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On-road traffic emissions of polycyclic aromatic hydrocarbons and their oxy- and nitro- derivative compounds measured in road tunnel environments



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HIGHLIGHTS

- Polycyclic aromatic compounds including PAH, oxy- and nitro-derivatives
- Includes several compounds not previously measured in road tunnels
- Measured in road tunnels and urban background
- Large decline in PAH, but not nitro-PAH since 1992–96
- 1-Nitropyrene promising specific marker of diesel exhaust

GRAPHICAL ABSTRACT



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ABSTRACT

Vehicular emissions are a key source of polycyclic aromatic compounds (PACs), including polycyclic aromatic hydrocarbons (PAHs) and their oxygenated (OPAH) and nitrated (NPAH) derivatives, in the urban environment. Road tunnels are a useful environment for the characterisation of on-road vehicular emissions, providing a realistic traffic fleet and a lack of direct sunlight, chemical reactivity and non-traffic sources. In the present investigation the concentrations of selected PAHs, OPAHs and NPAHs have been measured in the Parc des Princes Tunnel in Paris (PdPT, France), and at the Queensway Road Tunnel and an urban background site in Birmingham (QT, U.K.). A higher proportion of semi-volatile (3–4 ring) PAH, OPAH and NPAH compounds are associated with the particulate phase compared with samples from the ambient environment. A large (~85%) decline in total PAH concentrations is observed between 1992 and 2012 measurements in QT. This is attributed primarily to the introduction of catalytic converters in the U.K. as well as increasingly stringent EU vehicle emissions legislation. In contrast, NPAH concentrations measured in 2012 are similar to those measured in 1996. This observation, in addition to an increased proportion of (Phe + Flt + Pyr) in the observed PAH burden in the tunnel, is attributed to the increased number of diesel passenger vehicles in the U.K. during this period. Except for OPAHs,

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comparable PAH and NPAH concentrations are observed in both investigated tunnels (QT and PdP). Significant differences are shown for specific substances between PAC chemical profiles in relation with the national traffic fleet differences (33% diesel passenger cars in U.K. vs 69% in France and up to 80% taking into account all vehicle categories). The dominating and sole contribution of 1-Nitropyrene observed in the PdPT NPAH profile strengthens the promising use of this compound as a diesel exhaust marker for PM source apportionment studies.

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1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are a class of atmospheric pollutant, identified as being carcinogenic in humans (IARC, 2010). Exposure to PAHs is associated with excess risk of lung cancer (WHO, 2000) as well as other adverse health effects including bronchitis, asthma, heart disease and reproductive toxicity (Choi et al., 2010). PAHs therefore contribute to poor ambient air quality, particularly in urban areas and require careful monitoring and investigation to understand their concentrations, behaviour and fate in the environment.

The PAH congener benzo[a]pyrene (BaP) is widely used as a marker for PAHs in the atmosphere as BaP constitutes a substantial proportion of the total carcinogenic potential of the total PAH burden (Delgado-Saborit et al., 2011). The European Directive 2004/107/EC sets a target value of 1 ng m^{-3} in the PM_{10} fraction for the annual mean concentration of BaP. In the United Kingdom (U.K.), an air quality standard of a 0.25 ng m^{-3} annual average is included in the National Air Quality Strategy.

The World Health Organisation (WHO) has recommended guidelines for concentrations of BaP producing excess lifetime cancer risks of 1/10,000, 1/100,000 and 1/1,000,000 of 1.2, 0.12 and 0.012 ng m^{-3} , respectively (WHO, 2000). It is estimated that 20% of the population of the EU is exposed to BaP levels higher than the EU target of 1 ng m^{-3} and 88% is exposed to levels higher than the reference level of 0.12 ng m^{-3} (EEA, 2015).

PAHs are typically generated as by-products from the incomplete combustion and pyrolysis of fossil fuels and wood as well as the release of petroleum products. PAHs can therefore originate from domestic, industrial, transport and accidental combustion sources as well as natural processes (Ravindra et al., 2008; Jang et al., 2013; Alam et al., 2015). Anthropogenic sources are expected to dominate the PAH burden in the ambient air over the naturally occurring component (Wild and Jones, 1995). PAHs are chemically reactive with atmospheric lifetimes of hours to days (Keyte et al., 2013). Consequently, urban PAH concentrations are primarily influenced by local and regional emissions and processes.

A range of compounds receiving increasing interest are PAH derivative compounds such as oxygenated (OPAH) and nitrated (NPAH) polycyclic aromatic hydrocarbons. NPAH and OPAH are also shown to exert cytotoxicity, immunotoxicity and carcinogenicity (IARC, 2012, 2013; Durant et al., 1996; WHO, 2000), and are a particular concern due to their direct acting mutagenicity (Bolton et al., 2000; Fiedler and Mücke, 1991).

OPAHs and NPAHs result from primary emission from combustion processes (Gullett et al., 2003; Shen et al., 2012b, 2012c; Sidhu et al., 2005; Simoneit et al., 2007; Fine et al., 2002; Fitzpatrick et al., 2007; IARC, 2012, 2013; Cho et al., 2004; Jakober et al., 2007; Tang et al., 2002; WHO, 2000) although compared with primary PAHs, relatively few data are available. A comprehensive overview of currently available data on primary combustion sources of individual OPAH and NPAH compounds was recently provided by Keyte et al. (2013).

In addition to direct combustion sources, OPAHs and NPAHs also result from gas-phase and heterogeneous reactions of primary PAH with atmospheric oxidants (e.g. OH, NO_3 , N_2O_5 and O_3) (Keyte et al., 2013; Atkinson and Arey, 1994, 2007). It has been shown that this atmospheric processing of PAH can be an important secondary source of NPAH and OPAH congeners that contributes significantly to their observed

atmospheric concentrations (Albinet et al., 2007, 2008a; Ringuet et al., 2012a; Reisen and Arey, 2005; Eiguren-Fernandez et al., 2008; Arey et al., 1990; Atkinson and Arey, 2007).

Numerous studies have suggested PAHs can contribute significantly to the observed carcinogenicity and/or mutagenicity of ambient air (Albinet et al., 2008a; Bethel et al., 2001; Durant et al., 1998; Gupta et al., 1996; Hannigan et al., 1998; Pedersen et al., 2004, 2005; Tuominen et al., 1988; Umbuzeiro et al., 2008; Wang et al., 2011; Bonfanti et al., 1996; Harrison et al., 2004).

However, it has been indicated in some studies that semi-polar fractions of atmospheric PM extracts (likely to contain OPAH and NPAH compounds) can display higher direct acting mutagenicity than non-polar extracts (likely to contain PAH compounds) (Jariyasopit et al., 2014a, 2014b; Lewtas et al., 1990; Nishioka et al., 1985; Pedersen et al., 2004; Umbuzeiro et al., 2008; Wang et al., 2011). These studies therefore suggest that NPAH and OPAH may pose more toxic hazard in the urban environment than PAH.

Road traffic is considered a key primary source of PAHs, OPAHs, NPAHs in urban areas (Fraser et al., 1998; Jakober et al., 2007; Lim et al., 1999; Oda et al., 1998; Rogge et al., 1993a; Staehelin et al., 1998; Zhu et al., 2003). For example, it has been estimated that motor vehicle emissions account for between 46 and 90% of total PAHs in ambient PM in urban areas (Nikolaou et al., 1984; Jang et al., 2013).

There is therefore a need accurately to assess the relative and overall contribution of road traffic makes to the concentrations of different PAHs, OPAHs and NPAHs in the ambient urban atmosphere in relation to other primary combustion sources (e.g. industrial emissions and domestic burning), secondary sources (e.g. reactive input and volatilisation from surfaces) as well as other influencing factors such as reactive or photolytic loss processes.

However, accurately measuring on-road vehicular emissions is complicated by the mixture of engine and fuel types and emission control technologies present. Furthermore, experimental studies in a laboratory will only yield data on specific vehicles, engine characteristics and/or fuel formulations (e.g. Zielinska et al., 2004a, 2004b).

Sampling in road tunnels is expected to provide a more realistic traffic profile than using dynamometer tests (Oda et al., 2001; Wingfors et al., 2001). Road tunnels provide the advantage of a realistic distribution of on-road vehicles; relatively low rates of dispersion and chemical reactivity; and a lack of inputs from other primary sources. Additionally, repeated monitoring in a tunnel environment can assess historic changes in PAH emission profiles in response to changes in fuel usage or emission control measures (Ravindra et al., 2008).

Relatively few studies have characterised the on-road emission profile of PAHs, NPAHs and OPAHs in tunnel environments (Wingfors et al., 2001; Dimashki et al., 2000; Smith and Harrison, 1996; Ho et al., 2009; Fraser et al., 1998). Furthermore, many previous on-road emission studies have sampled only the particle-phase component (Chen et al., 2013; Eiguren-Fernandez and Miguel, 2012; Marr et al., 1999; Miguel et al., 1998; Phuleria et al., 2006) and a large number of studies report results in terms of PAH emission factors i.e. mass emitted per unit volume/weight of fuel consumed (Marr et al., 1999; Miguel et al., 1998) or unit distance of vehicle travel (Fraser et al., 1998; Kam et al., 2012; Staehelin et al., 1998).

In the present investigation, the total (gas + particle phase) concentrations of selected PAHs, OPAHs and NPAHs were measured in a road

tunnel environment in central Birmingham, U.K and simultaneously at an urban background site in southwest Birmingham. Comparative measurements (only particle phase) were performed in a tunnel of the Paris ring road (France). The specific aims were to i) obtain realistic 'traffic signatures' for these compounds; ii) compare investigated tunnel concentrations and chemical profiles in relation to the national vehicle fleet compositions; iii) compare these tunnel concentrations with those observed in the ambient urban environment; and iv) assess the temporal trend of these compounds in the tunnel and relate this to observed changes in traffic characteristics during this period.

2. Experimental

2.1. Study location

Sampling was conducted inside the Queensway Road Tunnel (QT) in Birmingham, U.K. in September 2012 and inside the Parc des Princes Tunnel (PdPT) of the Paris ring road, France in June 2013. The sampling locations are shown in Figs. S1 and S2 of the Supplementary information (SI). The main differences between both sampling locations lie in the traffic fleet composition. In UK, gasoline vehicles are dominant and diesel powered passenger cars accounted for about 32% of total cars in 2012 (DfT, 2014) (Fig. S3). In France among the 38 million vehicles, 68.6% were diesel in 2013. Taking into account all vehicle categories including heavy trucks, this proportion was about 80% for diesel (CCFA, 2014).

The QT in Birmingham passes under the city centre, providing a main through route for a dual carriageway, which constitutes part of a major highway through the city. The tunnel is approximately 544 m long with natural ventilation, with the north- and south-bound traffic separated by a concrete dividing wall. The speed limit in the tunnel is 30 mph.

Concurrent air sampling was conducted at a background site at Elms Road Observatory Site (EROS) on the University of Birmingham campus, approximately 3 km south of the city centre. These samples provide an 'ambient background' concentration to be subtracted from the tunnel concentrations to calculate a 'traffic' concentration. During the sampling campaign the average temperature was about 11.5 ± 2.2 °C. A description and details of the background site have been discussed previously by Harrad et al. (2003) and Alam et al. (2015).

The PdPT is part of the Paris ring road which constitutes the major road around the French capital. The tunnel passes under the Parc des Princes football stadium and is 580 m long with forced ventilation. It is about 5 m high and 52 m wide divided into two carriageways separated by a wall, comprising the internal (clockwise direction) and external ring roads (anticlockwise direction). Tunnel speed limit in 2013 was 80 km h⁻¹.

Daily traffic flow data are not available for the QT itself and traffic counts were not performed during sampling. Traffic counts, supplied by the Department of Transport are available for sites on the same road at a distance of approximately 200 m from either end of the tunnel. Daily traffic counts in 2012 at these sites were estimated at ~75,000 and ~25,000 vehicles per day for roads to the south and north east of the tunnel respectively. It is assumed, based on the number of potential traffic routes/origins available, that the latter of these traffic counts will be a better approximation of tunnel traffic flow for the sampling days conducted.

For PdPT, traffic data including vehicle counts, average speed and tunnel fill rate, were recorded during the sampling campaign and provided by the Paris city council (Marie de Paris). Total average daily traffic was about 210,000 vehicles per day with an equal distribution for the internal and external ring roads (Fig. S5). Mean vehicle speed was slightly higher for the external ring road than for the internal one (69 and 57 km h⁻¹, respectively) and inversely for tunnel fill rate (12 and 18%, respectively). The latter is a measure of congestion and indicates freely flowing traffic.

2.2. Sampling procedures

Air samples were collected in QT, following a procedure utilised previously in air monitoring studies in Birmingham by members of this research group (Smith and Harrison, 1996; Lim et al., 1999; Dimashki et al., 2000, 2001; Harrad et al., 2003; Harrad and Laurie, 2005). A high volume air sampler (PM₁₀, Tisch Environmental Inc., Cleves, Ohio, USA), adapted to sample both particle-phase and gas-phase pollutants was deployed in an emergency breakdown lay-by in the southbound section of the tunnel. 24 h air samples were taken on four separate weekdays, in order to include both morning and evening rush hour periods. Total air volume sampled during ~24 h sampling periods during this study varied from ~800–1200 m³.

In PdPT, PM₁₀ particulate samples were collected on 9 consecutive days using a high volume sampler DA-80 (with cooled sample storage, ≈ 10 °C) (Digitel, Hegnau, Switzerland) (sampling duration 24 h, started at midnight, 30 m³ · h⁻¹). The sampler was located in the middle of the tunnel on an emergency exit of the internal ring road.

Total particulate matter was collected on quartz fibre filters (for QT: Whatman, obtained from VWR International, Lutterworth, Leicestershire, UK; dimensions, 8" × 10"; retention efficiency >99%; for the PdPT: Tissu quartz Pallflex, Ø = 150 mm). For QT, gas-phase sample was collected using cylindrical polyurethane foam (PUF) plugs (dimensions 3" × 3 3/8", flame retardant-free, Tisch Environmental Inc., Cleves, Ohio, USA). Two PUF plugs were loaded in series inside a cylindrical metal tube (PUF holder) fitted downstream of the filter holder.

Prior to sampling, filters were heated at 450 °C for 24 h to reduce organic impurities. PUFs were pre-cleaned by ultrasonication twice in a solvent mixture of DCM, hexane and methanol (1:1:1 by volume) followed by ultrasonication in hexane only. After collection, samples were wrapped in aluminium foils, sealed in polyethylene bags and stored at <– 10 °C prior to extraction and analysis.

2.3. Sample extraction and clean-up

QT and EROS samples were analysed for 18 PAHs, 4 OPAHs and 12 NPAHs (Table S1) using similar methodologies to those described previously (Delgado-Saborit et al., 2013). PdP samples were analysed for 21 PAHs, 30 OPAHs and 32 NPAHs (Tables S2, S3, S4 and S5) using similar procedures described in previous work (Albinet et al., 2006, 2007, 2008a, 2008b, 2013, 2014; Ringuet et al., 2012a, 2012b) and standard methods EN 15549 and TS 16645 for PAHs. All solvents (dichloromethane, hexane, pentane, methanol) used in sample extraction and cleanup were HPLC grade (purity >98%), obtained from Fisher Scientific or Aldrich. Filter and PUF samples were extracted separately in order to determine particulate and gas phase analyte concentrations independently.

Briefly, QT and EROS filters and PUFs were spiked with 1000 pg μL⁻¹ deuterated internal standards for quantification. Samples were placed in a glass flask, immersed in DCM and ultrasonicated at room temperature (25 °C) for 20 min. Sample extracts were then reduced under a gentle stream of nitrogen to a volume of 1 mL prior to sample clean-up. Due to the large volume of solvent required for PUF extractions, these sample extracts were initially transferred to Turbovap apparatus (Biotage Ltd., Uppsala, Sweden) and blown down under a gentle stream of nitrogen (20 °C) to 5 mL. Sample extracts were initially cleaned by filtration using a clean glass Pasteur pipette chromatography column filled with a small amount of glass wool and 0.5 g of fine anhydrous sodium sulphate (puriss grade for HPLC, Sigma-Aldrich Company Ltd., Gillingham, U.K.). Sample extracts then underwent further concentration to almost dryness under a gentle nitrogen flow and were made up to a volume of 1 mL with hexane. Sample extracts were then subject to a solid phase extraction step, based on the methodology described by Albinet et al. (2006) and Cochran et al. (2012). An aminopropyl solid phase extraction tube (Sigma-Aldrich Company Ltd., Gillingham, UK) was pre-eluted with 3 × 1 mL aliquots of DCM followed by the same measure of hexane.

The sample was then passed through the column and target compounds were eluted by the sequential DCM/hexane solvent gradient (3×1 mL) of 20/80%, 35/65%, 50/50%. This resulted in optimum recovery of PAH, NPAH and OPAH compounds in one sample extract for analysis.

PdPT filters were cut into punches of 47 mm diameter. A punch was used for PAH analysis and extracted using ASE 200, Dionex (3 DCM cycles: 120 °C, 140 bars, 6 min heat time, 6 min static time). Extracts were then blow down under a gentle stream of nitrogen (Zymark, Turbopap II) and redissolved in acetonitrile for UPLC/Fluorescence analysis. The second punch filter was used for NPAH and OPAH analysis. Filters were extracted using QuEChERS-like procedure developed previously for particulate-bound PAH and PAH derivatives analysis (Albinet et al., 2013, 2014). Briefly, punches were placed in centrifuge glass tubes and 7 mL of acetonitrile were added to perform the extraction using a Multi-tube Vortexer (DVX-2500 Multi Tube Vortexer, VWR) during 1.5 min. After extraction, samples were centrifuged for 5 min at 4500 rpm (Sigma 3–16 PK centrifuge). The supernatant extract was collected and reduced near to dryness under a gentle nitrogen stream. Reduced extracts were then dissolved in dichloromethane (100–200 μ L). A clean up step was applied for extracts dedicated to GC/NICI-MS analysis of NPAHs and OPAHs. The clean-up was performed on silica SPE cartridge (SiOH chromabond, Macherey Nagel, 3 mL, 500 mg) with a first elution of pentane (1 mL discarded) and then the collection of eluted extract with 9 mL of 65:35 (v/v) pentane-DCM. Purified extracts were then reduced near to dryness under a gentle stream of nitrogen and then reconstituted in about 100 μ L of acetonitrile.

2.4. Sample analysis

QT and EROS samples were analysed for PAH compounds using Gas Chromatography (GC – 6890 N Agilent Technologies) fitted with a non-polar capillary column (Agilent HP-5MS, 30 m, 0.25 mm ID, 0.25 μ m film thickness – 5% phenylpolysiloxane) in tandem with a Mass Spectrometer (5973 N, Agilent Technologies) operated in electronic ionisation (EI) and selective ion monitoring (SIM) mode. For OPAH and NPAH analysis an Agilent Technologies GC–MS (GC 6890 W and 5973 MSD) equipped with a Restek Rxi-PAH column (60 m, 0.25 mm ID, 0.1 μ m film thickness) was operated in negative ion chemical ionisation (NICI) and SIM mode. Methane (99.9% purity; Argo International Ltd., UK.) was used as the reagent gas for the NICI analysis.

Quantification of all target compounds was based upon the ratios of analyte response peak area to that of an appropriate deuterated internal standard. Standards of perdeuterated and native PAH (all compounds) and NPAH compounds (>98% purity in toluene or isoctane) (1-nitronaphthalene-d7; 3-nitrofluoranthene-d9; 1-nitropyrene-d9 and 6-nitrochrysene-d11) and *p*-terphenyl-d14 recovery standard (>99% purity, in toluene) were obtained from Greyhound Chromatography, Merseyside, UK, as pre-prepared solutions by Chiron AS, Trondheim, Norway. Perdeuterated (9-fluorenone-d8 and anthraquinone-d8) and native OPAH internal standards and 1-fluoro-7-nitrofluorene recovery standard (purity >98%) were obtained initially as solids from Sigma-Aldrich Company Ltd., Gillingham, UK and solutions prepared by dilution with hexane.

PAHs of the PdPT samples were analysed by UPLC/UV-Fluorescence (Thermo Scientific, Dionex Ultimate 3000) using a C18 UPLC column (Zorbax Eclipse PAH, 2.1 mm \times 150 mm \times 1.8 μ m). 23 PAHs were quantified using external standard solution calibration. Recovery control; before extraction a known amount of 6-methylchrysene was added to the samples and used as standard extraction recovery control (Table S2). NPAHs and OPAHs were analysed by GC/NICI-MS (Agilent 7890 A GC coupled to 5975C MS, methane as reagent gas) (Albinet et al., 2006, 2014) using an Optima-5MS Accent column (30 m \times 250 μ m \times 0.25 μ m) and operated in SIM mode. Quantification of OPAHs and NPAHs was performed by internal standard calibration using native standards and deuterated surrogate compounds added before extraction (Table S3 and S4).

9-Fluorenone-d9 and 1-nitropyrene-d9 were used as surrogate standards.

Quality assurance experiments were performed to assess the accuracy, precision and reproducibility of the extraction, clean-up and analysis methods. Replicate analysis of Standard Reference Material 1649b (urban dust), provided by the National Institute of Standards and Technology (NIST), was conducted using the procedures outlined above. The mean concentrations of 6 (INERIS, PdPT) and 10 (University of Birmingham, QT and EROS) SRM samples were in good agreement with reference concentrations provided by NIST for PAHs and those reported in the literature for NPAHs and OPAHs (Albinet et al., 2014 and references therein). Field blank filters and PUFs ($n = 1$ for each phase, at each site) were collected in order to evaluate any contamination during the sampling and analytical procedures. Compounds showing field blank sample concentrations higher than 30% of mean tunnel sample concentrations were excluded. All results presented here were corrected for field blank concentration values.

3. Results and discussion

3.1. Concentrations of PAHs, OPAHs and NPAHs

Mean concentrations of the same PAHs, OPAHs and NPAHs measured in the QT and PdPT and the proportion of each compound present in the particle-phase for QT, are presented in Table 1. Concentrations of additional NPAHs and OPAHs analysed in PdPT samples are presented in Table S5. Compounds below quantification limit are not reported in the table.

Lower molecular weight (LMW) PAHs (MW < 203) comprised ~93% of average total PAH mass (QT, gaseous and particulate phases), consistent with previous measurements in tunnel and roadside locations (Harrad and Laurie, 2005; Smith and Harrison, 1996; Benner et al., 1989; Ho et al., 2009; Fraser et al., 1998; Khalili et al., 1995), and emission studies of gasoline and diesel vehicles (Schauer et al., 1999, 2002; Zhu et al., 2003; Zielinska et al., 2004a, 2004b). Focusing on compounds mainly associated with the particulate phase (from BaA to Cor), results obtained for both tunnels showed comparable individual PAH concentration levels.

Previous studies by Alam et al. (2013) and Harrad and Laurie (2005) have reported 'traffic increment' concentrations of PAHs in Birmingham. These were derived by subtracting concentrations at the Elms Road background site (EROS), from those measured simultaneously at a nearby roadside location. The relative concentrations of individual PAHs in the tunnel are similar to those of the 'traffic increment' reported in these previous studies.

In QT, 9F was the dominant OPAH compound measured. BaAQ was present at very low concentration, indicating a relatively low traffic input of this compound, in agreement with previous road tunnel measurements (Fraser et al., 1998). 9F was observed predominantly in the gas phase, while AQ, MAQ and BaAQ were present mainly in the particulate phase. Interestingly, OPAH concentration levels observed in the PdPT were significantly lower notably for AQ and MAQ.

1 and 2NNap isomers were the most abundant NPAHs compounds measured, predominantly present in the gas-phase (QT). The observed ratio of 1NNap/2NNap was ~1.8. This ratio is slightly higher than previously observed in the same tunnel by Dimashki et al. (2000). 1NPy and 9NANt were the dominant particle-phase NPAHs measured in both tunnels. These compounds have been identified as the two principal NPAHs present in diesel emissions (Campbell and Lee, 1984; Paputa-Peck et al., 1983; Ratcliff et al., 2010; Schuetzle et al., 1982; Zhu et al., 2003; Zielinska et al., 2004b).

2NPyr and 2NFlt are found in relatively low levels in the tunnels. These compounds are generally not observed in vehicular emissions and are the principal products of gas-phase (OH and/or NO₃ initiated) reactions of Pyr and Flth respectively (Atkinson and Arey, 1994). The low concentration of these compounds in the tunnel is in agreement

Table 1Mean \pm standard deviation of PAH, OPAH and NPAH concentrations measured in the Queensway Road Tunnel (n = 4), Parc des Princes Tunnel (n = 9) and at EROS (n = 4).

PAHs	Mean QT (ng m ⁻³) ^a	% Particle-phase	Mean PdPT (ng m ⁻³) ^b	Mean EROS (ng m ⁻³) ^c	% Particle-phase
Acy	10.0 \pm 3.7	1	nm	0.2 \pm 0.1	2
Ace	3.3 \pm 1.6	3	0.1 \pm 0.1	0.4 \pm 0.2	4
Flo	12.0 \pm 13.0	1	0.2 \pm 0.0	3.8 \pm 1.1	1
Phe	81.1 \pm 25.7	5	3.8 \pm 0.6	25.8 \pm 1.3	4
Ant	8.0 \pm 3.4	7	0.6 \pm 0.1	2.0 \pm 1.0	5
Flt	13.6 \pm 2.9	49	6.8 \pm 1.0	3.0 \pm 1.0	10
Pyr	11.1 \pm 3.6	67	7.5 \pm 1.0	3.7 \pm 0.6	11
Ret	0.8 \pm 0.4	67	0.6 \pm 0.0	2.0 \pm 0.3	18
BaA	1.0 \pm 0.1	72	0.7 \pm 0.1	0.1 \pm 0.0	69
Chr	1.6 \pm 0.6	70	1.2 \pm 0.4	0.1 \pm 0.0	75
BbF	0.8 \pm 0.2	88	0.8 \pm 0.2	0.4 \pm 0.2	71
BkF	1.2 \pm 0.2	79	1.0 \pm 0.3	0.2 \pm 0.0	72
BeP	0.8 \pm 0.1	90	0.8 \pm 0.2	0.1 \pm 0.0	77
BaP	0.9 \pm 0.3	91	0.8 \pm 0.3	0.1 \pm 0.0	80
IPy	0.8 \pm 0.4	95	0.9 \pm 0.4	0.2 \pm 0.1	78
DBA	0.2 \pm 0.1	65	0.2 \pm 0.1	0.1 \pm 0.1	91
Bpy	1.7 \pm 0.5	95	1.7 \pm 0.6	0.3 \pm 0.1	81
Cor	0.8 \pm 0.2	99	0.8 \pm 0.2	0.1 \pm 0.0	91
OPAHS	Mean QT (ng m ⁻³) ^a	% Particle-phase	Mean PdPT (ng m ⁻³) ^b	Mean EROS (ng m ⁻³) ^c	% Particle-phase
9F	7.1 \pm 1.9	18	0.1 \pm 0.0	1.1 \pm 0.4	6
AQ	3.7 \pm 1.3	94	0.2 \pm 0.0	0.7 \pm 0.2	61
MAQ	1.7 \pm 0.5	100	0.1 \pm 0.1	0.4 \pm 0.1	78
BaAQ	0.0 \pm 0.0	100	0.0 \pm 0.0	0.1 \pm 0.0	95
NPAHS	Mean QT (ng m ⁻³) ^a	% Particle-phase	Mean PdPT (ng m ⁻³) ^b	Mean EROS (ng m ⁻³) ^c	% Particle-phase
1NNap	1918 \pm 438	2	<QL ^d	118 \pm 58	2
2NNap	980 \pm 816	3	<QL	135 \pm 103	2
2NFlo	94 \pm 87	95	31 \pm 5	13 \pm 10	50
9NAnt	294 \pm 154	88	41 \pm 11	34 \pm 16	59
1NFlt	1916	75	nm	13 \pm 15	79
2NFlt	9 \pm 8	100	19 \pm 14 ^e	11 \pm 4	83
3NFlt	18 \pm 15	95	nm	1 \pm 0	76
4NPyr	8 \pm 0	89	3 \pm 4	2 \pm 1	80
1NPyr	343 \pm 148	96	287 \pm 94	5 \pm 3	86
2NPyr	15 \pm 3	86	<QL	6 \pm 3	81
7NBaA	2 \pm 3	94	18 \pm 13	1 \pm 1	96
6NChr	5 \pm 2	88	7 \pm 9	0 \pm 0	94

nm - not measured.

^a - Gaseous + particulate phases, n = 4.^b - Only particulate phase, n = 9.^c - Gaseous + particulate phases, n = 4.^d - Below quantification limit.^e - 2 + 3-Nitrofluoranthene concentrations.

with previous measurements by Dimashki et al. (2000) and is consistent with the absence of direct sunlight and low oxidant concentrations resulting in negligible photochemical reactivity in the tunnels.

3.2. Comparison with previous tunnel studies

Table 2 provides a comparison between PAH levels observed in the present study (QT) with three previous road tunnel measurements of total (particulate + gas phase) PAH concentrations.

Considerable differences can be noted between these studies. Pollutant concentrations can be expected to vary considerably in different tunnel environments due to differences in traffic fleet composition (e.g. relative level of gasoline- and diesel-fuelled vehicles), level of traffic congestion, fuel formulations, emission control measures (e.g. legislative requirements), tunnel characteristics (e.g. dimensions, level of ventilation) and meteorological conditions (e.g. relative humidity, temperature). For example, the relatively high concentrations of PAHs observed in the Baltimore Harbour Tunnel by Benner et al. (1989) compared with other studies may be attributed to the higher proportion of gasoline-fuelled vehicles in this location at this time.

The concentration of semi-volatile (3–4 ring) PAHs is considerably lower in the present study than reported in previous studies. Semi-volatile PAHs Acy, Ace, Flo, Phe, Ant, Flt and Pyr have been

observed in relatively high concentrations in diesel emissions (Ratcliff et al., 2010; Rogge et al., 1993a; Schauer et al., 1999; Zhu et al., 2003; Zielinska et al., 2004b). The estimated proportions of diesel heavy duty vehicles (HDVs) in the relevant studies were <3% (present study); 9% (Benner et al., 1989); 8–24% (Wingfors et al., 2001); and 47% (Ho et al., 2009). The low relative contribution of diesel HDVs may therefore be a contributing factor to the reported concentrations of LMW PAHs in these tunnel studies.

The PAH concentrations measured in the QT were linearly regressed against corresponding road tunnel emission factors derived by Wingfors et al. (2001) and Ho et al. (2009). A very good correlation ($R^2 > 0.9$) was observed between measured concentrations in this study and the emission factors calculated by Wingfors et al. (2001) for a road tunnel in Gothenberg, Sweden. This can possibly be attributed to similarities in tunnel characteristics, sampling techniques, traffic fleet composition (vehicle types and fuel compositions) and emission controls measures present in the two locations.

No correlation was found between measured concentrations in the QT and the emission factors derived by Ho et al. (2009) in the Shing Mun Tunnel, Hong Kong. This suggests very different traffic fleet composition, emission control measures and/or fuel formulations exist between the two locations and this causes considerable differences in PAH emission profiles.

Table 2
Comparison of total (P + V) PAH concentrations and percentage of concentration in the particulate phase (%P) in different road tunnel measurements.

	This study ^a		Ho et al. (2009) ^b		Benner et al. (1989) ^c		Wingfors et al. (2001) ^d	
	ng m ⁻³	%P	ng m ⁻³	%P	ng m ⁻³	%P	ng m ⁻³	%P
Acy	10	1.2	645	0	nm	nm	12	4
Ace	3	3	1748	0	nm	nm	8	15
Flo	12	1.2	209	0.7	nm	nm	46	3
Phe	81	5	205	4	209	12	179	21
Ant	8	7	32	4	38	14	15	51
Flt	14	49	45	46	56	55	73	84
Pyr	11	67	45	59	58	51	87	87
Ret	0.8	67	nm	nm	nm	nm	0.3	100
BaA	1	72	5	99	8	99	3	100
Chr	2	70	8	74	14	85	4	97
BbF	0.8	88	1	100	11	100	1	100
BkF	1	79	0.3	100	11	100	0.1	100
BeP	0.8	90	0	nm	5	100	1	100
BaP	0.9	91	1	100	6	100	1	100
IPy	0.8	95	0.2	100	5	100	0.5	100
DBA	0.2	65	0.3	100	nm	nm	0.2	100
BPy	2	95	0	nm	8	100	2	100
Cor	0.8	99	nm	nm	nm	nm	0.5	100

nm – not measured.

^a – Queensway Road Tunnel, Birmingham; Sept. 2012; estimated 25,000 vehicles per day.

^b – Shing Mun Tunnel, Hong Kong; Weekday noon samples; summer 2003; 53,000 vehicles per day.

^c – Baltimore Harbor Tunnel, USA; 1985–86; mechanical ventilation; traffic flow unknown.

^d – Ludby Road Tunnel in Gothenberg, Sweden; April 2000; 20,000 vehicles per day.

Measured concentrations of OPAHs and NPAHs in road tunnels are relatively lacking in the literature. Gorse et al. (1983) measured 1NPy concentrations in the Allegheny Mountain Tunnel in Pennsylvania, USA in 1981. The maximum reported concentration was ~3 times lower than the mean concentrations measured in the present investigation (QT and PdPT). Benner (1988) measured mean concentrations of ~0.3 ng/m³ for 1NPy and 9NAnt in the Baltimore Harbour Tunnel in 1985, in good agreement with the levels observed in the present study.

3.3. Comparison of chemical profiles of both investigated tunnels

Particulate phase PAH, OPAH and NPAH chemical profiles obtained for both tunnels are presented in Fig. 1.

OPAH chemical profiles were similar for both tunnels. Significant differences in the contribution of specific substances were observed for PAHs and NPAHs. For instance, larger contributions of Pyr and 1NPy were observed for the PdPT while the contributions of heavier PAHs (BPy, IPy, Cor) and 9NAnt were lower than in the QT. Differences observed could be explained by the national traffic fleet differences between both tunnels with a significant higher proportion of diesel vehicles in France (PdPT, up to 80%) and, conversely, a larger proportion of gasoline cars in U.K. (QT, about 66%). Pyr (Ratcliff et al., 2010; Zhu et al., 2003) and especially 1NPy (Paputa-Peck et al., 1983; Hayakawa et al., 1994; Zielinska et al., 2004a, 2004b; Schulte et al., 2015), are compounds mainly associated with diesel emissions while heavier PAHs are described in the literature as compounds mainly emitted by gasoline engines (Li and Kamens, 1993; Miguel et al., 1998; Rogge et al., 1993a).

Complete profiles obtained at PdPT taking into account all the quantified OPAHs or NPAHs are presented on Figs. S6 and S7. 1-Naphthaldehyde and benanthrone were the dominating compounds for OPAHs. Among all the quantified NPAHs, 1NPy was the dominating and sole contributor to the NPAH chemical profile in such a highly diesel impacted environment. These findings suggest the use of this compound as specific diesel exhaust marker for aerosol source apportionment studies (Schulte et al., 2015).

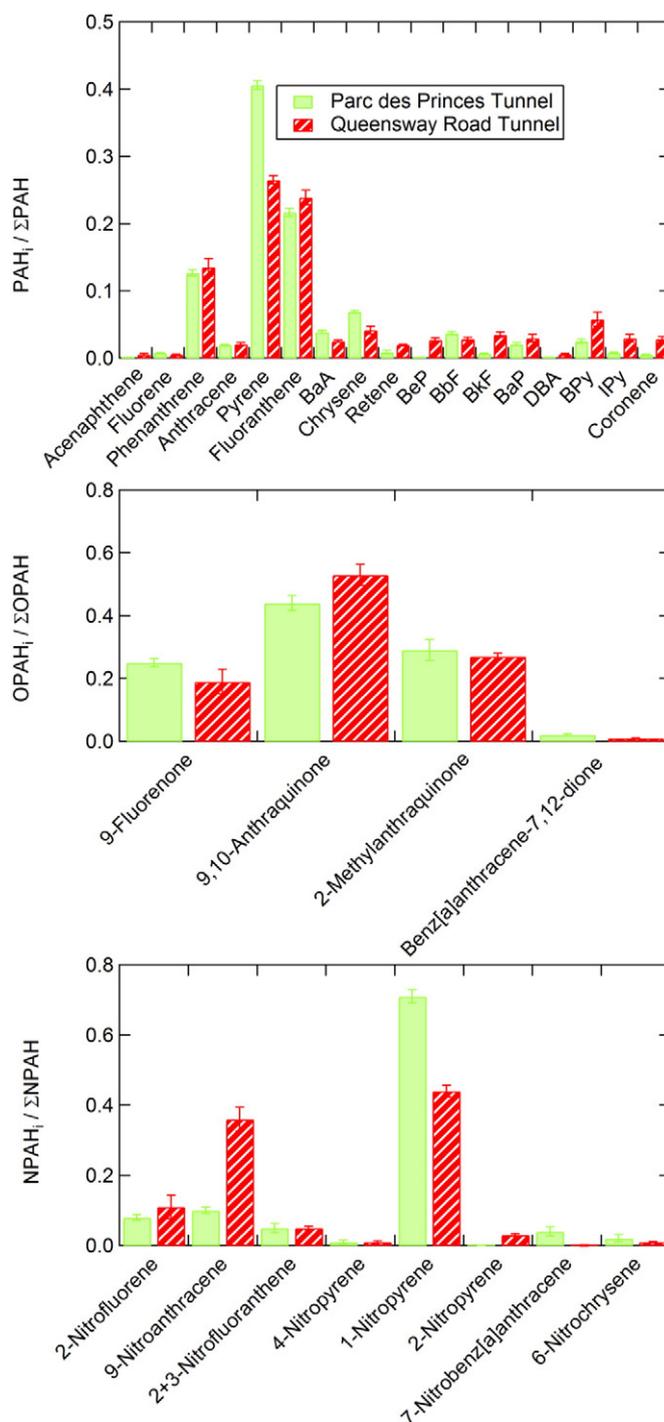


Fig. 1. Comparison of particulate phase PAH, OPAH and NPAH chemical profiles obtained for both investigated tunnel environments (Parc des Princes and Queenway road tunnels; n = 9 and 4, respectively).

3.4. Gas-particle phase partitioning of PAH, OPAH and NPAH

The phase partitioning behaviour of PAH, OPAH and NPAH in QT and ambient measurements are different (Table 1).

For most LMW 3-ring compounds and HMW 5 + ring compounds, the proportion of compounds in the particle phase in the QT is similar to that observed at background site EROS. However, semi-volatile compounds (e.g. Pyr, Flt, Ret, 9F, AQ, MAQ, 2NFlo) display markedly higher proportions in the particle phase in the tunnel than in the ambient atmosphere. The phase partitioning behaviour of PAH, OPAH and NPAH

as a function of compound MW is therefore markedly different for the tunnel and ambient samples (Fig. 2) with greater proportions of each compound class present in the particulate phase.

Higher particulate phase contributions may reflect the more dominant role of direct emissions from vehicles in the tunnel, which may be associated to a greater extent with fine particles (Albinet et al.,

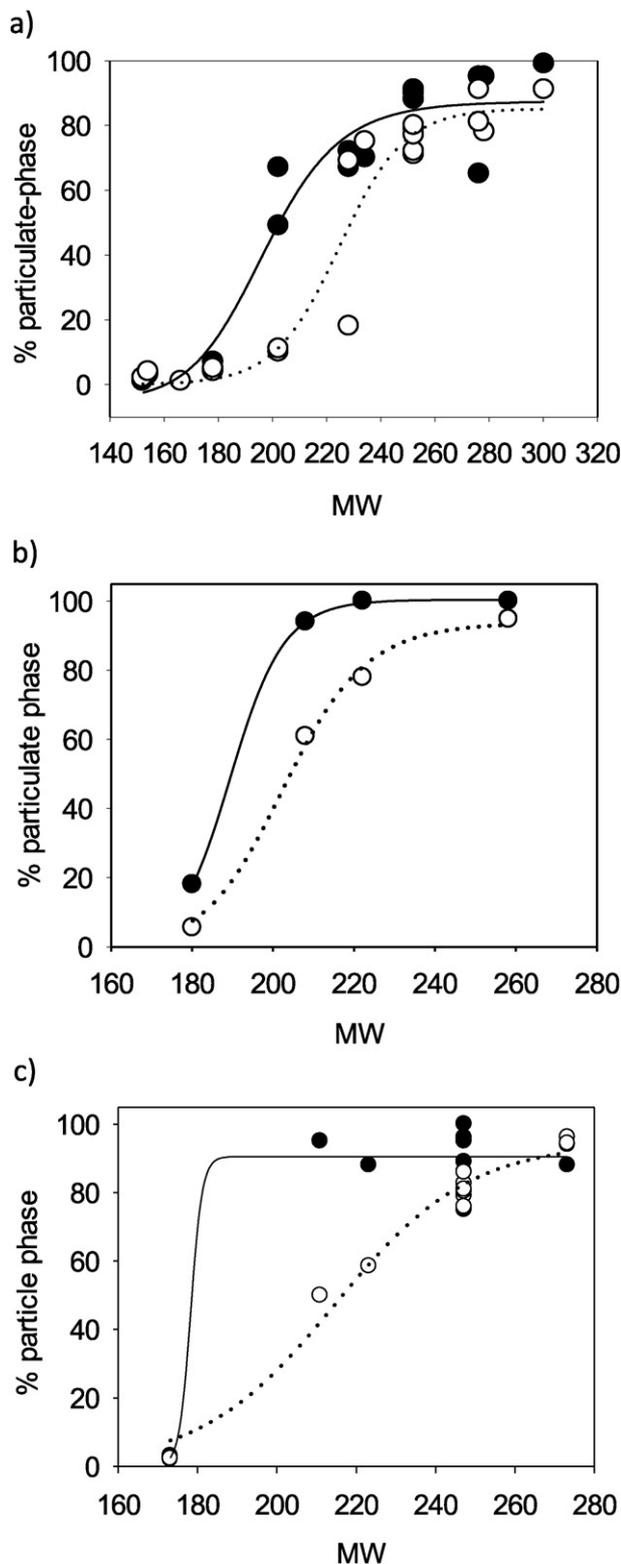


Fig. 2. Plots of % of component in the particulate phase vs. molecular weight for a) PAHs, b) OPAHs and c) NPAHs, measured in the tunnel (black dots, solid black line) and at EROS (white dots, dotted line).

2008b). Zielinska et al. (2004a) suggest that Flt and Pyr emissions were predominantly in the gas-phase when vehicles were idle or at low engine loads but at higher vehicle load, a much larger proportion of these compounds were present in the particulate phase, particularly for diesel vehicles. This could indicate vehicles in the tunnel were operating under relatively higher load, thus contributing to higher particulate concentrations of these compounds. However, lower daytime temperatures and higher particulate matter concentrations in the tunnel favour partitioning into the condensed phase (Yamasaki et al., 1982) and this is a more likely explanation.

Retene (Ret) is not commonly associated with road traffic (Wingfors et al., 2001) and is typically a marker for wood combustion (Ramdahl, 1983) and recently described as highly emitted during coal combustion (Shen et al., 2012a). The lower Ret concentrations observed in the QT relative to EROS suggest non-traffic sources dominate and transportation of Ret from the ambient atmosphere outside the tunnel may be responsible for observed tunnel concentrations. The higher proportion of Ret in the particulate phase in the tunnel relative to EROS is therefore unlikely to be source-driven. This observation supports the argument that temperature and particle loading are the dominant factors, as suggested above.

3.5. Comparison of QT and ambient concentrations

It is assumed that concentrations of PAHs, OPAHs and NPAHs measured in the tunnel result entirely from on-road vehicular emissions (including exhaust and non-exhaust emissions). Comparing levels of compounds measured in the QT with those observed at the background site EROS (tunnel/ambient ratios) will allow the assessment of other influencing factors (e.g. non-traffic sources, relative rates of atmospheric loss processes) to their overall and relative concentrations in the urban atmosphere. The tunnel/ambient ratios measured in the present study are shown in Fig. 3. It can be seen that these ratios vary considerably for different individual compounds.

Mean total PAH concentration was ~4.5 times higher in the tunnel than the mean concentration at EROS. Similarly, Kim et al. (2012) noted that PAH concentrations were ~6 and 10 times higher in the Bukak Tunnel in Seoul, South Korea, than were measured at an ambient roadside location during spring and winter respectively. Wingfors et al. (2001) also noted total PAH concentrations in the Ludby Tunnel in Gothenburg, Sweden were an order of magnitude higher than those measured in heavily trafficked urban areas. These observations are generally consistent with the lower rate of dispersion and lower chemical reactivity in the tunnel environment compared with the ambient atmosphere.

The considerable variability in tunnel/ambient ratios between different PAHs, can be attributed to differences in traffic source contribution at the ambient site, physiochemical properties, and/or relative reactivity rates of individual PAH compounds. The only PAH compound to exhibit a tunnel/ambient ratio of <1 was Ret. This is consistent with this compound resulting primarily from wood or coal combustion used for residential heating in this period rather than road traffic (Shen et al., 2012a; Bari et al., 2010; Fine et al., 2002; McDonald et al., 2000; Ramdahl, 1983).

LMW (3–4 ring) compounds Flo, Phe, Ant, Flth, Pyr display relatively low (3 to 4.5) tunnel/ambient ratios. Given that these compounds, are expected to be relatively abundant in traffic emissions this observation is somewhat surprising. For example, Phe, Flt and Pyr are the dominant PAHs in diesel exhaust (Ratcliff et al., 2010; Zhu et al., 2003 and PdPT results) and therefore may be expected to display enhanced ratios. This observation suggests non-traffic sources (e.g. domestic wood and coal combustion or revolatilisation of pollutants from road and or soil/vegetation surfaces) may contribute significantly at the ambient site, resulting in relatively low tunnel/ambient ratios.

It has been previously been indicated that PAH concentrations measured in the U.K. atmosphere can be influenced by the secondary input

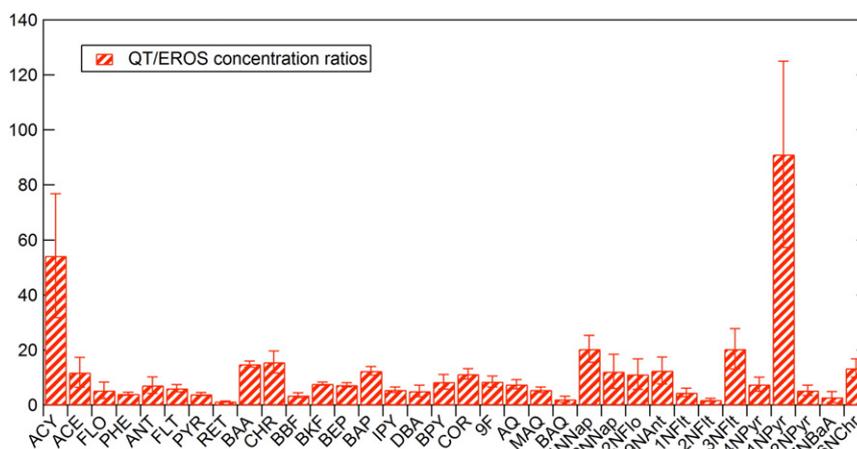


Fig. 3. Mean ratios of concentrations measured in the Queensway Road Tunnel to those measured simultaneously at the Elms Road background (n = 4).

due to volatilisation from soil, vegetation and/or road surfaces (Dimashki et al., 2001; Harrad and Laurie, 2005; Lee and Jones, 1999). For example, Lee and Jones (1999) noted a significant positive correlation between the concentration of Phe, Flt and Pyr and temperature in a semi rural site in northern England, indicating the possibility of temperature-driven evaporation from vegetation and/or soils influencing concentrations.

Evidence for secondary surface volatilisation at the Birmingham University site has been discussed by Dimashki et al. (2001) and Lim et al. (1999). It was indicated however, that volatilisation from surfaces was more significant in the city centre than at the University site. However, it is possible that PAH concentrations at the EROS background site are influenced by secondary input from surface volatilisation and that this has influenced the observed tunnel/ambient ratios of LMW PAHs.

Interestingly, the tunnel/ambient ratio of Flt is higher than that of Pyr, despite higher OH reactivity noted for Pyr relative to Flt (Atkinson et al., 1990; Brubaker and Hites, 1998). This may suggest Pyr concentrations at EROS may be 'buffered' by volatilisation from soil or vegetation surfaces to a much greater degree than Flt resulting in lower tunnel/ambient ratio.

The tunnel/ambient ratio of Acy is considerably higher than those of other PAHs. This is consistent with relatively high gas-phase OH reactivity of this compound (Brubaker and Hites, 1998; Reisen and Arey, 2002). The lack of direct sunlight inside the tunnel is likely to result in minimal reactivity, leading to enhanced ratios. However, while Ant is shown to display similarly fast reactivity towards OH (Brubaker and Hites, 1998), the observed tunnel/ambient ratio is lower than expected. This may suggest the ambient concentration of Ant is substantially influenced by non-traffic sources, either primary or non-combustion related.

Most HMW PAHs (MW > 228) display relatively high tunnel/ambient ratios compared with LMW PAHs. BaA and Chr display particularly high ratios compared with other PAHs, which may reflect a relatively low contribution of non-traffic sources of these compounds at the ambient sites, and/or low atmospheric reactivity.

The relative differences in tunnel/ambient ratios between HMW PAHs may arise in part from the relative stability of these compounds towards atmospheric degradation. For example, BaP displays a relatively high tunnel/ambient ratio compared with other 5 ring PAH compounds. This may be attributed to greater susceptibility of BaP to heterogeneous reactivity in the ambient atmosphere (Jariyasopit et al., 2014a; Ringuet et al., 2012b; Cazaunau et al., 2010; Perraudin et al., 2007).

DBA displays a relatively low tunnel/ambient ratio. This is consistent with a relatively low input from road traffic, as indicated by Jang et al. (2013) who assessed a 'traffic' profile at London monitoring sites, and may indicate an alternative seasonally-dependent combustion source influencing the ambient sites.

The low (<1) ratios observed for BaAQ indicate that this compound is not emitted to a significant degree by road vehicles and is present in higher levels in the ambient atmosphere. This suggests levels of this compound observed at EROS result primarily from a non-traffic combustion source such as natural gas home appliances (Rogge et al., 1993b), wood or coal combustion (Shen et al., 2013) or uncontrolled domestic waste combustion (Sidhu et al., 2005).

NPAHs generally display higher tunnel/ambient ratios than unsubstituted PAHs, although there is wide variability between individual compounds. Relatively high ratios were observed for 1NNap, 2NNAp, 2NFlo, 9NAnt, 3NFlt, 1NPyr and 6NChy. These compounds are expected to be predominantly associated with diesel exhaust emissions (Ball and Young, 1992; Campbell and Lee, 1984; IARC, 2013; Paputa-Peck et al., 1983; Rappaport et al., 1982; Schuetzle et al., 1982; Schuetzle and Perez, 1983; Zhu et al., 2003; Zielinska et al., 2004a, 2004b) with lower input from other combustion sources (WHO, 2000).

The principal atmospheric loss process for NPAHs is expected to be photoreactivity including direct photolysis (Atkinson et al., 1989; Fan et al., 1995, 1996a, 1996b; Phouongphouang and Arey, 2003; Ringuet et al., 2012b; Jariyasopit et al., 2014a). For example, Atkinson et al. (1989) noted atmospheric lifetimes for 1NNap and 2NNAp due to photolysis were ~38 and ~28 times shorter respectively than the corresponding gas-phase reactions with OH.

Photolysis is not expected to occur significantly in the tunnel environment where direct sunlight is absent. It is expected that the principal source of NPAHs in the urban environment is diesel vehicle exhaust with a much lower input from other combustion sources (Ciccioli et al., 1989; WHO, 2000; Keyte et al., 2013). The very high tunnel/ambient ratios for a number of NPAH compounds may therefore reflect more rapid photolytic and/or reactive losses in the ambient atmosphere.

While Holloway et al. (1987) noted relatively long photolysis half lives for 1NPyr and 3NFlt of 1.2 to 6 days and 12.5 to >20 days respectively, other studies suggest this process can be a potentially significant atmospheric sink for particle-bound NPAHs. Fan et al. (1996a) derived half-lives due to photolytic decay for 1NPyr, 2NFlt and 2NPyr on diesel soot and wood smoke in an outdoor chamber of 0.8 to 1.2 h with faster reaction noted for 1NPyr on wood smoke particles.

The results of the present study suggest 1NPyr is degraded more rapidly than other NPAHs. While Fan et al. (1996a) indicated that the structure of particle-associated NPAH compounds does not influence the rate of degradation, it has been suggested elsewhere that the isomeric structure of the compound does influence the rate of photolytic decay (Pitts, 1983). For example, Holloway et al. (1987) and Feilberg and Nielsen (2000) have indicated 1NPyr decays up to 10 times more rapidly than other MW 247 NPAHs.

Dimashki et al. (2000) observed levels of 1NPyr and 9NAnt in the tunnel ~6 and ~2 times higher in the Queensway Road Tunnel than in

the ambient urban atmosphere of Birmingham respectively. This previous study was conducted in central Birmingham during winter. The QT/EROS ratio in the present study is shown to be a factor ~10 and ~4.5 higher than the previous study for 1NPyr and 9NAnt respectively. This may partly be attributed to higher input of pollutants in the city centre compared to the background EROS site and the fact that sampling in the present study was conducted in the late summer leading to potentially faster rates of photolytic degradation in the ambient atmosphere.

The tunnel/ambient ratio of 1NNap is a factor ~2.2 higher than that of 2NNap. Experimental studies indicate 1NNap will exhibit a rate of photolysis ~1.3–8 times higher than that of 2NNap (Atkinson et al., 1989; Phouongphouang and Arey, 2003). This would suggest the observed difference in ratios for the two NNap isomers is due to differences in the rates of photolytic degradation and the relatively long exposure time of air samples collected at EROS.

The relatively low ratios observed for 7NBaA indicate only a minor contribution from traffic for this compound at the ambient site. 7NBaA has been measured in vehicular emissions (Karavalakis et al., 2009; Zhu et al., 2003). However, the previous study in Birmingham did not detect this compound in the QT but did observe measureable levels in the city centre (Dimashki et al., 2000).

2NFlt and 2NPyr are expected to result from atmospheric reactions with minor input from road traffic (Atkinson and Arey, 1994). A tunnel/ambient ratio of <1 was observed for 2NFlt, consistent with little formation in the tunnel. However, 2NPyr displays a ratio of ~5 which is unexpected.

3.6. Temporal trend in PAH and NPAH in QT concentrations

Previous measurements of PAH (Smith and Harrison, 1996) and NPAH (Dimashki et al., 2000) concentrations have been made in the Queensway Road Tunnel. A comparison between the results of the present study and these previous investigations could therefore provide an assessment of temporal changes in emission profiles. Some caution is needed in interpreting these changes as both sets of data derive from relatively short periods of measurement and hence week-to-week variability cannot be assessed. Concentrations of OPAHs have not previously been measured in the tunnel.

A comparison of total (gas + particle phase) PAH levels measured in the tunnel in 2012 and 1992 is shown in Table 3. A decline of ~85% for total PAH concentration is noted between 1992 and 2012 measurements. This observation is in agreement with the historical reduction in PAH levels reported in road tunnel studies in the United States (Benner et al., 1989; Eiguren-Fernandez and Miguel, 2012). The magnitude of concentration reduction varies considerably between individual compounds. The majority of compounds (Ace, Flo and HMW PAHs) exhibit a decline of >90% while Phe, Flt and Pyr exhibit a decline of <80%.

A number of factors have been shown to be responsible for reduction of PAHs from road vehicles. These include changes to fuel formulations (Westerholm and Egeback, 1994) e.g. use of biofuels (Ratcliff et al., 2010) or use of additives to enhance the cetane or octane number (Williams et al., 1986; Zhu et al., 2003); innovations in engine design e.g. use of three-way catalysts (Rogge et al., 1993a; Schauer et al., 2002; Westerholm and Egeback, 1994; Zielinska et al., 2004b) and improvement in exhaust emission control measures e.g. particulate filters (Hu et al., 2013), with their implementation being principally driven by increasingly strict government legislation (Perrone et al., 2014). Other factors e.g. state of vehicle maintenance and ambient conditions (e.g. temperature) are also shown to influence PAH emissions from road traffic (Zielinska et al., 2004b).

The observed reduction of PAH levels in the QT can be attributed, to a large degree, to the introduction of mandatory catalytic converters to the U.K in 1993. Catalytic converters have been shown to reduce the emissions of PAHs in gasoline-fuelled vehicles by 92–99% (Rogge et al., 1993a; Schauer et al., 2002; Westerholm and Egeback, 1994; Zielinska et al., 2004b). For example, Benner et al. (1989) measured PAH

Table 3

Comparison of mean total (particulate + vapour) PAH concentrations measured in the Queensway Road Tunnel in 1992 (Smith and Harrison, 1996) and 2012 (present study).

	Tunnel concentration (ng m ⁻³)		% Decline
	1992 (n = 8)	2012 (n = 4)	
Acy	95	10	90
Ace	114	3	97
Flo	167	12	93
Phe	333	81	76
Ant	51	8	84
Flt	48	14	71
Pyr	55	11	80
BaA	14	1	93
Chr	26	2	94
BbF	13	0.8	93
BkF	5	1	88
BaP	13	0.9	93
IPy	22	0.8	96
DBA	4	0.2	95
BPy	35	2	95
Cor	12	1	94
∑ PAH	1122	158	86

concentrations in the Baltimore Harbour Tunnel, USA, a factor 5–10 lower than a study conducted 10 years earlier (Fox and Stanley, 1976). This was attributed to the introduction of catalytic converters which were first used in the USA in 1974.

However, progressively stringent legislation pertaining to vehicular emissions of both gasoline and diesel vehicles is also likely to have contributed to PAH emission reductions. It is indicated that different stages of EU legislation on new vehicle emission limits (91/441/EEC) has resulted in progressively reduced PAH emissions since 1993 (Perrone et al., 2014).

The relative concentration of individual PAHs has changed significantly over this period. Indeed, the combined contribution of (Phe + Flt + Pyr) to ∑PAH burden has increased from ~44% in 1992 to ~72% in 2012. Gasoline-fuelled vehicles are shown to emit higher levels of HMW compounds e.g. BaP, IPy, BPy, Cor (Marr et al., 1999; Miguel and Pereira, 1989; Miguel et al., 1998) while diesel is generally shown to be a greater source of semi-volatile compounds such as Phe, Flt, and Pyr (Chen et al., 2013; Harrison et al., 1996; Miguel et al., 1998). This observation could therefore suggest a greater contribution of diesel emissions over the previous 20 years in the tunnel.

In the period 1994 to 2012, the number of gasoline-fuelled cars in the U.K decreased by ~500,000 while the number of diesel-fuelled passenger cars increased by ~7.8 million (DfT, 2014). This trend has seen the relative proportion of diesel cars in the U.K traffic fleet increase from ~7% in 1994 to ~33% in 2012 (see Fig. S3).

The trend in the number of gasoline and diesel vehicles on the road is reflected in the volume of gasoline and diesel fuel supplied to the U.K market (see Fig. S4) and national fuel sales. In the UK, sales of gasoline fuel decreased by ~43% between 1990 and 2011, from 33 billion litres to 19 billion litres. Meanwhile the sales of diesel fuel more than doubled over this period, from ~12 billion litres in 1992 to ~25 billion litres in 2011 (UKPIA, 2012).

A comparison in concentrations of four NPAHs measured in the present study in 2012 and those measured by Dimashki et al. (2000) in 1996 is shown in Table 4. The previous measurements were made on only one sampling day, while the current study is the average of four separate sampling days so comparison of results must be done with caution.

In contrast to the significant historical decline noted for PAH concentrations, little or no decline in NPAH concentration is noted. The mean levels of NNap isomers measured in the present study fall within the range of concentrations measured in 1996 while the concentrations of 9NAnt and 1NPyr were within 1 standard deviation of the lower range of concentrations measured in 1996.

Table 4

Comparison of total (particulate + vapour) NPAH concentrations measured in the Queensway Road Tunnel in 1996 (Dimashki et al., 2000) and 2012 (present study).

	Tunnel concentration (pg m ⁻³)	
	2012 (This study)	1996 (Dimashki et al., 2000)
1NNap	1918 ± 461	560–2120
2NNap	980 ± 820	620–1570
9NAnt	294 ± 165	370–760
1NPy	343 ± 157	440–690

1NNap, 2NNap, 9NAnt and 1NPy are all present in diesel exhaust emissions in relatively high levels (Campbell and Lee, 1984; Draper, 1986; Paputa-Peck et al., 1983; Zhu et al., 2003) and are present in low/negligible emissions from gasoline vehicles (Zielinska et al., 2004b). The increase in relative contribution of diesel vehicles in the U.K traffic fleet from 1996 to 2012 may therefore have a stronger influence on changes in observed NPAH concentrations relative to PAHs.

Evidence for the increased importance of NPAH in urban air over time has been indicated previously. For example, Matsumoto et al. (1998) noted the concentration of BaP declined significantly in the period 1975 to 1992 in the heavily trafficked region of Sapporo, Japan, while the mutagenicity of collected particles remained unchanged. The authors suggested this could be attributed to an increase in diesel traffic and the possible associated increase in NPAH concentrations.

The lack of increase in observed NPAH levels in the tunnel over this time may suggest that while the volume of diesel traffic has increased, the emissions of NPAHs from individual diesel vehicles may have declined. Indeed, improved exhaust after-treatment (e.g. use of catalytic devices or particulate traps) and fuel formulation has been shown to reduce NPAH and OPAH emissions (Fiedler and Mücke, 1991; Marinov et al., 2009; Nielsen et al., 1999; Ratcliff et al., 2010; Westerholm and Egeback, 1994; Zhu et al., 2003).

The results of the present study therefore suggest that the temporal variation in PAH and NPAH concentrations in the QT have been influenced by both an increase in the number of diesel vehicles in the U.K traffic fleet and a net reduction in emissions from individual vehicles in response to changes in fuel formulation and engine/exhaust system design. The results suggest the NPAH/PAH ratio from on-road vehicular emissions in the U.K. has increased substantially in the last 20 years. This demonstrates the need to monitor more carefully the concentrations of NPAHs and their contribution to poor ambient air quality in urban areas.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <http://dx.doi.org/10.1016/j.scitotenv.2016.05.152>.

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