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## Mechanisms of reactivity of benzo(a)pyrene and other PAH inferred from field measurements

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## ABSTRACT

Semi-volatile polycyclic aromatic hydrocarbons (PAHs) partition between the vapour and condensed phases, both of which undergo oxidation. However, the relative contributions of oxidation in the vapour and condensed phases remain controversial. This is particularly important in respect of benzo(a)pyrene, which is responsible for a substantial proportion of the carcinogenic risk associated with airborne PAHs and is used as a marker for the PAH mixture in air quality standards. There is substantial evidence from field measurements that B(a)P is less reactive in the atmosphere than low molecular weight PAHs, but many uncertainties remain regarding the rate and determinants of its atmospheric decay. Using novel methodology, changes in the ratios of PAHs during atmospheric transport are used to infer the concentrations of OH and NO<sub>3</sub> radicals responsible for the gas phase oxidation of low molecular weight PAHs. These are then used to examine the reactivity of B(a)P during atmospheric transport, and it is concluded that the loss of B(a)P can plausibly be described by the vapour phase reaction with the OH radical. These results offer an alternative mechanism to some others involving heterogeneous chemistry proposed in the literature.

## 1. Introduction

Polycyclic aromatic compounds (PAHs) are a group of semi-volatile compounds which undergo atmospheric transport, but the main mechanisms by which they are oxidised are a matter of controversy, despite considerable research. In this study, we use atmospheric field measurements to make inferences as to the mechanism of oxidation of the semi-volatile PAH congener, benzo(a)pyrene, generating results which may be of relevance to the atmospheric oxidation of semi-volatile compounds more generally.

PAHs range from two and three ring compounds (most notably phenanthrene and anthracene) which exist predominantly (typically > 90%) in the vapour phase to compounds of five or more rings (such as benzo(a)pyrene) which exist with typically 90% or more in the condensed phase. It is probable that PAHs make an appreciable contribution to the carcinogenicity of PM<sub>2.5</sub> in ambient air (Harrison et al., 2004). Acknowledging the known carcinogenicity of PAHs, the European Union has set a target level of 1 ng m<sup>-3</sup> of benzo(a)pyrene (B(a)P) taken as a representative of the entire mixture (European Union,

2004). The UK Air Quality Objective for PAHs is somewhat stricter, i.e. 0.25 ng m<sup>-3</sup> of B(a)P taken as a representative of the mixture (EPAQS, 1995). The WHO Unit Risk Factor for the PAH mixture is set in terms of a concentration of B(a)P, and the WHO Review of the Health Aspects of Air Pollution (REVIHAAP, 2013) highlighted the relatively high level of risk associated with exposure to 1 ng m<sup>-3</sup> of B(a)P and implicitly recommended consideration of a stricter guideline. It is estimated that 85–91% of the population of Europe live in areas exceeding the EU target value (UNECE, 2016). A modelling study of the continental US concluded that the incremental lifetime cancer risk from B(a)P exposure exceeds 1 × 10<sup>-5</sup> in many areas (Zhang et al., 2016).

Delgado-Saborit et al. (2011) have estimated the contributions of individual PAH congeners to carcinogenicity of the mixture found in UK urban air using relative potency factors deriving from a number of sources. Although the attribution of carcinogenic potency varies with the source of the Potency Equivalency Factors (PEF), two compounds make a dominant contribution, benzo(a)pyrene and dibenzo(a,l)pyrene (Delgado-Saborit et al., 2011). B(a)P represents a large proportion (typically around 50%) of the carcinogenic activity of commonly

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measured PAHs in the atmosphere (Delgado-Saborit et al., 2011), and because of this, and its use as a marker for the health risk of the mixture, B(a)P has a special importance amongst the PAHs.

A great deal of work has been conducted in the laboratory in order to determine rate coefficients and mechanisms for atmospherically relevant reactions of PAHs (Keyte et al., 2013). The main oxidising species in the atmosphere are the hydroxyl radical and the nitrate radical, with reactions with ozone appreciably slower in the case of most congeners (Keyte et al., 2013). The products of atmospheric reactions are most characteristically oxy-derivatives and nitro-derivatives, the latter arising both from reactions of PAHs with the NO<sub>3</sub> radical and with the OH radical followed by addition of nitrogen dioxide. While the literature abounds with measurements of PAH concentrations, there have been very few field studies of their atmospheric degradation, and there are only modest numbers of studies in which oxy and nitro-derivatives of PAHs have been measured (Harrison et al., 2016; Ringuet et al., 2012; Keyte et al., 2016). One factor complicating the study of PAH reactions in the atmosphere is the fact that many PAH congeners are present in both vapour and particulate phases and can transfer relatively rapidly between the two. Consequently, studies of reactivity need to take account of both phases in order to estimate reaction rates.

There have been a large number of studies of atmospherically relevant reactions of the vapour of lower molecular weight PAHs conducted in the laboratory and the rate coefficients are fairly well defined (Keyte et al., 2013). The picture is less clear with respect to particle-associated forms of PAHs. There have been many studies in the laboratory of reactions of PAHs adsorbed upon model substrates such as silica and carbon with atmospherically relevant gases and free radical species, some of which have shown appreciable rates of reaction (Keyte et al., 2013). However, the relevance of such heterogeneous processes to reactivity in the atmosphere is not clearly understood because of the difficulties of extrapolation to real-atmosphere substrates and consideration of the mass transfer limitations which affect reactions of gas phase oxidants with constituents of atmospheric particles.

Lohmann and Lammel (2004) have commented on the fact that when moving between urban source areas and remote atmosphere locations, there are reductions in concentrations of lower molecular weight PAHs by a large factor, while concentrations of the higher molecular weight species, most notably benzo(a)pyrene diminish by a much smaller ratio. They cite a case of relative annual mean concentrations of phenanthrene (63-fold higher in the central European background than the Arctic) compared to B(a)P with a ratio of only 1.5 between the two locations (Lohmann and Lammel, 2004). Anttila et al. (2016) report PAH concentrations measured at a site in southern Sweden (Rao) and a remote rural site in sub-Arctic Finland (Pallas). In the mean of data for 2012, the ratio of Phe/B(a)P is 15 and 23 respectively. This can be compared with 124 in the urban source area of Birmingham, UK (Alam et al., 2013), which reduces to 41 in winter at the rural UK site of Weybourne (Alam et al., 2013). Similarly, Halsall et al. (1997) and Hung et al. (2005) report ratios of Phe/B(a)P of around 10 at Alert in the high Arctic.

Clearly, phenanthrene is lost more rapidly than B(a)P during atmospheric transport. Some workers have interpreted this phenomenon as being due to the inaccessibility of PAH molecules within airborne particles due to having been coated with a less reactive surface layer. Zhou et al. (2012) used laboratory studies to show that liquid organic coatings could suppress the reaction of condensed phase B(a)P with ozone, but solid EC coatings were able to suppress the reaction entirely. In subsequent studies it was shown that a coating of secondary organic aerosol (from ozonolysis of  $\alpha$ -pinene) was able to slow the oxidation of B(a)P at low relative humidities, but then an increase in relative humidity led to a reduction in viscosity of the coating, and a more rapid reaction of the B(a)P (Zhou et al., 2013). An alternative explanation is provided by the theoretical constructs of Donahue et al. (2013) who demonstrate that the relatively long atmospheric lifetime of semi-volatile organic compounds can be explained by slow mass transfer from

the gas phase to the particle causing a severe limitation to the rate of oxidation of PAHs present in the condensed phase, with the overall rate of loss being determined by reaction of the small proportion of the compound present as vapour. Currently, both the “coating protection” and “vapour-only reaction” theories appear viable and there is no clear knowledge of the factors determining the atmospheric lifetimes of some of the more carcinogenic high molecular weight PAH compounds.

Numerical modellers have used a number of approaches to describing the atmospheric reactivity of PAHs. Van Jaarsfeld et al. (2007) set the conversion rate of B(a)P to zero in relation to photo-oxidation. Halsall et al. (2001) simulated the reaction of gas-phase PAH (only) with the hydroxyl radical, as did Galarneau et al. (2014). Taking a very different approach, Matthias et al. (2009) and Bieser et al. (2012) used kinetic data from Kwamena et al. (2004) which describe a heterogeneous reaction of B(a)P and ozone on the particle surface. Lammel et al. (2009) tested three scenarios for vapour-particle partitioning and oxidation. In two scenarios, oxidation reactions were set to zero for B(a)P in the condensed phase, and in the third scenario gas phase rate coefficients for reaction with OH (daytime) and NO<sub>3</sub> (nighttime) were applied for both phases of anthracene and fluoranthene with a lesser rate in the case of B(a)P. The scenario giving the best agreement with measured data was that describing absorption into organic matter, adsorption to black carbon and no reactivity of particle-bound B(a)P. Friedman et al. (2014) compared three approaches to modelling the oxidation of pyrene by hydroxyl radical and ozone. In the first scheme, PAHs achieved instant equilibrium between vapour and absorption by primary organic matter and adsorption to black carbon. In the second, PAHs were trapped in SOA when emitted and slowly evaporated from the SOA, and in the third, PAHs were trapped in primary organic matter and black carbon upon emission and slowly evaporated. The third option gave the closest simulation of measured concentrations of pyrene. In this scenario, 80% of PAHs remained within the particles after 24 h. In a recent paper, Shrivastava et al. (2017) fitted global B(a)P measurement data with predictions from a numerical model in which the key process is oxidation by ozone in the condensed phase, which is suppressed by a shielding layer of organic aerosol of variable viscosity at a threshold humidity and temperature. The comparison of modelled and measured data is generally good, with some substantial outliers. A general weakness of such modelling approaches is their dependence upon emissions inventories which carry substantial uncertainties.

In order to better understand the factors determining the lifetime of high molecular weight PAHs in the atmosphere, there is a pressing need for high quality experimental data, which could be from carefully designed laboratory experiments, but would most usefully derive from field measurements. In this paper, we use a novel approach with data from a carefully constructed field campaign to shed new light on this question for B(a)P.

## 2. Methods

The data used in this research have been reported previously (Alam et al., 2014). Briefly, they comprise concentration data for polycyclic aromatic hydrocarbons measured at the Weybourne Atmospheric Observatory (see Fig. 1) on the North Sea coast in eastern England. Individual PAHs congeners were measured in both particle and vapour form using methods previously described (Alam et al., 2014). This involved collection of PAHs in two separate sampling trains, one using a parallel plate denuder to collect vapour before filtration (Delgado-Saborit et al., 2014), the other a PUF plug placed after a filter. Data were taken primarily from the winter campaign due to higher concentrations and back trajectories were calculated according to the methods described by Alam et al. (2014) and used to estimate transit times between major UK source areas and the receptor point at Weybourne Atmospheric Observatory. Specific cluster mean trajectories for each 24-hour period analysed appear in Fig. S1. As the concentrations of hydroxyl radical were not known, ratios of compounds were used in

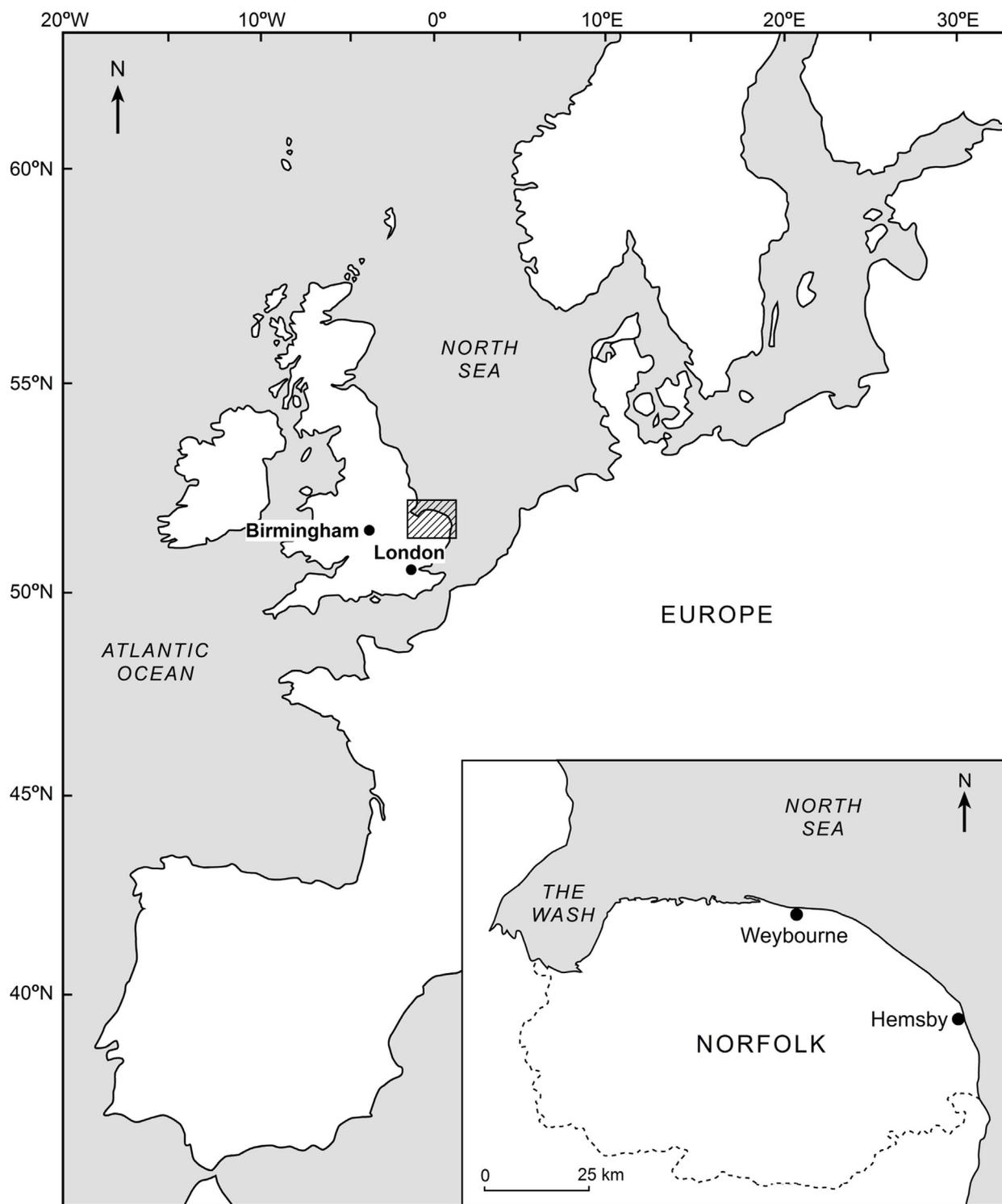


Fig. 1. Site map.

order to allow estimation of the OH radical concentration. Therefore the data analysis used measurements of phenanthrene, fluoranthene and pyrene which are PAHs existing primarily in the vapour phase with appreciably different rate coefficients for reaction with hydroxyl, together with data for B(a)P. In the case of the summer campaign, concentrations of B(a)P vapour were below detection limit and calculations used chrysene data. For all compounds, the partitioning between the particle phase and vapour phase was measured both within the source region and at the receptor point. This partitioning was assumed to change linearly with time between the source and receptor location and

the partitioning was recalculated at every hourly time step.

### 2.1. The air sampling location

The Weybourne Atmospheric Observatory (Penkett et al., 1999) is located on the north Norfolk coast of England (Fig. 1). It is located at 20 m above mean sea level, less than 100 metres from the shoreline in a rural area with few local pollution sources, and none of any magnitude. The terrain is relatively flat, allowing air masses to approach relatively intact from appreciable distances over land or sea. Cardenas et al.

(1998) were able to discern the diurnal features of emissions from London in an air mass advected to Weybourne with a 9-hour time offset corresponding to the travel time of the air mass. A mean hydroxyl radical concentration was calculated from the change in VOC ratios between London and Weybourne (Cardenas et al., 1998). This feature of Weybourne is facilitated by the low local road traffic and population density, together with lack of industry. Fig. S2 shows population densities in England and serves to highlight the high population densities in the London area and the West Midlands conurbation in comparison to the areas between London and Weybourne. This is an area with few industrial sources, and few emissions of air pollutants associated with high population density (e.g. NO<sub>x</sub>, CO, PM from traffic). This feature allows the pursuit of pseudo-Lagrangian experiments in which changes in air mass composition can be observed.

## 2.2. The source regions

The main source regions in this study are the West Midlands/East Midlands conurbations and the London area in England, and locations across the North Sea in mainland Europe. Extensive data are available of measurements made in the UK West Midlands using methods directly comparable with those used at Weybourne. Mari et al. (2010) have noted the considerable similarity in the congener profiles of PAHs measured at UK urban sites. In a receptor modelling study of PAHs at sites across the UK, Jang et al. (2013) noted that the relative contribution of source categories influencing PAHs at UK urban sites varied little across England, Wales and Scotland, implying a similar congener profile. This proposition was further tested by calculating monthly ratios of chrysene/B(a)P in monthly particle phase samples (as this is the only phase measured) collected at UK national network sites in 2015. The sites selected were Birmingham Tyburn and London Brent which are both background sites within these cities. The chrysene/B(a)P ratios were  $2.2 \pm 0.5$  and  $2.4 \pm 0.5$  for Birmingham and London respectively. In February 2010 when the Weybourne samples were collected, the ratios were 1.9 and 2.0 respectively. Consequently, average weekday congener profiles determined at an urban background site in Birmingham, West Midlands in weekday air samples collected in January 2010 (as reported by Alam et al., 2013, 2014) were used as representative of the source area samples. Such data were also used for mainland European source areas, but this is likely to have led to increased uncertainty.

## 2.3. Model calculations

A simple model was implemented via a spreadsheet which was based upon the following assumptions:

- air is advected from urban source regions to Weybourne (the receptor site), and the dominant removal mechanism for PAHs is reaction of vapour with the hydroxyl radical. Rate coefficients appear in Table S1;
- the mean hydroxyl radical concentration averaged along the trajectory can be estimated from the change in ratios of lower molecular weight compounds. The concentration of OH was calculated initially from:

$$\ln \left[ \frac{[PAH_1]_t}{[PAH_2]_t} \right] = \ln \left[ \frac{[PAH_1]_0}{[PAH_2]_0} \right] + [OH](k_2 - k_1)t \quad (1)$$

in which [PAH<sub>1,2</sub>] refers to the concentration of vapour of the two PAH congeners at time  $t = 0$  (i.e. in the source region) and  $t = t$ , and  $k_1$  and  $k_2$  are the respective rate coefficients for reaction of PAH 1 and 2 for reaction with OH. As this ignores re-partitioning, OH concentrations were varied iteratively to obtain the best fit to the measured PAH data.

- reaction is assumed between PAH vapour and hydroxyl radical

which is first order in each;

- the fraction of each PAH present in the vapour phase changes linearly with time during transport from the source area to the receptor site and is interpolated based on field measurements.
- the particulate component of the PAH is considered to be chemically unreactive, but is able to re-partition to the vapour phase.
- Deposition rates of PAH vapour and fine aerosol are both low and of comparable magnitude for similar compounds; only relative deposition rates are relevant. Volatilisation from soils may influence the low molecular weight compounds, but will be small, and of similar magnitude for congeners of similar mass. Both processes are ignored in the model.

Deposition processes will play a minor role in determining PAH concentrations, but these are unlikely to compete with chemical reactivity in determining relative concentrations, particularly as vapour deposition rates are likely to be similar for the various congeners, and particle-phase deposition will be very modest due to the small sizes of the particles (accumulation mode) with which PAH are largely associated.

Although a more sophisticated model would be desirable, the lack of a spatially disaggregated emissions inventory for all PAH precludes this. Use of compound ratios avoids the need to model dispersion processes, as all compounds are diluted similarly by such processes.

The model is implemented in hourly time steps and Fig. S3 shows typical changes in normalised concentrations of three constituents by reaction with OH over a trajectory of 15 h.

## 3. Results and discussion

This study builds upon earlier work in our group which was focussed initially upon development of procedures for the analysis of low concentrations of particulate PAHs in low volume air samples (Delgado Saborit et al., 2010), development of advanced procedures for sampling both vapour and condensed phase PAH (Delgado-Saborit et al., 2014), procedures for measurements of quinone derivatives including some not previously measured in the atmosphere (Delgado-Saborit et al., 2013), receptor modelling of airborne PAH concentrations (Jang et al., 2013) and the application of the analytical techniques to studying the reactivity of PAHs both in the urban background (Alam et al., 2013) and at the rural Weybourne site (Alam et al., 2014). The urban studies (Alam et al., 2013) demonstrated that the ratio of concentrations of individual low molecular weight PAH congeners between a roadside and a nearby urban background site increased monotonically with the rate coefficient for reaction of the PAH congener with the hydroxyl radical. This was interpreted as due to concentrations at the urban background site being reduced relative to the local traffic source in a direct relationship to their reactivity with OH, hence leading to higher roadside to background ratios for the more reactive compounds. Application of the same conceptual thinking to PAH concentrations measured at the coastal rural Weybourne site showed that the ratio between concentrations of individual quinones and their parent PAH was inversely related to the PAH concentration indicating a relative increase in quinones relative to PAH in the more aged air masses (Alam et al., 2014). When concentration ratios for specific three ring PAHs and for specific four ring PAHs between urban source regions and rural Weybourne were calculated, there was once again a monotonic increase in ratio with PAH vapour phase reactivity as represented by the rate coefficient for PAH congener vapour with the hydroxyl radical (Alam et al., 2014). Dachs et al. (2002) have shown that diurnal trends in concentrations of low molecular weight PAH measured in Baltimore are consistent with removal by reaction with the OH radical.

While our published analyses of these data have considered reactivity only of the lower molecular weight compounds existing predominantly as vapour, we now report analyses of our data extending to the higher molecular weight compound benzo(a)pyrene which is

**Table 1**

Results of estimation of OH radical concentrations from fluoranthene/pyrene ratios (winter campaign).

Date	Air mass origin	Reaction time (h)	Estimated OH (molecules cm <sup>-3</sup> )
Feb 5	London	9	$7.98 \times 10^5$
Feb 8	Hamburg	24	$2.87 \times 10^5$
Feb 15	London	7	$1.11 \times 10^6$
Feb 16	London	7	$1.12 \times 10^6$
Feb 19	Leeds	9	$8.22 \times 10^5$
Feb 23	Amsterdam	12	$4.76 \times 10^5$
Feb 24	London	8	$6.63 \times 10^5$
Feb 25	London	9	$7.53 \times 10^5$
Feb 26	Leicester	4	$9.88 \times 10^5$

present predominantly in the condensed phase.

Mean backward air mass trajectories for 5, 15, 16, 24 and 25 February passed through or close to the London conurbation *en route* to Weybourne. The map of population density shown in Fig. S2 reveals a relatively sparse population in the intermediate area between London and Weybourne. Consequently, our initial analysis assumed London as the main PAH source area for these samples and transit times were calculated for the air mass between London and Weybourne. For other samples, predominant source areas within the UK or European mainland were identified (see Table 1). Combining the transit times with measured fluoranthene/pyrene ratios from a source region (the West Midlands conurbation) and Weybourne in equation (1), an iterative approach, which was needed because the vapour/particle ratio changed between every time step of the model, showed that the ratio of concentrations measured at Weybourne could be explained well by using a hydroxyl radical concentration in the range of  $(2.9\text{--}11) \times 10^5$  (average  $7.8 \times 10^5$ ) cm<sup>-3</sup>, and reactions solely with PAH vapour (see Table 1).

A small dataset was also available from a summer campaign at Weybourne. Concentrations were generally lower than in the winter campaign, and data quality not so high. However, data for phenanthrene, pyrene and chrysene appeared to be good and have been modelled in Table 2. In this case, the estimated hydroxyl radical concentrations range from  $(1.50\text{--}1.63) \times 10^6$  cm<sup>-3</sup>.

In the next set of calculations, phenanthrene and B(a)P vapour were paired in equation (1) with the hydroxyl radical concentrations calculated from the fluoranthene/pyrene ratios to calculate phenanthrene/B(a)P ratios at our Weybourne receptor point. This gave phenanthrene/B(a)P ratios which were far too high (i.e. phenanthrene was reacting too slowly or B(a)P too rapidly). Unlike most low molecular weight PAHs, phenanthrene has a relatively rapid gas phase reaction with the NO<sub>3</sub> radical for which Kwok et al. (1994) determined a rate coefficient of  $1.2 \times 10^{-13}$  cm<sup>3</sup> molecules<sup>-1</sup> s<sup>-1</sup>. This reaction was added into equation (1), which was then used to optimise the NO<sub>3</sub> concentration in combination with the previously determined OH concentration, and gave NO<sub>3</sub> concentrations within the range of  $(0.91\text{--}6.95) \times 10^8$  cm<sup>-3</sup> (mean  $3.6 \times 10^8$  cm<sup>-3</sup>), shown in Table 3.

The calculated OH concentrations of  $(2.9\text{--}11) \times 10^5$  (average  $7.8 \times 10^5$ ) cm<sup>-3</sup> can be compared with measured data. Heard et al. (2004) have reported measurements of hydroxyl radical in the winter

**Table 2**

Measured and modelled congener ratios for samples collected in the summer campaign.

Date	Phe/Pyr		Phe/Chr		Estimated hydroxyl (molecules cm <sup>-3</sup> )
	Measured	Modelled	Measured	Modelled	
6 Aug	6.8	6.8	18	20	$1.5 \times 10^6$
10 Aug	7.3	6.9	21	19	$1.6 \times 10^6$
19 Aug	7.8	6.7	20	18	$1.63 \times 10^6$
20 Aug	7.2	6.6	21	18	$1.59 \times 10^6$
23 Aug	8.6	7.3	21	19	$1.68 \times 10^6$

**Table 3**

Results of estimation of NO<sub>3</sub> radical concentrations from the measured ratios of phenanthrene to B(a)P (winter campaign).

Date	Measured Phe/B(a)P	Calculated Phe/B(a)P (1) <sup>a</sup>	Calculated Phe/B(a)P (2) <sup>a</sup>	Estimated NO <sub>3</sub> (molecules cm <sup>-3</sup> )
Feb 5	37.2	107.7	37.2	$3.10 \times 10^8$
Feb 8	49.5	109.1	49.7	$0.91 \times 10^8$
Feb 15	65.1	109.4	65.1	$1.88 \times 10^8$
Feb 16	97.9	141.1	97.9	$1.35 \times 10^8$
Feb 19	44.2	106.7	44.3	$2.83 \times 10^8$
Feb 23	12.7	120.3	12.7	$5.53 \times 10^8$
Feb 24	34.1	134.2	34.0	$4.53 \times 10^8$
Feb 25	53.1	116.9	53.1	$2.32 \times 10^8$
Feb 26	48.9	147.7	48.9	$6.95 \times 10^8$

<sup>a</sup> Note: Phe/B(a)P (1) – calculated value using OH radical concentration from Table 1 without inclusion of NO<sub>3</sub> reaction. Phe/B(a)P (2) – calculated value using OH radical concentrations from Table 1 with inclusion of NO<sub>3</sub> reaction.

urban troposphere in the UK. The measurements were made in Birmingham, a city in the UK West Midlands. Although the measurements were made in suburban Birmingham, it is likely that they would be relevant to a significant proportion of the travel of the urban plume. During the winter measurement period (16 January to 18 February 2000) measurable concentrations of hydroxyl radical were found between approximately 06:00 and 18:00 h with a peak concentration of about  $1.8 \times 10^6$  cm<sup>-3</sup> and a daytime average of around  $8 \times 10^5$  cm<sup>-3</sup>. This would imply a 24-hour average concentration of OH of around  $4 \times 10^5$  cm<sup>-3</sup>. In an earlier study including members of our group (Cardenas et al. 1998), evidence was shown from temporal air pollutant profiles for advection of a highly polluted air mass from London to the Weybourne Observatory taking 9 h in November 1993. From changes in the ratios of hydrocarbons, it was inferred that the daytime average concentration of hydroxyl was  $3.2 \times 10^5$  cm<sup>-3</sup>. The conditions at that time were very highly polluted, which is likely to have suppressed the hydroxyl radical concentrations relative to the less polluted atmospheres sampled in the much more recent PAH study. The only other available winter data are few, as most studies have measured in the summer months. Kim et al. (2014), measured noon concentrations of OH in Boulder, Colorado of  $\sim 27 \times 10^5$  cm<sup>-3</sup>, with 24-hour averages (judged from their Fig. 1) of  $\sim 12 \times 10^5$  cm<sup>-3</sup> in February 2011. Ren et al. (2006) reported maximum winter daytime mixing ratios in New York City for OH of  $14 \times 10^5$  cm<sup>-3</sup>. Diurnally-averaged mean concentrations were not reported, but appear to be  $\sim 5 \times 10^5$  cm<sup>-3</sup>.

Measurements of OH made in summer 1999 by Heard et al. (2004) showed peak concentrations of around  $3 \times 10^6$  cm<sup>-3</sup> and a 24-hour mean of around  $1.5 \times 10^6$  cm<sup>-3</sup> and hence relatively consistent with that estimated from our PAH data (Table 2). Summer data from New York City reported by Ren et al. (2003) show a 24-hour mean of around  $2.0 \times 10^6$  cm<sup>-3</sup>, as do those from the MEGAPOLI campaign in Paris reported by Michoud et al. (2012). The OH radical concentrations calculated from the PAH decay data are broadly consistent with the measured data summarised above. Hence, although some more aged PAHs will be present from locations upwind of our putative source areas, and some less aged PAHs from locations closer to the receptor point, the average level of reaction is consistent with the source areas and congener ratios used in our simulation.

Stone et al. (2014) have recently measured NO<sub>3</sub> concentrations in the UK atmosphere and report winter night-time concentrations in the range of 0–80 ppt ( $0\text{--}2.2 \times 10^9$  cm<sup>-3</sup>) with most data lying below 50 ppt ( $1.3 \times 10^9$  cm<sup>-3</sup>). Their mean value of 18.9 ppt ( $5.1 \times 10^8$  cm<sup>-3</sup>) is very consistent with our 24-hour range of  $(0.9\text{--}6.95) \times 10^8$  cm<sup>-3</sup> and mean of  $3.6 \times 10^8$  cm<sup>-3</sup>.

As explained above, ignoring the reaction of phenanthrene with NO<sub>3</sub> leads to high calculated phenanthrene/B(a)P ratios, which could be explained by an unaccounted for reaction of phenanthrene, or a more rapid loss of B(a)P than from the vapour phase reaction with

**Table 4**

The estimated half-life of B(a)P as function of the percentage in the particle phase (%P) and OH concentration.

%P B(a)P	99%			95%			90%		
OH concentration (molecules cm <sup>-3</sup> )	0.5 × 10 <sup>6</sup>	2 × 10 <sup>6</sup>	5 × 10 <sup>6</sup>	0.5 × 10 <sup>6</sup>	2 × 10 <sup>6</sup>	5 × 10 <sup>6</sup>	0.5 × 10 <sup>6</sup>	2 × 10 <sup>6</sup>	5 × 10 <sup>6</sup>
Half-life time (h)	770	192	77	154	38	15	77	19	8

hydroxyl. There are two reasons for thinking that the former explanation is correct. Firstly, inclusion of the phenanthrene-NO<sub>3</sub> reaction gives correct congener ratios when using plausible NO<sub>3</sub> radical concentrations. Secondly, when phenanthrene was paired with fluoranthene or pyrene in calculations of OH radical concentration (without inclusion of the NO<sub>3</sub> reaction), the calculated OH concentrations always appeared too high, by a factor of around two, as with B(a)P, suggesting a deficiency in the phenanthrene reaction rate.

Using the same method to estimate decay, i.e. reacting only in the vapour phase, and re-partitioning after every time-step, the atmospheric half life of B(a)P has been calculated. Plausible ranges of % particulate (90–99%) and hydroxyl radical concentrations (0.5 × 10<sup>6</sup> to 5 × 10<sup>6</sup> cm<sup>-3</sup>) have been used. Results appear in Table 4. These show half lives as long as 770 h at 99% particle-association (probably corresponding to very low temperatures) and low OH radical concentrations (low insolation). This would be consistent with the observed persistence of B(a)P and high B(a)P/phenanthrene ratios observed at remote, and especially at polar sites noted in the Introduction. However, as anticipated, half lives can be relatively short (8 h) under high temperature and more oxidising (higher OH) conditions.

#### 4. Conclusions

The measured data on low molecular weight PAH ratios (fluoranthene and pyrene) can be explained in terms of an atmospheric reaction with the OH radical at concentrations of the same order as those measured in the UK atmosphere in the relevant season. In the case of phenanthrene, it is necessary also to include the reaction with NO<sub>3</sub> which can then account for the relative concentrations of this compound. The use of congener ratios in these calculations removes the need to account for atmospheric dispersion/dilution processes, and their associated uncertainties. Taking Tables 1 and 3 together shows that there is consistency between the reaction rates of fluoranthene, pyrene, phenanthrene and B(a)P when these react only in the vapour phase. Table 2 shows consistency also with the reactivity of chrysene as vapour.

In the case of B(a)P, atmospheric reactivity can be explained by reaction of the vapour phase only with hydroxyl radicals at the rate coefficient of 5 × 10<sup>-11</sup> cm<sup>3</sup> molecules<sup>-1</sup> s<sup>-1</sup> determined from structure-activity relationships. This finding provides an alternative to the much-studied condensed phase reactions of B(a)P which may prove to be of little if any relevance to behaviour in the atmosphere. The role of condensed phase reactions is very hard to assess, as their rate is highly variable, dependent upon the distribution of the B(a)P upon and within the substrate, and the presence of protective layers (Poschl et al., 2001; Zhou et al., 2012, 2013). On the contrary, provided the concentration of vapour is known, the reaction rate can be estimated from a known (or modelled) concentration of the hydroxyl radical. A key challenge for numerical modellers seeking to simulate the behaviour of B(a)P during long-range transport is to estimate the particle-vapour partitioning, which was not an issue in this study as it was derived directly from measurements.

While there will inevitably be exceptions, this work suggests strongly that the oxidation of semi-volatile compounds in the atmosphere will, for many compounds, be dominated by reaction of the vapour component, with little contribution of reactions in the condensed phase, which are of limited relevance due to diffusion limitations of the attack by oxidant species (Donahue et al., 2013). This may

not be the case for compounds with very low vapour pressures (such as oleic acid) (Al-Kindi et al., 2016), and hence modelling approaches which account fully for partitioning between the vapour and condensed phases are essential to reliable predictions.

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#### Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.apr.2018.05.009>.

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