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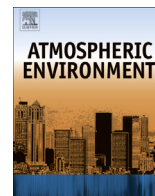
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Using atmospheric measurements of PAH and quinone compounds at roadside and urban background sites to assess sources and reactivity[☆]



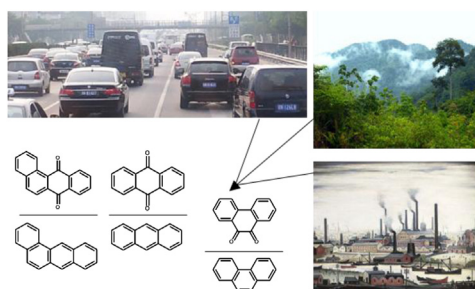
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HIGHLIGHTS

- Fourteen PAH and 11 quinone compound measurements at roadside and suburban sites.
- PAH and quinone congener traffic profile determined from measurements.
- PAH diagnostic ratios evaluated and utilised to assess reactivity.
- Simultaneous quinone to parent PAH ratios explored signifying importance of reactivity.

GRAPHICAL ABSTRACT



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ABSTRACT

The sources of polycyclic aromatic hydrocarbon (PAH) in various environmental media have commonly been identified based on the ratios of concentrations of selected PAH congeners. These ratios are applicable to various environmental media and distinguish between sources originating from vehicular emissions, petroleum products, petroleum combustion, coal and biomass burning. In this study an evaluation of PAH diagnostic ratios is provided for vapour and particulate phase samples collected simultaneously at well defined roadside and suburban sites in Birmingham, UK. It focuses on 14 PAH and 11 quinone compounds which were measured at both sites to obtain information upon traffic emissions (and subsequently a PAH congener traffic profile) and to evaluate the validity of PAH diagnostic ratios. The results suggest that PAH ratios of the low molecular weight compounds are less stable and more susceptible to atmospheric processing, indicating the importance of determining PAH ratio threshold values based on well defined samples. Quinone to parent-PAH ratios were also examined to assess the potential reactivity of PAH compounds, where the results suggest that significant atmospheric processing occurs during transport, altering the ratios between both sites, in a manner related to the relative reactivity of different PAH congeners.

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1. Introduction

Polycyclic aromatic hydrocarbons (PAH) are a class of ubiquitous semi-volatile organic compounds, partitioned between the vapour and particulate phase. The vapour phase tends to contain predominantly low molecular weight (LMW) PAH, comprising two to four fused benzene rings (<228 Da); whereas high molecular weight (HMW) PAH with five or more fused rings (>252 Da) are

mainly associated with particulate matter (PM). They are produced mainly through incomplete combustion or pyrolysis of organic material. Major anthropogenic sources include coal and wood burning, petrol and diesel oil combustion and various industrial processes (Mastral and Callen, 2000; Bzdusek et al., 2004). Some combustion processes are however, natural such as volcanic eruptions and biomass burning (van de Schootbrugge et al., 2009; Iinuma et al., 2007). The ubiquitous and semi-volatile nature of PAH, means that previous emissions that have deposited on various media (e.g. soil and vegetation) may be re-emitted into the atmosphere; with some studies reporting LMW PAH being formed naturally in soils and subsequently volatilizing into the atmosphere (Cabrerizo et al., 2011). PAH can also undergo long-range transport reaching rural areas and high altitudes and latitudes (Alam et al., 2013; Lammel et al., 2009; Dvorska et al., 2011).

The mutagenic and carcinogenic properties that many PAH possess have led to many human health concerns (Collins et al., 1998). Consequently, the European Union has set specific target concentrations for airborne PAH (e.g. benzo(a)pyrene taken as a marker of the mixture has a target of 1 ng/m^3 as an annual mean concentration) and action internationally aims to reduce emissions to the atmosphere. PAH are emitted into the environment as a complex mixture containing many structural isomers and derivatives. Recently, PAH quinone derivatives have also become a focus of interest, primarily because they can contribute to oxidative stress and are believed by some to be more toxic than their parent PAH (Sidhu et al., 2005; Walgraevae et al., 2010). Although oxygenated-PAH (OPAH) including quinones are released into the atmosphere during incomplete combustion processes along with PAH, they are also formed *via* atmospheric processing. PAH can react with atmospheric oxidants including OH, O₃ and NO₃ to form a variety of OPAH and nitro-PAH (Atkinson and Arey, 2007). However, the relative contribution to the observed atmospheric burden of PAH quinone (and nitro-PAH) derivatives from direct combustion emissions and secondary atmospheric reactions is far from fully understood.

Apportioning PAH and quinones to different sources is an essential part of their risk assessment and management, and many source and receptor orientated techniques have been developed to evaluate source contributions (Watson et al., 2002). Traditionally PAH source apportionment investigations have distinguished between petrogenic and pyrogenic sources using molecular fingerprints of PAH isomers within the same molecular class (Yunker et al., 2002). The ratios of defined pairs of individual PAH compounds, also known as diagnostic ratios, have been extensively used as markers of different sources, since outlined by Yunker et al. (2002). It has been suggested that some PAH compounds are emitted in reasonably regular proportions and it is assumed that the paired compounds are diluted to a similar extent during transport, and thus their subsequent ratios remain constant between the source and receptor. It is on this principle that diagnostic ratios are exploited by researchers as recently reviewed by Tobiszewski and Namiesnik (2012).

Diagnostic ratios have been used to identify pyrogenic or petrogenic sources (Zhang et al., 2005), diesel or gasoline emission (Ravindra et al., 2008), fuel or wood combustion (De La Torre-Roche et al., 2009) and traffic related sources (Katsoyiannis et al., 2007; Akyuz and Cabuk, 2010). However, PAH diagnostic ratios that are attributed to each hypothetical source are not definitive, as many studies have highlighted the variable range of emission factors and compound ratios from given source categories. For example, a ratio between 0.4 and 0.5 for FLU/(FLU + PYR) may indicate possible sources including cement production, metal manufacturing, fertiliser production, diesel combustion and road dust, while another diagnostic ratio from the same data set may show a strong variation

for a particular source, e.g. BbF/BkF = 2.5–2.9 for aluminium smelter emissions. Diagnostic ratios have further been questioned as a reliable source apportionment tool, owing to the variation in combustion conditions and atmospheric processes that can cause substantial variation in the emission and degradation of individual compounds (Katsoyiannis et al., 2011). Atmospheric processes can hinder these diagnostic ratios as individual PAH compounds have different atmospheric lifetimes and reactivities (Atkinson and Arey, 2007; Arey, 1998). For example, ANT, B(a)A and B(e)P have significantly shorter lifetimes than their isomeric PAH compounds when exposed to atmospheric oxidants such as ozone (Perraudin et al., 2007). Ratios such as ANT/(ANT + PHE) may therefore be strongly influenced by photochemical reactions leading to ratios which approach zero. Further limitations of diagnostic ratios are that their interpretation is dependent upon the source profile chosen and the ratio considered, but this is minimised by selecting ratios with similar physicochemical properties of PAH compounds.

In this study an evaluation of PAH diagnostic ratios is provided for vapour and particulate phase samples collected simultaneously at roadside and suburban sites in Birmingham, UK. It focuses on 14 PAH and 11 quinone compounds which are measured at both sites to obtain information upon traffic emissions and to evaluate the validity of diagnostic ratios.

2. Experimental

2.1. Site location

Sampling was conducted simultaneously at two locations in Birmingham, the major city within the West Midlands conurbation, the second largest urban centre in the UK with a population of ca. 2.5 million. One location was the Bristol Road Observatory Site (BROS), located on the perimeter of the University of Birmingham campus, ca. 5 m from the heavily trafficked A38, which has an annual average daily flow of traffic (total volume of vehicle traffic a year divided by 365 days) of ca. 28,000 vehicles. The sampler was located at a height of ca. 5 m above street level at BROS. The second location was the Elms Road Observatory Site (EROS), located ca. 800 m west of BROS, ca. 3.5 km southwest of Birmingham city centre. EROS is an urban background site within the “green space” of the University of Birmingham campus and is subject to anthropogenic emissions from some moderately busy roads (nearest road ca. 500 m away) and surrounding activities from local residents. The sampler was located at a height of ca. 2 m above street level at EROS.

2.2. Particulate matter sampling

Daily (24 h) samples were measured simultaneously at the two sampling locations between 7th January 2010 and 26th January 2010, using two identical sampling trains that consisted of a denuder collecting the vapour phase fraction of species, upstream of a Micro-Orifice Uniform Deposition Impactor (MOUDI) collecting the particulate phase fraction, with a polyurethane foam (PUF) located at the end of the sampling train. The detailed description of the denuder design is found elsewhere (Delgado-Saborit et al., 2013a). Briefly, the denuder consists of a set of parallel metal plates coated with XAD-4 (Gundel et al., 1995) to collect the gas phase PAH and quinone species. The MOUDI 110R (MSP Copley Scientific, UK) collected the particulate phase PAH and quinones in the size fractions, <0.56 μm , 0.56–1.8 μm and 1.8–10 μm for 24 h at 30 L min⁻¹, using polypropylene backed PTFE 47 mm filters (Whatman, Maidstone, UK). Particulate concentrations reported in this work hereafter, refer to the total sum of compounds in all three size fractions.

2.3. Sampling analyses

Prior to sampling, the PUFs were pre-cleaned in a Soxhlet using dichloromethane for 24 h. The solvent was later drained and the PUFs were left to dry in a sealed metal container under a stream of nitrogen. The cleaned and dried PUFs were wrapped in pre-heated aluminium foil and were sealed in airtight plastic bags and stored in a freezer. After exposure, the filters and PUFs were wrapped separately with clean pre-heated foil, enclosed in airtight plastic bags and stored under conditions of approximately $-18\text{ }^{\circ}\text{C}$ until analysis.

Samples were analysed for 14 PAHs and 11 quinones using the methodology described elsewhere (Delgado-Saborit et al., 2013b). A list of measured species, abbreviations and properties can be found in Annex 1. Briefly, filters and PUFs were spiked with $1000\text{ pg }\mu\text{L}^{-1}$ deuterated internal standards for quantification. Filters were immersed in dichloromethane (DCM), ultrasonicated at $20\text{ }^{\circ}\text{C}$ for 15 min and dried and cleaned with a chromatography column filled with 0.5 g of anhydrous sodium sulphate (Puriss grade for HPLC). The cleaned extract was split into two equal parts, where one half was further concentrated to $50\text{ }\mu\text{L}$ under a gentle nitrogen flow and the other derivatised as outlined below. PUFs were immersed in 100 mL of DCM, ultrasonicated at $20\text{ }^{\circ}\text{C}$ for 20 min, concentrated to 10 mL using nitrogen and subsequently dried and cleaned as described for the filters above. The second part of the extract was derivatised in order to convert five LMW quinones to their diacetyl derivatives as described previously (Cho et al., 2004; Chung et al., 2006; Delgado-Saborit et al., 2013b).

The samples were analysed for PAH and quinone compounds using an Agilent Technologies 6890 Gas Chromatograph (GC) equipped with an Agilent HP-5MS, non-polar capillary column (30 m , 0.25 mm ID, $0.25\text{ }\mu\text{m}$ film thickness – 5% phenyl-polysiloxane), in tandem with a 5973N Mass Spectrometer (MS). Quality assurance, limits of detection, recoveries and more information regarding the analytical procedure can be found in Delgado-Saborit et al. (2013b).

Annex 1

PAH and quinone compound abbreviations and characteristic properties.

| Compound | Abbreviation | Molecular weight (Da) | No. of rings |
|-------------------------------|--------------|-----------------------|--------------|
| Phenanthrene | PHE | 178.23 | 3 |
| Anthracene | ANT | 178.23 | 3 |
| Fluoranthene | FLU | 202.25 | 4 |
| Pyrene | PYR | 202.25 | 4 |
| Benzo(a)anthracene | B(a)A | 228.29 | 4 |
| Chrysene | CHR | 228.29 | 4 |
| Benzo(b)fluoranthene | B(b)F | 252.31 | 5 |
| Benzo(k)fluoranthene | B(k)F | 252.31 | 5 |
| Benzo(e)pyrene | B(e)P | 252.31 | 5 |
| Benzo(a)pyrene | B(a)P | 252.31 | 5 |
| Indeno(1,2,3-cd)pyrene | IND | 276.33 | 6 |
| Dibenz(a,h)anthracene | D(a,h)A | 276.33 | 6 |
| Benzo(ghi)perylene | B(ghi)P | 278.35 | 6 |
| Coronene | COR | 300.35 | 7 |
| 1,2-Naphthoquinone | 1,2-NQ | 158.15 | 2 |
| 1,4-Naphthoquinone | 1,4-NQ | 158.15 | 2 |
| 2-Methyl-1,4-naphthoquinone | 2-M-14-NQ | 172.18 | 2 |
| Phenanthraquinone | PQ | 208.22 | 3 |
| Anthracenequinone | AQ | 208.22 | 3 |
| 2-Methylanthraquinone | 2-MAQ | 222.24 | 3 |
| 2,3-Dimethylanthraquinone | 2,3-DMAQ | 236.27 | 3 |
| Benzo(a)anthracene-7,12-dione | B(a)AQ | 258.27 | 4 |
| 5,12-Naphthacenequinone | 5,12-NQ | 258.27 | 4 |
| Benzo(a)pyrene-6,12-dione | B(a)P-6,12 | 282.30 | 5 |
| Benzo(a)pyrene-1,6-dione | B(a)P-1,6 | 282.30 | 5 |

3. Results and discussion

3.1. PAH concentrations

The average total (vapour and particulate) concentrations of PAH compounds measured at EROS and BROS during the winter campaign (7 Jan 2010 to 26 Jan 2010) are illustrated in Fig. 1 (A). High molecular weight (HMW) PAH compounds were present in relatively lower concentrations than compounds of lower molecular weights (LMW). For example, the total (vapour and particulate) concentration of PHE (MW = 178.23 Da) at BROS and EROS was 23.6 and 20.6 ng m^{-3} , respectively; whereas the total concentration of B(a)P (MW = 252.31 Da) at BROS and EROS were 2 orders of magnitude lower at 0.26 and 0.18 ng m^{-3} , respectively. The concentrations of B(a)P are consistent with previous measurements made at the same sites (Harrad and Laurie, 2005) and exceed the UK EPAQS standard of 0.25 ng m^{-3} as an annual average. Although PAH congener profiles are very similar for both sites (see Fig. 1(A)), the average total concentrations for all measured PAH compounds at BROS exceeded those at EROS, with a paired *t*-test revealing these roadside increments to be significant ($p < 0.05$) for all PAH compounds, thus demonstrating the importance of traffic emissions of PAH. The magnitude of the increment varies for different PAH compounds; for example the average total concentration for B(e)P (a relatively stable PAH) was 11% lower at EROS than that measured at BROS, the smallest observed difference between the two sites. ANT, however, was approximately 51% lower at EROS in comparison to that measured at BROS. Although these observations could reflect greater relative road traffic emissions of ANT, the variable lower concentrations of different PAH at EROS may also reflect their relative stabilities/atmospheric lifetimes (Harrad et al., 2003). Previous studies have shown that the lower roadside increments for HMW PAH may arise from their reduced reactivity, with the result that advected regional inputs “buffer” their concentrations at locations removed from the immediate impact of line and point sources (Harrad and Laurie, 2005).

LMW (<228 Da) PAH compounds were predominantly in the vapour phase (see Fig. 1(B)), where the most abundant PAH measured at BROS and EROS were PHE (22.0 and 19.8 ng m^{-3} , respectively), PYR (12.0 and 9.9 ng m^{-3} , respectively) and FLU (9.2 and 8.5 ng m^{-3} , respectively). Vapour phase concentrations of HMW (>252 Da) PAH compounds ranged between 0.27 ng m^{-3} for B(b)F at BROS to 4.4 pg m^{-3} for COR at EROS. Interestingly, vapour phase concentrations did not vary greatly between sites, albeit being statistically significant (*t*-test, $p < 0.05$), with BROS:EROS mean concentration ratios ranging from 1.07 (FLU) to 2.11 (ANT).

The average particulate phase PAH concentrations are illustrated in Fig. 1(C), where a significant difference is observed between EROS and BROS for LMW PAH compounds. Largest BROS:EROS mean concentration ratios were observed for PYR (5.2), FLU (4.2), ANT (2.2) and PHE (2.1), which suggests that these particles may be largely traffic related. This behaviour is consistent with incorporation of PAH into particles as exhaust gases cool, with slow downwind release into the vapour phase as dilution reduces the concentration of vapour allowing vaporisation to proceed. It must be noted, however, that these compounds are predominantly in the vapour phase (see Fig. 1(B) and (C)). BROS:EROS mean concentration ratios for HMW particulate phase PAH were between 1.1 and 1.4 in good agreement with previous studies (Harrad and Laurie, 2005).

The average PUF concentrations observed at EROS and BROS are shown in Fig. 1(D). The low concentrations demonstrate the efficiency of the denuder upstream that collects the majority of the vapour phase PAH compounds and Delgado-Saborit et al. (2013a) conclude that PAH on the PUF arise from evaporation from particles collected in the impactor.

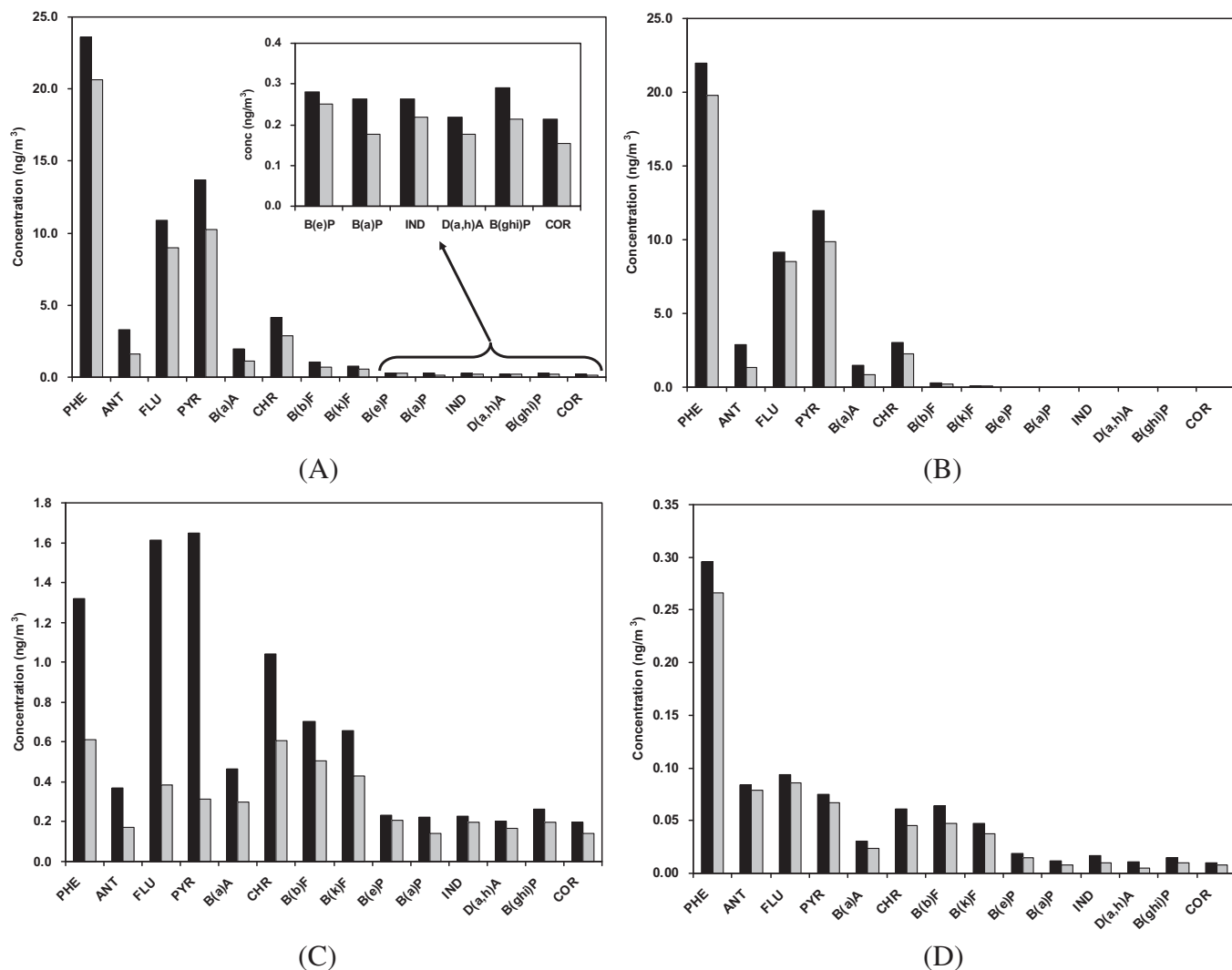


Fig. 1. (A) Average total (vapour + particulate) concentrations; (B) average vapour phase concentrations; (C) average particle phase concentrations; and (D) average PUF concentrations of PAH compounds measured at BROS (black) and EROS (grey). Note different scales.

3.2. Quinone concentrations

The average total (vapour and particulate) concentrations of quinone compounds measured at EROS and BROS during the winter campaign (7 Jan 2010 to 26 Jan 2010) are illustrated in Fig. 2(A). The most abundantly determined quinone compounds measured at BROS and EROS were PQ (6.1 and 4.5 ng m^{-3} , respectively), 1,2-NAPQ (3.0 and 1.2 ng m^{-3} , respectively) and 1,4-NAPQ (2.1 and 0.8 ng m^{-3} , respectively); while 2-MAQ was found in abundance at BROS (2.8 ng m^{-3}) only. LMW quinones (<208 Da) were mainly found in the vapour phase, which explains why the total measurements in this study for 1,2-NAPQ and 1,4-NAPQ are considerably higher than those previously determined (Chung et al., 2006; Valavanidis et al., 2006; Wingfors et al., 2011). The average total concentrations for PQ determined at BROS and EROS are also significantly higher than previously reported (Schnelle-Kreis et al., 2001; Chung et al., 2006; Mirivel et al., 2010). The higher concentrations determined in this study indicate the importance of measuring both vapour and particulate phases, as although these previous measurements have determined quinone concentrations at urban background sites, concentrations are reported in the particulate phase only. Previous observations of AQ, however, have been reported for both vapour and particulate phases, ranging from 0.03 to 9.9 ng m^{-3} measured

at sampling locations including rural, urban background, urban and traffic roadside (Niederer, 1998; Schnelle-Kreis et al., 2005; Sienna, 2006; Albinet et al., 2006, 2008; Wingfors et al., 2011) and are in line with the concentrations reported in this study. A comprehensive literature review of previous OPAH measurements has been reported by Walgraeve et al. (2010).

The average total concentrations for all measured quinones at BROS exceeded those at EROS, with a paired *t*-test revealing these roadside increments to be statistically significant ($p < 0.05$) for all quinones except for 2,3-DMAQ, B(a)P-1,6 and B(a)P-6,12. This may demonstrate the importance of traffic emissions of quinone compounds, in particularly 2-MAQ, where average concentrations at BROS exceeded EROS by an order of magnitude. Surprisingly, approximately 20% of 2-MAQ was found in the particulate phase at BROS in comparison to 50% at EROS, where the measured vapour phase concentration of 2-MAQ at BROS exceeded that of EROS by a factor of 10. This suggests that roadside emissions of 2-MAQ are predominantly in the vapour phase and do not equilibrate rapidly with the condensed phase.

The distribution of vapour to particulate phase for PAH and quinone compounds is illustrated in Fig. 3. Statistically significant differences (*t*-test, $p < 0.05$) between the vapour and particulate phase distributions at both sites were observed for FLU, PYR and

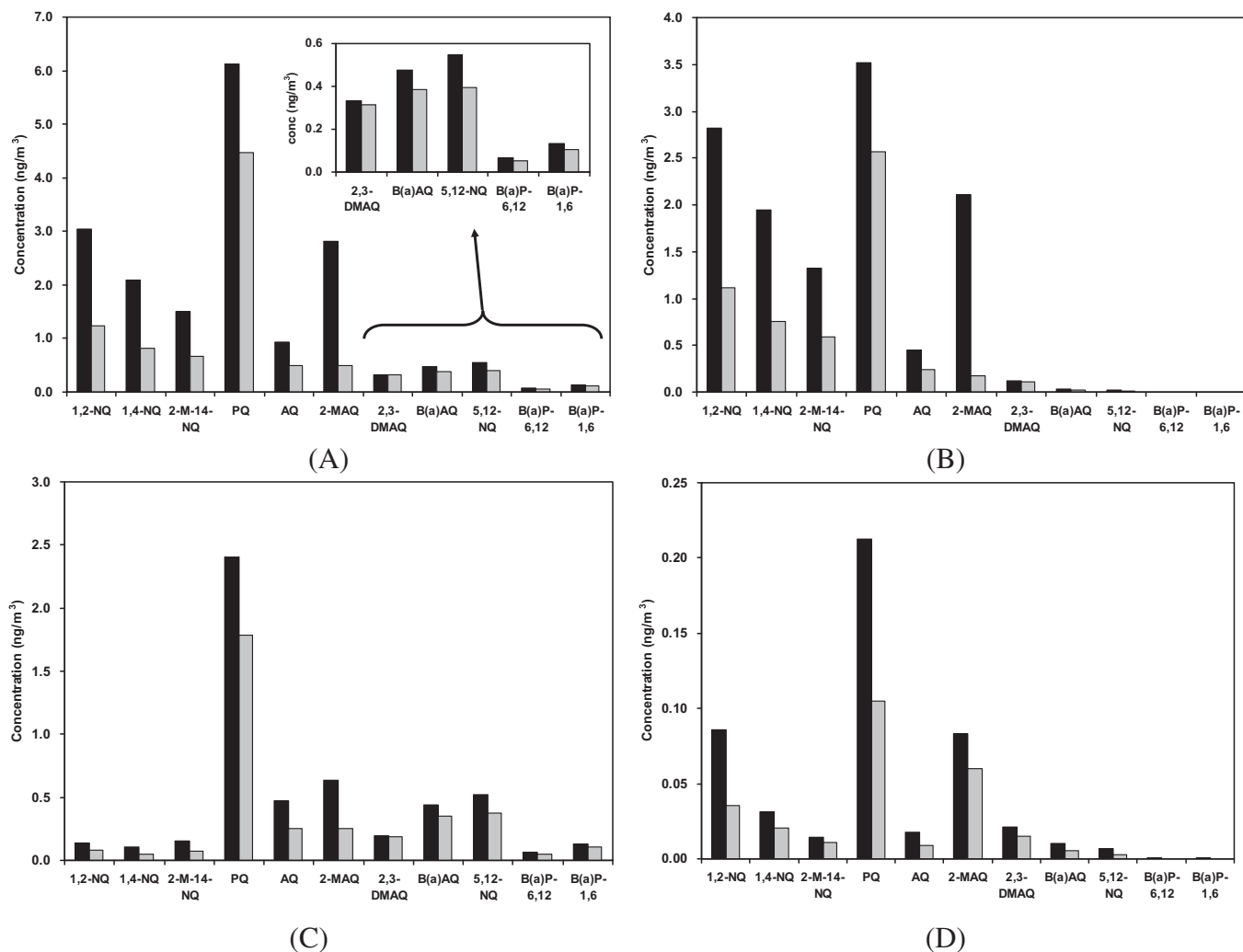


Fig. 2. (A) Average total (vapour + particulate) concentrations; (B) average vapour phase concentrations; (C) average particle phase concentrations; and (D) average PUF concentrations of quinone compounds measured at BROS (black) and EROS (grey). Note different scales.

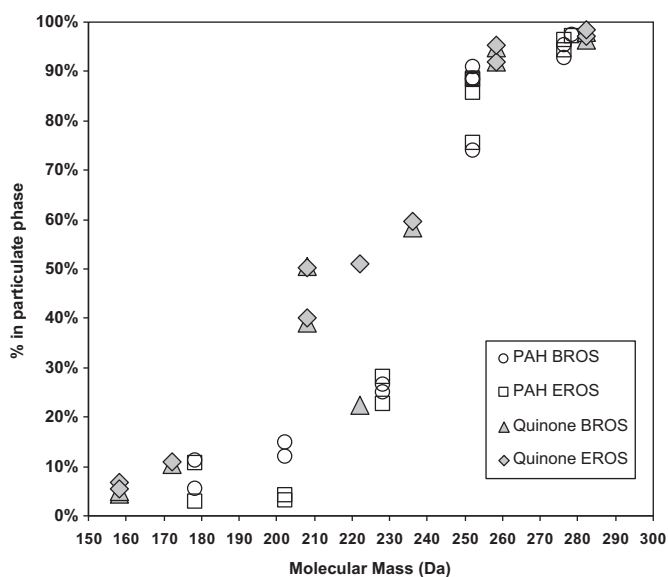


Fig. 3. Distribution of measured compounds in particulate phase as a function of molecular weight. Open circles – PAH measured at BROS; open squares – PAH measured at EROS; grey triangles – quinones measured at BROS; grey diamonds – quinones measured at EROS.

2-MAQ. Approximately 12–15% of FLU (MW = 202.25 Da) and PYR (MW = 202.25 Da) were in the particulate phase at BROS in comparison to < 5% at EROS, suggesting a larger proportion of particulate FLU and PYR emissions at the roadside location. PQ and AQ were consistently both distributed at 40 and 50% in the particulate phase respectively at both sites.

3.3. Traffic profile

The observations of PAH and quinone compounds were measured simultaneously at roadside (BROS) and urban background (EROS) areas, enabling a traffic profile to be obtained by calculating the difference between the two sites. The traffic profile measured for PAH and quinone compounds, is shown in Fig. 4, where the PAH and quinone compounds are shown with increasing molecular mass (from left to right). The most abundant PAH compounds in the vapour phase in the traffic profile were in the order PHE > PYR > ANT while the most abundant PAH compounds in the particulate phase were FLU > PYR > PHE, indicating that PYR and PHE are relatively good traffic source indicators, in agreement with previous studies (Duval and Friedlander, 1981). Data from the National Atmospheric Emissions Inventory (NAEI, <http://naei.defra.gov.uk/data/>) from 1990 to 2009 suggests that the emission of PYR is only greater from the production of aluminium and the

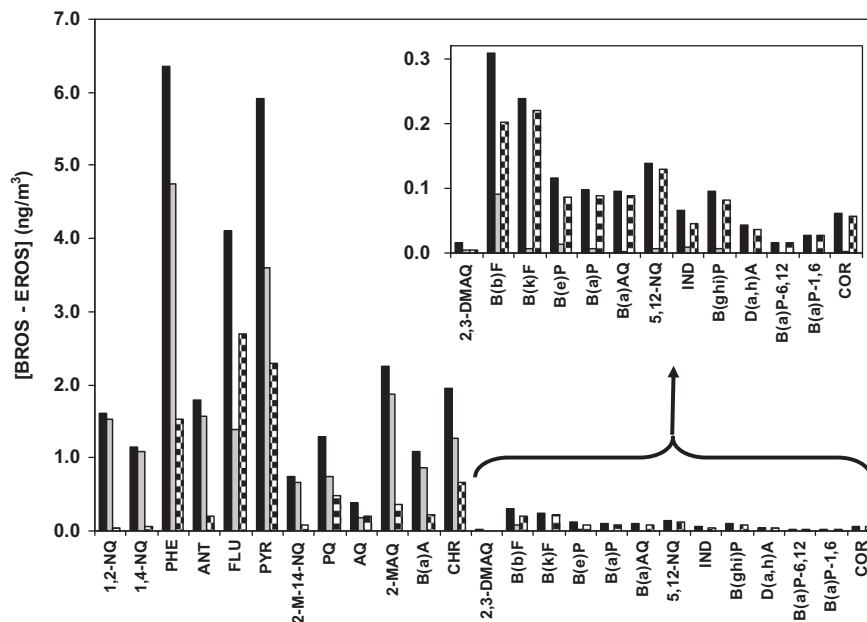


Fig. 4. Traffic profile of total mean concentration of PAH and quinone compounds (black); vapour phase mean concentration (grey); and particulate phase mean concentrations (checkered).

burning of domestic wood; while the largest source for PHE is domestic wood burning followed by vehicular emissions. Many studies have suggested that B(ghi)P and COR could potentially be used as vehicular emission tracers (Greenberg et al., 1981; Harkov et al., 1984); however, the results from this present study show little difference of these PAH between the two sites. These compounds are however of relatively low volatility and subject to the “buffering effect” discussed above. Recently, Gao et al. (2011) conducted roadside measurements of PAH in $PM_{2.5}$ in urban Guangzhou. Their results indicated that approximately 55% of the total PAH concentration was accounted for by HMW PAH (>252 Da), significantly larger than that measured in this study. This demonstrates the importance of measuring both vapour and particulate phase PAH, as shown by the larger proportion of LMW PAH measurements in Fig. 4.

The most abundant quinone compounds measured in the vapour phase from the traffic profile (Fig. 4), were in the order 2-MAQ > 1,2-NQ > 1,4-NQ; while the most abundant quinone in the particulate phase were PQ > 5,12-NQ. As discussed previously, the largest observed difference between the two sites was that of vapour phase 2-MAQ, suggesting that 2-MAQ could potentially be used as a vehicular emission tracer. The only compound that did not show a significant traffic increment was that of 2,3-DMAQ, suggesting that the source of this quinone compound is not traffic-related.

3.4. Diagnostic ratios

Five bi-variate plots are illustrated in Fig. 5 (A–E), which include all 20 days of simultaneous samples at BROS, EROS as well as the traffic increment calculated ratios. The PAH ratio ranges that correspond to different source types are included in the axes of each of bi-variate plots within Fig. 5 (taken from Yunker et al., 2002; Sofowote et al., 2010).

The ANT/(ANT + PHE) ratio is reported as being indicative of unburned fossil fuels (petroleum sources) when <0.1 and combustion sources (pyrogenic sources) when >0.1 (Yunker et al., 2002). Fig. 5(A) and (C) both show a significant difference (ANOVA, $p < 0.05$) in the ANT/(ANT + PHE) ratio for samples

collected at both sites and the traffic increment. Approximately 80% of samples collected at BROS (trafficked roadside) were >0.1, whereas all of the samples collected at EROS were <0.1. Interestingly the ratios calculated from the traffic increment concentrations were all >0.1, where 90% of the ratios were >0.15. This is surprising as according to the diagnostic ratio thresholds calculated by Yunker et al. (2002), one would expect that roadside (BROS) measurements would be more representative of petrogenic sources (ratio < 0.1) owing to the larger traffic source. In an evaluation of PAH diagnostic ratios collected in an urban-industrial environment, it was reported that the majority of samples were related to combustion sources (Sofowote et al., 2010). However, in another evaluation of two decades of source inventory and air concentration data from the UK the ANT/(ANT + PHE) ratio was quite uniform, consistently < 0.1 (Katsoyiannis et al., 2011). The latter evaluation reported PAH diagnostic ratios from multiple sites including, rural, semi-rural, urban and urban-industrial sites and no significant differences were observed. The authors, however, did report a strong seasonal trend where winter seasons showed significantly larger ANT/(ANT + PHE) ratios than in summer. One interpretation for this finding was the seasonal differences in sources, e.g. increased domestic burning of coal and wood during winter. However, it could not have been ruled out that this seasonal variation could have been owing to seasonal differences in the relative rates of loss of these compounds, i.e. higher reaction rates with atmospheric oxidants (Katsoyiannis et al., 2011). PAH compounds can react with OH forming their respective quinone compounds where the reactions rate coefficients for the gas phase reaction of PHE + OH is $3.2 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, an order of magnitude slower than ANT + OH ($1.3 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$). This corresponds to absolute rates of $6.4 \times 10^{-5} \text{ s}^{-1}$ and $2.6 \times 10^{-4} \text{ s}^{-1}$ ($[\text{OH}] = 2 \times 10^6 \text{ molecule cm}^{-3}$; global 12 h average (Atkinson and Arey, 2007) for PHE and ANT, respectively). It seems more likely therefore, that the lower ratios at EROS may be indicative of atmospheric processing/degradation of PAH, and is also demonstrated by the largest observed difference in the magnitude of the concentrations of ANT at both sites (51% lower concentration measured at EROS in comparison to BROS, see Fig. 1). This is in

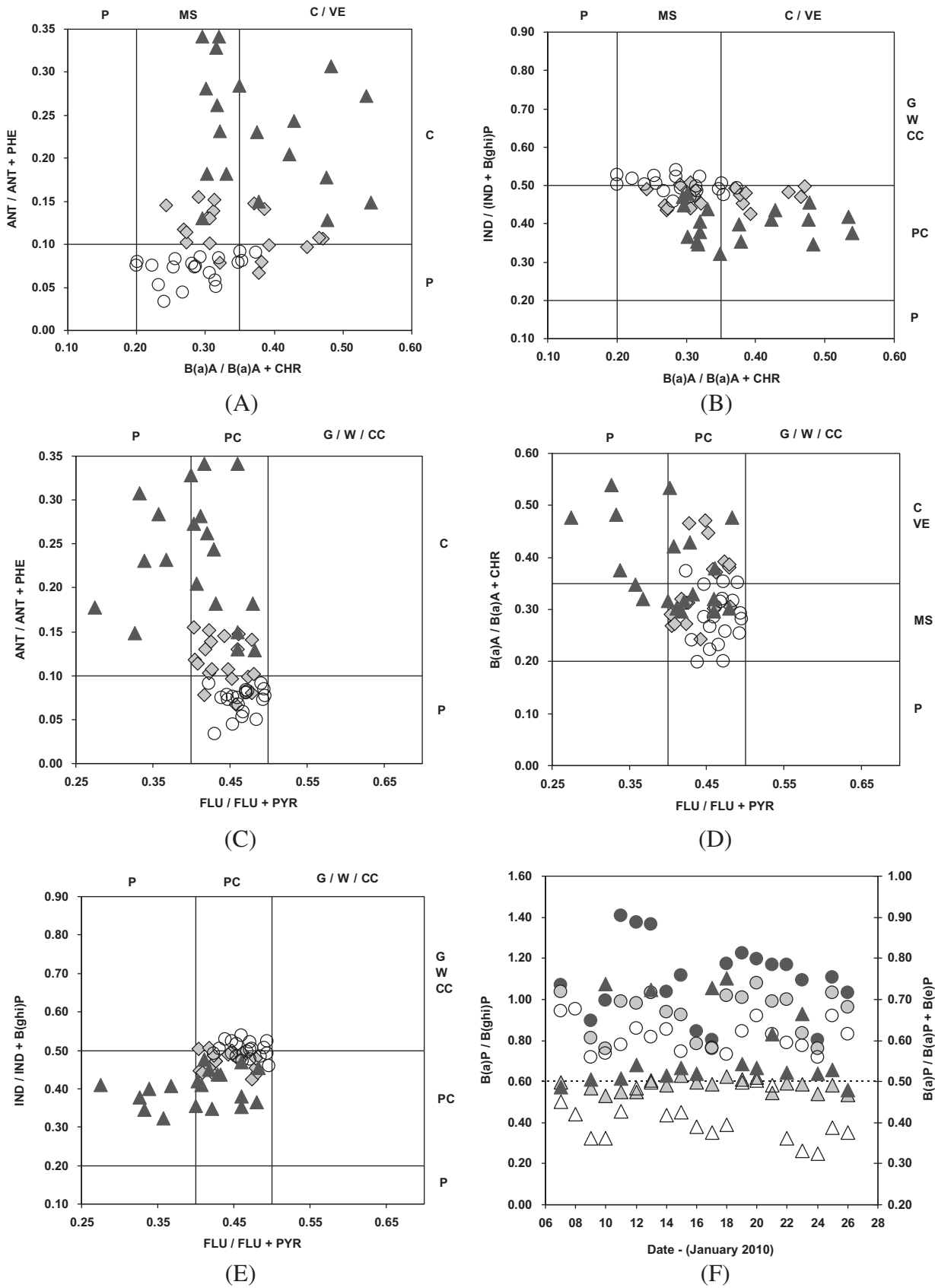


Fig. 5. (A–E) Bi-variate plots of diagnostic ratios for traffic increment (black triangles), BROS (grey diamonds) and EROS (open circles) samples. Dotted lines signify threshold values and source designations, taken from Yunker et al. (2002) and Sofowote et al. (2010). P = petroleum; PC = petroleum combustion; C = combustion; WC = wood combustion; MS = mixed sources; VE = vehicular emission; G/W/CC = grass, wood & coal combustion. (F) Time series of diagnostic ratios of $\text{B(a)P} / \text{B(ghi)P}$ (primary y axis) for traffic increment (black circles), BROS (grey circles) and EROS (open circles) samples; and $\text{B(a)P} / (\text{B(a)P} + \text{B(e)P})$ (secondary axis) for traffic increment (black triangles), BROS (grey triangles) and EROS (open triangles) samples.

agreement with Tobiszewski and Namiesnik (2012), who demonstrated that $ANT/(ANT + PHE)$ may be strongly influenced by reactions leading to ratios approaching zero. However, the samples collected at BROS could also be more influenced by domestic burning than EROS, with local residential buildings within a relative close proximity of the sampling location, which would lead to an increase in the $ANT/(ANT + PHE)$ ratio, as observed in Fig. 5(A) and (C) for the calculated traffic profile.

The $B(a)A/(B(a)A + CHR)$ ratio is reported as being indicative of unburned fossil fuels, combustion sources and mixed sources (Yunker et al., 2002). This ratio is often reported in the range of 0.2–0.4, which does not clearly show a dominance of petrogenic or combustion sources *i.e.* shows mixed sources (see Katsoyiannis et al., 2011). Sofowote et al. (2010) investigated the diagnostic ratios of 3 NIST Standard Reference Materials (SRM) and found that the $B(a)A/(B(a)A + CHR)$ ratio was approximately 0.2–0.25, 0.3–0.35 and 0.55–0.60 for diesel exhaust particulate, urban dust and coal tar/combustion emissions SRMs, respectively. Fig. 5(A) and (B) illustrate that when applying the thresholds proposed by Yunker et al. (2002), 95 and 58% of the samples imply mixed sources for EROS and BROS, respectively (between 0.2 and 0.35); while 42% of samples at BROS indicate coal combustion (Yunker et al., 2002). The traffic increment calculated ratios however are between 0.3 and 0.55, where 53% of the calculated ratios indicate coal combustion sources according to the threshold values (>0.35). Recently, Akyuz and Cabuk (2008) investigated particle associated PAH in Turkey, where their calculated $B(a)A/(B(a)A + CHR)$ ratios were 0.52 and 0.55 for $PM_{2.5}$ and $PM_{2.5-10}$, respectively. After conducting principal component analysis (PCA) the authors suggested that this was due to coal combustion as well as vehicular emissions; a result that was later reproduced when studying both vapour and particulate phases (Akyuz and Cabuk, 2010). If the ratio $B(a)A/(B(a)A + CHR)$ was truly reflective of source type then ratios collected from the samples collected at BROS should be relatively smaller than EROS, indicating an increased petrogenic source. As the sampling sites are well characterised, it is unlikely that the calculated ratios for BROS (42%) and the traffic increment (53%) indicate coal combustion sources, as the predominant domestic fuel is natural gas, and thus any impact upon PAH concentration is likely to be small. The derived ratios at the two sites together with the traffic increment ratio calculations were statistically different (ANOVA, $p < 0.05$); therefore the ratio may be influenced by atmospheric chemical reactions, as has been reported previously. For example, the half lives of $B(a)A$ and CHR are 650 and 690 h for particles absorbed onto carbon black, 2 and 78 h for alumina and 4 and 100 h for silica gel, respectively (Behymer and Hites, 1985). Unfortunately, to the author's knowledge, vapour phase rates of reaction for these compounds have not been investigated. In addition the concentration difference of $B(a)A$ between the two sites was 42%, the largest calculated difference after ANT . An alternative consideration, however, is that these compound ratios are influenced by domestic combustion, the extent of which is larger at BROS than EROS, owing to the closer proximity of local residential buildings. However, as the predominant domestic fuel is natural gas, any impact upon PAH concentrations are likely to be small.

The calculated $FLU/(FLU + PYR)$ ratio is illustrated in Fig. 5(C) and (D) and was on average 10% lower at BROS. All of the ratios calculated were between 0.4 and 0.5, signifying petroleum combustion sources (Kavouras et al., 1999; Yunker et al., 2002; Zencak et al., 2007; De La Torre-Roche et al., 2009). The calculated ratios for the traffic increment, however, were statistically different from the two sites (t -test, $p < 0.05$), where 37% of the ratios were <0.4 , indicative of petrogenic sources. The slightly larger ratios measured at EROS could reflect a larger proportion of grass/wood/coal combustion from local residential buildings close by. However, as

observed for the LMW ratios above, BROS may also be susceptible to domestic combustion processes from local residential buildings and thus it is more likely that the larger ratios calculated at EROS could signify photochemical reactivity (De La Torre-Roche et al., 2009). As mentioned previously approximately 12–15% of FLU and PYR were present in the particulate phase at BROS in comparison to $<5\%$ at EROS, signifying a larger proportion of particulate FLU and PYR emissions from presumably vehicular emissions, as shown in Fig. 4. The average FLU/PYR ratios calculated at BROS and EROS were 0.78 and 0.87, respectively. FLU and PYR mean total (vapour and particulate) concentrations were 17 and 25% lower at EROS, respectively. If these differences were due to atmospheric processing only, then this would suggest that PYR is more reactive than FLU , consistent with previous gas and heterogeneous kinetic measurements (Brubaker and Hites, 1998; Atkinson et al., 1990; Esteve et al., 2004, 2006; Perraudin et al., 2005, 2007; Bedjanian et al., 2010). This is also consistent with our recent results from a rural site in the UK, Weybourne, where FLU/PYR ratios are considerably larger (2.06) (Alam et al., 2013). However, owing to the large differences in particulate phase FLU and PYR between the two sites (76 and 81% lower in EROS, respectively); it is more plausible that the differences in the $FLU/(FLU + PYR)$ ratios may reflect major source differences more than chemical reactivity. Chemical reactions are, however, expected to shift the ratio slightly towards larger values (Tobiszewski and Namiesnik, 2012).

The HMW PAH diagnostic ratio, $IND/(IND + B(ghi)P)$, is reported as being less influenced by reactivity than LMW PAH diagnostic ratios (Zhang et al., 2005), as these PAH are relatively stable. The ratio is reported as assisting in the differentiation of petroleum, petroleum combustion and grass/wood/coal combustion sources (Yunker et al., 2002), and often gives the same indication as the $FLU/(FLU + PYR)$ ratio (Katsoyiannis et al., 2011), see Fig. 5(E). Fig. 5(B) and (E) shows that 95 and 40% of the samples collected at BROS and EROS respectively, fall into the petroleum combustion source (0.2–0.5) range; while 60% of the samples from EROS are supposedly influenced by grass/wood/coal combustion, similar to the ratio $FLU/(FLU + PYR)$. 75% of the calculated traffic increment ratios are lower than those derived at BROS, although the ratios fall into the same petroleum combustion source category. The $IND/(IND + B(ghi)P)$ ratios are an average of 11% larger at EROS, which is due to the increased $B(ghi)P$ emissions at BROS, and is also demonstrated by the ratio $B(a)P/B(ghi)P$ in Fig. 5(F). The ratio $B(a)P/B(ghi)P$ is reported as signifying traffic (>0.6) and non-traffic (<0.6) emissions (Braendli et al., 2007). Although Fig. 5(F) shows that both BROS and EROS are influenced by traffic related emissions, the apparent lower ratios calculated at EROS (and low ratios at BROS during weekends), demonstrate that traffic-related emissions are more important at BROS, and that the ratio threshold is perhaps too low. Moreover, the calculated traffic increment ratios are significantly larger than both BROS and EROS for all the sampling days. Braendli et al. (2007) suggested this ratio ($B(a)P/B(ghi)P$) to be used as a traffic related indicator after investigating organic waste in compost. It has since been exploited for source apportionment for sewage sludge and soil samples (Katsoyiannis et al., 2007; Tobiszewski and Namiesnik, 2012). This study, however, suggests that for atmospheric measurements the threshold value of this ratio should be increased to approximately 0.8, see Fig. 5(F).

Another ratio that is of importance is $B(a)P/(B(a)P + B(e)P)$. This ratio signifies the ageing of the emitted particles (Grimmer et al., 1983; Oliveira et al., 2011; Tobiszewski and Namiesnik, 2012) and is shown in Fig. 5(F). Since this ratio is photosensitive, it is often considered to be a marker of atmospheric ageing and photo-degradation of PAH. Ratios of approximately 0.5 are reported as being freshly emitted whereas ratios <0.5 may have undergone ageing. Interestingly, Fig. 5(F) indicates that samples collected at

BROS are freshly emitted with ratios very close to 0.5, whereas the samples collected at EROS have lower ratios (<0.5), particularly during the weekend. The calculated traffic increment ratios are also approximately 0.5 with the exception of 6 days where the ratios are between 0.8 and 1.0. This result indicates that atmospheric processing may be an important factor and may explain why the smallest observed concentration difference between the two sites was that of B(e)P, the most stable of all the PAH compounds. Alternatively, this ratio may represent the extent of emissions from traffic, where the larger ratio may be indicative of more traffic related emissions, particularly for the 6 days where the calculated traffic increment ratios were between 0.8 and 1.0.

3.5. PAH reactivity and quinone/parent-PAH ratios

To investigate the atmospheric reactivity of PAH compounds, the average $[BROS]/[EROS]$ ratios were calculated and are presented in Fig. 6(A) and (B) for PAH predominantly in the vapour and particulate phase, respectively. Fig. 6(A) shows a substantial difference in the ratios which are dependent upon their respective reactivities. If it is assumed that the ratios of emitted PAH are similar, the larger ratios may be attributed to the occurrence of oxidation reactions of PAH occurring during transport, whereas the smaller ratios determined are modified less. The largest calculated ratios are those of the fast reacting species. According to the stand alone ratios calculated (see Fig. 6(A)), the reactivity of the vapour phase PAH compounds are in the following order: ANT > B[a]A > CHR > PYR > PHE > FLU, which is consistent with the relative magnitudes of vapour phase reaction rate coefficients with respect to OH (Atkinson and Arey, 2007; Atkinson et al., 1990, 1989; Biermann et al., 1985; Brubaker and Hites, 1998; Kwok et al., 1994), as shown in Table 1.

For the particulate phase, however, Fig. 6(B) indicates that B(e)P and IND are the slowest reacting compounds, while B(a)P and B(k)F are the fastest. Although this is consistent with the heterogeneous second order rate coefficients with respect to ozone reported by Perraudin et al. (2007) for PAH absorbed on graphite particles, and with respect to NO_2 for PAH absorbed on silica particles (Perraudin et al., 2005), it is not definitive as there is a large variation between studies calculating the heterogeneous rate constants of HMW PAH. Moreover, the larger ratios in this case may simply be owing to large emission differences between the two sites. HMW PAH are reported as being more stable than LMW PAH due to the vapour-

Table 1

Average gas phase rate coefficients of LMW PAH compounds found in literature and their corresponding calculated BROS/EROS concentration ratios.

| PAH | BROS/EROS ratios ^a | Second order rate constant, k (cm^3 molecules ⁻¹ s ⁻¹) ^b |
|--------------------|-------------------------------|---|
| ANT | 2.11 | 1.29E-10 |
| B[a]A ^c | 1.81 | |
| CHR ^c | 1.37 | |
| PYR | 1.21 | 5.00E-11 |
| PHE | 1.11 | 2.54E-11 |
| FLU | 1.07 | 1.10E-11 |

^a Vapour phase BROS/EROS ratios, see Fig. 5(A).

^b Average second order rate coefficient calculated from NIST kinetics database, <http://kinetics.nist.gov/kinetics/index.jsp>.

^c No gas phase rate coefficient data reported in literature.

particle partitioning, *i.e.* LMW PAH tend to be present predominantly in the vapour phase and thus more susceptible to atmospheric processing (Tobiszewski and Namiesnik, 2012).

Although the concentrations of all quinone compounds were larger at the roadside sampling site (BROS), the ratio of the concentration of some oxidation product quinones to those of their parent PAH were smaller, see Fig. 7. These quinone to parent-PAH ratios can be used to assess the contribution of atmospheric reactions to the concentration of quinones in the atmosphere (McKinney et al., 1999). Like PAH diagnostic ratios, quinone to parent-PAH ratios can be indicative of the rate of transformation of PAH into quinones, but are not definitive since quinones can also be emitted directly from combustion process and vehicular emissions, as shown in Fig. 4 and demonstrated by various studies (Walgraeve et al., 2010; Layshock et al., 2010) and quinones are also likely to be reactive. Furthermore, this ratio can be influenced by the sampling location and temperature, as this may influence the gas to particle partitioning of PAHs and OPAHs. For example, Walgraeve et al. (2010) reviewed a number of OPAH/PAH ratios measured during the summer and winter seasons, and found that ratios ranged between 0.0002 and 27, the general trend being explained by the greater photochemical activity of PAH during the summer.

The observed concentration ratios of AQ, PQ and B(a)AQ to parent-PAH are shown in Fig. 7, where the scatter of the PQ/PHE ratios calculated for the traffic increment, BROS and EROS, makes it difficult to draw conclusions regarding atmospheric processing of PHE to PQ. However, 95% and 85% of the ratios AQ/ANT and B(a)AQ/

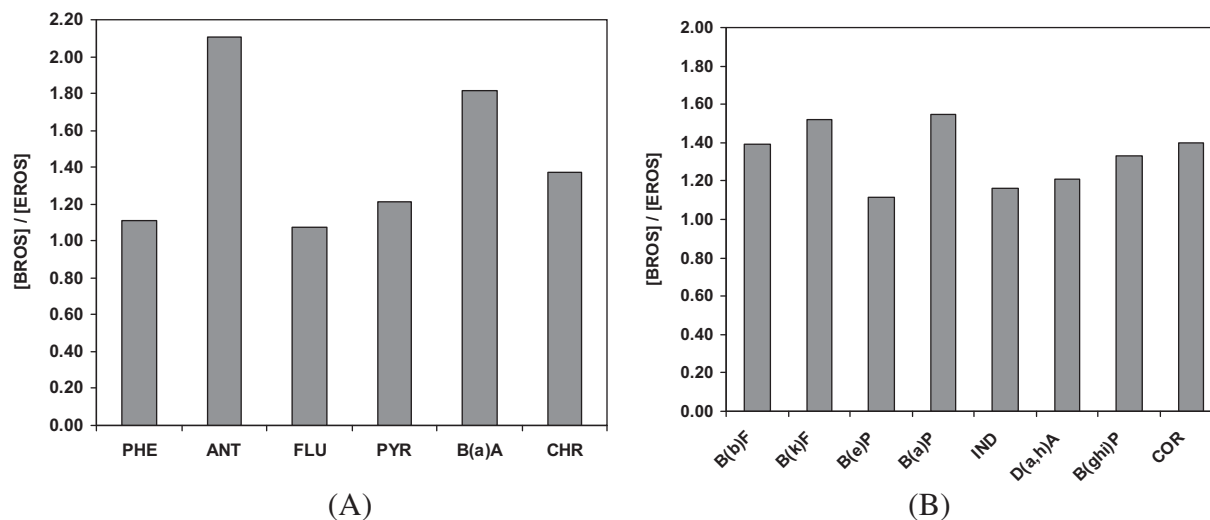


Fig. 6. Average $[BROS]/[EROS]$ ratios for (A) predominantly vapour phase PAH and (B) predominantly particulate phase PAH compounds.

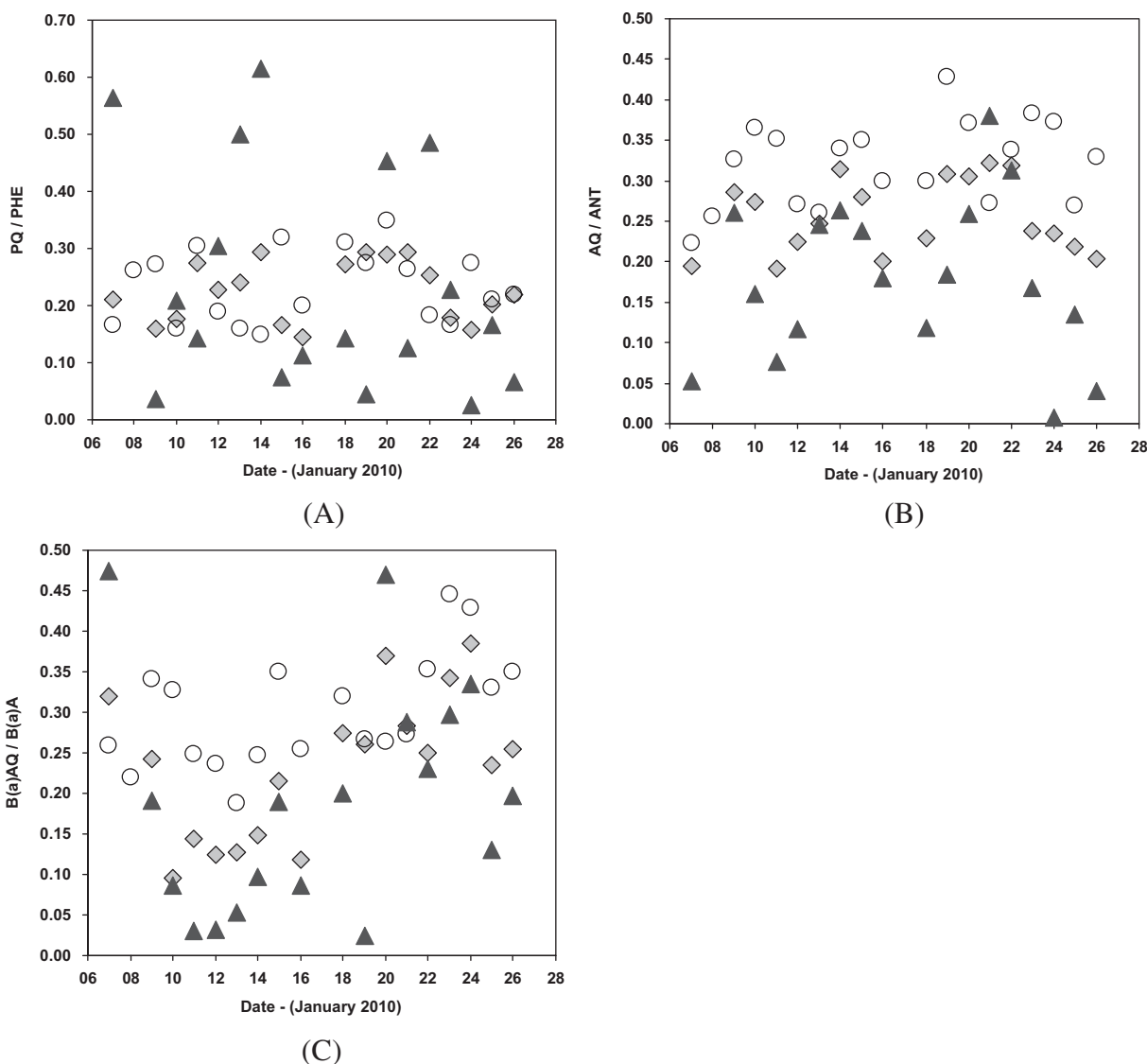


Fig. 7. Calculated concentration ratios of (A) PQ/PHE (B) AQ/ANT and (C) B(a)AQ/B(a)A for samples collected at BROS (grey diamonds), EROS (open circles) and traffic increment (black triangles) between 7 January 2010 and 26 January 2010.

B(a)A, respectively, were larger at EROS indicating either more rapid loss processes for PAH, or formation of quinones (or possibly both). The traffic increment ratios are also 95% and 85% larger than BROS for AQ/ANT and B(a)AQ/B(a)A, respectively. This is in agreement with McKinney et al. (1999), who showed a change in AQ/ANT ratios with increasing distance from the emission source. In contrast, Wingfors et al. (2011), also calculated concentration ratios for AQ and B(a)AQ to their parent PAH at two different sites, and found that they did not differ significantly (*t*-test, $p = 0.05$). These two sites, however, were at equal distances from the source of emission.

4. Conclusion

The vapour and particulate phase of 14 PAH and 11 quinone compounds have been measured simultaneously at well defined roadside (BROS) and urban background (EROS) sites in Birmingham, UK. Vapour phase partitioning of these compounds have been assessed as a function of molecular mass (Da), where significant differences were observed for the phase distribution for 2-MAQ between the two sites. Concentrations for all species measured at

BROS were found to be larger than EROS, with the exception of 2,3-DMAQ, suggesting that 2,3-DMAQ is not traffic related. Largest traffic increments were found for PAH – PHE, PYR, FLU and quinone – 2-MAQ, indicating their suitability for use as traffic markers.

An evaluation of PAH diagnostic ratios has been conducted to examine all samples collected during the 20 day sampling period. The results presented in this study indicate that PAH diagnostic ratios have to be utilised with great care with interpretation that must take into account various source factors including atmospheric processing. The concentrations and diagnostic ratios measured at BROS and EROS look similar but are in fact significantly different as discussed; strong indications are seen of the importance of atmospheric reactivity of PAH, particularly for LMW PAH. It is suggested therefore, that ratios such as ANT/(ANT + PHE) and B(a)A/(B(a)A + CHR) should not be utilised at all as source apportionment tools, while HMW PAH diagnostic ratios may be exploited with greater confidence owing to their increased stability. Nonetheless, it should be borne in mind that there are likely to be differing ratios between apparently similar sources using different processes or abatement measures, and that the composition of road traffic emissions has changed markedly in recent years (Hesterberg

et al., 2011). Therefore ratio thresholds that are widely used in the literature should also be treated with great caution and amended to specific source sites that are well defined. PAH ratios provide only a crude and qualitative source apportionment assessment and where available should accompany more qualitative methods such as multivariate factor analysis.

Acknowledgments

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