the effect of primary emissions from residential heating from the area of housing to the south of the BROS site during the winter evening.

Some of the profiles (e.g. 1-nitronaphthalene (Fig. 5f)), show rapid increases in concentration at the EROS site at the lowest temperatures which may be the result of transformation from vapour to the particulate form at low temperatures. This effect is not apparent for these metrics at the BROS site where

concentrations are generally higher. However, the overall temperature range is quite small (Figure S2), and expected to lead to relatively small changes in partitioning.

3.6. Variation of concentration with wind speed

All concentration data were sorted by wind speed and the mean values of concentration of selected congeners at each wind speed are plotted against wind speed in Figure S13 to S16. The error bars show the standard error in the means. Unlike the distribution of data by time of day, the distribution of wind speed is heavily weighted to moderate wind speeds (Table S3) resulting in higher values of standard error at low and high wind speeds where the quantity of data is less. However, the relatively small values of standard error at these moderate wind speeds (Figures S13 to S16) compared to those at all times of day are less than would occur simply as a result of the greater availability of data, and are indicative of a strong relationship between concentration and wind speed.

Previous work (Jones et al., 2010) has shown that increased

Table 4
Median ratios of 18:00–21:00 concentrations to those at 06:00–09:00 at both sites for each congener (winter campaign).

	EROS Median	BROS Median
Fluorene	1.26	0.78
Phenanthrene	1.51	0.73
Anthracene	1.58	0.94
Fluoranthene	2.32	0.60
Pyrene	2.93	0.60
Benzo(a)anthracene	4.56	2.29
Chrysene	3.37	2.29
Benzo(b)fluoranthene	5.79	3.38
Benzo(k)fluoranthene	5.22	2.95
Benzo(e)pyrene	5.69	2.95
Benzo(a)pyrene	5.16	2.68
Indeno(1,2,3-cd)pyrene	4.73	2.48
Dibenz(a,h)anthracene	7.97	4.39
Benzo(ghi)perylene	3.53	1.94
Coronene	3.09	1.63
Retene	2.32	1.37
1,4-Naphthoquinone	0.61	0.89
2-Methyl-1,4-naphthoquinone	0.75	0.88
Anthraquinone	1.94	1.73
2-Methyl-anthraquinone	1.88	1.58
Phenanthraquinone	1.94	1.72
2,3-Dimethyl-anthraquinone	1.39	1.73
Benz(a)anthracenequinone-7,12-dione	4.26	4.83
5,12-Naphthacenequinone	2.21	2.81
1-Nitronaphthalene	0.91	0.88
2-Nitronaphthalene	1.21	0.80
1,5-Dinitronaphthalene	2.21	1.32
2-Nitrofluorene	0.98	0.86
9-Nitroanthracene	1.49	3.60

Key: Group A; Group B; Group C:

wind speed results in a general reduction of concentrations of airborne particulate due to increased vertical dispersion, with more rapid reductions of concentration in the vicinity of discrete point or line sources at low wind speed due to dilution at source, and increases in concentration at high wind speeds due to material being raised from the surface by the action of the wind. An increase of concentration at moderate wind speeds may also be seen where particulate matter from a buoyant source (Carslaw et al., 2006), or material from an elevated source is mixed downwards more rapidly.

Some of the plots of concentration versus wind speed show concentrations increasing with wind speed at the highest wind speeds (e.g. Figure S13a) – evidence of some resuspension. The plots of indeno(1,2,3-cd)pyrene and benzo(a)pyrene versus wind speed (Figure S13a and b) show higher background concentrations

at the EROS site than the roadside BROS site at low wind speed, while for benz(a)anthracenequinone-7,12-dione (Figure S13e) concentrations are higher at the roadside site than at the background site. However, this result is based on only three observations at the lowest wind speed and may be affected by other factors such as the poor air-quality event which occurred at the end of the campaign, and the standard errors are notably large.

3.7. Comparison with standard air quality metrics

Similar analyses of PM₁₀ and NO_x (as NO₂) from the Tyburn and Tyburn Roadside AURN sites are shown in Figure S17. The equivalent results for all AQ metrics measured at Tyburn and Tyburn Roadside AURN sites are also presented in the Supplementary Information (Figures S18 to S21). The concentration trends of

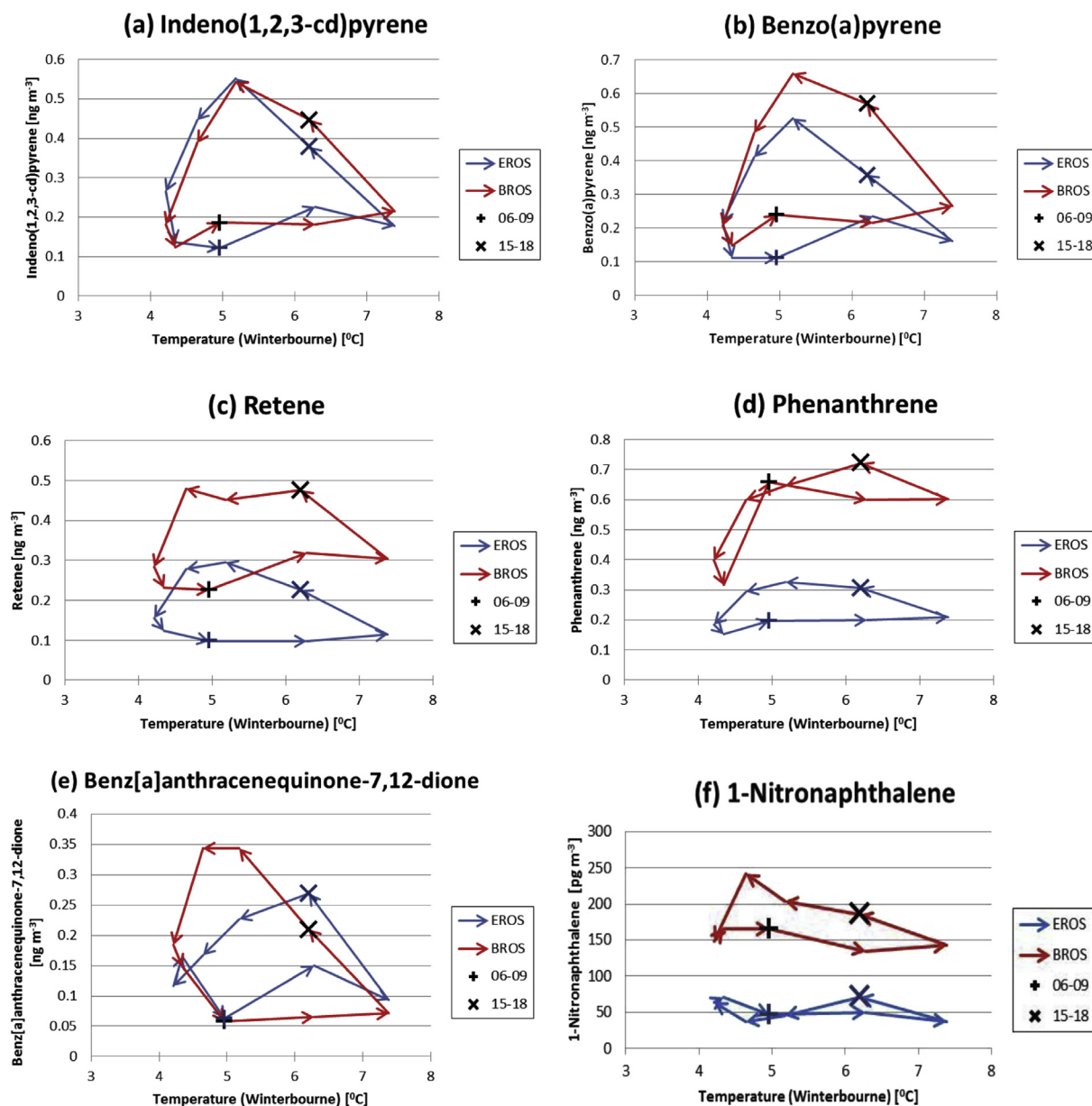


Fig. 5. Variation of diurnal concentration of selected PAHs, quinones and nitro-PAHs with diurnal temperature: (a) Indeno(1,2,3-cd)pyrene; (b) Benzo(a)pyrene; (c) Retene; (d) Phenanthrene; (e) Benz(a)anthracenequinone-7,12-dione; (f) 1-Nitronaphthalene.

these metrics are similar to those of the PAHs with high concentrations in the final six hour period of the campaign (Figure S17a–b).

The diurnal plots of the air quality metrics (excluding the final six hours of data) show similar roadside and background concentrations of PM₁₀ (Figure S17c), and elevated roadside concentrations of NO_x (Figure S17d) commensurate with the latter being more dependent on primary traffic emissions. In general there are higher concentrations of each metric around the morning and evening commuting periods (06:00–09:00; 15:00–18:00). The plots of the diurnal mean concentrations of NO_x against diurnal temperature (Figure S17f) are similar to those of phenanthrene, (Fig. 5d), identified above as being heavily traffic influenced.

The plots of PM₁₀ and NO_x concentrations against wind speed (Figure S17g and h) show a more rapid reduction of NO_x concentration with wind speed at low wind speeds at the roadside site (Figure S17 h) – consistent with a traffic generated pollutant, and

increases in the concentrations of PM₁₀ at higher wind speeds – consistent with the resuspension of particulate matter.

3.8. Summer campaign

This was less substantial, but had the advantage of including the sampling of vapour. Most compounds showed a broadly similar pattern of behaviour, exemplified by data for benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(e)pyrene and benzo(a)pyrene at the roadside site (BROS) in Fig. 6. This shows a substantial morning rush hour (07:00–11:00) maximum, with much reduced concentrations through the remainder of the day. The quinones and nitro-PAH showed a broadly similar pattern. Some PAH showed a modest increase in the afternoon (15:00–19:00) relative to the daytime (11:00–15:00) sample, possibly reflective of higher traffic levels at this time.

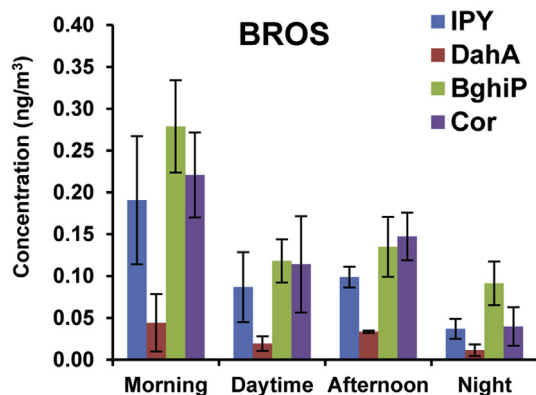
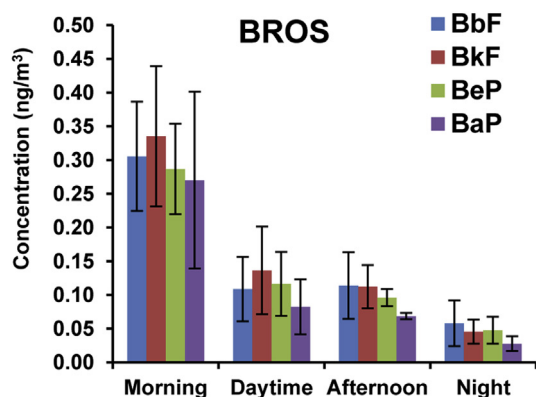
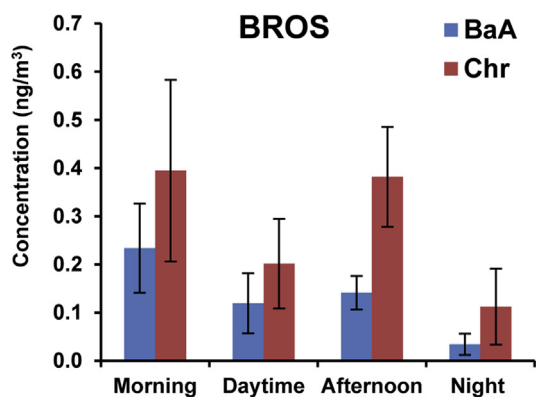


Fig. 6. Diurnal profiles of PAHs at BROS. Morning = 0700–1100; Daytime = 1100–1500; Afternoon = 1500–1900; Night = 1900–0700 (summer campaign).

When concentrations were normalised by concentrations of NO_x , measured at the Tyburn station, shown for benzo(b)fluoranthene in Fig. 7, the diurnal profile flattens, especially at the background site, EROS, with a reduction in the nighttime sample. This reflects a decrease in the PAH/ NO_x ratio at night, probably as a result of lower emissions or greater reactivity of PAH. This is contrary to the behaviour seen in the winter data, but readily explained by the lack of a residential combustion source in summer. Some nitro-PAH (9-nitroanthracene, 1-nitronaphthalene and 2-nitronaphthalene) show similar behaviour to PAH in the PAH/ NO_x plots, reflective of combustion sources, while other derivatives (9-fluorenone, anthraquinone and most notably 2-nitrofluoranthene and 2-nitropyrene) show a substantial increase in the daytime (11.00–15.00) sample relative to the other samples (Fig. 8),

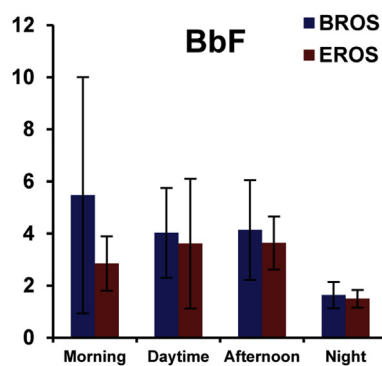


Fig. 7. Diurnal concentration profiles for benzo(b)fluoranthene (summer campaign) normalised by NO_x concentration ($\text{pg m}^{-3}/\mu\text{g m}^{-3}$).

probably reflecting daytime formation involving the hydroxyl radical, as also reported by Ciccioli et al. (1996) and Tsapakis and Stephanou (2007).

3.9. Sources of quinones and nitro-PAH

In the Supplementary information to their review, Keyte et al. (2013) list the reported sources of quinones and nitro-PAH. Of those compounds measured in this work, road traffic sources are reported for all except 2,3-dimethylantraquinone and 1,5-dinitronaphthalene, which are not listed by Keyte et al. (2013). Emissions from wood and coal combustion are listed for very few of the compounds, but this may reflect a lack of measurements, and where data are reported, the relative magnitude of emissions from traffic exhaust and coal/wood combustion is not evaluated. Consequently, our study breaks new ground in demonstrating the

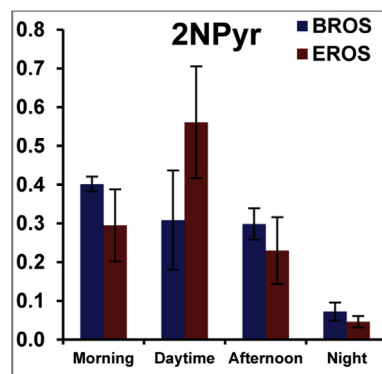
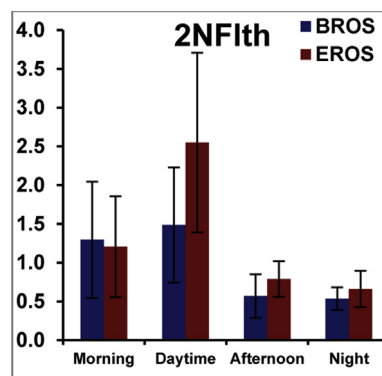


Fig. 8. Diurnal concentration profiles for 2-nitrofluoranthene and 2-nitropyrene (summer campaign) normalised by NO_x concentration ($\text{pg m}^{-3}/\mu\text{g m}^{-3}$).

importance of the Group C compounds in Table 4 as emissions from combustion of these solid fuels. For those in Group A, it is likely that traffic emissions dominate strongly relative to solid fuels. Some secondary nitro-PAH formation from nocturnal pathways involving the NO₃ radical may also be an important influence in the winter data, but from the diurnal profiles in Figure S9, this does not appear to be important. On the contrary, daytime formation of 2-nitropyrene, 2-nitrofluoranthene, 9-fluorenone and anthraquinone does appear to be significant in summer.

3.10. Ratios of nitrofluoranthene to nitropyrenes

Keyte et al. (2013) report that 2-nitrofluoranthene (2N-Flt) and 2-nitropyrene (2N-Pyr) have been widely observed in the atmosphere, but are not generally observed in primary emissions, implying that they are atmospheric reaction products. On the other hand, 1-nitropyrene (1N-Pyr) is widely observed in emissions and in this work shows a highly elevated BROS/EROS ratio (Table 3) and low (Group A) ratio of 18.00–21.00/06.00–09.00 concentrations (Table 4) consistent with a major road traffic source. As reviewed by Keyte et al. (2013), the 2N-Flt/1N-Pyr ratio can be indicative of the relative importance of atmospheric formation as compared to direct emission. Ratios of >5 are considered to indicate the dominance of atmospheric reactions over emissions. From the winter data, the mean and median 2N-Flt/1N-Pyr ratios are 1.5 and 1.1 at BROS and 5.0 and 4.3 at EROS. The daytime mean 2N-Flt/1N-Pyr ratios are 0.7 at BROS and 3.5 at EROS, whilst night time ratios are 2.4 at BROS and 6.7 at EROS. This suggests that atmospheric reactions are of limited importance at this time of year, but can be dominant over emissions at night, particularly at EROS. In the summer data, the 2N-Flt/2N-Pyr ratios remain low (<5) throughout the diurnal cycle at BROS, but at EROS climbed to >9 during the daytime (11.00–16.00) and nighttime (19.00–07.00) periods, indicative of formation from atmospheric reactions at these times.

Information on the relative importance of daytime (OH radical) and nighttime (NO₃ radical) reactions can be inferred from the 2N-Flt/2N-Pyr ratio as 2N-Flt can be formed from both OH and NO₃ reactions while only OH-initiated reactions are important for 2N-Pyr formation. According to Albinet et al. (2008) a ratio of 5–10 is indicative of a dominant OH radical pathway, while values above 100 are consistent with the NO₃ reaction pathway. In the winter data mean and median values of the 2N-Flt/2N-Pyr ratio are respectively 6.5 and 8.1 at BROS, and 7.5 and 8.8 at EROS. The day and night mean 2N-Flt/2N-Pyr ratios are 5.8 and 7.0 at BROS, and 6.7 and 11.9 at EROS, indicating a dominant OH radical pathway. In summer, mean ratios are low (<7) at both sites during daylight hours (samples between 07.00 and 19.00) consistent with the yield ratio from OH reaction for equal concentrations of parent compounds in the atmosphere (Atkinson and Arey, 1994). In the nighttime (19.00–07.00) samples, the mean ratio is >12 at both sites, indicative of NO₃ reactions influencing formation, but far higher ratios have been reported in some other studies (Keyte et al., 2013).

There is some, limited evidence for atmospheric formation of compounds such as 2-nitrofluoranthene and 2-nitropyrene, especially in summer with both OH and NO₃-initiated reactions playing a role. In general, however, such reactions do not make a major contribution to quinone and nitro-PAH concentrations at our sites, consistent with a sampling location with many influential local sources, especially road traffic throughout the year, and residential heating in the winter season.

4. Discussion and conclusions

Variability in the concentrations of airborne material may be a

consequence of:

- changes in the rate of emission of primary material which may be due to the human-influenced diurnal cycle of the working and domestic day, or to the effect of the solar day on the emission of natural material,
- chemical or physical changes in the state of the airborne material that may occur due to the diurnal cycle of meteorological variables such as temperature,
- changes in the ability of the atmosphere to disperse material due to changes in atmospheric stability or airflow.

There are congeners for which concentrations are higher at the roadside site than at the background site, although this difference falls into three different patterns. In the case of phenanthrene (Fig. 5d), fluorene, pyrene and anthracene the roadside increase occurs primarily during the working day – presumably as a result of higher traffic levels, while for some other congeners such as retene (Fig. 5c), 1-nitronaphthalene, and 2-nitronaphthalene the higher concentration is consistent throughout the 24-h period. In contrast, the higher concentrations of benz(a)anthracenequinone-7,12-dione (Fig. 5e) occur during the evening, and may be a consequence of domestic activity (heating or cooking) in the housing to the south of the road.

The increase in concentration of some quinones and nitro-PAHs such as 1-nitronaphthalene (Fig. 5f) which occurs at the lowest air temperatures at the EROS site may in part be a consequence of changes in vapour-particulate partitioning at low temperatures. That this occurs at the EROS site but not at the BROS site suggests that re-partitioning due to temperature is not a major factor. Due to the southerly wind direction, the minimum mean night-time air temperature was in excess of 4 °C, which is relatively high for January, and diurnal temperature variations were modest (Figure S2).

The relatively small standard errors in the mean concentrations at moderate wind speeds compared to those obtained at different times of day, are in part a result of there being twice the data available at these wind speeds. The greater dispersion of material at higher wind speeds has an important effect on the airborne concentrations. Although a limited amount of data is available at higher wind speeds, the small increase in concentrations at the highest measured wind speed is indicative of a contribution of wind resuspended dust to PAHs such as indeno(1,2,3-cd)pyrene (Figure S13a), quinones and nitro-PAHs.

The analysis of the ratio of concentrations at 18:00–21:00 relative to that at 06:00–09:00 h is particularly instructive. This shows results consistent with those from the receptor modelling of Jang et al. (2013) and of the UK National Atmospheric Emissions Inventory (<http://naei.defra.gov.uk/>; Mari et al., 2010; Katsoyiannis et al., 2011) which shows road traffic and residential fuel combustion to be the major sources of PAH emissions. Jang et al. (2013) found that a factor associated with evaporation of automotive fuels explained a large proportion of the variation in the low molecular weight PAH species and this is consistent with the results seen in Fig. 4 and Table 4 in which it is interpreted that the Group A compounds are associated predominantly with traffic emissions. In that work, both the coal combustion and wood combustion factors explained a large proportion of the variation in the high molecular weight PAH, again consistent with the results in Table 4 in which Group C is interpreted as heavily associated with domestic heating emissions. As explained above, the compounds in Group B probably have appreciable contributions from both road traffic and domestic heating emissions with the exception of retene which is likely to be solely associated with wood burning and indicates that wood burning is only partially responsible for the high evening

concentrations with another residential heating source, most probably coal combustion, also responsible. This work extends the results from the other studies in showing that groups of quinones and nitro-PAH have strong associations with traffic emissions on the one hand (Group A) (Alam et al., 2013; Ringuet et al., 2012) and residential heating emissions on the other (Group C) (Shen et al., 2012, 2013). Many of these compounds are rarely measured in field studies.

There is some, limited evidence for atmospheric formation of compounds such as 2-nitrofluoranthene and 2-nitropyrene, especially in summer with both OH and NO₃-initiated reactions playing a role. In general, however, such reactions do not make a major contribution to quinone and nitro-PAH concentrations at our sites, consistent with a sampling location with many influential local sources, especially road traffic throughout the year, and residential heating in the winter season.

Acknowledgements

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Appendix A. Supplementary information

Supplementary information related to this article can be found at <http://dx.doi.org/10.1016/j.atmosenv.2015.09.050>.

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