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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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4 **ON-ROAD TRAFFIC EMISSIONS OF POLYCYCLIC**
5 **AROMATIC HYDROCARBONS AND THEIR OXY-**
6 **AND NITRO- DERIVATIVE COMPOUNDS**
7 **MEASURED IN ROAD TUNNEL ENVIRONMENTS**
8
9

10 **Ian J. Keyte^a, Alexandre Albinet^{b,*} and Roy M. Harrison^{a,*,†}**
11

12
13 **^a Division of Environmental Health and Risk Management**
14 **School of Geography, Earth and Environmental Sciences**
15 **University of Birmingham**
16 **Edgbaston, Birmingham B15 2TT**
17 **United Kingdom**

18
19 **^b INERIS**
20 **(Institut National de l'Environnement industriel et des RISques)**
21 **Parc technologique Alata, BP 2**
22 **60550 Verneuil en Halatte**
23 **France**
24

* To whom correspondence should be addressed.

Tel: +44 121 414 3494; Fax: +44 121 414 3708; Email: r.m.harrison@bham.ac.uk
Tel: +33344556485; Email: alexandre.albinet@ineris.fr, alexandre.albinet@gmail.com

†Also at: Department of Environmental Sciences / Center of Excellence in Environmental Studies, King Abdulaziz University, PO Box 80203, Jeddah, 21589, Saudi Arabia

25 **HIGHLIGHTS**

- 26 • Polycyclic aromatic compounds including PAH, oxy- and nitro-derivatives
- 27 • Includes several compounds not previously measured in road tunnels
- 28 • Measured in road tunnels and urban background
- 29 • Large decline in PAH, but not nitro-PAH since 1992-96
- 30 • 1-Nitropyrene promising specific marker of diesel exhaust
- 31

32 **ABSTRACT**

33 Vehicular emissions are a key source of polycyclic aromatic compounds (PACs), including
34 polycyclic aromatic hydrocarbons (PAHs) and their oxygenated (OPAH) and nitrated (NPAH)
35 derivatives, in the urban environment. Road tunnels are a useful environment for the
36 characterisation of on-road vehicular emissions, providing a realistic traffic fleet and a lack of direct
37 sunlight, chemical reactivity and non-traffic sources. In the present investigation the concentrations
38 of selected PAHs, OPAHs and NPAHs have been measured in the Parc des Princes Tunnel in Paris
39 (PdPT, France), and at the Queensway Road Tunnel and urban background site in Birmingham
40 (QT, U.K). A higher proportion of semi-volatile (3-4 ring) PAH, OPAH and NPAH compounds are
41 associated with the particulate phase compared with samples from the ambient environment. A
42 large (~85%) decline in total PAH concentrations is observed between 1992 and 2012
43 measurements in QT. This is attributed primarily to the introduction of catalytic converters in the
44 U.K as well as increasingly stringent EU vehicle emissions legislation. In contrast, NPAH
45 concentrations measured in 2012 are similar to those measured in 1996. This observation, in
46 addition to an increased proportion of (Phe + Flt + Pyr) in the observed PAH burden in the tunnel,
47 is attributed to the increased number of diesel passenger vehicles in the U.K during this period.
48 Except for OPAHs, comparable PAH and NPAH concentrations are observed in both investigated
49 tunnels (QT and PdP). Significant differences are shown for specific substances between PAC
50 chemical profiles in relation with the national traffic fleet differences (33% diesel passenger cars in
51 U.K. vs 69 % in France and up to 80% taking into account all vehicle categories). The dominating
52 and sole contribution of 1-Nitropyrene observed in the PdPT NPAH profile strengthens the
53 promising use of this compound as a diesel exhaust marker for PM source apportionment studies.

54

55 **Capsule Abstract:** Polycyclic aromatic hydrocarbons and their oxy- and nitro-derivatives have
56 been determined in a road tunnels and an external background site to elucidate sources and temporal
57 trends.

58 **Keywords:** Polycyclic aromatic hydrocarbons; Nitro-PAH; Oxy-PAH; Vehicular emissions, Diesel
59 exhaust.

60
61 **1. INTRODUCTION**

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

68
69 The PAH congener benzo[a]pyrene (BaP) is widely used as a marker for PAHs in the atmosphere as
70 BaP constitutes a substantial proportion of the total carcinogenic potential of the total PAH burden
71 (Delgado-Saborit et al., 2011). The European Directive 2004/107/EC sets a target value of 1 ng m^{-3}
72 in the PM_{10} fraction for the annual mean concentration of BaP. In the United Kingdom (U.K.), an
73 air quality standard of a 0.25 ng m^{-3} annual average is included in the National Air Quality Strategy.

74
75 The World Health Organisation (WHO) has recommended guidelines for concentrations of BaP
76 producing excess lifetime cancer risks of 1/10 000, 1/100 000 and 1/1 000 000 of 1.2, 0.12 and
77 0.012 ng m^{-3} , respectively (WHO, 2000). It is estimated that 20% of the population of the EU is
78 exposed to BaP levels higher than the EU target of 1 ng m^{-3} and 88% is exposed to levels higher
79 than the reference level of 0.12 ng m^{-3} (EEA, 2015).

80
81 PAHs are typically generated as by-products from the incomplete combustion and pyrolysis of
82 fossil fuels and wood as well as the release of petroleum products. PAHs can therefore originate
83 from domestic, industrial, transport and accidental combustion sources as well as natural processes
84 (Ravindra et al., 2008; Jang et al., 2013; Alam et al., 2015). Anthropogenic sources are expected to

85 dominate the PAH burden in the ambient air over the naturally occurring component (Wild and
86 Jones, 1995). PAHs are chemically reactive with atmospheric lifetimes of hours to days (Keyte et
87 al., 2013). Consequently, urban PAH concentrations are primarily influenced by local and regional
88 emissions and processes.

89
90 A range of compounds receiving increasing interest are PAH derivative compounds such as
91 oxygenated (OPAH) and nitrated (NPAH) polycyclic aromatic hydrocarbons. NPAH and OPAH are
92 also shown to exert cytotoxicity, immunotoxicity and carcinogenicity (IARC, 2012, 2013; Durant et
93 al., 1996; WHO, 2000), and are a particular concern due to their direct acting mutagenicity (Bolton
94 et al., 2000; Fiedler and Mücke, 1991).

95
96 OPAHs and NPAHs result from primary emission from combustion processes (Gullet et al., 2003;
97 Shen et al., 2012b, c; Sidhu et al., 2005; Simoneit et al., 2007; Fine et al., 2002; Fitzpatrick et al.,
98 2007; IARC, 2012, 2013; Cho et al., 2004; Jakober et al., 2007; Tang et al., 2002; WHO, 2000)
99 although compared with primary PAHs, relatively few data are available. A comprehensive
100 overview of currently available data on primary combustion sources of individual OPAH and
101 NPAH compounds was recently provided by Keyte et al. (2013).

102
103 In addition to direct combustion sources, OPAHs and NPAHs also result from gas-phase and
104 heterogeneous reactions of primary PAH with atmospheric oxidants (e.g. OH, NO₃, N₂O₅ and O₃)
105 (Keyte et al., 2013 ; Atkinson and Arey, 1994; 2007). It has been shown that this atmospheric
106 processing of PAH can be an important secondary source of NPAH and OPAH congeners that
107 contributes significantly to their observed atmospheric concentrations (Albinet et al., 2007, 2008a;
108 Ringuet et al., 2012a; Reisen and Arey, 2005; Eiguren-Fernandez et al., 2008; Arey et al., 1990;
109 Atkinson and Arey, 2007).

110

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

115
116 However, it has been indicated in some studies that semi-polar fractions of atmospheric PM extracts
117 (likely to contain OPAH and NPAH compounds) can display higher direct acting mutagenicity than
118 non-polar extracts (likely to contain PAH compounds) (Jariyasopit et al., 2014a,b; Lewtas et al.,
119 1990; Nishioka et al., 1985; Pedersen et al., 2004; Umbuzeiro et al., 2008; Wang et al., 2011).

120 These studies therefore suggest that NPAH and OPAH may pose more toxic hazard in the urban
121 environment than PAH.

122
123 Road traffic is considered a key primary source of PAHs, OPAHs, NPAHs in urban areas (Fraser et
124 al., 1998; Jakober et al., 2007; Lim et al., 1999; Oda et al., 1998; Rogge et al., 1993a; Staehelin et
125 al., 1998; Zhu et al., 2003). For example, it has been estimated that motor vehicle emissions account
126 for between 46 and 90% of total PAHs in ambient PM in urban areas (Nikolaou et al., 1984; Jang et
127 al., 2013).

128
129 There is therefore a need accurately to assess the relative and overall contribution of road traffic
130 makes to the concentrations of different PAHs, OPAHs and NPAHs in the ambient urban
131 atmosphere in relation to other primary combustion sources (e.g. industrial emissions and domestic
132 burning), secondary sources (e.g. reactive input and volatilisation from surfaces) as well as other
133 influencing factors such as reactive or photolytic loss processes.

134
135 However, accurately measuring on-road vehicular emissions is complicated by the mixture of
136 engine and fuel types and emission control technologies present. Furthermore, experimental studies

137 in a laboratory will only yield data on specific vehicles, engine characteristics and/or fuel
138 formulations (e.g. Zielinska et al., 2004a,b).

139
140 Sampling in road tunnels is expected to provide a more realistic traffic profile than using
141 dynamometer tests (Oda et al., 2001; Wingfors et al., 2001). Road tunnels provide the advantage of
142 a realistic distribution of on-road vehicles ; relatively low rates of dispersion and chemical reactivity
143 ; and a lack of inputs from other primary sources. Additionally, repeated monitoring in a tunnel
144 environment can assess historic changes in PAH emission profiles in response to changes in fuel
145 usage or emission control measures (Ravindra et al., 2008).

146
147 Relatively few studies have characterised the on-road emission profile of PAHs, NPAHs and
148 OPAHs in tunnel environments (Wingfors et al., 2001; Dimashki et al., 2000; Smith and Harrison,
149 1996; Ho et al., 2009; Fraser et al., 1998). Furthermore, many previous on-road emission studies
150 have sampled only the particle-phase component (Chen et al., 2013; Eiguren-Fernandez and
151 Miguel, 2012; Marr et al., 1999; Miguel et al., 1998; Phuleria et al., 2006) and a large number of
152 studies report results in terms of PAH emission factors i.e. mass emitted per unit volume/weight of
153 fuel consumed (Marr et al., 1999; Miguel et al., 1998) or unit distance of vehicle travel (Fraser et
154 al., 1998; Kam et al., 2012; Staehelin et al., 1998).

155
156 In the present investigation, the total (gas + particle phase) concentrations of selected PAHs,
157 OPAHs and NPAHs were measured in a road tunnel environment in central Birmingham, U.K and
158 simultaneously at an urban background site in southwest Birmingham. Comparative measurements
159 (only particle phase) were performed in a tunnel of the Paris ring road (France). The specific aims
160 were to i) obtain realistic ‘traffic signatures’ for these compounds; ii) compare investigated tunnel
161 concentrations and chemical profiles in relation to the national vehicle fleet compositions; iii)
162 compare these tunnel concentrations with those observed in the ambient urban environment ; and

163 iv) assess the temporal trend of these compounds in the tunnel and relate this to observed changes in
164 traffic characteristics during this period.

165
166

167 **2. EXPERIMENTAL**

168 **2.1 Study Location**

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

177
178 The QT in Birmingham passes under the city centre, providing a main through route for a dual
179 carriageway, which constitutes part of a major highway through the city. The tunnel is
180 approximately 544 m long with natural ventilation, with the north- and south-bound traffic
181 separated by a concrete dividing wall. The speed limit in the tunnel is 30 mph.

182
183 Concurrent air sampling was conducted at a background site at Elms Road Observatory Site
184 (EROS) on the University of Birmingham campus, approximately 3 km south of the city centre.
185 These samples provide an ‘ambient background’ concentration to be subtracted from the tunnel
186 concentrations to calculate a ‘traffic’ concentration. During the sampling campaign the average
187 temperature was about 11.5 ± 2.2 °C. A description and details of the background site have been
188 discussed previously by Harrad et al. (2003) and Alam et al. (2015).

189

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

195
196 Daily traffic flow data are not available for the QT itself and traffic counts were not performed
197 during sampling. Traffic counts, supplied by the Department of Transport are available for sites on
198 the same road at a distance of approximately 200m from either end of the tunnel. Daily traffic
199 counts in 2012 at these sites were estimated at ~75 000 and ~25 000 vehicles per day for roads to
200 the south and north east of the tunnel respectively. It is assumed, based on the number of potential
201 traffic routes/origins available, that the latter of these traffic counts will be a better approximation of
202 tunnel traffic flow for the sampling days conducted.

203
204 For PdPT, traffic data including vehicle counts, average speed and tunnel fill rate, were recorded
205 during the sampling campaign and provided by the Paris city council (Marie de Paris). Total
206 average daily traffic was about 210 000 vehicles per day with an equal distribution for the internal
207 and external ring roads (Figure S5). Mean vehicle speed was slightly higher for the external ring
208 road than for the internal one (69 and 57 km h⁻¹, respectively) and inversely for tunnel fill rate (12
209 and 18%, respectively). The latter is a measure of congestion and indicates freely flowing traffic.

210
211

212 **2.2 Sampling Procedures**

213 Air samples were collected in QT, following a procedure utilised previously in air monitoring
214 studies in Birmingham by members of this research group (Smith and Harrison, 1996; Lim et al.,
215 1999; Dimashki et al., 2000; 2001; Harrad et al., 2003; Harrad and Laurie, 2005). A high volume air
216 sampler (PM₁₀, Tisch Environmental Inc., Cleves, Ohio, USA), adapted to sample both particle-

217 phase and gas-phase pollutants was deployed in an emergency breakdown lay-by in the southbound
218 section of the tunnel. 24 hour air samples were taken on four separate weekdays, in order to include
219 both morning and evening rush hour periods. Total air volume sampled during ~24 hour sampling
220 periods during this study varied from ~800-1200 m³.

221
222 In PdPT, PM₁₀ particulate samples were collected on 9 consecutive days using a high volume
223 sampler DA-80 (with cooled sample storage, ≈ 10°C) (Digitel, Hegnau, Switzerland) (sampling
224 duration 24 hours, started at midnight, 30 m³.h⁻¹). The sampler was located in the middle of the
225 tunnel on an emergency exit of the internal ring road.

226
227 Total particulate matter was collected on quartz fibre filters (for QT: Whatman, obtained from
228 VWR International, Lutterworth, Leicestershire, UK; dimensions, 8" x 10"; retention efficiency
229 >99%; for the PdPT: Tissu quartz Pallflex, Ø = 150 mm). For QT, Gas-phase sample was collected
230 using cylindrical polyurethane foam (PUF) plugs (dimensions 3" x 3 3/8", flame retardant-free,
231 Tisch Environmental Inc., Cleves, Ohio, USA). Two PUF plugs were loaded in series inside a
232 cylindrical metal tube (PUF holder) fitted downstream of the filter holder.

233
234 Prior to sampling, filters were heated at 450°C for 24 hours to reduce organic impurities. PUFs were
235 pre-cleaned by ultrasonication twice in a solvent mixture of DCM, hexane and methanol (1:1:1 by
236 volume) followed by ultrasonication in hexane only. After collection, samples were wrapped in
237 aluminium foils, sealed in polyethylene bags and stored at < -10°C prior to extraction and analysis.

238
239

240 **2.3 Sample Extraction and Clean-Up**

241 QT and EROS samples were analysed for 18 PAHs, 4 OPAHs and 12 NPAHs (Table S1) using
242 similar methodologies to those described previously (Delgado-Saborit et al., 2013). PdP samples
243 were analysed for 21 PAHs, 30 OPAHs and 32 NPAHs (Tables S2, S3, S4 and S5) using similar

244 procedures described in previous works (Albinet et al., 2006, 2007, 2008a, b, 2013, 2014; Ringuet
245 et al., 2012 a, b) and standard methods EN 15549 and TS 16645 for PAHs. All solvents
246 (dichloromethane, hexane, pentane, methanol) used in sample extraction and cleanup were HPLC
247 grade (purity >98%), obtained from Fisher Scientific or Aldrich. Filter and PUF samples were
248 extracted separately in order to determine particulate and gas phase analyte concentrations
249 independently.

250

251 Briefly, QT and EROS filters and PUFs were spiked with 1000 pg μL^{-1} deuterated internal
252 standards for quantification. Samples were placed in a glass flask, immersed in DCM and
253 ultrasonicated at room temperature (25°C) for 20 min. Sample extracts were then reduced under a
254 gentle stream of nitrogen to a volume of 1 mL prior to sample clean-up. Due to the large volume of
255 solvent required for PUF extractions, these sample extracts were initially transferred to Turbovap
256 apparatus (Biotage Ltd, Uppsala, Sweden) and blown down under a gentle stream of nitrogen
257 (20°C) to 5 mL. Sample extracts were initially cleaned by filtration using a clean glass Pasteur
258 pipette chromatography column filled with a small amount of glass wool and 0.5 g of fine
259 anhydrous sodium sulphate (puriss grade for HPLC, Sigma-Aldrich Company Ltd., Gillingham,
260 U.K.). Sample extracts then underwent further concentration to almost dryness under a gentle
261 nitrogen flow and were made up to a volume of 1 mL with hexane. Sample extracts were then
262 subject to a solid phase extraction step, based on the methodology described by Albinet et al. (2006)
263 and Cochran et al., (2012). An aminopropyl solid phase extraction tube (Sigma-Aldrich Company
264 Ltd., Gillingham, UK.) was pre-eluted with 3x 1 mL aliquots of DCM followed by the same
265 measure of hexane. The sample was then passed through the column and target compounds were
266 eluted by the sequential DCM/hexane solvent gradient (3 x 1 mL) of 20/80%, 35/65%, 50/50%. This
267 resulted in optimum recovery of PAH, NPAH and OPAH compounds in one sample extract for
268 analysis.

269

270 PdPT filters were cut into punches of 47 mm diameter. A punch was used for PAH analysis and
271 extracted using ASE 200, Dionex (3 DCM cycles: 120 °C, 140 bars, 6 min heat time, 6 min static
272 time) . Extracts were then blow down under a gentle stream of nitrogen (Zymark, Turbovap II) and
273 redissolved in acetonitrile for UPLC/Fluorescence analysis. The second punch filter was used for
274 NPAH and OPAH analysis. Filters were extracted using QuEChERS-like procedure developed
275 previously for particulate-bound PAH and PAH derivatives analysis (Albinet et al., 2013; 2014).
276 Briefly, punches were placed in centrifuge glass tubes and 7 ml of acetonitrile were added to
277 perform the extraction using a Multi-tube Vortexer (DVX-2500 Multi Tube Vortexer, VWR) during
278 1.5 min. After extraction, samples were centrifuged for 5 min at 4500 rpm (Sigma 3-16 PK
279 centrifuge). The supernatant extract was collected and reduced near to dryness under a gentle
280 nitrogen stream. Reduced extracts were then dissolved in dichloromethane (100-200 µl). A clean up
281 step was applied for extracts dedicated to GC/NICI-MS analysis of NPAHs and OPAHs. The clean-
282 up was performed on silica SPE cartridge (SiOH chromabond, Macherey Nagel, 3 ml, 500 mg) with
283 a first elution of pentane (1 ml discarded) and then the collection of eluted extract with 9 ml of
284 65:35 (v/v/) pentane-DCM. Purified extracts were then reduced near to dryness under a gentle
285 stream of nitrogen and then reconstituted in about 100 µL of acetonitrile.

286

287 **2.3 Sample Analysis**

288 QT and EROS samples were analysed for PAH compounds using Gas Chromatography (GC –
289 6890N Agilent Technologies) fitted with a non-polar capillary column (Agilent HP-5MS, 30 m,
290 0.25 mm ID, 0.25 µm film thickness – 5% phenylpolysiloxane) in tandem with a Mass
291 Spectrometer (5973 N, Agilent Technologies) operated in electronic ionisation (EI) and selective
292 ion monitoring (SIM) mode. For OPAH and NPAH analysis an Agilent Technologies GC-MS (GC
293 6890W and 5973 MSD) equipped with a Restek Rxi-PAH column (60 m, 0.25 mm ID, 0.1 µm film
294 thickness) was operated in negative ion chemical ionisation (NICI) and SIM mode. Methane (99.9%
295 purity; Argo International Ltd, UK.) was used as the reagent gas for the NICI analysis.

296 Quantification of all target compounds was based upon the ratios of analyte response peak area to
297 that of an appropriate deuterated internal standard. Standards of perdeuterated and native PAH (all
298 compounds) and NPAH compounds (>98% purity in toluene or isooctane) (1-nitronaphthalene-d7;
299 3-nitrofluoranthene-d9; 1-nitropyrene-d9 and 6-nitrochrysene-d11) and p-terphenyl-d14 recovery
300 standard (>99% purity, in toluene) were obtained from Greyhound Chromatography, Merseyside,
301 UK, as pre-prepared solutions by Chiron AS, Trondheim, Norway. Perdeuterated (9-fluorenone-d8
302 and anthraquinone-d8) and native OPAH internal standards and 1-fluoro-7-nitrofluorene recovery
303 standard (purity >98%) were obtained initially as solids from Sigma-Aldrich Company Ltd.,
304 Gillingham, UK and solutions prepared by dilution with hexane.

305

306 PAHs of the PdPT samples were analyzed by UPLC/UV-Fluorescence (Thermo Scientific, Dionex
307 Ultimate 3000) using a C18 UPLC column (Zorbax Eclipse PAH, 2.1 mm x 150 mm x 1.8 µm. 23
308 PAHs were quantified using external standard solution calibration. recovery control. Before
309 extraction a known amount of 6-methylchrysene was added to the samples and used as standard
310 extraction recovery control (Table S2). NPAHs and OPAHs were analyzed by GC/NICI-MS
311 (Agilent 7890A GC coupled to 5975C MS, methane as reagent gas) (Albinet et al., 2006, 2014)
312 using an Optima-5MS Accent column (30 m x 250 µm x 0.25 µm) and operated in SIM mode.
313 Quantification of OPAHs and NPAHs was performed by internal standard calibration using native
314 standards and deuterated surrogate compounds added before extraction (Table S3 and S4). 9-
315 Fluorenone-d9 and 1-nitropyrene-d9 were used as surrogate standards.

316

317 Quality assurance experiments were performed to assess the accuracy, precision and reproducibility
318 of the extraction, clean-up and analysis methods. Replicate analysis of Standard Reference Material
319 1649b (urban dust), provided by the National Institute of Standards and Technology (NIST), was
320 conducted using the procedures outlined above. The mean concentrations of 6 (INERIS, PdPT) and
321 10 (University of Birmingham, QT and EROS) SRM samples were in good agreement with

322 reference concentrations provided by NIST for PAHs and those reported in the literature for NPAHs
323 and OPAHs (Albinet et al., 2014 and references therein). Field blank filters and PUFs (n=1 for each
324 phase, at each site) were collected in order to evaluate any contamination during the sampling and
325 analytical procedures. Compounds showing field blank sample concentrations higher than 30% of
326 mean tunnel sample concentrations were excluded. All results presented here were corrected for
327 field blank concentration values.

328

329 **3. RESULTS AND DISCUSSION**

330 **3.1 Concentrations of PAHs, OPAHs and NPAHs**

331 Mean concentrations of the same PAHs, OPAHs and NPAHs measured in the QT and PdPT and the
332 proportion of each compound present in the particle-phase for QT, are presented in Table 1.

333 Concentrations of additional NPAHs and OPAHs analysed in PdPT samples are presented in Table
334 S5. Compounds below quantification limit are not reported in the table.

335

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

343

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

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

354
355 1 and 2NNap isomers were the most abundant NPAHs compounds measured, predominantly
356 present in the gas-phase (QT). The observed ratio of 1NNap/2NNap was ~1.8. This ratio is slightly
357 higher than previously observed in the same tunnel by Dimashki et al. (2000). 1NPyr and 9NAnt
358 were the dominant particle-phase NPAHs measured in both tunnels. These compounds have been
359 identified as the two principal NPAHs present in diesel emissions (Campbell and Lee, 1984;
360 Paputa-Peck et al., 1983; Ratcliff et al., 2010; Schuetzle et al., 1982; Zhu et al., 2003; Zielinska et
361 al., 2004b).

362
363 2NPyr and 2NFlt are found in relatively low levels in the tunnels. These compounds are generally
364 not observed in vehicular emissions and are the principal products of gas-phase (OH and/or NO₃
365 initiated) reactions of Pyr and Flth respectively (Atkinson and Arey, 1994). The low concentration
366 of these compounds in the tunnel is in agreement with previous measurements by Dimashki et al.
367 (2000) and is consistent with the absence of direct sunlight and low oxidant concentrations resulting
368 in negligible photochemical reactivity in the tunnels.

369 370 **3.2 Comparison with Previous Tunnel Studies**

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

373

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

382
383 The concentration of semi-volatile (3-4 ring) PAHs is considerably lower in the present study than
384 reported in previous studies. Semi-volatile PAHs Acy, Ace, Flo, Phe, Ant, Flt and Pyr have been
385 observed in relatively high concentrations in diesel emissions (Ratcliff et al., 2010; Rogge et al.,
386 1993a; Schauer et al., 1999; Zhu et al., 2003; Zielinska et al., 2004b). The estimated proportions of
387 diesel heavy duty vehicles (HDVs) in the relevant studies were <3% (present study); 9% (Benner et
388 al., 1989); 8-24% (Wingfors et al., 2001); and 47% (Ho et al., 2009). The low relative contribution
389 of diesel HDVs may therefore be a contributing factor to the reported concentrations of LMW
390 PAHs in these tunnel studies.

391
392 The PAH concentrations measured in the QT were linearly regressed against corresponding road
393 tunnel emission factors derived by Wingfors et al. (2001) and Ho et al. (2009). A very good
394 correlation ($R^2 > 0.9$) was observed between measured concentrations in this study and the emission
395 factors calculated by Wingfors et al. (2001) for a road tunnel in Gothenberg, Sweden. This can
396 possibly be attributed to similarities in tunnel characteristics, sampling techniques, traffic fleet
397 composition (vehicle types and fuel compositions) and emission controls measures present in the
398 two locations.

399

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

404
405 Measured concentrations of OPAHs and NPAHs in road tunnels are relatively lacking in the
406 literature. Gorse et al. (1983) measured 1NPyr concentrations in the Allegheny Mountain Tunnel in
407 Pennsylvania, USA in 1981. The maximum reported concentration was ~3 times lower than the
408 mean concentrations measured in the present investigation (QT and PdPT). Benner (1988)
409 measured mean concentrations of ~0.3 ng/m³ for 1NPyr and 9NAnt in the Baltimore Harbour
410 Tunnel in 1985, in good agreement with the levels observed in the present study.

411
412
413 **3.3 Comparison of chemical profiles of both investigated tunnels**

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

416
417 OPAH chemical profiles were similar for both tunnels. Significant differences in the contribution of
418 specific substances were observed for PAHs and NPAHs. For instance, larger contributions of Pyr
419 and 1NPyr were observed for the PdPT while the contributions of heavier PAHs (BPy, IPy, Cor)
420 and 9NAnt were lower than in the QT. Differences observed could be explained by the national
421 traffic fleet differences between both tunnels with a significant higher proportion of diesel vehicles
422 in France (PdPT, up to 80%) and, conversely, a larger proportion of gasoline cars in U.K. (QT,
423 about 66%). Pyr (Ratcliff et al., 2010; Zhu et al., 2003) and especially 1NPyr (Paputa-Peck et al.,
424 1983; Hayakawa et al., 1994; Zielinska et al., 2004a,b; Schulte et al., 2015), are compounds mainly
425 associated with diesel emissions while heavier PAHs are described in the literature as compounds

426 mainly emitted by gasoline engines (Li and Kamens, 1993; Miguel et al., 1998; Rogge et al.,
427 1993a).

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

434
435
436 **3.4 Gas-Particle Phase Partitioning of PAH, OPAH and NPAH**

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

439
440 For most LMW 3-ring compounds and HMW 5+ ring compounds, the proportion of compounds in
441 the particle phase in the QT is similar to that observed at background site EROS. However, semi-
442 volatile compounds (e.g. Pyr, Flt, Ret, 9F, AQ, MAQ, 2NFlo) display markedly higher proportions
443 in the particle phase in the tunnel than in the ambient atmosphere. The phase partitioning behaviour
444 of PAH, OPAH and NPAH as a function of compound MW is therefore markedly different for the
445 tunnel and ambient samples (Figure 2) with greater proportions of each compound class present in
446 the particulate phase.

447
448 Higher particulate phase contributions may reflect the more dominant role of direct emissions from
449 vehicles in the tunnel, which may be associated to a greater extent with fine particles (Albinet et al.,
450 2008b). Zielinska et al. (2004a) suggest that Flt and Pyr emissions were predominantly in the gas-
451 phase when vehicles were idle or at low engine loads but at higher vehicle load, a much larger
452 proportion of these compounds were present in the particulate phase, particularly for diesel

453 vehicles. This could indicate vehicles in the tunnel were operating under relatively higher load, thus
454 contributing to higher particulate concentrations of these compounds. However, lower daytime
455 temperatures and higher particulate matter concentrations in the tunnel favour partitioning into the
456 condensed phase (Yamasaki et al., 1982) and this is a more likely explanation.

457
458 Retene (Ret) is not commonly associated with road traffic (Wingfors et al., 2001) and is typically a
459 marker for wood combustion (Ramdahl, 1983) and recently described as highly emitted during coal
460 combustion (Shen et al., 2012a). The lower Ret concentrations observed in the QT relative EROS
461 suggest non-traffic sources dominate and transportation of Ret from the ambient atmosphere outside
462 the tunnel may be responsible for observed tunnel concentrations. The higher proportion of Ret in
463 the particulate phase in the tunnel relative to EROS is therefore unlikely to be source-driven. This
464 observation supports the argument that temperature and particle loading are the dominant factors, as
465 suggested above.

466 467 **3.5 Comparison of QT and Ambient Concentrations**

468 It is assumed that concentrations of PAHs, OPAHs and NPAHs measured in the tunnel result
469 entirely from on-road vehicular emissions (including exhaust and non-exhaust emissions).

470 Comparing levels of compounds measured in the QT with those observed at the background site
471 EROS (tunnel/ambient ratios) will allow the assessment of other influencing factors (e.g. non-traffic
472 sources, relative rates of atmospheric loss processes) to their overall and relative concentrations in
473 the urban atmosphere. The tunnel/ambient ratios measured in the present study are shown in Figure
474 3. It can be seen that these ratios vary considerably for different individual compounds.

475
476
477 Mean total PAH concentration was ~4.5 times higher in the tunnel than the mean concentration at
478 EROS. Similarly, Kim et al. (2012) noted that PAH concentrations were ~6 and 10 times higher in
479 the Bukak Tunnel in Seoul, South Korea, than were measured at an ambient roadside location
480 during spring and winter respectively. Wingfors et al. (2001) also noted total PAH concentrations in

481 the Ludby Tunnel in Gothenburg, Sweden were an order of magnitude higher than those measured
482 in heavily trafficked urban areas. These observations are generally consistent with the lower rate of
483 dispersion and lower chemical reactivity in the tunnel environment compared with the ambient
484 atmosphere.

485
486 The considerable variability in tunnel/ambient ratios between different PAHs, can be attributed to
487 differences in traffic source contribution at the ambient site, physiochemical properties, and/or
488 relative reactivity rates of individual PAH compounds. The only PAH compound to exhibit a
489 tunnel/ambient ratio of <1 was Ret. This is consistent with this compound resulting primarily from
490 wood or coal combustion used for residential heating in this period rather than road traffic (Shen et
491 al., 2012a; Bari et al., 2010; Fine et al., 2002; McDonald et al., 2000; Ramdahl, 1983).

492
493 LMW (3-4 ring) compounds Flo, Phe, Ant, Flth, Pyr display relatively low (3 to 4.5) tunnel/ambient
494 ratios. Given that these compounds, are expected to be relatively abundant in traffic emissions this
495 observation is somewhat surprising. For example, Phe, Flt and Pyr are the dominant PAHs in diesel
496 exhaust (Ratcliff et al., 2010; Zhu et al., 2003 and PdPT results) and therefore may be expected to
497 display enhanced ratios. This observation suggests non-traffic sources (e.g. domestic wood and coal
498 combustion or revolatilisation of pollutants from road and or soil/vegetation surfaces) may
499 contribute significantly at the ambient site, resulting in relatively low tunnel/ambient ratios.

500
501 It has been previously been indicated that PAH concentrations measured in the U.K. atmosphere
502 can be influenced by the secondary input due to volatilisation from soil, vegetation and/or road
503 surfaces (Dimashki et al., 2001; Harrad and Laurie, 2005; Lee and Jones, 1999). For example, Lee
504 and Jones (1999) noted a significant positive correlation between the concentration of Phe, Flt and
505 Pyr and temperature in a semi rural site in northern England, indicating the possibility of
506 temperature-driven evaporation from vegetation and/or soils influencing concentrations.

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

513
514 Interestingly, the tunnel/ambient ratio of Flt is higher than that of Pyr, despite higher OH reactivity
515 noted for Pyr relative to Flt (Atkinson et al., 1990; Brubaker and Hites, 1998). This may suggest Pyr
516 concentrations at EROS may be ‘buffered’ by volatilisation from soil or vegetation surfaces to a
517 much greater degree than Flt resulting in lower tunnel/ambient ratio.

518
519 The tunnel/ambient ratio of Acy is considerably higher than those of other PAHs. This is consistent
520 with relatively high gas-phase OH reactivity of this compound (Brubaker and Hites, 1998; Reisen
521 and Arey, 2002). The lack of direct sunlight inside the tunnel is likely to result in minimal
522 reactivity, leading to enhanced ratios. However, while Ant is shown to display similarly fast
523 reactivity towards OH (Brubaker and Hites, 1998), the observed tunnel/ambient ratio is lower than
524 expected. This may suggest the ambient concentration of Ant is substantially influenced by non-
525 traffic sources, either primary or non-combustion related.

526
527 Most HMW PAHs (MW>228) display relatively high tunnel/ambient ratios compared with LMW
528 PAHs. BaA and Chr display particularly high ratios compared with other PAHs, which may reflect
529 a relatively low contribution of non-traffic sources of these compounds at the ambient sites, and/or
530 low atmospheric reactivity.

531
532 The relative differences in tunnel/ambient ratios between HMW PAHs may arise in part from the
533 relative stability of these compounds towards atmospheric degradation. For example, BaP displays a

534 relatively high tunnel/ambient ratio compared with other 5 ring PAH compounds. This may be
535 attributed to greater susceptibility of BaP to heterogeneous reactivity in the ambient atmosphere
536 (Jariyasopit et al., 2014a; Ringuet et al., 2012b; Cazaunau et al., 2010; Perraudin et al., 2007).

537
538 DBA displays a relatively low tunnel/ambient ratio. This is consistent with a relatively low input
539 from road traffic, as indicated by Jang et al. (2013) who assessed a ‘traffic’ profile at London
540 monitoring sites, and may indicate an alternative seasonally-dependent combustion source
541 influencing the ambient sites.

542
543 The low (<1) ratios observed for BaAQ indicate that this compound is not emitted to a significant
544 degree by road vehicles and is present in higher levels in the ambient atmosphere. This suggests
545 levels of this compound observed at EROS result primarily from a non-traffic combustion source
546 such as natural gas home appliances (Rogge et al., 1993b), wood or coal combustion (Shen et al.,
547 2013) or uncontrolled domestic waste combustion (Sidhu et al., 2005).

548
549 NPAHs generally display higher tunnel/ambient ratios than unsubstituted PAHs, although there is
550 wide variability between individual compounds. Relatively high ratios were observed for 1NNap,
551 2NNap, 2NFlo, 9NAnt, 3NFIt, 1NPyr and 6NChy. These compounds are expected to be
552 predominantly associated with diesel exhaust emissions (Ball and Young, 1992; Campbell and Lee,
553 1984; IARC, 2013; Paputa-Peck et al., 1983; Rappaport et al., 1982; Schuetzle et al., 1982;
554 Schuetzle and Perez, 1983; Zhu et al., 2003; Zielinska et al., 2004a,b with lower input from other
555 combustion sources (WHO, 2000).

556
557 The principal atmospheric loss process for NPAHs is expected to be photoreactivity including direct
558 photolysis (Atkinson et al., 1989; Fan et al., 1995; 1996a,b; Phousongphouang and Arey, 2003;
559 Ringuet et al., 2012b; Jariyasopit et al., 2014a). For example, Atkinson et al. (1989) noted

560 atmospheric lifetimes for 1NNap and 2NNap due to photolysis were ~38 and ~28 times shorter
561 respectively than the corresponding gas-phase reactions with OH.

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

567
568 While Holloway et al. (1987) noted relatively long photolysis half lives for 1NPyr and 3NFlt of 1.2
569 to 6 days and 12.5 to >20 days respectively, other studies suggest this process can be a potentially
570 significant atmospheric sink for particle-bound NPAHs. Fan et al. (1996a) derived half-lives due to
571 photolytic decay for 1NPyr, 2NFlt and 2NPyr on diesel soot and wood smoke in an outdoor
572 chamber of 0.8 to 1.2 hr with faster reaction noted for 1NPyr on wood smoke particles.

573
574 The results of the present study suggest 1NPyr is degraded more rapidly than other NPAHs. While
575 Fan et al. (1996a) indicated the structure of particle-associated NPAH compounds does not
576 influence the rate of degradation, it has been suggested elsewhere that the isomeric structure of the
577 compound does influence the rate of photolytic decay (Pitts, 1983). For example, Holloway et al.
578 (1987) and Feilberg and Nielsen (2000) have indicated 1NPyr decays up to 10 times more rapidly
579 than other MW 247 NPAHs.

580
581 Dimashki et al. (2000) observed levels of 1NPyr and 9NAnt in the tunnel ~6 and ~2 times higher in
582 the Queensway Road Tunnel than in the ambient urban atmosphere of Birmingham respectively.
583 This previous study was conducted in central Birmingham during winter. The QT/EROS ratio in the
584 present study is shown to be a factor ~10 and ~4.5 higher than the previous study for 1NPyr and
585 9NAnt respectively. This may partly be attributed to higher input of pollutants in the city centre

586 compared to the background EROS site and the fact that sampling in the present study was
587 conducted in the late summer leading to potentially faster rates of photolytic degradation in the
588 ambient atmosphere.

589
590 The tunnel/ambient ratio of 1NNap is a factor ~2.2 higher than that of 2NNap. Experimental studies
591 indicate 1NNap will exhibit a rate of photolysis ~1.3 – 8 times higher than that of 2NNap (Atkinson
592 et al., 1989; Phouongphouang and Arey, 2003). This would suggest the observed difference in
593 ratios for the two NNap isomers is due to differences in the rates of photolytic degradation and the
594 relatively long exposure time of air samples collected at EROS.

595
596 The relatively low ratios observed for 7NBaA indicate only a minor contribution from traffic for
597 this compound at the ambient site. 7NBaA has been measured in vehicular emissions (Karavalakis
598 et al., 2009; Zhu et al., 2003). However, the previous study in Birmingham did not detect this
599 compound in the QT but did observe measureable levels in the city centre (Dimashki et al., 2000).

600
601 2NFlt and 2NPyr are expected to result from atmospheric reactions with minor input from road
602 traffic (Atkinson and Arey, 1994). A tunnel/ambient ratio of <1 was observed for 2NFlt, consistent
603 with little formation in the tunnel. However, 2NPyr displays a ratio of ~5 which is unexpected.

604 605 **3.6 Temporal Trend in PAH and NPAH in QT Concentrations**

606 Previous measurements of PAH (Smith and Harrison, 1996) and NPAH (Dimashki et al., 2000)
607 concentrations have been made in the Queensway Road Tunnel. A comparison between the results
608 of the present study and these previous investigations could therefore provide an assessment of
609 temporal changes in emission profiles. Some caution is needed in interpreting these changes as
610 both sets of data derive from relatively short periods of measurement and hence week-to-week

611 variability cannot be assessed. Concentrations of OPAHs have not previously been measured in the
612 tunnel.

613

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

621

622 A number of factors have been shown to be responsible for reduction of PAHs from road vehicles.
623 These include changes to fuel formulations (Westerholm and Egeback, 1994) e.g. use of biofuels
624 (Ratcliff et al., 2010) or use of additives to enhance the cetane or octane number (Williams et al.,
625 1986; Zhu et al., 2003); innovations in engine design e.g. use of three-way catalysts (Rogge et al.,
626 1993a; Schauer et al., 2002; Westerholm and Egeback, 1994; Zielinska et al., 2004b) and
627 improvement in exhaust emission control measures e.g. particulate filters (Hu et al., 2013), with
628 their implementation being principally driven by increasingly strict government legislation (Perrone
629 et al., 2014). Other factors e.g. state of vehicle maintenance and ambient conditions (e.g.
630 temperature) are also shown to influence PAH emissions from road traffic (Zielinska et al., 2004b).

631

632 The observed reduction of PAH levels in the QT can be attributed, to a large degree, to the
633 introduction of mandatory catalytic converters to the U.K in 1993. Catalytic converters have been
634 shown to reduce the emissions of PAHs in gasoline-fuelled vehicles by 92-99% (Rogge et al.,
635 1993a; Schauer et al., 2002; Westerholm and Egeback, 1994; Zielinska et al., 2004b). For example,
636 Benner et al. (1989) measured PAH concentrations in the Baltimore Harbour Tunnel, USA, a factor

637 5-10 lower than a study conducted 10 years earlier (Fox and Stanley, 1976). This was attributed to
638 the introduction of catalytic converters which were first used in the USA in 1974.

639
640 However, progressively stringent legislation pertaining to vehicular emissions of both gasoline and
641 diesel vehicles is also likely to have contributed to PAH emission reductions. It is indicated that
642 different stages of EU legislation on new vehicle emission limits (91/441/EEC) has resulted in
643 progressively reduced PAH emissions since 1993 (Perrone et al., 2014).

644
645 The relative concentration of individual PAHs has changed significantly over this period. Indeed,
646 the combined contribution of (Phe + Flt + Pyr) to Σ PAH burden has increased from ~44% in 1992
647 to ~72% in 2012. Gasoline-fuelled vehicles are shown to emit higher levels of HMW compounds
648 e.g. BaP, IPy, BPy, Cor (Marr et al., 1999; Miguel and Pereira, 1989; Miguel et al., 1998) while
649 diesel is generally shown to be a greater source of semi-volatile compounds such as Phe, Flt, and
650 Pyr (Chen et al., 2013; Harrison et al., 1996; Miguel et al., 1998). This observation could therefore
651 suggest a greater contribution of diesel emissions over the previous 20 years in the tunnel.

652
653 In the period 1994 to 2012, the number of gasoline-fuelled cars in the U.K decreased by ~500,000
654 while the number of diesel-fuelled passenger cars increased by ~7.8 million (DfT, 2014). This trend
655 has seen the relative proportion of diesel cars in the U.K traffic fleet increase from ~7% in 1994 to
656 ~33% in 2012 (see Figure S3).

657
658 The trend in the number of gasoline and diesel vehicles on the road is reflected in the volume of
659 gasoline and diesel fuel supplied to the U.K market (see Figure S4) and national fuel sales. In the
660 UK, sales of gasoline fuel decreased by ~43% between 1990 and 2011, from 33 billion litres to 19
661 billion litres. Meanwhile the sales of diesel fuel more than doubled over this period, from ~12
662 billion litres in 1992 to ~25 billion litres in 2011 (UKPIA, 2012).

663
664 A comparison in concentrations of four NPAHs measured in the present study in 2012 and those
665 measured by Dimashki et al. (2000) in 1996 is shown in Table 4. The previous measurements were
666 made on only one sampling day, while the current study is the average of four separate sampling
667 days so comparison of results must be done with caution.

668
669 In contrast to the significant historical decline noted for PAH concentrations, little or no decline in
670 NPAH concentration is noted. The mean levels of NNap isomers measured in the present study fall
671 within the range of concentrations measured in 1996 while the concentrations of 9NAnt and 1NPyr
672 were within 1 standard deviation of the the lower range of concentrations measured in 1996.

673
674 1NNap, 2NNap, 9NAnt and 1NPyr are all present in diesel exhaust emissions in relatively high
675 levels (Campbell and Lee, 1984; Draper, 1986; Paputa-Peck et al., 1983; Zhu et al., 2003) and are
676 present in low/negligible emissions from gasoline vehicles (Zielinska et al., 2004b). The increase in
677 relative contribution of diesel vehicles in the U.K traffic fleet from 1996 to 2012 may therefore
678 have a stronger influence on changes in observed NPAH concentrations relative to PAHs.

679
680 Evidence for the increased importance of NPAH in urban air over time has been indicated
681 previously. For example, Matsumoto et al. (1998) noted the concentration of BaP declined
682 significantly in the period 1975 to 1992 in the heavily trafficked region of Sapporo, Japan, while the
683 mutagenicity of collected particles remained unchanged. The authors suggested this could be
684 attributed to an increase in diesel traffic and the possible associated increase in NPAH
685 concentrations.

686
687 The lack of increase in observed NPAH levels in the tunnel over this time may suggest that while
688 the volume of diesel traffic has increased, the emissions of NPAHs from individual diesel vehicles
689 may have declined. Indeed, improved exhaust after-treatment (e.g. use of catalytic devices or

690 particulate traps) and fuel formulation has been shown to reduce NPAH and OPAH emissions
691 (Fiedler and Mücke, 1991; Marinov et al., 2009; Nielsen et al., 1999; Ratcliff et al., 2010;
692 Westerholm and Egeback, 1994; Zhu et al., 2003).

693

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

701

702

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1224 **TABLE LEGENDS**

1225 **Table 1.** Mean±standard deviation of PAH, OPAH and NPAH concentrations measured in the
1226 Queensway Road Tunnel (n=4), Parc des Princes Tunnel (n=9) and at EROS (n=4).

1227
1228 **Table 2.** Comparison of total (P+V) PAH concentrations and percentage of concentration in the
1229 particulate phase (%P) in different road tunnel measurements.

1230
1231 **Table 3.** Comparison of mean total (particulate + vapour) PAH concentrations measured in the
1232 Queensway Road Tunnel in 1992 (Smith and Harrison, 1996) and 2012 (present
1233 study).

1234
1235 **Table 4.** Comparison of total (particulate + vapour) NPAH concentrations measured in the
1236 Queensway Tunnel in 1996 (Dimashki et al., 2000) and 2012 (present study).

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1239 **FIGURE LEGENDS**

1240

1241 **Figure 1.** Comparison of particulate phase PAH, OPAH and NPAH chemical profiles obtained
1242 for both investigated tunnel environments (Parc des Princes and Queenway road
1243 tunnels; n=9 and 4, respectively).

1244
1245 **Figure 2.** Plots of % of component in the particulate phase vs. molecular weigh for a) PAHs, b)
1246 OPAHs and c) NPAHs, measured in the tunnel (black dots, solid black line) and at
1247 EROS (white dots, dotted line).

1248
1249 **Figure 3.** Mean ratios of concentrations measured in the Queensway Road Tunnel to those
1250 measured simultaneously at the Elms Road background (n=4).

1251
1252

1253 **Table 1.** Mean±standard deviation of PAH, OPAH and NPAH concentrations measured in the
 1254 Queensway Road Tunnel (n=4), Parc des Princes Tunnel (n=9) and at EROS (n=4).

1255

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

1256 a – Gaseous + particulate phases, n=4

1257 b – Only particulate phase, n=9

1258 c - Gaseous + particulate phases, n=4

1259 d – below quantification limit

1260 e – 2+3-Nitrofluoranthene concentrations

1261 nm - not measured

1262 **Table 2.** Comparison of total (P+V) PAH concentrations and percentage of concentration in the
 1263 particulate phase (%P) in different road tunnel measurements.

	This study ^a		Ho <i>et al.</i> (2009) ^b		Benner <i>et al.</i> (1989) ^c		Wingfors <i>et al.</i> (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	n	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

1264

1265 a – Queensway Road Tunnel, Birmingham; Sept 2012; estimated 25 000 vehicles per day
 1266 b – Shing Mun Tunnel, Hong Kong; Weekday noon samples; summer 2003; 53 000 vehicles per day
 1267 c – Baltimore Harbor Tunnel, USA; 1985-86; mechanical ventilation; traffic flow unknown
 1268 d – Ludby Road Tunnel in Gothenberg, Sweden; April 2000; 20 000 vehicles per day
 1269 nm – not measured

1270

1271 **Table 3.** Comparison of mean total (particulate + vapour) PAH concentrations measured in the
 1272 Queensway Road Tunnel in 1992 (Smith and Harrison, 1996) and 2012 (present study).

1273

	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
ΣPAH	1122	158	86

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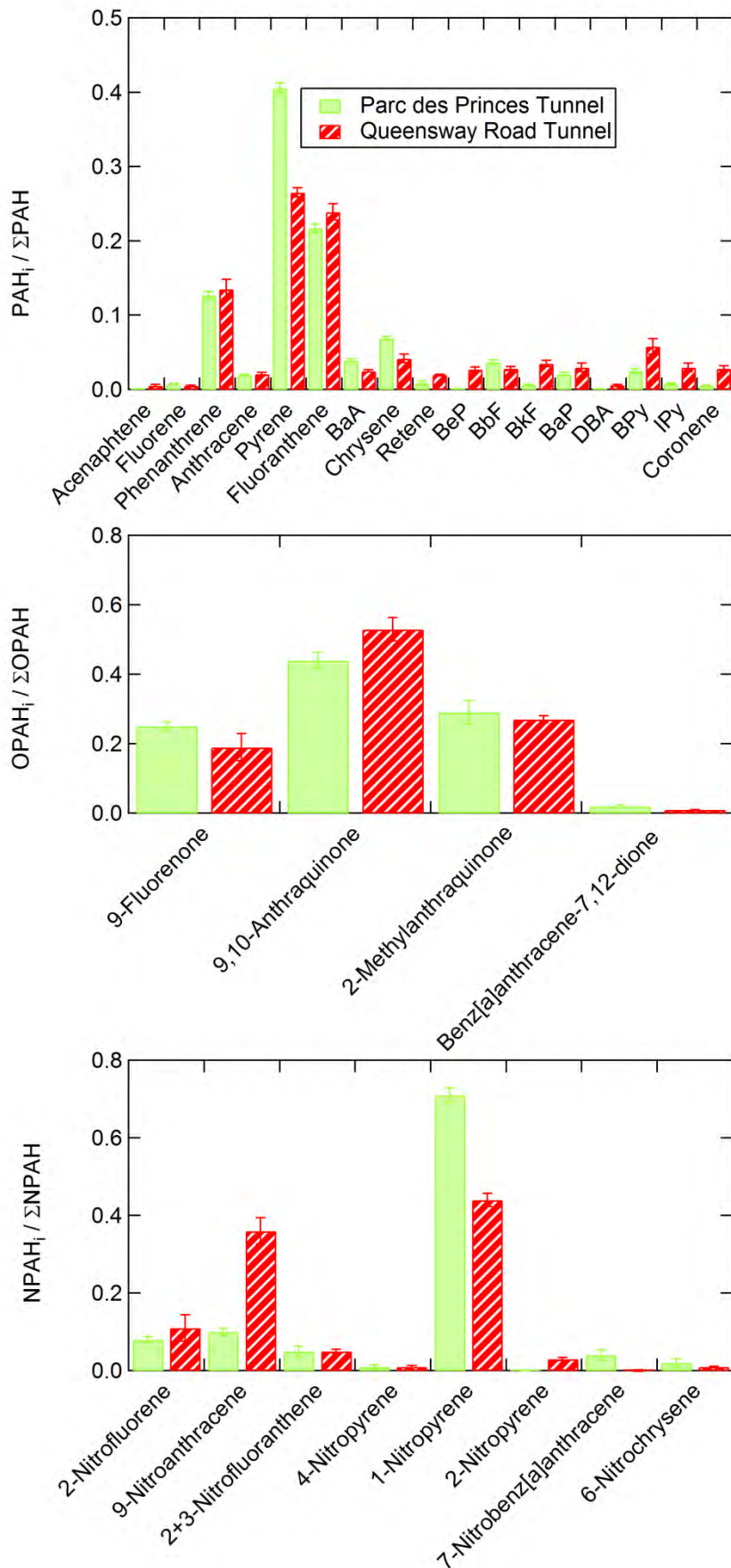
1276 **Table 4.** Comparison of total (particulate + vapour) NPAH concentrations measured in the
1277 Queensway Road Tunnel in 1996 (Dimashki et al., 2000) and 2012 (present study).

1278

	Tunnel concentration (pg m⁻³)	
	2012 (This Study)	1996 (Dimashki <i>et al.</i>, 2000)
1NNap	1918±461	560-2120
2NNap	980±820	620-1570
9NAnt	294±165	370-760
1NPyr	343±157	440-690

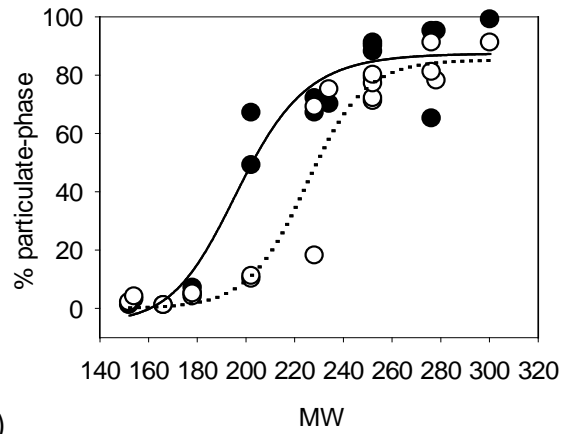
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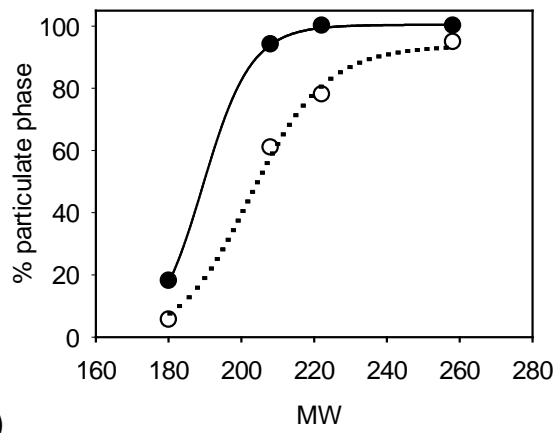
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1282 **Figure 1.** Comparison of particulate phase PAH, OPAH and NPAH chemical profiles obtained for
 1283 both investigated tunnel environments (Parc des Princes and Queenway road tunnels; n=9 and 4,
 1284 respectively).



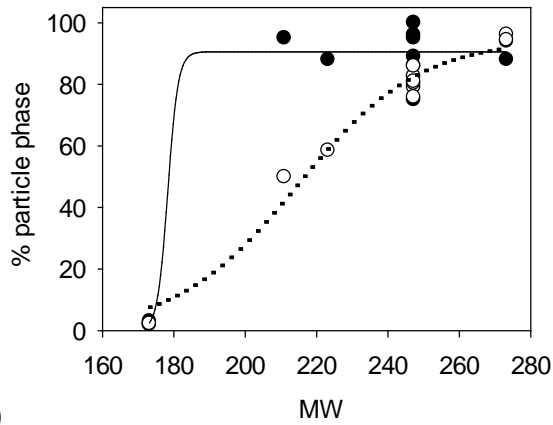
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a)



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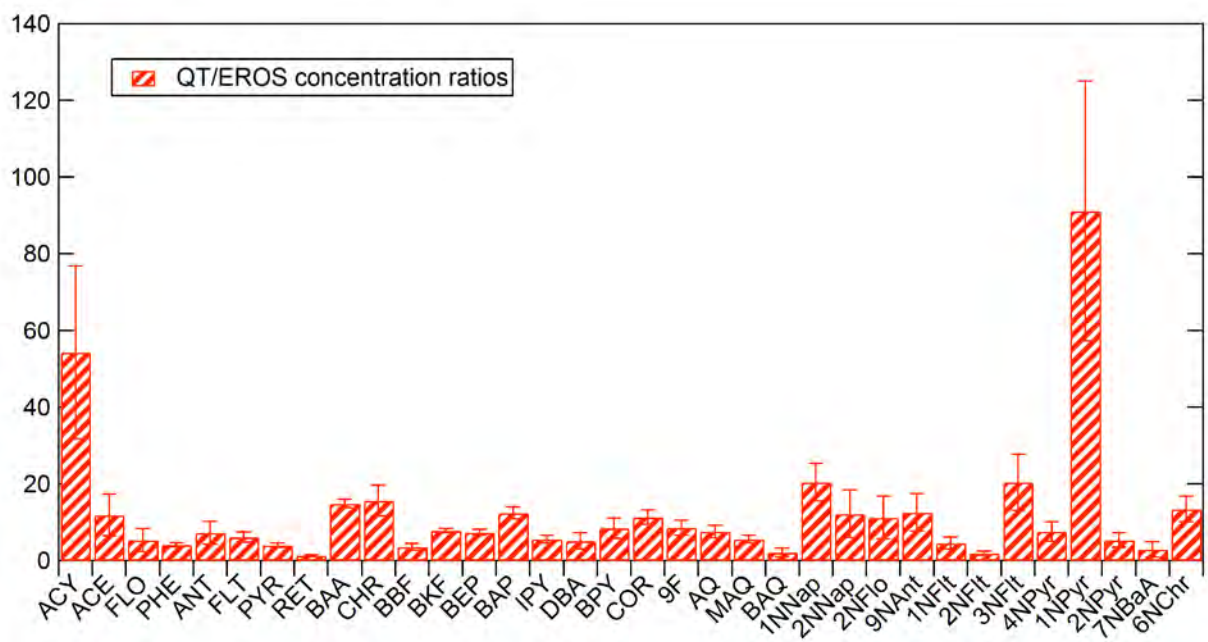
b)



1287

c)

1288 **Figure 2.** Plots of % of component in the particulate phase vs. molecular weigh for a) PAHs, b)
 1289 OPAHs and c) NPAHs, measured in the tunnel (black dots, solid black line) and at EROS (white
 1290 dots, dotted line).



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1292 **Figure 3.** Mean ratios of concentrations measured in the Queensway Road Tunnel to those
 1293 measured simultaneously at the Elms Road background (n=4).

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