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Pant, Pallavi; Shi, Zongbo; Pope, Francis D.; Harrison, Roy M.

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Characterization of Traffic-Related Particulate Matter Emissions in a Road Tunnel in Birmingham, UK: Trace Metals and Organic Molecular Markers

Pallavi Pant[‡], Zongbo Shi, Francis D. Pope, Roy M. Harrison^{*†}

Division of Environmental Health and Risk Management, School of Geography, Earth and Environmental Sciences, University of Birmingham, Edgbaston, Birmingham, B15 2TT, United Kingdom

ABSTRACT

Road traffic is one of the key sources of particulate matter (PM) in urban areas, and an understanding of the chemical composition of traffic emissions is important for source apportionment analysis. In this study, PM samples were collected simultaneously in a road tunnel and at a background site in Birmingham (UK) and analysed for a suite of elemental and organic species (hopanes, alkanes and PAH) with an aim to characterize the vehicular emissions in a tunnel environment and to prepare a composite mixed fleet profile for PM_{2.5} traffic emissions. Large enrichment was observed for many organic and elemental species in the case of the tunnel samples with respect to the background site. The tunnel samples show a large enrichment of trace elements relative to the urban background with a mode at ca. 3 μm in the mass size distribution, indicative of emissions resulting from resuspension/abrasion sources. Cu, Ba and Sb were found to have the characteristic non-exhaust (brake wear) emission peaks in the coarse size range in the tunnel. A composite PM_{2.5} traffic profile was prepared using the data from the two sites, and was compared against previously reported profiles. The profile was also compared against other traffic profiles from Europe and USA, and was found to be very similar to the previously-reported PM_{2.5} composite traffic profile from the UK. However, the uncertainties associated with the species were found to be much lower in the case of the tunnel profile from this study, and we conclude that this profile would be very suitable for use in Chemical Mass Balance Model analyses for the UK and other countries with a similar road traffic fleet mix.

Keywords: Molecular markers; Source profile; Europe; Traffic; Road tunnel.

INTRODUCTION

Road transport constitutes an important source of particulate matter (PM) emissions in urban areas, and motor vehicles are an important source of carbonaceous aerosols particularly for the particles in the fine size range (aerodynamic diameter < 2.5 μm) (Kam *et al.*, 2012; Keuken *et al.*, 2012). Average PM_{2.5} concentrations in the UK range between 12–15 μg m⁻³ (Harrison *et al.*, 2012a) and primary road traffic emissions contribute nearly 30% of the total PM_{2.5} and contribute 30–50% of the urban and

roadside increments of PM (AQEG, 2012). Health risk (in terms of toxicity) associated with air pollutants has been linked to concentrations of transition metals and polycyclic aromatic hydrocarbons (PAHs), both of which are present in high concentrations in traffic emissions (Ayres *et al.*, 2008). PM and diesel engine emissions have been classified as carcinogens by the International Agency for Research on Cancer (IARC), and several recent studies have linked vehicular emissions to adverse health effects (de Kok *et al.*, 2006; HEI, 2010; Godri *et al.*, 2011; Slezakova *et al.*, 2013).

Only a few studies have focused on the characterization of PM emissions from road traffic in the UK. Between the late 1990s and early 2000s, several papers reported concentrations of PAHs in the near-road environment (Smith and Harrison, 1996; Harrison *et al.*, 2003) and there are a very limited number of studies focusing on analysis of molecular markers in high traffic environments in the UK (Harrad *et al.*, 2003; Yin *et al.*, 2010). Recent research literature has focused on sources such as wood burning and secondary PM (Harrison *et al.*, 2012b; Fuller *et al.*, 2014; Charron *et al.*, 2013) apart from Lawrence *et al.* (2013) who reported chemical composition of PM₁₀ in a road tunnel in Hatfield (UK). The only receptor modelling study from the UK highlighted the need for generation of local representative source profiles

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

[‡] Now at Department of Environmental Health Sciences, School of Public Health and Health Sciences, University of Massachusetts, Amherst, MA 01003, USA

* Corresponding author.

Tel.: +44 121 414 3494; Fax: +44 121 414 3708
E-mail address: r.m.harrison@bham.ac.uk

to overcome the uncertainty introduced by profiles from North America (Yin *et al.*, 2010). AQEG (2012) also recommended detailed analysis of exhaust emissions in order to improve the understanding of emission characteristics and their potential contribution to ambient PM.

Traffic emissions can be characterized using a suite of methods including dynamometer emission studies in the laboratory and ambient measurements (details in Pant and Harrison, 2013; Giechaskiel *et al.*, 2014). Source profiles prepared using ambient data offer the advantage of being representative of the on-road fleet, and they reflect emissions in the real-world conditions better than laboratory-derived profiles. However, factors such as variations in speed and fleet characteristics (i.e., proportion of heavy duty vehicles (HDVs) and light duty vehicles (LDVs)) can cause variability in the ambient measurements. Particulate emissions from vehicles vary based on fleet composition (engine and fuel type), age and maintenance of the vehicle and driving conditions. Tunnels are often used for analysis of emissions from road vehicles including estimation of emission factors and physical and chemical characterization of vehicular emissions (El-Fadel and Hashisho, 2000). Several studies have been conducted for measurement of PM emissions in roadway tunnels in different parts of the world including the USA (Fraser *et al.*, 1998; Abu-Allaban *et al.*, 2002), China (He *et al.*, 2008), Europe (Weingartner *et al.*, 1997; Handler *et al.*, 2008; El Haddad *et al.*, 2009; Lawrence *et al.*, 2013; Pio *et al.*, 2013), New Zealand (Ancelet *et al.*, 2011), Japan (Funasaka *et al.*, 1998), Brazil (Brito *et al.*, 2013) and Mexico (Mancilla and Mendoza, 2012).

However, a detailed chemical characterization of traffic-associated PM emissions in the UK has not been reported in the scientific literature so far. In addition, there are no representative road traffic source profiles with the exception of that from Pant *et al.* (2014) who reported a composite PM_{2.5} traffic profile based on the Lenschow approach. The

objectives of this study include characterization of PM_{2.5} emissions from road traffic in a typical road tunnel in the UK and preparation of a composite PM_{2.5} road traffic (exhaust) source profile.

MATERIALS AND METHODOLOGY

Sampling was conducted simultaneously at the A38 Queensway Tunnel (QT) and the Elms Road Observatory Site (EROS) in Birmingham, United Kingdom between September 11 and 21, 2012.

Sampling Sites

A38 Queensway Tunnel, Birmingham (QT)

This twin bore tunnel is 545 metres in length and is one of the major road tunnels in Birmingham, running in the North/South direction. It has two lanes on each side and a cross-sectional area of 25 m². Average vehicle speed in the tunnel is 50 kilometres hour⁻¹ and the modal split is presented in Fig. 1. An estimated 25000 vehicles travel through the tunnel each day (Azzi, 2012). The tunnel is ventilated naturally and the samplers were placed in the emergency layby area at a distance of 1.5 m from the road in the southbound lane. At the time of the sampling, the tunnel was closed at night for maintenance work in the northbound lane between 10 pm and 6 am. A significant effect is not anticipated since the traffic volume during these hours is very low. The site has been used for PM measurements previously (Birmili *et al.*, 2006).

The modal split at the site was found to be similar to the country average, which is cars and taxis (82.1%), buses and coaches (1.51%), light vehicles (12.09%), goods vehicles (3.23%) and motorcycles (1.10%) (DfT, 2013). The fuel split at the national level is nearly 70:30 for gasoline and diesel (DfT, 2013). Data on the fuel split was not available for the tunnel or the background site.

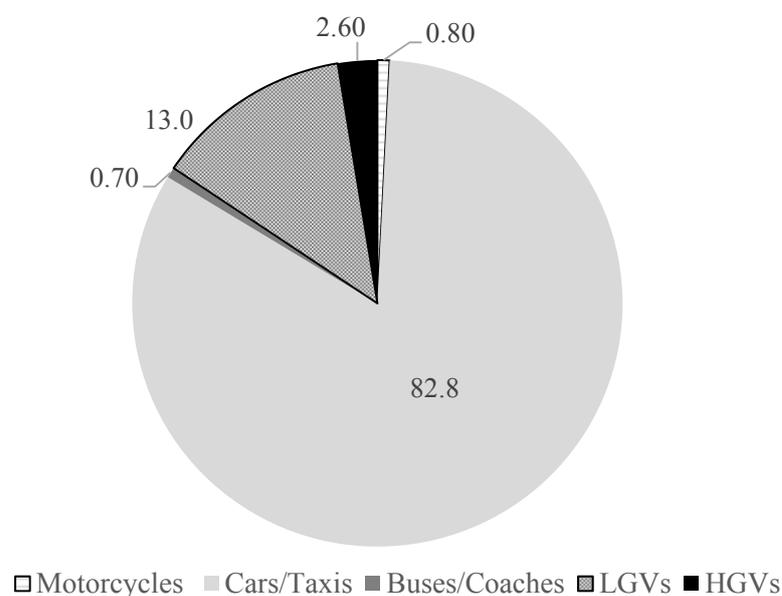


Fig. 1. Modal split at A38 Queensway Tunnel (%).

Elms Road Observatory Site (EROS)

This is an urban background site located in an open field within the University of Birmingham campus (52.45°N; 1.93°W). The site is about 3.5 km southwest of the centre of Birmingham. There are no significant PM sources in the vicinity, and the nearest anthropogenic sources are a nearby railway and some moderately trafficked roads. Occasionally, agricultural machinery is used in the open field. There is little residential accommodation within 300 m. The site has been used as an urban background site in a number of previous research studies (Yin *et al.*, 2010; Pant *et al.*, 2014).

Sampling

Integrated 24 hour PM_{2.5} (PM with aerodynamic diameter < 2.5 µm) samples were collected using high volume samplers (Digitel DHA-80) on pre-baked quartz filters (n = 12 at each site) while integrated 48-hour size-segregated PM samples were collected using a 8-stage rotating MOUDI (Model 100, MSP Corporation, Minneapolis, Minnesota, USA) using 47 mm PTFE and 37 mm quartz back-up filters (n = 4 at QT and n = 3 at EROS). Coarse and fine fractions of PM were also sampled using a dichotomous Partisol 2025 air sampler at flow rates of 15.0 and 1.7 L min⁻¹ respectively. Field blanks were collected for each sample type and processed using the same methods.

Average wind speed during the sampling period was 4.80 ± 1.23 m s⁻¹ with a predominant south, south-west direction.

Mass and Chemical Analysis

Gravimetric analysis was performed on the PTFE filter samples using an MC5 Sartorius microbalance. Before weighing, all filters were equilibrated in a humidity (35–45% RH) and temperature (25°C) controlled windowless room for 24 hours. An ionizing blower and an α-particle source (²¹⁰Po) were used to reduce the effects of static electricity.

Extraction of the trace metals from a segment of the Digitel filter was performed using reverse aqua regia solution using the procedure described by Allen *et al.* (2001). Briefly, each filter was extracted using 2 mL of 189 cm³ L⁻¹ Aristar Grade hydrochloric acid (HCl) and 66 cm³ L⁻¹ Aristar Grade nitric acid (HNO₃) per sample. The samples were heated followed by mild sonication and were diluted before analysis. Inductively Coupled Plasma Mass Spectrometry (ICP-MS, Agilent 7500ce with an Octopole Mass Spectrometer) was used to analyse the samples for Ti, V, Mn, Cu, Cr, Zn, Sb, Sn, Ba and Ca.

The MOUDI PTFE impaction substrates were first analysed using WD-XRF for Al, Si and Fe. The MOUDI samples were then extracted using HF and HNO₃ as described in Shi *et al.* (2011). To extract the total element fraction, the samples were placed in Teflon bombs and HF and HNO₃ were added (1:3) and the bombs were heated for 24 hours at 150°C. Subsequently, the HF was allowed to vaporise, 5 mL of 2M HNO₃ and 5 mL of DDW were added, and the bombs were heated for 24 hours at 150°C. The samples were then transferred into pre-cleaned and labelled LDPE tubes and stored at -4°C until analysis by ICP-MS for Fe, Mn, Sb, Ba, Cu, Zn, Cr, Pb and V.

For molecular marker analysis, the Digitel PM_{2.5} filter

samples were extracted using a standardized solvent extraction method and were corrected for blanks (Yin *et al.*, 2010). Briefly, each sample was spiked with 25 µL of the isotopically-labelled internal standard mixture including aaa-20R-cholestane-d4, dibenz(ah)anthracene-d14 and octacosane-d58 and extracted using 20 mL of dichloromethane (DCM) under mild sonication at 25°C using an ultrasonic bath. The extracts were then concentrated to 250 µL under a gentle stream of oxygen-free nitrogen. Chemical analysis was undertaken by direct injection of the sample into the GC-MS system and quantification was completed in SIM (selected ion monitoring) mode (Agilent GC- 6890N plus MSD-5973N fitted with a HP-5MS column). Hopanes analysed include 17α(H)-22,29,30-trisnorhopane (TNOHO), 17α(H)-21b(H)-30-norhopane (NHO), 17α(H)-21b(H)-hopane (HOP), C31αβS-hopane (SHHO), C31αβR-hopane (RHHO), C32αβS-hopane (SBHHO), C32αβR-hopane (RBHHO), 22S-trishomohopane (STHHO) and 22R-trishomohopane (RTHHO). Alkanes from C24-C35 were analysed and PAHs analysed include benzo(b)fluoranthene (BbF), benzo(k)fluoranthene (BkF), benzo(e)pyrene (BeP), benzo(a)pyrene (BaP), dibenzo(a,h)anthracene (DahA), perylene (Per), picene (Pic), indeno(1,2,3-cd)pyrene (IcdP), benzo(ghi)perylene (BghiPe) and coronene (Cor).

Organic carbon (OC) and elemental carbon (EC) were analysed using a Sunset Laboratory thermal/optical carbon analyser with quartz filter samples using the EUSAAR2 protocol (Cavalli *et al.*, 2010).

Additional detail is provided in the Supplementary Information.

Data Analysis

Data analysis was carried out using Microsoft Excel and SPSS (Version 21). Species with blank concentrations more than 10% were not included in the analysis (Cr was excluded). Species' correlation analysis was conducted using SPSS based on Pearson Correlation and the correlation values reported in the text are for p < 0.01 unless otherwise mentioned.

RESULTS

Mass Concentrations

Average 24-h PM_{2.5} (fine) and PM_{2.5-10} (coarse) concentrations based on Partisol sampler measurements were observed to be 56.1 and 46.9 µg m⁻³ at QT. The measurements from EROS for PM mass (Partisol samples) were unsuccessful, but those from a local national network site (Birmingham Tyburn) showed average fine and coarse fraction concentrations of 8.7 and 0.6 µg m⁻³ respectively. A bimodal particle size distribution (PSD) was observed for PM mass at both sites with peaks in coarse and accumulation modes (Fig. 2). The observation is broadly similar to previous studies across site types in the UK (Allen *et al.*, 2001; Gietl *et al.*, 2010; Taiwo *et al.*, 2014).

Carbonaceous Material

At QT, average 24-hour OC and EC concentrations in the PM_{2.5} fraction were observed to be 16.8 and 16.9 µg m⁻³

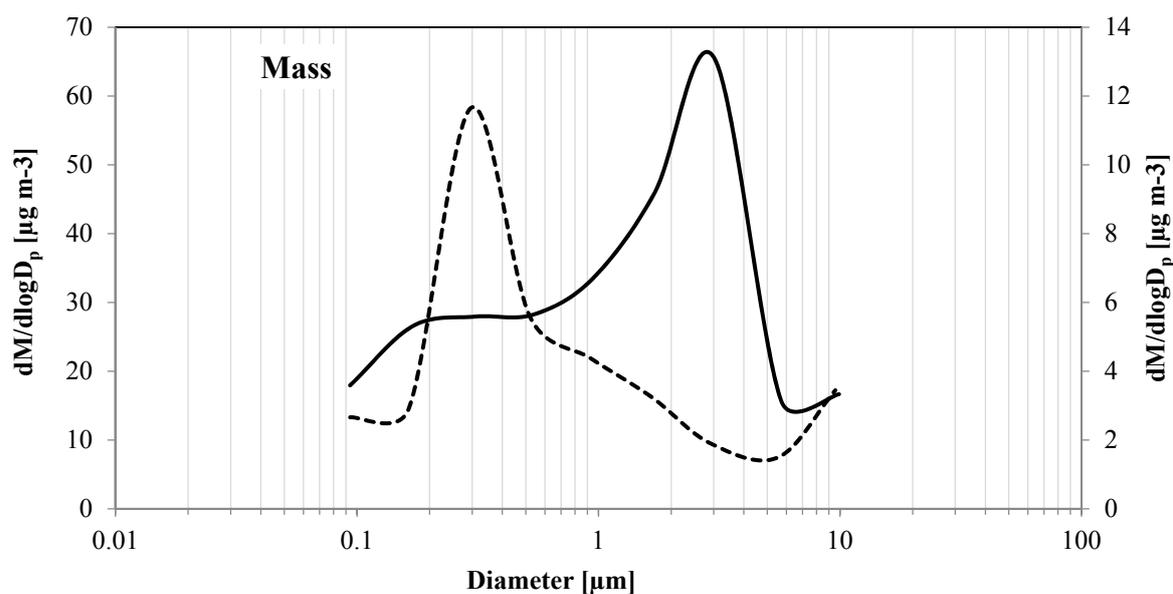


Fig. 2. Mass size distribution for PM at QT and EROS based on MOUDI samples (*solid line*-QT (*primary axis*), *dashed line*-EROS (*secondary axis*); in $\mu\text{g m}^{-3}$).

respectively, while at EROS the concentrations were 1.45 and 0.70 $\mu\text{g m}^{-3}$ (Table 1). OC and EC were strongly correlated at EROS ($r = 0.91$) but the correlation was weaker at QT ($r = 0.58$). This could be the result of variable amounts of resuspension of road dust in the tunnel.

EC is used as a marker for traffic, and is found in the atmosphere as a primary species. Previous research has utilized the ratio between OC and EC to determine the influence of traffic (Castro *et al.*, 1999), although the ratios have to be interpreted with respect to sampling site characteristics. Typically, a high OC/EC ratio indicates higher contribution of OC, indicating lower traffic emissions or a higher non-traffic contribution (e.g., biomass burning) whilst a low OC/EC ratio indicates a high contribution from traffic emissions. The OC/EC ratio was observed as 0.997 ± 0.16 for QT and 2.72 ± 1.45 for EROS. In comparison, He *et al.* (2008) observed a ratio of 0.49 ± 0.04 in a tunnel (~20% HDVs) in China while Ancelet *et al.* (2011) observed the OC/EC ratio of 1.7 in a tunnel in New Zealand. According to Pio *et al.* (2011), OC/EC values around 0.3–0.4 are typical for traffic-dominated locations in Europe, although the ratios are subject to temporal change, as vehicle technologies evolve.

Elements

Overall, concentrations of all of the metals measured in this study were higher at QT compared to EROS (Table 1). Cu, Zn and Ba were found to be the most abundant metals (of those analysed on the Digitel filters) at QT while at EROS, Mn and Zn had the highest concentrations (Table 1). In the Hatfield Tunnel (UK), Ba was found to be the most abundant trace element followed by Zn and Cu (Lawrence *et al.*, 2013). Concentrations in QT were similar in the case of Mn, V, Ca and Zn, although concentrations of Ba and Sb were higher in the case of the Hatfield Tunnel. This seems

plausible considering that the current study focused on $\text{PM}_{2.5}$ while the measurements in Hatfield were conducted on PM_{10} , and Ba and Sb, markers for brake wear, are expected to be present in higher concentrations in the coarse fraction of PM. Element concentrations observed at QT were also found to be similar to concentrations reported elsewhere in Europe (Laschober *et al.*, 2004; Fabretti *et al.*, 2009).

Significant correlations were observed between the elements at QT with the strong correlation between Cu and Sn ($r = 0.992$) while at EROS, brake-wear associated elements were also found to have significant correlations-Sb and Ba ($r = 0.85$) and Ba and Sn ($r = 0.65$). Ti and Cu were also correlated at EROS ($r = 0.78$) (Table 2). Several elements (e.g., Cu, Mn, Cr, V) were found to be moderately correlated to EC while Ti and Ca were found to have no correlation with EC. Weak or no correlation of trace elements with EC has also been observed elsewhere and it has been postulated that this could be due to the trace metal contribution from non-exhaust emissions (Funasaka *et al.*, 1998; He *et al.*, 2008; Ancelet *et al.*, 2011). It should be noted, however, that this observation cannot be directly interpreted as true for all types of road traffic emissions since contributors to PM emissions in a tunnel will differ from those in a normal roadway environment and both chemical composition and emission factors will be different.

Ratios between elements can be used to distinguish between different sources. From data collected in Sweden, Sternbeck *et al.* (2002) proposed a characteristic Cu/Sb ratio (4.6 ± 2.3) for brake wear particles. For the UK, Gietl *et al.* (2010) reported the Cu/Sb ratio of 9.1 ($\text{PM}_{2.5}$) for a heavy traffic road in London while Lawrence *et al.* (2013) reported the ratio value to be 7.2 (PM_{10}) for a tunnel site. In the current study, the Cu/Sb ratio was observed to be 8.95 ± 0.92 for QT and 6.84 ± 5.34 for EROS and broadly falls within the range of reported ratios. In comparison,

Brito *et al.* (2013) reported a Cu/Sb ratio of 8.2 for a road tunnel (PM_{2.5}) in Sao Paulo (Brazil). Brake pad composition varies both geographically, and with time, so differences between sites are to be expected.

The Cu/Zn ratios were observed to be 1.05 ± 0.13 and 0.31 ± 0.28 at QT and EROS respectively. Pulles *et al.* (2012) reported a Cu/Zn ratio of 0.13 for gasoline and 0.35 for diesel fuel in the UK, but non-exhaust sources are

likely to be far more important. At QT, both exhaust and non-exhaust sources contribute to Cu as well Zn, while at EROS, traffic is not a major local contributor.

Mass Size Distributions

Size distributions, measured in terms of mass, number or surface area, are helpful for determining sources of PM, and can be used to predict regional lung deposition

Table 1. Summary of 24-h concentrations at QT and EROS in the PM_{2.5} fraction (*OC, EC and Ca* in $\mu\text{g m}^{-3}$, others in ng m^{-3}) derived from analysis of Digital filters.

Species	QT				EROS			
	Mean	S.D.	Min	Max	Mean	S.D.	Min	Max
OC	16.8	3.29	11.7	22.9	1.45	0.76	0.44	3.12
EC	16.9	2.38	14.1	22.0	0.70	0.55	0.16	1.89
Hopanes								
TNOHO	1.1	0.25	0.75	1.54	0.04	0.02	0.02	0.07
NHO	4.49	1.13	2.94	6.55	0.12	0.09	0.09	0.3
HOP	6.49	1.7	4.12	10.03	0.17	0.11	0.11	0.39
SHHO	1.65	0.46	1.07	2.57	0.09	0.03	0.05	0.13
RHHO	1.46	0.42	0.96	2.35	0.11	0.02	0.06	0.14
SBHHO	1.49	0.45	0.93	2.43	0.05	0.09	0.09	0.26
RBHHO	1.12	0.32	0.78	1.79	0.05	0.09	0.08	0.21
STHHO	1.01	0.31	0.7	1.68	0.02	0.05	0.04	0.12
RTHHO	0.79	0.23	0.51	1.29	<i>Not detected in any sample</i>			
PAHs								
BbF	2.16	0.54	1.27	2.97	0.07	0.07	0.03	0.21
BkF	1.55	0.31	0.80	2.00	0.07	0.05	0.04	0.14
BeP	1.75	0.28	1.28	2.02	0.08	0.07	0.05	0.22
BaP	0.95	0.29	0.41	1.36	0.06	0.04	0.05	0.14
Per	0.24	0.06	0.18	0.34	0.05	0.01	0.06	0.07
IcdP	0.32	0.06	0.22	0.46	0.05	0.04	0.04	0.13
DbA	<i>detected in less than 20% samples</i>				0.02	0.02	0.00	0.04
Pic	<i>detected in less than 20% samples</i>				0.02	0.02	0.00	0.04
BghiPe	0.50	0.08	0.39	0.65	0.07	0.03	0.06	0.14
Cor	0.14	0.02	0.11	0.18	0.05	0.01	0.05	0.07
Alkanes								
C24	142.0	0.34	95.5	195.0	0.40	0.21	0.22	0.63
C25	127.0	1.11	81.9	186.0	0.50	0.28	0.29	0.82
C26	67.8	0.23	44.3	97.4	0.37	0.21	0.23	0.61
C27	43.8	0.56	26.2	57.4	0.54	0.22	0.4	0.8
C28	26.1	0.28	12.6	36.7	0.31	0.18	0.18	0.51
C29	48.5	1.01	32.2	62.9	0.66	0.3	0.44	0.99
C30	29.4	1.55	17.8	44.8	0.21	0.1	0.14	0.34
C31	40.7	1.66	24.9	56.6	0.5	0.28	0.29	0.82
C32	27.1	2.22	13.1	43.4	0.16	0.003	0.16	0.17
C33	28.8	3.88	15	47.1	0.35	0.23	0.16	0.61
Elements								
Ti	16.9	10.85	5.0	40.2	0.68	0.49	0.25	1.94
V	1.2	0.67	0.6	2.6	0.17	0.19	0.02	0.67
Mn	27.9	13.3	11.7	54.3	5.0	6.3	0.1	21.4
Cu	95.6	44.5	38.4	191	2.8	1.8	0.4	6.3
Zn	93.4	47.9	37.9	196	14.1	14.0	1.9	35.2
Sn	19.8	8.5	8.0	36.2	0.3	0.1	0.1	0.5
Sb	10.6	4.3	4.4	17.0	0.6	0.5	0.1	1.5
Ba	65.8	25.3	31.6	111	1.2	0.7	0.1	2.5
Ca	1.51	1.20	0.44	4.44	0.06	0.06	0.02	0.21

Note: For definitions of the abbreviations, see the sub-section on Chemical Analysis.

Table 1. Correlation coefficients between elemental species at QT (light grey) and EROS (dark grey) (*only correlations above 0.5 are reported*).

	Ti	V	Mn	Cu	Zn	Sn	Sb	Ba	Ca
Ti	1	.987**	.976**	.965**	.992**	.937**	.916**	.900**	.980**
V		1	.967**	.946**	.980**	.928**	.928**	.895**	.957**
Mn			1	.992**	.989**	.985**	.973**	.967**	.934**
Cu	.782**			1	.981**	.992**	.958**	.975**	.940**
Zn				.544	1	.959**	.938**	.931**	.962**
Sn					.725*	1	.976**	.991**	.896**
Sb						.717*	1	.979**	.848**
Ba				.545		.679*	.862**	1	.852**
Ca									1

(Harrison *et al.*, 2000). In a traffic environment, a number of factors can influence the size distribution including, but not limited to vehicle fleet mix, road type and grade, meteorological conditions (e.g., season type) and distance from the road (Zhu *et al.*, 2006; Beddows *et al.*, 2009; Hays *et al.*, 2011; Song and Gao, 2011).

Considerable differences were seen between different elements at the same sampling site, and for the same element between sampling sites. Some elements showed similar size distributions at both sites (e.g., Fe, Si) while others had distinct distributions at each site (e.g., Al, Cu). Fig. 3 presents the size distributions for the various elements at QT and EROS. The particle size distributions from the QT site show remarkable consistency (Fig. 3). The predominantly crustal elements (Al, Si and Fe) show a strong mode at 3 μm diameter, as do many of the elements expected to be associated with vehicle wear processes, such as Sb, Ba, Cu, Mn and Pb. Perhaps surprisingly, V also shows this mode despite not normally being associated with crustal or vehicle wear sources. Zn shows a slightly broader distribution with a mode at a little below 2 μm reflecting different sources, or source processes. Tyre wear is generally considered to be the main source of Zn in the roadside environment (Thorpe and Harrison, 2008; Harrison *et al.*, 2012c). Considering the EROS particle size distributions (Fig. 3), it is only for Al, Si and Fe that these are very similar to those from QT. The other elements show a much greater fine particle contribution (Fig. 3). This is suggestive of a regional pollution source from which coarser particles have been depleted by preferential deposition. Contributions from sources other than vehicle wear may also be important at this site, and especially the nearby railway line and station. The brake wear-related elements Ba, Sb and Cu (Gietl *et al.*, 2010) which show correlations in Table 2 also show a common sub-micrometre mode in their size distributions (Fig. 3). Similar results were reported by Taiwo *et al.* (2014) for Ba and V (bimodal size distribution, peaks in coarse and fine mode) in samples collected at EROS. While comparing size distributions at the two sites, it is important to consider that there are significant differences in site characteristics. While the tunnel site (QT) is predominantly influenced by traffic emissions (reflected in strong correlations between elements associated with vehicular emissions and characteristic size distributions), the urban background site (EROS) does not have specific sources in the vicinity, and the size distributions

observed there can reflect a mix of sources. Also, at EROS, the nearby railway line and station is probably influencing the metal concentrations at the site. Regionally transported accumulation mode aerosol will also influence this site, while making little contribution at the QT site.

Analyses of the fine/coarse ratios can also aid in understanding the contributions of natural and anthropogenic sources to a particular element. Soil-associated elements including Al, Si and Fe were found to have a higher fraction of coarse mass at both QT and EROS. However, all the other elements were predominantly in the fine fraction at EROS (Fig. 4). At QT, on the other hand, Pb and Zn had the highest fraction of fine mass while Sb and Ba had the highest fraction of coarse mass. The coarse fraction of Sb and Ba is expected to be associated with brake wear emissions. A higher percentage of elements in the fine fraction at EROS, with very similar peaks in the accumulation mode, could potentially be due to the emissions from the railway in the vicinity. Elements such as Al, Fe, Cu, Zn and Ca are reported to be enriched in emissions from railways (wheels, brake pads, rails etc.) with PM peaks in the fine range (0.25–0.6 μm) from brake discs used in railways (Abbasi *et al.*, 2011). Braking action upon approach to the University station and wear and tear of wheels, brakes and rail tracks can contribute to fine particle emissions in the vicinity of the site. In addition, most trains running along this route are electric, and particles can be released due to wear of the power lines. Martins *et al.* (2016) have recently reported high concentrations of Ba, Cu, Mn, Zn, Sb and Sn in European subway systems, although it is important to note that type of brake pads as well as composition of the rail (wheels, rails etc.) can influence the total emissions. Cu particles have also been attributed to railway emissions in cases where Cu wires are in use for electricity supply (Moreno *et al.*, 2016). There is need for further analysis at EROS to fully understand the impact of railway emissions.

Harrison *et al.* (2012c) proposed a methodology for estimation of the contribution of non-exhaust emissions to PM which involves the use of quantitative factors to estimate specific mass contributions based on specific source markers—Cu/Ba for brake wear, Zn for tyre wear and Si for resuspended dust. Based on this method, brake wear, tyre wear and resuspended dust were found to contribute 31.6%, 19.5% and 44.4% respectively at the tunnel site and 95.5% of the total PM mass was apportioned to the three

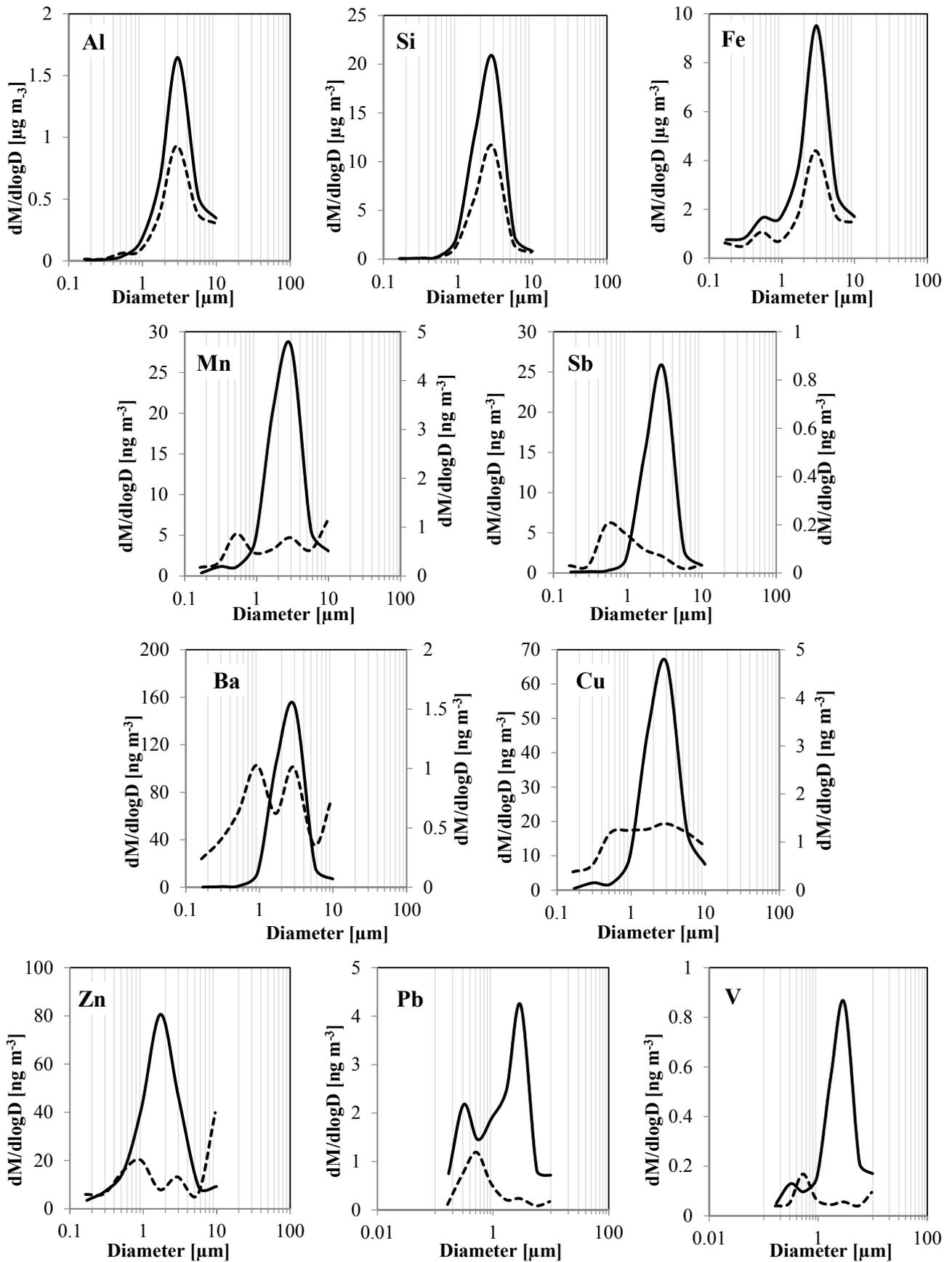


Fig. 3. Size distribution for various elements at QT and EROS (solid line- QT, dashed line-EROS; primary axis for QT and secondary axis for EROS; Al, Si, Fe in $\mu g m^{-3}$ and others in $ng m^{-3}$).

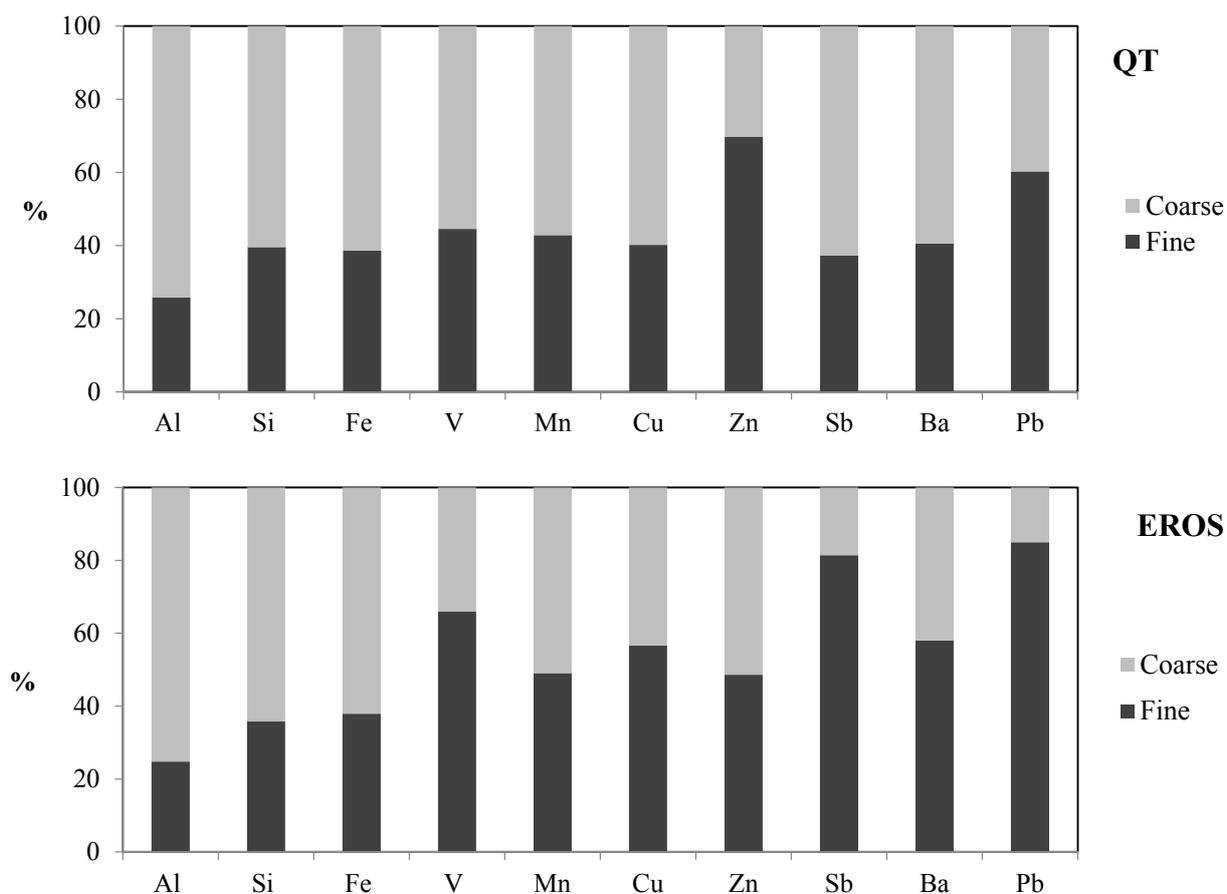


Fig. 4. Fraction of fine and coarse PM for elements at QT and EROS, estimated from MOUDI data.

sources. It is important to note that the tyre wear contribution might be overestimated since Zn is not a unique marker for tyre wear.

Molecular Markers

Hopanes

Hopanes are used as markers for traffic emission, and are typically released during the combustion process (Lin *et al.*, 2010; Pant and Harrison, 2013). They are normally found in lubricating oil used for vehicles, and can be used as markers for diesel as well as gasoline vehicles. The total hopane concentration was observed to be $19.6 \pm 5.2 \text{ ng m}^{-3}$ at QT and $0.62 \pm 0.48 \text{ ng m}^{-3}$ at EROS. HOP and NHO were the most abundant hopane species at both sites (Table 1).

Alkanes

Alkanes are emitted from natural as well as anthropogenic sources. Lower n-alkanes are typically associated with combustion emissions while higher alkanes, particularly the odd-numbered n-alkanes (C₂₉, C₃₁, C₃₃) are associated with biogenic (vegetative emissions) (Rogge *et al.*, 1993; Schauer *et al.*, 1996; Lin *et al.*, 2010). The alkane profiles for the sites were markedly different. Traffic emissions-associated alkanes such as C₂₄ and C₂₅ were the most abundant at QT while C₂₇ and C₂₉ were the most abundant at EROS (Table 1).

Carbon Preference Index (CPI) was calculated for a

qualitative estimate of contributing sources. CPI is defined as the ratio between odd and even numbered n-alkanes (in this case, C₂₄-C₃₃), and can be used to estimate the relative contribution of anthropogenic and biogenic sources. Higher index values are typically associated with vegetative material, while values around unity are associated with anthropogenic activities (Kavouras *et al.*, 1999). In this study, the index value for QT and EROS were observed to be 0.99 and 1.76 respectively indicating an anthropogenic contribution at both sites, with a ratio indicating wholly anthropogenic material at the tunnel site (QT).

PAHs

In case of PAHs, BbF and BkF were found to be the most abundant particulate PAHs (Table 1). The ratio between IcdP/IcdP + BghiPe (0.38 for QT and 0.41 for EROS) was similar to previously reported values (0.37 for diesel-Ravindra *et al.*, 2008). Pic and DbA were detected in less than 20% of the QT samples, and this is likely to be because these PAHs are typically associated with coal combustion.

Roadside Enrichment

In order to understand the contribution of traffic to the species' concentrations, roadside enrichment was calculated for the various elements based on the Eq. (1) (Amato *et al.*, 2011). This approach has been used previously to understand the enrichment due to traffic emissions in urban areas by

Oliviera *et al.* (2010) and Amato *et al.* (2011) although the level of enrichment was lower compared to the results from this study.

$$\text{Roadside enrichment} = \left(\frac{C_t - C_{ub}}{C_t} \right) \times 100 \quad (1)$$

where

C_t is concentration at QT (tunnel).

C_{ub} is the concentration at EROS (urban background).

In case of elements, more than 80% increment was observed for all the measured elements between EROS and QT with the highest increments for elements such as Sn (98.7%), Ba (98.2%) and Cu (97%) and lowest increment for Mn (82.1%). Surprisingly, the roadside enrichment for Zn was lower than for most other elements (83.6%). In the case of carbon, enrichment of 95.9% and 91.4% was observed for EC and OC respectively. Alkanes showed the highest enrichment among the molecular marker species, with almost 100% enrichment.

Source Profile

Source profiles are defined as “*the mass abundances, i.e., fraction of total mass of chemical species in source emissions, and such profiles are generally representative of source categories rather than individual emitters*” (Watson *et al.*, 2002). For vehicular emissions, source profiles are typically generated using dynamometer-based sampling. Composite (i.e., mixed gasoline and diesel) profiles can also be generated using the tunnel/roadway and twin-site studies. The profiles may be prepared with respect to PM as well as OC. In this case, a composite source profile ($\mu\text{g } \mu\text{g}^{-1}$

OC) was prepared for traffic emissions using the Eq. (2).

Profile value

$$= \frac{\text{Concentration}(X)_{QT} - \text{Concentration}(X)_{EROS}}{\text{Concentration}(OC)_{QT} - \text{Concentration}(OC)_{EROS}} \quad (2)$$

where

Concentration (X)_{QT} refers to the concentration of species X at QT.

Concentration (X)_{EROS} refers to the concentration of species X at EROS.

This method is based on the assumption that the roadside increment of PM and its constituents are a fingerprint of traffic emissions (where roadside increment refers to the difference in concentration between the roadside and urban background concentrations), and the calculated increment is then used to estimate the source profile. Uncertainty is represented as the standard deviation across individual samples. The approach is discussed in Pant *et al.* (2014), and has been used in previous studies (Yan *et al.*, 2009; Pant *et al.*, 2014). The profile is presented in Table 3.

Since different chemical species can be emitted from a range of sources, it is important to understand the variability in the species' concentration. This is also useful in the estimation of the reliability of a particular species as a source marker. In order to understand the stability of the species, ratios of individual values to mean values were calculated, and a value of 1 represents absolute similarity. The variation within the different compound classes is presented in Fig. 5. Hopane species and EC exhibit the least variability, while several elements (e.g., Mn) exhibited

Table 3. Composite traffic profile based on tunnel measurements ($\mu\text{g } \mu\text{g}^{-1}$ OC) derived from analysis of Digital PM_{2.5} filters.

Species Class	Species	Concentration	Uncertainty
Carbon	EC	1.0487	0.1724
Elements	Ca	0.1007	0.0516
	Ti	0.0011	0.0005
	V	0.0001	0.00003
	Mn	0.0015	0.0008
	Cu	0.0062	0.0019
	Zn	0.0057	0.0023
	Sn	0.0013	0.0004
	Sb	0.0007	0.0002
	Ba	0.0044	0.0011
	Alkanes	C24	0.0093
C25		0.0083	0.0024
Hopanes	TNOHO	0.0001	0.00001
	NHO	0.0003	0.00004
	HOP	0.0004	0.0001
	HHO	0.0002	0.00003
	BHHO	0.0002	0.00002
	THHO	0.0001	0.00002
PAHs	IcdP	0.00002	0.00001
	BghiPe	0.00003	0.00001
	Cor	0.00001	0.00000

Note: For definitions of the abbreviations, see the sub-section on Chemical Analysis.

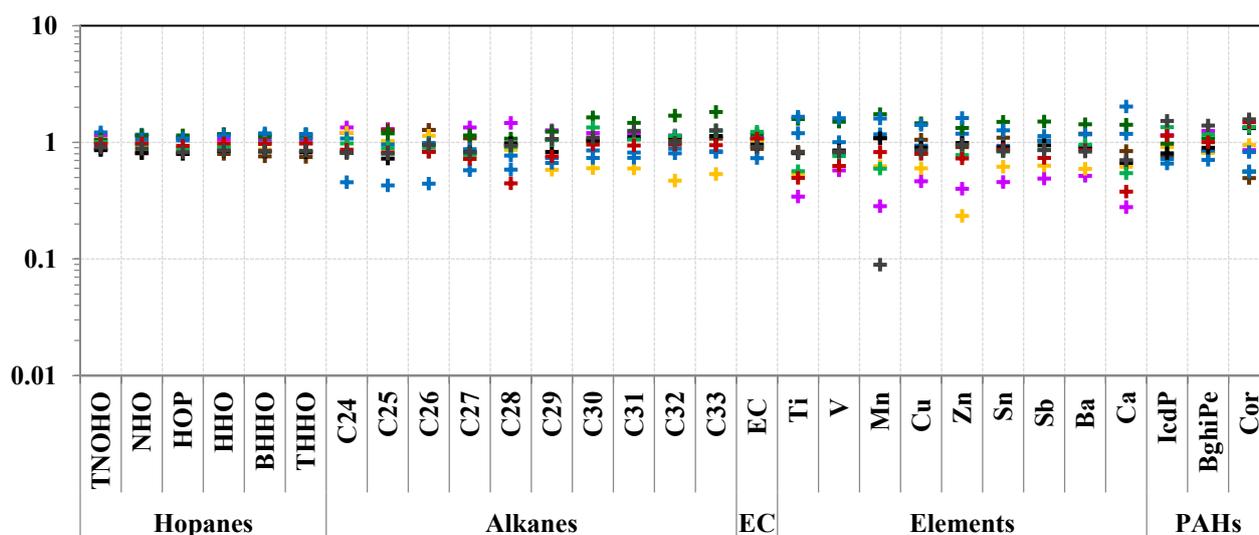


Fig. 5. Variations within species classes (represented as ratio between individual value to mean value where a value of 1 indicates absolute similarity).

a higher degree of variability. Higher variability in the case of elements can be due to the various emission sources (including soil, non-exhaust and exhaust emissions) which contribute to the $PM_{2.5}$ fraction and can lead to higher uncertainties while hopanes are emitted almost solely as exhaust emissions. The data supports the argument that carbonaceous species are less variable as markers for exhaust emissions, and are better suited for use in receptor modelling.

The tunnel profile was compared against the twin-site profile reported in Pant *et al.* (2014) and other traffic profiles including some derived from ambient measurements (France (tunnel)- El Haddad *et al.*, 2009; USA (twin-site)- Yan *et al.*, 2009) and dynamometer-based profiles (Lough *et al.*, 2007). The profile was found to be broadly similar to the other ambient data-based profiles (Fig. 6).

Coefficient of divergence (COD), a self-normalizing statistic, is often used to understand the degree of similarity between PM observations across sites (Wongphatarakul *et al.*, 1998). More recently, it has been also used to calculate the degree of similarity between source profiles (Kong *et al.*, 2011). For the current study, COD was calculated using the following formula (Wongphatarakul *et al.*, 1998). A COD value of zero represents identical data, while a maximum value approaching one indicates a large difference:

$$COD = \sqrt{\frac{1}{n} \sum_{i=1}^k \frac{(x_{ij} - x_{ik})^2}{(x_{ij} + x_{ik})^2}} \quad (3)$$

where

x_{ij} is the concentration of species i in profile j

x_{ik} is the concentration of species i in profile k

n is the number of species used in calculation

Highest similarity was observed for the two UK profiles (COD = 0.32) while the highest variation was observed for the UK tunnel profile and the USA dynamometer profile (COD = 0.65) (Fig. 7). A number of factors can contribute to

the differences between vehicle emissions profiles including fleet age and composition, fuel types and sampling locations. Among the profiles analysed in this study, while EC and hopane congener concentrations were relatively similar across profiles, differences were observed in concentrations of BghiPe, and alkanes. Some difference in PAH concentrations is expected due to the differences in fleet composition (diesel/gasoline split) across the countries. The lowest concentration of BghiPe was observed in France, where the diesel:gasoline ratio is exceptionally high. Furthermore, the US profiles used in this study were collected more than a decade ago, and the emission patterns are expected to have changed with improvements in engine technology and fuel quality.

CONCLUSIONS

PM samples ($PM_{2.5}$ and size-segregated) were analysed at a road tunnel and an urban background site in Birmingham (UK). The samples were analysed for traffic-associated elements and molecular markers and a large enrichment was observed both for elemental and organic species at the tunnel site.

Si and Fe were found to be the most abundant elements in the tunnel, and Cu, Zn and Ba were the most abundant trace elements. Unimodal size distribution were observed for Si and Al at QT but a smaller secondary peak was also observed for Al at EROS. Analysis of size distribution data indicates potential impact from the nearby railway tracks at EROS, but this needs to be analysed further. Characteristic coarse-mode peaks were observed for tracers of non-exhaust emissions- Cu, Sb and Ba, indicating the contribution of non-exhaust emissions. The Cu/Sb ratio was found to be broadly similar to previously reported characteristic ratios for brake wear emissions.

A composite traffic source profile for organic markers was prepared using the Lenschow approach, and compared against other reported profiles. Overall, the profile prepared

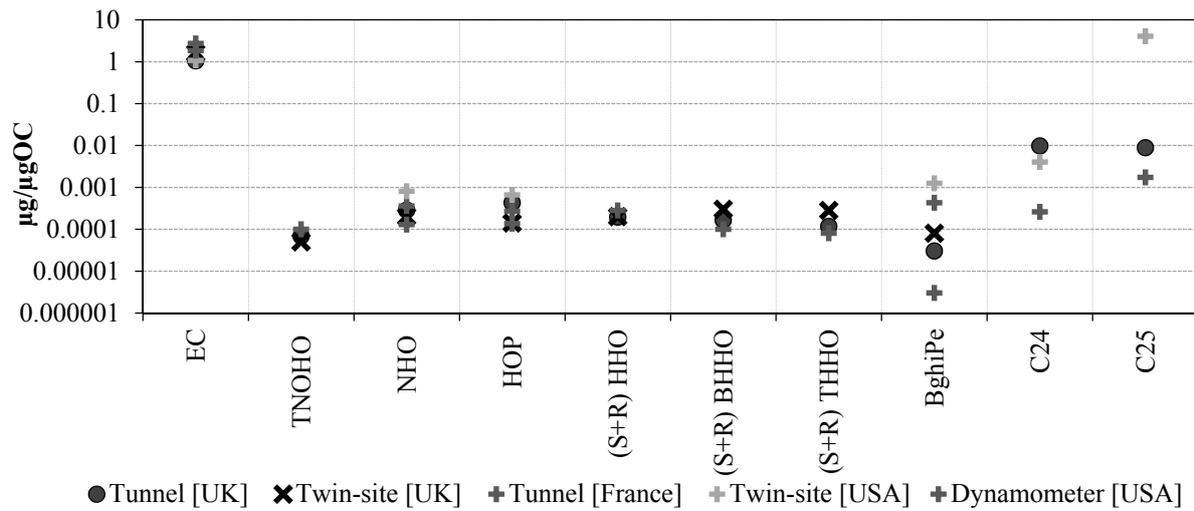


Fig. 6. Comparison of tunnel profile with other ambient and dynamometer-based profiles. (Data from: Pant *et al.* (2014) – Twin Site; El Haddad *et al.* (2009) – Tunnel, France; Yan *et al.* (2009) – Twin Site, USA; Lough *et al.* (2007) – Dynamometer, USA).

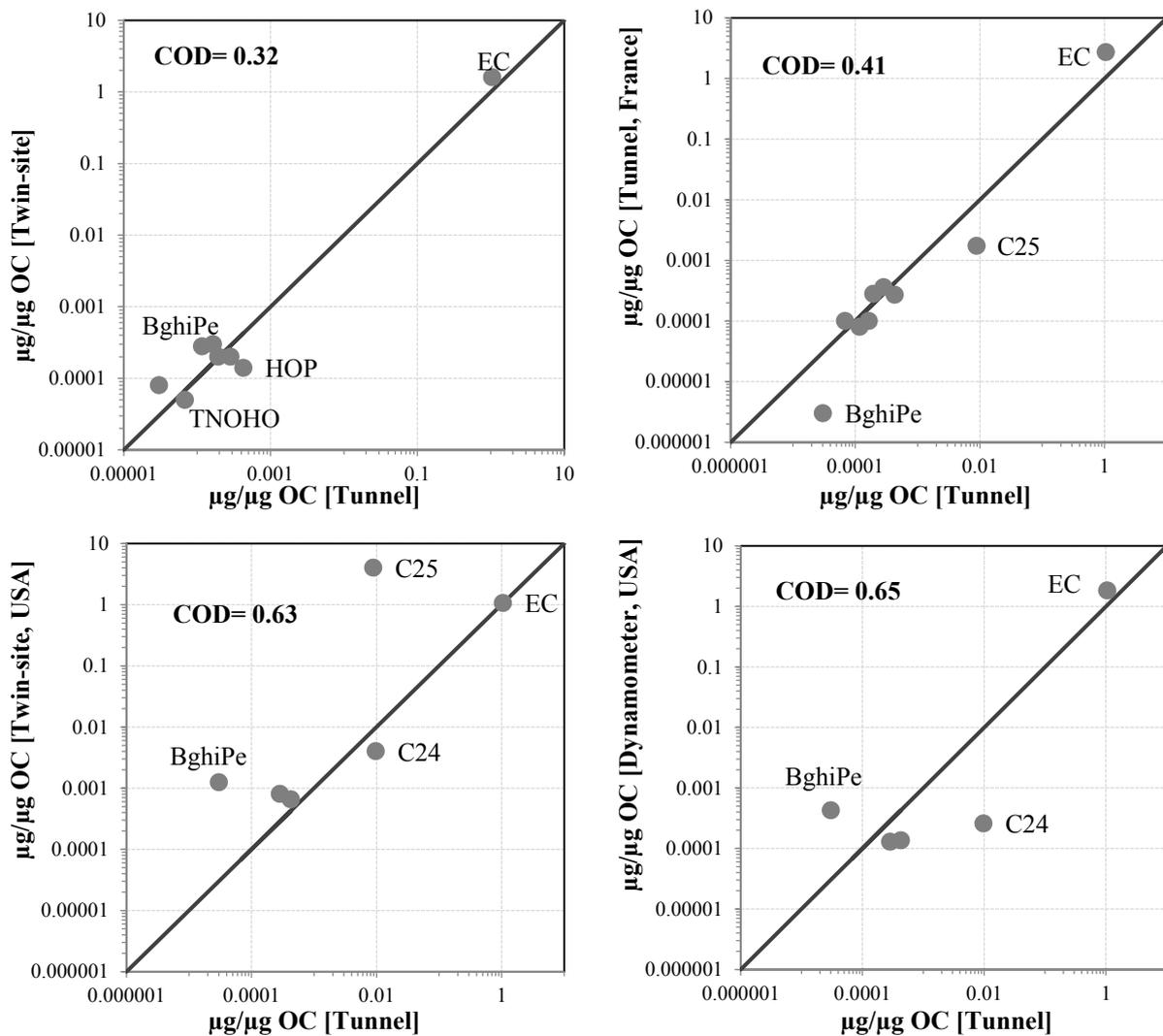


Fig. 7. Comparison between the tunnel profile and other reported source profiles (see legend to Fig. 6 for identity of comparator studies).

using the tunnel measurement was similar to another UK composite profile derived from roadside measurements (reported in Pant *et al.*, 2014) as well as other reported profiles. However, a key difference was the lower uncertainty estimates (based on standard deviation across samples in both cases) for the individual species for this profile compared to the other profile (discussed in Pant *et al.*, 2014) prepared using the ambient measurements at outdoor sites. High uncertainties associated with species in a source profile can introduce errors during receptor modelling with CMB, as the statistics associated with the model are dependent on the uncertainty estimate. Preparation of source profiles using monitoring data from tunnels offers an advantage over monitoring data from other ambient sites (e.g., kerbside) since the influence of other sources as well as meteorology is more limited. Comparison among the profiles indicates distinct advantage in the case of tunnel profiles in the lower uncertainties associated with the individual species.

This is the first study on characterization of PM_{2.5} exhaust emissions in a road tunnel in the UK. The source profile prepared as a part of this study can be used for future receptor modelling studies as well as for improvement of emission inventories in the UK and in those countries of Europe where the vehicle fleet mix and age profile are similar to this study.

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SUPPLEMENTARY MATERIAL

Supplementary data associated with this article can be found in the online version at <http://www.aaqr.org>.

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