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Alam, M. S.; Delgado Saborit, Juana Maria; Stark, C.; Harrison, Roy

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# Investigating PAH relative reactivity using congener profiles, quinone measurements and back trajectories

M. S. Alam<sup>1</sup>, J. M. Delgado-Saborit<sup>1</sup>, C. Stark<sup>1</sup>, and R. M. Harrison<sup>1,2</sup>

<sup>1</sup>Division of Environmental Health & Risk Management School of Geography, Earth & Environmental Sciences University of Birmingham Edgbaston, Birmingham, B15 2TT, UK

<sup>2</sup>Department of Environmental Sciences/Center of Excellence in Environmental Studies, King Abdulaziz University, Jeddah, 21589, Saudi Arabia

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Correspondence to: R. M. Harrison (r.m.harrison@bham.ac.uk)

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## Abstract

Vapour and particle-associated concentrations of 15 polycyclic aromatic hydrocarbons (PAH) and 11 PAH quinones have been measured in winter and summer campaigns at the rural site, Weybourne in eastern England. Concentrations of individual PAH are 20–140 times smaller than average concentrations at an English urban site. The concentrations of PAH are greatest in air masses originating from southern England relative to those from Scandinavia and the North Atlantic, while quinone to parent PAH ratios show an inverse behaviour, being highest in the more aged North Atlantic polar air masses. While concentration of 1,2-naphthoquinone decline from summer to winter, those of 1,4-naphthoquinone and anthraquinone increase suggesting a photochemical formation pathway. A comparison of congener concentration profiles measured at Weybourne with those from an urban source area (Birmingham) reveals differential losses at the rural site, especially evident in fluoranthene: pyrene ratios and consistent with the known rates of vapour phase reactions of 3 and 4 ring compounds with hydroxyl radical. The ratios of quinones to their parent PAH at Weybourne are greater than those in the urban source area indicating either more rapid loss processes for PAH, or formation of quinones during advection of the air mass, or probably both.

## 1 Introduction

Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous organic pollutants, present in the atmosphere both in the vapour phase and associated with particulate matter (PM). PAHs are often measured in studies of atmospheric chemistry or health effects of air pollution, owing to their known carcinogenic effects (Yu, 2002). 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 compounds (Sidhu et al., 2005; Walgraeve et al., 2010). Rarely however, are such

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compounds measured in the same airborne samples, despite the need to do so to elucidate atmospheric processing of PAH.

Oxygenated PAH, including quinones are released into the atmosphere along with PAH during incomplete combustion processes (Iinuma et al., 2007; Layshock et al., 2010; Valavanidis et al., 2006). Vapour phase and heterogeneous atmospheric processing of PAHs can yield further quinone products via reactions with atmospheric oxidants including OH, NO<sub>3</sub> and O<sub>3</sub> (Atkinson and Arey, 2007). However, the relative contribution to the observed atmospheric burden of PAH quinone derivatives from direct combustion emissions and secondary atmospheric reactions is far from fully understood.

Although there are many reports of oxygenated-PAHs measured in airborne analyses (Walgraeve et al., 2010), which include ketones, carboxaldehydes and diones, limited measurements of quinones alongside PAH have been reported. Wang et al. (2011) reported the measurements of three quinones, nitro-PAH (NPAH) and associated parent PAH compounds, in a toxicity study of PM<sub>2.5</sub> during the Beijing Olympic Games. They found that although most of the parent PAH, NPAH and oxygenated-PAH (OPAH) concentrations correlated with NO and NO<sub>2</sub>, only the parent PAHs were correlated with CO and SO<sub>2</sub> concentrations. The authors suggested that the OPAHs were therefore primarily associated with local emissions and local photochemical formation. Albinet and co-workers reported the measurement of 15 PAH compounds using HPLC with fluorescence/UV detection, while determining 17 NPAH and 9 OPAH (2 of which were quinone) compounds simultaneously using GC-MS with negative ion chemical ionisation (NICI) (Albinet et al., 2006, 2007a, b, 2008a, b). More recently, Wingfors et al. (2011) measured 18 OPAHs, 6 of which were quinones, in an urban environment, but were only able to measure 3 of the associated parent PAH compounds. The most common of the measured airborne quinone compounds reported in the literature to date are 9,10-anthraquinone and 9,10-phenanthraquinone; however, many studies have also reported quinone compounds including 1,2-naphthoquinone and 1,4-

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naphthoquinone from diesel and gasoline vehicle emissions (Cho et al., 2004; Jakober et al., 2007).

Recently, in a study from this laboratory, we reported a methodology to measure quinones and PAHs in the gaseous and particulate phases in ambient air, utilising GC-MS (Delgado-Saborit et al., 2013a). This included the first measurements for a range of quinones with a comparison of vapour and particulate phases, at an urban site in Birmingham with concentrations being of the same order of magnitude as their parent PAHs. In the present study we utilise the previously reported methodology to determine the airborne concentrations of 15 PAHs and 11 quinones, at a rural site on the North Sea coast, Weybourne, UK. Quinone to parent-PAH ratios combined with back trajectories are used to assess the long range chemical transport and relative contribution of potential sources for measurements made at the site.

## 2 Experimental

### 2.1 Site location

Sampling was conducted at the Weybourne Atmospheric Observatory (52°57' N 1°07' E) located on the North Norfolk coast. The observatory is located in a field approximately 100 m from the sea and 1 km away (north-west) from the nearest village. The area is surrounded by agricultural land with the closest city, Norwich, approximately 50 km SSE. The location receives a variety of Atlantic, Arctic, European, UK and North Sea air masses, owing to the rapidly changing wind directions. A comprehensive description of the site is given elsewhere (Penkett et al., 1999).

### 2.2 Particle and vapour phase sampling

Daily particulate (PM<sub>2.5</sub> and PM<sub>2.5-10</sub>) and vapour phase (PUFs) samples were collected over two one month periods, during winter (2 February 2010–2 March 2010) and summer (6 August 2010–2 September 2010), using a high volume air sampler TE-6070

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the vapour phase during the winter and summer, respectively. This may reflect faster gas phase reaction rates with atmospheric oxidants (OH, O<sub>3</sub> and NO<sub>3</sub>) in the summer where oxidant levels are higher. Equilibration between the phases seems likely to be relatively slow.

The average total concentration of PAH in the summer campaign was approximately 70% of the winter campaign sum. There is scatter around this value for individual compounds, the most marked difference being for retene. The very high winter/summer ratio for retene is likely to reflect its emission during wood burning (Bari et al., 2009). The seasonal difference for the other compounds is seen in the high MW as well as the low MW compounds and is not explicable purely by greater partitioning to vapour in the warmer summer campaign, although this will be a factor. Other reasons include greater emissions in the winter due to increased fossil fuel usage, the usual seasonal increase in primary pollutants in winter due to poorer dispersion conditions, and a different frequency of air mass types, as this strongly influences concentrations during an episode (see below).

### 3.2 Quinone concentration

The average concentrations of vapour and particulate phase quinone compounds measured during summer and winter are shown in Table 1. We report the first remote site observations for 2-methylantraquinone (2MAQ), 2,3-dimethylantraquinone (2,3DMAQ), benzo(a)pyrene-6,12-dione (B(a)P-6,12) and benzo(a)pyrene-1,6-dione (B(a)P-1,6) using GC-MS. Quinones with molecular mass < 208 Da were mainly found in the vapour phase, consistent with previous studies, who reported that > 50% LMW OPAH compounds (MW < 202 Da) were present in the gas phase (Albinet et al., 2008a). Approximately 95% of 1,2-naphthoquinone (1,2NQ) 1,4-naphthoquinone (1,4NQ) and 2-methyl-1,4-naphthoquinone (2MNQ) were measured in the vapour phase, irrespective of seasons. A smaller percentage of vapour phase, approximately 50 and 20%, was measured for phenanthraquinone (PQ) and anthraquinone (AQ) during the winter, respectively; but vapour phase AQ during the summer was approxi-

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spheric transport, irrespective of the reaction products. Figure 2a illustrates that 53 % of the quinone to parent-PAH ratios during the winter sampling period were in the order B(a)A-7,12/B(a)A > AQ/ANT > PQ/PHE. This may be indicative of the atmospheric processing rates for these compounds. For example, PAHs can react with OH forming their respective quinone compounds where the second order reaction rate coefficient for the gas phase reaction of PHE + OH is  $3.2 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (Lee et al., 2003) which is an order of magnitude slower than ANT + OH ( $1.3 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ) (Atkinson and Arey, 1994). This corresponds to daytime lifetimes of 4.3 h and 1.1 h for PHE and ANT respectively, for  $[\text{OH}] = 2 \times 10^6 \text{ molecule cm}^{-3}$ ; global 12 h average (Atkinson and Arey, 2007); and may account for the smaller ratios of PQ/PHE in comparison with AQ/ANT and B(a)A-7,12/B(a)A. To date, however, no gas phase reaction rate coefficient has been measured for B(a)A with atmospheric oxidants, OH, O<sub>3</sub> or NO<sub>3</sub>, even though a significant proportion of B(a)A is found to be present in the gas phase during winter (see Table 1). The ratios of B(a)P-6,12 and B(a)P-1,6 to B(a)P did not show a strong variation as demonstrated for AQ, PQ and B(a)A-7,12, with approximately 85 % of the sampled ratios less than 0.5. The observed ratios of particulate phase AQ, PQ and B(a)A-7,12 to parent-PAH during the winter sampling campaign (not shown) were found to be strongly related to their air mass origins, as shown in Fig. 2 for the sum of particulate and vapour. However, 77 % of the particulate quinone to parent-PAH ratios were in the order AQ/ANT > B(a)A-7,12/B(a)A > PQ/PHE and the ratios were in the order of 0.1–2.9, larger than the ratios determined for the sum of vapour and particulate compounds of 0.04–1.8 shown in Fig. 2a.

During the summer a more pronounced difference was observed between total quinone/PAH ratios of air masses originating from “polluted” and “non-polluted” regions, see Fig. 2b. Again, relatively larger quinone/PAH ratios were observed when air masses originated from remote areas away from regions with high primary emissions (see Fig. 2b, 13 August 2010 to 16 August 2010 and 29 August 2010 to 2 September 2010), particularly for ratios AQ/ANT and B(a)A-7,12/B(a)A. Unlike the winter data, however, 88 % of the quinone to parent-PAH ratios were in the order AQ/ANT > B(a)A-

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7,12/B(a)A > PQ/PHE. To assess whether atmospheric processing rates were at all responsible for this observation during the summer, total AQ/ANT : PQ/PHE ratios were calculated for the three cluster trajectories. The average total AQ/ANT : PQ/PHE ratios determined for green (remote, North Sea), blue (London and Western Europe) and red (mainland UK and Ireland) trajectories were 5.1, 2.5 and 2.2, respectively. The larger ratio calculated for remote areas, as well as the higher concentrations of AQ observed during the summer relative to the winter, suggests greater atmospheric processing rates for faster reacting PAHs during long range transport.

Approximately 77 and 56% of the particulate quinone to parent-PAH ratios during the winter and summer sampling period were also in the order AQ/ANT > B(a)A-7,12/B(a)A > PQ/PHE, respectively. This is consistent with relative rates of heterogeneous processing for these compounds. For example, Perraudin et al. (2005, 2007) investigated the kinetics of the reactions of atmospheric oxidants and PAHs adsorbed on model atmospheric particles. They found that whatever the conditions of the particle loading, the ozone concentration and nature of the particles, ANT and B(a)A were the most reactive towards ozone oxidation (Perraudin et al., 2007), where the absolute reaction rates for ANT + O<sub>3</sub> was an order to magnitude faster than PHE + O<sub>3</sub>. Similarly, particulate PHE was found to be less reactive towards NO<sub>2</sub> and not considered to be degraded at atmospherically relevant NO<sub>2</sub> concentrations (Perraudin et al., 2005). ANT and B(a)A, however, were found to react up to 3 orders of magnitude faster, and when adsorbed on silica particles, their lifetime relative to NO<sub>2</sub> oxidation may be shorter than a few hours in polluted conditions. Calculated lifetimes for ANT, B(a)A and PHE with respect to NO<sub>2</sub> using the reaction rate coefficients determined by Perraudin et al. (2005) and a yearly average [NO<sub>2</sub>] of 1.3 × 10<sup>11</sup> molecule cm<sup>-3</sup>, determined at Harwell, UK (2011) are 4 h, 60 h and 1460 h, respectively. These kinetic observations may explain the ordering of the particulate ratios and the relatively low PQ to PHE particulate ratios determined during the summer sampling campaign. However, the variation in the literature for heterogeneous reaction rate coefficients of PAHs means that it is difficult to infer the rates of PAH conversion to their derivative compounds.







NO<sub>3</sub> (Atkinson et al., 1990) and heterogeneous absolute rates calculated with respect to OH (Bedjanian et al., 2010; Esteve et al., 2006), NO<sub>2</sub> (Esteve et al., 2004, 2006; Perraudin et al., 2005) and O<sub>3</sub> (Perraudin et al., 2007), suggesting that PYR may have a higher susceptibility to atmospheric processing than FLU.

A difference in the ranking relating to PQ was also observed between the two sites (see Fig. 3), where elevated levels of PQ were observed at EROS. This could indicate a direct emission source of this species from traffic (Alam et al., 2013). The average quinone to parent-PAH ratios for PQ/PHE, AQ/ANT and B(a)A-7,12/B(a)A are shown in Table S2. The elevated ratios observed at Weybourne for AQ/ANT and B(a)A-7,12/B(a)A may be attributed to the occurrence of oxidation reactions of PAHs occurring during long range transport. The more similar ratios obtained at the two sites for PQ/PHE suggests that the atmospheric processing rate of PHE may be slower than ANT and B(a)A, consistent with the ordering of quinone/parent-PAH ratios discussed for Fig. 2.

The ratios of urban/rural PAH and quinone concentrations are illustrated in Fig. 4. This ratio can be used to assess the reactivity of PAH and quinone compounds. Figure 4 shows a substantial difference in the ratios depending upon where the air masses are originating from. For example, the ratios calculated using rural data where air masses originate from relatively local source areas, such as London/mainland UK (Fig. 4, blue bars) and mainland Europe (Fig. 4, green bars) are very similar and relatively small, in comparison to the larger ratios calculated when the air masses originate from “remote” areas, such as the North Sea (Fig. 4, red bars). 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 PAHs occurring during long range transport from these remote areas, whereas the smaller ratios determined from polluted areas will be modified less. Lohmann and Lammel (2004) point out that the annual mean concentration of B(a)P measured at a background site in central Europe is only slightly higher than that measured in the Canadian Arctic while for PHE the European site has a vastly higher concentration. They cite evidence that particle-bound PAH are not depleted dur-

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ing their transport. The largest calculated ratios are those of the LMW species, which is consistent with these species being subject to more rapid vapour phase loss due to greater reactivity. According to the stand-alone ratios calculated using remote air mass rural data (see Fig. 4), the reactivity of the LMW PAHs are in the following order: ANT > PYR > B(a)A > CHR > 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., 1989, 1990; Biermann et al., 1985; Brubaker and Hites, 1998; Kwok et al., 1994), as shown in Table 2. The lower ratio for most quinones in Fig. 4 relative to their parent PAH can be explained either by the production of these compounds by atmospheric reactions or their greater stability relative to PAH, which has yet to be established adequately, but which is suggested by laboratory studies of their formation.

## 4 Conclusions

The choice of Weybourne as a site for measurements was based upon its exposure both to polluted air masses advected from southern England, continental European air masses and far cleaner air traversing the North Sea from the Arctic. In the event, air masses representative of all three sources were sampled, and show interesting differential behaviour, particularly during the summer. The fact that the losses of 3/4 ring PAH correlate with their vapour phase reactivity towards the hydroxyl radical confirms the results of laboratory studies suggesting this as the key reactant. The far smaller loss of high molecular weight compounds in comparison to the lower molecular weight species confirms the relative stability of the former and that the high reaction rates in heterogeneous processes seen in some laboratory studies are probably not occurring in the atmosphere.

The far greater relative losses of low molecular weight PAH than of quinones in the more aged air masses indicate either a greater atmospheric stability of the quinones, or their formation during atmospheric transport, or both processes. Some quinones,

notably 1,4-naphthaquinone, and anthraquinone show evidence of atmospheric formation in their considerably greater relative abundance in the summer than the winter campaign.

**Supplementary material related to this article is available online at**  
[http://www.atmos-chem-phys-discuss.net/13/25741/2013/  
acpd-13-25741-2013-supplement.pdf](http://www.atmos-chem-phys-discuss.net/13/25741/2013/acpd-13-25741-2013-supplement.pdf).

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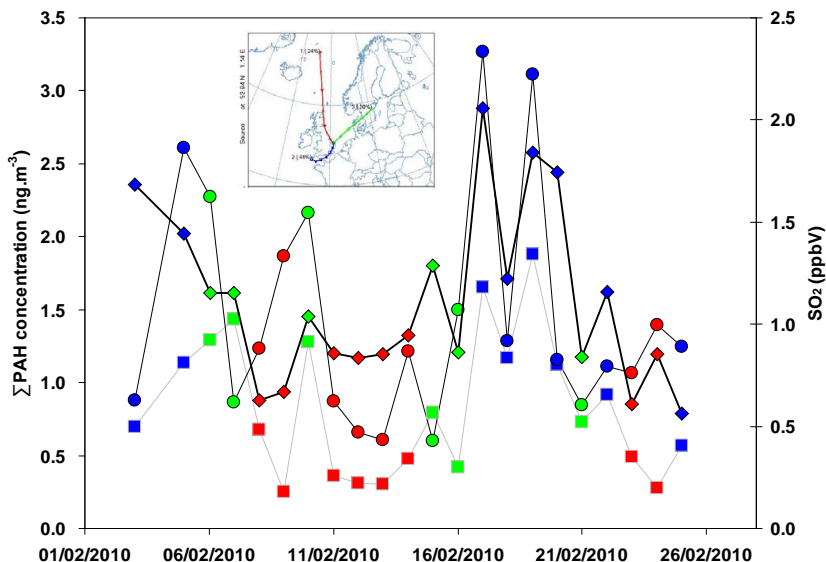
**Table 2.** Average gas phase rate coefficients of LMW PAH compounds found in literature and their corresponding calculated urban/rural reactivity ratios

PAH	Urban/Rural <sup>a</sup> Ratios	Second order rate constant, $k$ cm <sup>3</sup> molecules <sup>-1</sup> s <sup>-1</sup> <sup>b</sup>	Absolute rate s <sup>-1</sup> <sup>c</sup>
ANT	143	$1.29 \times 10^{-10}$	$2.59 \times 10^{-4}$
PYR	131	$5.00 \times 10^{-11}$	$1.00 \times 10^{-4}$
B(a)A <sup>d</sup>	118		
CHR <sup>d</sup>	103		
PHE	102	$2.54 \times 10^{-11}$	$5.09 \times 10^{-5}$
FLU	100	$1.10 \times 10^{-11}$	$2.20 \times 10^{-5}$

<sup>a</sup> Urban/rural ratios calculated using remote air mass rural data (see Fig. 4, red bars). <sup>b</sup> Average second order rate coefficient calculated from NIST kinetics database, <http://kinetics.nist.gov/kinetics/index.jsp>. <sup>c</sup> Absolute rate with respect to OH. [OH] =  $2 \times 10^6$  molecules cm<sup>-3</sup>. <sup>d</sup> No gas phase rate coefficient data reported in literature.

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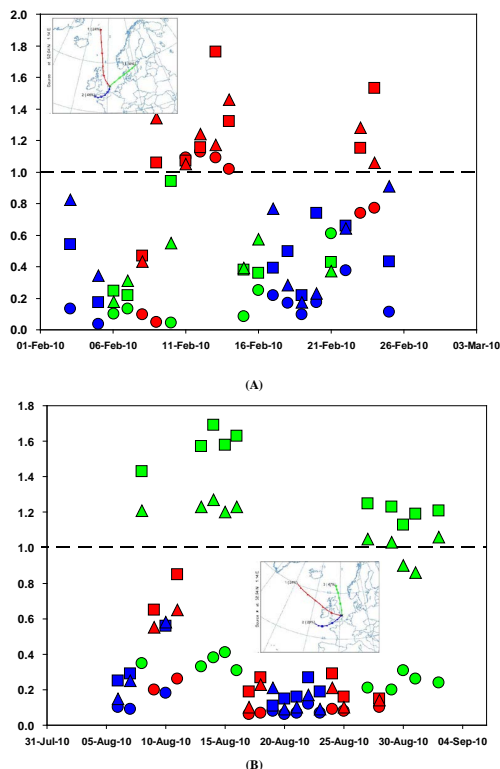
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**Fig. 1.** Temporal trend of SO<sub>2</sub> (secondary axis, diamonds), ΣPAH particulate phase (squares) and vapour phase (circles) for the winter sampling period 2 February 2010 to 25 February 2010. Colours signify three air masses determined by cluster analysis, see embedded image and/or Fig. S1A for colour codes.

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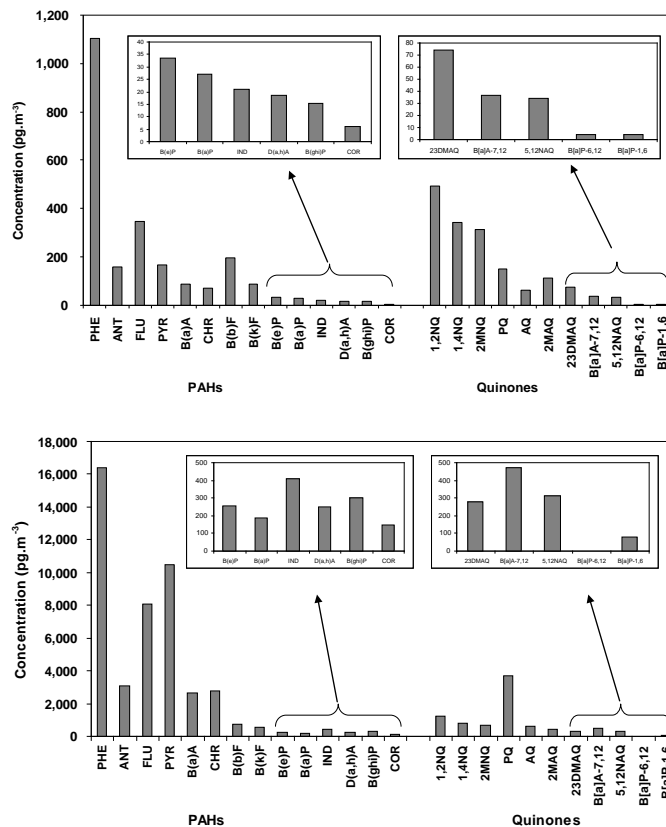
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**Fig. 2.** Quinone to parent-PAH ratios (sum of vapour and particulate phases) during **(A)** winter and **(B)** summer. Circles – PQ/PHE; squares – AQ/ANT and triangles – B(a)A-7,12/B(a)A. Colours signify three different air masses determined by cluster analysis, see embedded image and/or Figure S1A and S1B for colour codes.

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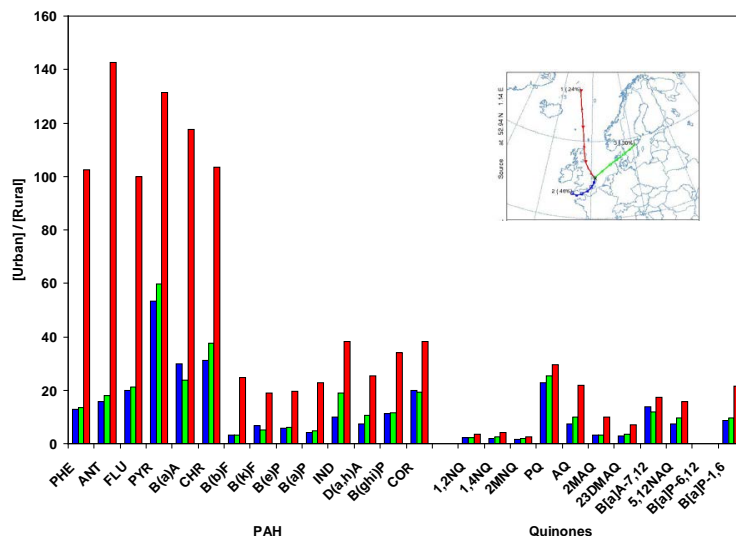


**Fig. 3.** Average PAH profile (sum of particulate and vapour phase) from (top graph) Weybourne and (lower graph) Elms Road Observatory site (Birmingham).

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**Fig. 4.** Winter ratio of compound concentrations measured at EROS, Birmingham, UK to species concentrations measured at Weybourne, UK. Blue – ratios determined using average concentrations of air masses travelling from mainland UK and London; Green – ratios determined using average concentrations calculated from air masses arriving from mainland Europe; Red – ratios determined using average concentrations calculated from air masses travelling from the North Sea.