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Chemically-speciated on-road $PM_{2.5}$ motor vehicle emission factors in Hong Kong

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ABSTRACT

$PM_{2.5}$ (particle with an aerodynamic diameter less than 2.5 μm) was measured in different microenvironments of Hong Kong (including one urban tunnel, one Hong Kong/Mainland boundary roadside site, two urban roadside sites, and one urban ambient site) in 2003. The concentrations of organic carbon (OC), elemental carbon (EC), water-soluble ions, and up to 40 elements (Na to U) were determined. The average $PM_{2.5}$ mass concentrations were 229 ± 90, 129 ± 95, 69 ± 12, 49 ± 18 μg m^{-3} in the urban tunnel, cross boundary roadside, urban roadside, and urban ambient environments, respectively. Carbonaceous particles (sum of organic material [OM] and EC) were the dominant constituents, on average, accounting for ~82% of $PM_{2.5}$ emissions in the tunnel, ~70% at the three roadside sites, and ~48% at the ambient site, respectively. The OC/EC ratios were 0.6 ± 0.2 and 0.8 ± 0.1 at the tunnel and roadside sites, respectively, suggesting carbonaceous aerosols were mainly from vehicle exhausts. Higher OC/EC ratio (1.9 ± 0.7) occurred at the ambient site, indicating contributions from secondary organic aerosols. The $PM_{2.5}$ emission factor for on-road diesel-fueled vehicles in the urban area of Hong Kong was 257 ± 31 mg veh^{-1} km^{-1}, with a composition of ~51% EC, ~26% OC, and ~9% $SO_4^{=}$. The other inorganic ions and elements made up ~11% of the total $PM_{2.5}$ emissions. OC composed the largest fraction (~51%) in gasoline and liquid petroleum gas (LPG) emissions, followed by EC (~19%). Diesel engines showed higher emission rates than did gasoline and LPG engines for most pollutants, except for V, Br, Sb, and Ba.

1. Introduction

Hong Kong is one of the most populated cities in Asia, with seven million people within its 1100 km^2 territory. Streets with heavy traffic are close to sidewalks and residential and commercial buildings. On-road pollutants are trapped in between high rise structures along the streets, leading to poor dispersion and high human exposure. Previous particulate matter (PM) studies (Cao et al., 2003, 2004; Guo et al., 2009; Ho et al., 2003, 2006; Lee et al., 2006; Louie et al., 2005; Yuan et al., 2006) have verified vehicle engine exhausts as important contributors to particulate pollution, accounting for 20–51% of $PM_{2.5}$ (particle with an aerodynamic diameter less than 2.5 μm). Although the Government has been working for years to control emissions from motor vehicles, improvements from those measures have tended to be offset by the increasing emission levels from the continuously growing vehicle numbers and kilometers driven.

In recent years, the problem of fine particles in the urban areas of Hong Kong has attracted increased concern, since the evidence from epidemiology and toxicology studies (Dockery et al. 1993; Schwartz et al. 1996) has suggested statistically significant association between morbidity and ambient fine particle concentrations. Diaz-Sanchez et al. (1999) found that real-world diesel exhaust particles may increase people's allergic sensitization. Thus, on-road pollutants pose risks to the environment and human health in Hong Kong (Ou et al., 2008; Wong et al., 2008).

Past PM studies at roadside and tunnel sites in Hong Kong have provided limited information on chemically-speciated $PM_{2.5}$. Chan et al. (2000) collected three 24h PM_{10} (particle with an aerodynamic diameter less than 10 μm) samples at 62 roadside sites in 14 districts of Hong Kong, with an average PM_{10} level of 129, 92, 84 and 119 μg m^{-3} for urban commercial, urban residential, urban industrial and new town areas, respectively. Cheng et al. (2006) reported $PM_{2.5}$ mass concentrations of 229, 69, and 49 μg m^{-3} in tunnel, roadside, and ambient microenvironments, respectively. Higher $PM_{2.5}$ levels were associated with increasing proportions of diesel-fueled vehicles. At the northern

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entrance to the cross-harbor tunnel, Lee et al. (2006) showed that carbonaceous particles (sum of organic carbon [OC] and elemental carbon [EC]) were mainly from fresh vehicle exhausts from January to May, 2004, accounting for ~46% of $PM_{1.0}$ and ~44% of $PM_{2.5}$. At the Mok Kok (MK) roadside site, located in a crowded commercial area with heavy traffic (Louie et al., 2005), decreasing trends in $PM_{2.5}$ mass, OC, and EC levels were found from 2000 to 2005. In contrast, $SO_4^=$ and NH_4^+ levels increased during the same period (So et al., 2007).

In Hong Kong, emission factors for $PM_{2.5}$ mass, carbonyls, and dicarboxylic acid/ketoacids/dicarbonyls had been previously reported by Cheng et al. (2006), Ho et al. (2007), and Wang et al. (2006), respectively. However, real-world emission factors and source profiles for chemically-speciated $PM_{2.5}$ are still unavailable. This information is important for policy and decision makers involved in the formulation and development of effective control policy and measures for reducing emissions from mobile sources. Reported here are chemically-speciated $PM_{2.5}$ measured along Hong Kong roadsides and in tunnels, and chemically-speciated $PM_{2.5}$ emission factors.

2. Methodology

2.1. Roadside and ambient measurements

$PM_{2.5}$ samples were collected at two urban roadside sites (the Hong Kong Polytechnic University, [PU] and Mok Kok [MK]), one cross boundary roadside site (Lok Ma Chau [LMC]), and one urban ambient site (Tsuen Wan [TW]) (Fig. 1). Fig. 1 specifies the tunnel, roadside, and ambient sampling sites where samples were taken in summer and winter 2003. Traffic composition and volume were determined by manual-counts at 15-min intervals during the sampling periods. Traffic videos were used to verify the counts. The vehicle types were classified into three major categories, namely gasoline-fueled vehicles (motor cycle and private car), LPG-fueled taxis and diesel-fueled vehicles (big bus, heavy goods vehicle, light goods vehicle and minibus). Diesel-fueled vehicles accounted for ~38% and ~51% of the traffic fleet at PU and MK, respectively, with ~40% and ~28% for gasoline-fueled vehicles and ~22% and ~21% for LPG-fueled vehicles. The PU and MK sites experience 5000 to 6000 vehicles per hour during sampling periods. The LMC site is a boundary-crossing point between Hong Kong and mainland China, with ~2500 vehicles per hour during sampling periods, of which ~80% are fueled with diesel and the remaining ~20% fueled with gasoline. Diesel-fueled vehicles at this boundary-crossing point could be fueled with either mainland diesel or Hong Kong diesel. Mainland China diesel fuel contains 500 ppmw sulfur (maximum) while Hong Kong diesel contains 50 ppmw sulfur. For the PU, MK, and LMC roadside sites, the $PM_{2.5}$ sampling inlet was located at a height of 1.5 m, within ~1 m to the main roads. The TW site is on the rooftop of a 20-m high building. Average values were reported for each season and location due to the limited number of samples (ranged from 11 to 32 samples).

$PM_{2.5}$ samples were collected on parallel 47 mm Teflon membranes (Gelman. Inc., USA) and quartz-fiber filters (Whatman, UK), using Desert Research Institute (DRI, Reno, NV, USA) portable samplers, with a flow of 113 $L\,min^{-1}$ through a Bendix 240 cyclone $PM_{2.5}$ inlet; the flow was divided so that 66.56 $L\,min^{-1}$ went through each filter. The sampling durations were 3 h (08:00–11:00 and 15:00–18:00) at the roadside sites and 6 h (10:00–16:00) at the TW ambient site. Traffic counts, temperature, and relative humidity (RH) were monitored during each of the sampling period.

2.2. Tunnel measurements

Tunnel measurements were taken inside the south bore of the Shing Mun (SM) tunnel in the New Territories (Fig. 1). This tunnel carries traffic from the New Territories Eastern Area (Shatin) to the Western Area (Tsuen Wan). On average, approximately 1600 vehicles per hour traversed the tunnel during sampling periods, with ~50% diesel-fueled vehicles, ~41% gasoline-fueled vehicles, and ~9% LPG-fueled vehicles. Sixteen sets of sample, including 4 in the summer of 2003 and 12 in the winter of 2003, were sampled (Cheng et al., 2006). Samples were taken simultaneously at the entrance and exit of the tunnel. Sampling durations were 2 h in the summer, and 1 h in the winter to avoid

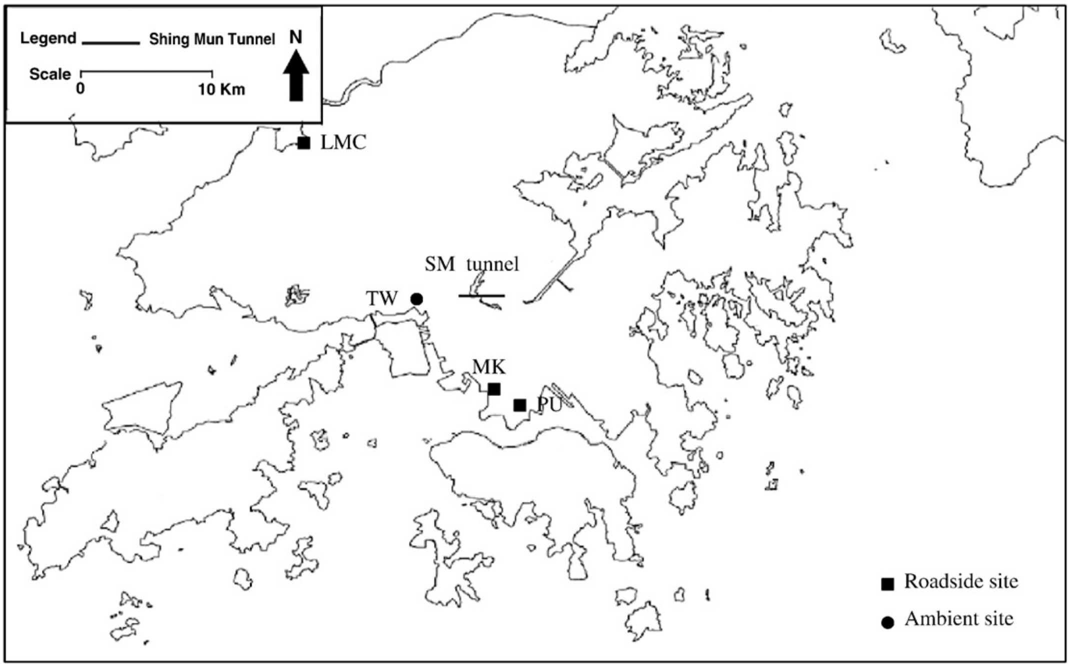

Fig. 1. Sampling locations of the Shing Mun (SM) tunnel, the Lok Ma Chau (LMC) cross boundary (Hong Kong/Mainland boundary) roadside site, the Mong Kok (MK) urban roadside site, the Hong Kong Polytechnic University (PU) urban roadside site, and the Tusen Wan (TW) ambient site. The south bore of the SM tunnel is approximately 1.6 km in length, with an upgrade of 1.054% towards the exit from the entrance. The cross sectional area of the tunnel is 70 m^2. The LMC cross boundary roadside site is a boundary-crossing point between Hong Kong and mainland China, which is located in a suburban area without major sources in vicinity. The urban roadside sites (PU and MK) are in commercial and residential area. The TW ambient site is in a residential area.

overloading the filters. Sample periods covered a wide range of diesel-fueled vehicle proportions, including morning rush hours (8:00–10:00), mid-day hours (11:00–13:00 and 14:00–16:00), evening rush hours (17:00–19:00), and late evening hours (21:00–23:00).

2.3. Chemical analyses

Filters were analyzed by DRI's Environmental Analysis Facility. $PM_{2.5}$ samples were analyzed for mass by gravimetry and for 40 elements (Na to U) by X-ray fluorescence (XRF) (Watson et al., 1999) on the Teflon membrane filters; for chloride (Cl^-), NO_3^-, and $SO_4^=$ by ion chromatography (Chow and Watson, 1999), for NH_4^+ by automated colorimetry, for soluble sodium (Na^+) and potassium (K^+) by atomic absorption spectrophotometry (AAS), and for OC and EC and eight carbon fractions by thermal/optical reflectance (TOR) carbon analysis following the Interagency Monitoring of Protected Visual Environments (IMPROVE) protocol (Chow et al., 1993, 2004) on the quartz-fiber filters.

2.4. Calculation of emission factors

Emission factors for vehicle mixture were derived from the Pierson and Brachaczek (1983) procedure and for diesel- and non-diesel-fueled vehicles (the combination of gasoline- and LPG-fueled vehicles) from the Pierson et al. (1996) procedure, with details for this study described by Cheng et al. (2006). The estimated emission factors for diesel-fueled vehicles from this method generally agree with the measured emission factors for 100% diesel-fueled vehicles according to the experiment results in the Caldecott Tunnel located in the San Francisco Bay area, CA, USA (Allen et al., 2001).

3. Results and discussion

3.1. $PM_{2.5}$ chemical composition

As shown in Table 1, average $PM_{2.5}$ mass concentrations were 229 ± 90, 129 ± 95, 69 ± 12, 67 ± 12, 49 ± 18 µg m^{-3} at the SM, LMC, MK, PU, and TW sites, respectively. Fig. 2 shows the $PM_{2.5}$ material balances for each microenvironment. Organic material (OM = 1.2 × OC), sulfate ($SO_4^=$) and EC were major constituents at the TW ambient site, accounting for ~33%, ~23%, and ~15% of $PM_{2.5}$, respectively. EC abundances were higher and $SO_4^=$ abundances were lower at the roadside sites (i.e., LMC, MK, and PU) than at the ambient site, consistent with enhanced influences of vehicular emissions. OM and EC were major constituents at the three roadside sites, accounting for 32–35% and 34–36% of $PM_{2.5}$ mass, respectively. $PM_{2.5}$ $SO_4^=$ was also an important component in the urban roadside microenvironment, making

Table 1
Average $PM_{2.5}$ mass and chemical composition in different microenvironments.

Site	Urban tunnel site	Cross boundary roadside site	Urban roadside site		Urban ambient site
	SM	LMC	MK	PU	TW
	Average ± SD[a]	Average ± SD[a]	Average ± SD[a]	Average ± SD[a]	Average ± SD[a]
Unit	(µg m^{-3})				
Vehicle percentage (diesel-/gasoline-/LPG-fueled vehicles)	50/41/9%	80/20/0%	51/28/21%	38/40/22%	NA[b]
N[c]	32	11	16	13	20
Mass[d]	229.1 ± 90.1	128.9 ± 94.8	69.3 ± 11.8	66.9 ± 12.3	49.3 ± 17.9
OC	58.5 ± 25.2	37.5 ± 24.9	19.4 ± 4.0	17.6 ± 3.5	13.8 ± 6.5
EC	114.1 ± 39.9	43.9 ± 21.1	28.4 ± 2.9	20.1 ± 4.3	7.3 ± 3.0
Cl^-	0.87 ± 0.61	0.62 ± 1.0	0.29 ± 0.072	0.32 ± 0.12	0.17 ± 0.12
NO_3^-	3.1 ± 2.5	5.7 ± 10.8	1.7 ± 0.84	1.6 ± 0.84	0.79 ± 0.59
$SO_4^=$	23.7 ± 9.3	10.4 ± 11.5	11.1 ± 5.6	13.3 ± 5.8	11.6 ± 5.7
NH_4^+	8.3 ± 3.1	5.0 ± 6.8	4.4 ± 2.0	5.5 ± 2.3	4.3 ± 2.1
Na^+	0.46 ± 0.35	0.27 ± 0.17	0.34 ± 0.12	0.29 ± 0.17	0.26 ± 0.075
K^+	0.73 ± 0.52	0.62 ± 0.91	0.56 ± 0.48	0.54 ± 0.31	0.67 ± 0.57
Na	1.4 ± 1.1	0.68 ± 0.49	0.59 ± 0.42	0.58 ± 0.41	0.27 ± 0.21
Mg	0.15 ± 0.16	0.096 ± 0.077	0.12 ± 0.066	0.11 ± 0.056	0.045 ± 0.028
Al	0.26 ± 0.33	0.19 ± 0.11	0.072 ± 0.059	0.085 ± 0.068	0.064 ± 0.057
Si	0.99 ± 1.2	0.88 ± 0.66	0.35 ± 0.22	0.34 ± 0.16	0.32 ± 0.23
P	0.041 ± 0.049	0.0010 ± 0.0011	0.012 ± 0.011	0.0080 ± 0.0010	0.0073 ± 0.0013
S	9.0 ± 4.2	4.1 ± 4.3	4.4 ± 1.9	5.38 ± 2.47	4.5 ± 2.4
Cl	0.19 ± 0.26	0.60 ± 1.26	0.12 ± 0.058	0.080 ± 0.040	0.072±0.037
K	0.77 ± 0.63	0.66 ± 0.88	0.57 ± 0.51	0.57 ± 0.27	0.74 ± 0.67
Ca	0.69 ± 0.60	0.35 ± 0.21	0.19 ± 0.093	0.16 ± 0.060	0.13 ± 0.052
Ti	0.046 ± 0.055	0.037 ± 0.032	0.017 ± 0.0082	0.016 ± 0.0081	0.012 ± 0.0079
V	0.012 ± 0.010	0.023 ± 0.025	0.013 ± 0.0040	0.014 ± 0.0062	0.015 ± 0.012
Cr	0.0065 ± 0.010	0.0066 ± 0.010	0.0047 ± 0.0044	0.0020 ± 0.0010	0.0012±0.00028
Mn	0.028 ± 0.024	0.032 ± 0.025	0.015 ± 0.0063	0.015 ± 0.0055	0.019 ± 0.012
Fe	1.1 ± 1.1	0.65 ± 0.41	0.30 ± 0.14	0.32 ± 0.10	0.20 ± 0.11
Co	0.0056 ± 0.0067	0.0044 ± 0.0034	0.0029 ± 0.0026	0.0025 ± 0.0025	0.0011 ± 0.00079
Ni	0.0053 ± 0.0037	0.0065 ± 0.0077	0.0072±0.0042	0.0056 ± 0.0029	0.0064 ± 0.0046
Cu	0.063 ± 0.035	0.020 ± 0.016	0.015 ± 0.0063	0.028 ± 0.012	0.033 ± 0.013
Zn	0.43 ± 0.26	0.40 ± 0.35	0.31 ± 0.14	0.21 ± 0.09	0.31 ± 0.21
Br	0.013 ± 0.0063	0.013 ± 0.020	0.015 ± 0.0088	0.0091 ± 0.0060	0.0089 ± 0.0064
Rb	0.0049 ± 0.0075	0.0058 ± 0.0061	0.0073 ± 0.0059	0.0049 ± 0.0035	0.0056 ± 0.0059
Yt	0.00084 ± 0.0015	0.0031 ± 0.0011	0.00010 ± 0.00008	0.00060 ± 0.00010	0.00010 ± 0.00010
Zr	0.0025 ± 0.0043	0.0017 ± 0.0012	0.00090 ± 0.00071	0.0019 ± 0.00086	0.0019 ± 0.0036
Sn	0.018 ± 0.019	0.028 ± 0.039	0.018 ± 0.013	0.016 ± 0.0077	0.021 ± 0.012
Sb	0.0086 ± 0.012	0.010 ± 0.0037	0.0093 ± 0.0024	0.012±0.0047	0.0068 ± 0.0041
Ba	0.037 ± 0.044	0.025 ± 0.021	0.030 ± 0.010	0.030 ± 0.010	0.017 ± 0.0074
Pb	0.072 ± 0.063	0.068 ± 0.10	0.056 ± 0.048	0.054 ± 0.036	0.080 ± 0.078

[a] Standard deviation.
[b] None.
[c] Number of samples.
[d] (Cheng et al., 2006).

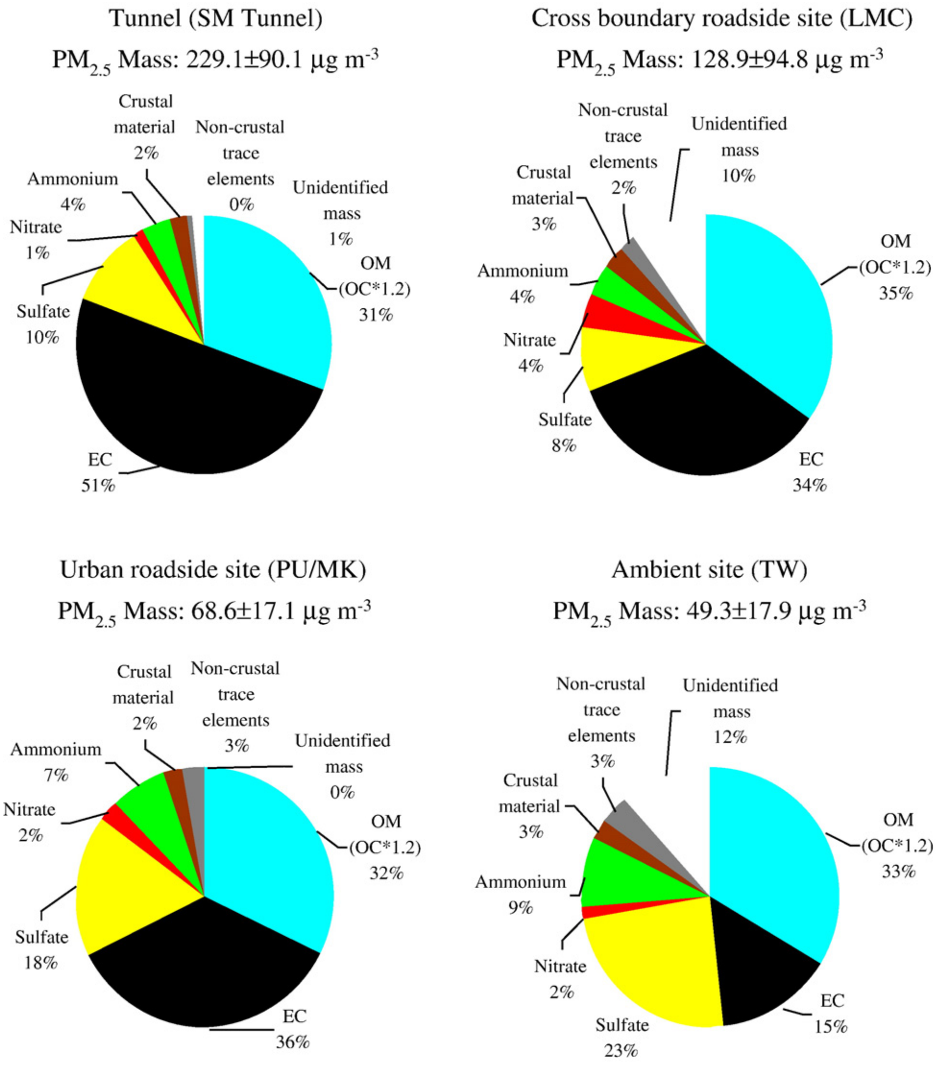

Fig. 2. Material balances of $PM_{2.5}$ in tunnel, cross boundary roadside, urban roadside, and ambient microenvironments. OM = 1.2 × OC (Russell, 2003), Crustal material = [1.89 × Al] + [2.14 × Si] + [1.4 × Ca] + [1.43 × Fe] (Solomon et al., 1989).

up ~18% of $PM_{2.5}$. EC was most abundant (~51%) of $PM_{2.5}$ in tunnel samples, followed by OM (~31%). $PM_{2.5}$ $SO_4^=$ contributed ~10% and the remaining ~5% was consisted of other inorganic ions and elements.

Average OC/EC ratios ranged from 0.6 ± 0.2 in the SM tunnel to 1.9 ± 0.7 in ambient air, with the ratios at the roadside sites being 0.9 ± 0.4 at LMC and 0.8 ± 0.1 at MK and PU. Higher OC/EC ratios were observed in ambient air owing a mixture of OC contribution from vehicle exhausts, industrial combustion sources, vegetative burning, and secondary organic aerosols. Ambient OC/EC ratios that far exceed similarities in source emission may indicate contributions from secondary organic aerosols.

3.2. Spatial distributions of chemical species

As shown in Table 1, $PM_{2.5}$ OC varied by 4-fold and EC by 16-fold among sampling sites. Average EC concentrations were 114 ± 40 µg m^{-3} in the SM tunnel, 44 ± 21 µg m^{-3} at LMC, 28 ± 3 µg m^{-3} at MK, 21 ± 4 µg m^{-3} at PU, and 7 ± 3 µg m^{-3} at TW. EC is often regarded as a marker for diesel-fueled vehicle emissions, especially at roadside sites. As shown in Fig. 3, the spatial differences in the EC (from 44 ± 21 µg m^{-3} at LMC to 28 ± 3 µg m^{-3} at MK and 20 ± 4 µg m^{-3} at PU) at the three roadside environments corresponded with the fraction of diesel-fueled vehicles, which were ~80%, ~51%, and ~38% at LMC, MK, and PU roadside sites, respectively.

$PM_{2.5}$ $SO_4^=$ and NH_4^+ in the tunnel were about two times higher than at other sites. $PM_{2.5}$ $SO_4^=$ and NH_4^+ levels were similar among the three roadside sites (LMC, MK, PU) and at the ambient (TW) site, as shown in Table 1. One way analysis of variance (ANOVA) (Conover and Iman, 1981) showed that the average $SO_4^=$ and NH_4^+ concentrations at the SM tunnel site differed from the other sites at 0.05 significant level. $(NH_4)_2SO_4$ in the SM tunnel were mainly from the tunnel dilution air, and, to some extent, in the vehicle exhausts. The homogeneous secondary aerosols at outdoor sites derived from the dominant regional sources. Prior studies (Louie et al., 2005; Pathak et al., 2003) found $(NH_4)_2SO_4$ mainly transported from the upwind area outside of Hong Kong.

$PM_{2.5}$ NO_3^- was highest at the LMC cross boundary roadside, followed in decreasing concentrations by the SM tunnel, MK/PU urban roadside, and TW ambient sites. One way ANOVA analysis showed that the average NO_3^- concentration at LMC statistically differed from the other sites at 0.05 significant level. LMC NO_3^- concentration at 5.7 ± 4.8 µg m^{-3} was nearly twice the SM level at 3.1 ± 2.5 µg m^{-3}. The LMC roadside site represents considerable number of heavy goods vehicles fueled with mainland diesel fuel in the area. The fuel specification and vehicle emission standards were much tighter in Hong Kong than mainland China. The mainland diesel-fueled vehicles may emit higher nitrogen oxygen (NO_x) due to the poor diesel fuel quality. Thus high atmospheric NO_3^-, arising from the oxidation of NO_x, was observed.

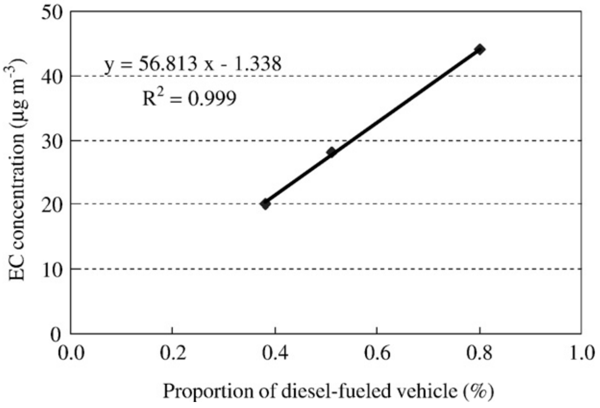

Fig. 3. Measured EC as a function of proportion of diesel-fueled vehicle.

$PM_{2.5}$ elemental Al, Si, Ca, Ti, Cr, and Fe showed similar spatial variations with carbonaceous aerosols. Enrichment factors ($EF = [X/Al]_{air}/[X/Al]_{crust}$) suggested that Al, Si, Ca, and Ti were crustal, possibly road dust, with enrichment factors close to unity. $PM_{2.5}$ Cr and Fe had enrichment factors exceeding five, suggesting the influence of non-crustal sources. Water-soluble K^+ concentrations ranged from 0.5 ± 0.3 μg m^{-3} at PU to 0.7 ± 0.5 μg m^{-3} at SM and Pb levels ranged from 0.05 ± 0.004 μg m^{-3} at PU to 0.08 ± 0.07 μg m^{-3} at TW. The sources of ambient K^+ and Pb in Hong Kong have been reported originated from chemical waste incinerator emissions that transported from the upwind areas, neighboring mainland China, and the Macao Special Administrative Region (Louie et al., 2005). Zheng and Fang (2000) also found K^+ and Pb, in regional pollution, correlated with each other with correlation coefficient (r) higher than 0.8. Mg and Ba levels in the tunnel samples were 32–58% and 25–48% higher than those in the cross boundary and urban roadside samples, and 236% and 116% higher than those in the ambient samples. This may suggest that traffic-related emissions are major sources.

3.3. Speciated emission factors for mixed vehicles

Table 2 summarizes Hong Kong emission factors of $PM_{2.5}$ mass (Cheng et al., 2006) and individual chemical species from mixed vehicles. More than half of $PM_{2.5}$ was from EC (66 ± 18 mg veh^{-1} km^{-1}) and about one third from OC (36 ± 12 mg veh^{-1} km^{-1}). $PM_{2.5}$ $SO_4^=$ accounted for ~6% of $PM_{2.5}$, followed by NH_4^+ (~2%) and Fe (~1%). Crustal elements accounted for ~2% of $PM_{2.5}$ emissions, probably from road dust. Inorganic ions (e.g., Cl^-, NO_3^-, and Na^+) contributed ~2%, and the remaining trace elements and unidentified material made up ~10% of $PM_{2.5}$ emissions. Seasonal differences were not statistically significant for the $PM_{2.5}$ mass and chemically speciated emission factors (all of p-values are larger than 0.05, t-test).

Speciated vehicle emission factors among tunnel studies could differ owing to: 1) fuel composition (Nelson et al., 2008), 2) fleet composition (Grieshop et al., 2006; Lough et al., 2005), 3) vehicle model (Norbeck et al., 1998), and 4) vehicle speed (Gillies et al., 2001). Gillies et al. (2001) reported lower emission factors measured in the Sepulveda Tunnel for EC (26 ± 5 mg veh^{-1} km^{-1}), OC (19 ± 9 mg veh^{-1} km^{-1}), and $SO_4^=$ (2 ± 2 mg veh^{-1} km^{-1}), but higher emission factors for NO_3^- (3 ± 1 mg veh^{-1} km^{-1}), Fe (3 ± 0 mg veh^{-1} km^{-1}), and some heavy metals. Cadle et al. (1997) measured PM_{10} speciated emissions in dynamometer tests and reported lower emission factors for most elements, such as for S (0.2 ± 0.2 mg veh^{-1} km^{-1}), Cl (0.3 ± 2.3 mg veh^{-1} km^{-1}), Ca (0.1 ± 0.1 mg veh^{-1} km^{-1}), Fe (0.2 ± 0.4 mg veh^{-1} km^{-1}), Zn (0.1 ± 0.2 mg veh^{-1} km^{-1}), etc.

Fleet composition affects emission factors. Average OC and EC emission factors were 46 ± 15 and 81 ± 10 mg veh^{-1} km^{-1} during the diesel-fueled vehicle dominated mid-day hours (11:00–16:00), ~1.8 times higher than those during the gasoline-dominated morning rush hours (8:00–10:00) and late evening period (21:00–23:00), with 28 ± 10 mg veh^{-1} km^{-1} for OC and 45 ± 7 mg veh^{-1} km^{-1} for EC (Fig. 4). This may imply that the speciated emission factors from diesel-fueled vehicles were higher than those from gasoline-fueled vehicles. As shown in Fig. 4, variability between measurements made on different days during the same sampling periods is insignificant since the day-to-day fluctuations of fleet composition were small.

Table 2
$PM_{2.5}$ speciated emission factor (EF) for mixed, diesel-, and non-diesel-fueled (gasoline and LPG) vehicles in the Shing Mun Tunnel.

$PM_{2.5}$	EF for mixed vehicles[a]	EF for diesel-fueled vehicles	EF for non-diesel-fueled vehicles[b]
	EF ± SE[c] in mg veh^{-1} km^{-1}		
Mass	131.0 ± 36.9	256.7 ± 31.3	16.6 ± 28.5
OC	35.7 ± 11.7	67.9 ± 10.2	8.5 ± 9.3
EC	65.8 ± 18.4	131.0 ± 14.1	3.2 ± 13.3
Cl^-	0.59 ± 0.51	0.000 ± 0.001	NA[d]
NO_3^-	1.1 ± 0.86	3.6 ± 1.1	NA
$SO_4^=$	7.1 ± 3.3	21.9 ± 7.0	NA
NH_4^+	2.8 ± 0.88	5.5 ± 1.3	0.57 ± 1.21
Na^+	0.26 ± 0.22	0.78 ± 0.29	NA
K^+	0.22 ± 0.17	0.76 ± 0.30	NA
Na	1.0 ± 1.2	0.54 ± 3.1	0.36 ± 2.02
Mg	0.35 ± 0.21	0.63 ± 0.43	0.055 ± 0.51
Al	0.22 ± 0.15	0.77 ± 0.12	NA
Si	0.45 ± 0.27	1.4 ± 0.3	NA
P	0.067 ± 0.037	0.000 ± 0.031	0.16 ± 0.025
S	2.7 ± 1.6	8.9 ± 1.0	NA
Cl	0.35 ± 0.34	0.54 ± 1.1	0.17 ± 0.90
K	0.29 ± 0.42	2.0 ± 0.57	NA
Ca	0.55 ± 0.48	1.6 ± 0.56	NA
Ti	0.084 ± 0.099	0.50 ± 0.15	NA
V	0.012 ± 0.0074	0.0062 ± 0.0010	0.019 ± 0.000
Cr	0.013 ± 0.018	0.038 ± 0.0010	NA
Mn	0.020 ± 0.020	0.088 ± 0.023	NA
Fe	0.95 ± 0.76	2.6 ± 0.89	NA
Co	0.013 ± 0.0094	0.030 ± 0.010	NA
Ni	0.0037 ± 0.0037	0.0087 ± 0.0010	NA
Cu	0.048 ± 0.023	0.071 ± 0.038	0.027 ± 0.030
Zn	0.20 ± 0.093	0.48 ± 0.097	NA
Br	0.0056 ± 0.0042	0.0035 ± 0.0000	0.008 ± 0.000
Rb	0.0080 ± 0.013	0.021±0.00	NA
Yt	0.0033 ± 0.0042	0.000 ± 0.000	0.019 ± 0.000
Zr	0.0080 ± 0.0089	0.023 ± 0.000	NA
Sn	0.030 ± 0.020	0.097 ± 0.000	NA
Sb	0.024 ± 0.016	0.014 ± 0.000	0.035 ± 0.000
Ba	0.073 ± 0.050	0.0013 ± 0.0000	0.14 ± 0.00
Pb	0.024 ± 0.026	0.093 ± 0.000	NA

[a] Mixed vehicles with 50% diesel-fueled vehicles, 41% gasoline-fueled vehicles, and 9% LPG-fueled vehicles.
[b] Gasoline- and LPG-fueled vehicles.
[c] Standard error.
[d] None.

3.4. Speciated emission factors for diesel- and non-diesel-fueled vehicles

For diesel emissions in Table 2, EC (131 ± 14 mg veh^{-1} km^{-1}) was the most abundant in $PM_{2.5}$ emissions, followed by OC (68 ± 10 mg veh^{-1} km^{-1}), $SO_4^=$ (22 ± 7 mg veh^{-1} km^{-1}), NH_4^+ (6 ± 1 mg veh^{-1} km^{-1}), and NO_3^- (4 ± 1 mg veh^{-1} km^{-1}), which constituted ~51%, ~26%, ~9%, ~2%, and ~1% of $PM_{2.5}$ emissions, respectively. The sum of the major elements, i.e., Fe, K, Ca, Si, Na, Al, Mg, Cl, and Zn, accounted for less than 9% of the $PM_{2.5}$ emissions. This chemical profile is similar to that derived from the Caldecott tunnel in 1997 by Kirchstetter et al. (1999) and from the dynamometer tests of individual diesel engines in 1992 by Lowenthal et al. (1994). Carbon content is within the range of 71–99.8% from the previous studies (Allen et al., 2001; Gertler et al., 2001; Lowenthal et al., 1994; Norbeck et al., 1998). The abundance of EC (51%) in this study is higher than the 41% abundance of Hildemann et al. (1991) for dynamometer tests.

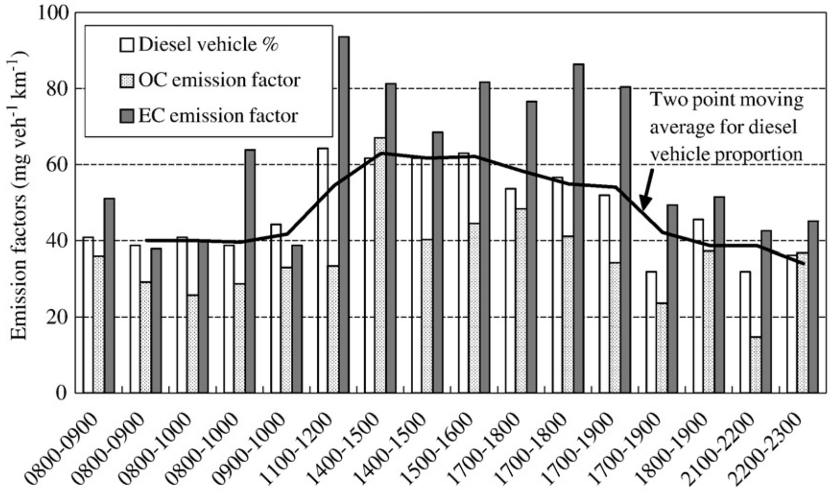

Fig. 4. Temporal variations for the emission factors of OC and EC versus percentage of diesel-fueled vehicles during the 16 runs.

The speciated emission factors for non-diesel-fueled vehicles (Table 2) were obtained, which represent a combined emission factors for gasoline- and LPG-fueled vehicles. For species such as OC, EC, Na, Mg, NH_4^+, and Cu, gasoline and LPG engines showed much lower emission rates than did diesel engine. For instance, EC emission factor was 3.2 ± 13.3 mg veh^{-1} km^{-1} for non-diesel-fueled vehicles, which was 40-fold lower than for diesel-fueled vehicles. However, for species such as V, Br, Sb, and Ba, gasoline and LPG emissions showed higher emission rates than did diesel emissions. These may indicate the marker species for gasoline and LPG engines. Carbonaceous aerosols were the primary constituents for gasoline and LPG emissions. OC (8.5 ± 9.3 mg veh^{-1} km^{-1}) composed the largest fraction, accounting for ~51% of $PM_{2.5}$. EC (3.2 ± 13.3 mg veh^{-1} km^{-1}) was the second fraction, consisting of ~19% of $PM_{2.5}$. Inorganic species, including ions and trace elements, composed an average of ~10% of $PM_{2.5}$ emissions. The rest of ~20% was the uncertainty or unidentified materials.

4. Conclusions

To characterize the speciated $PM_{2.5}$ in different microenvironments, experimental studies at the urban SM tunnel, cross boundary LMC roadside, urban MK/PU roadside, and TW ambient sites were conducted. Tunnel samples represented fresh emissions from vehicles, containing the highest proportion of carbonaceous aerosols, which accounted for ~84% of $PM_{2.5}$ emissions, with the lowest average OC/EC ratio of 0.6 ± 0.2. On the other hand, ambient samples indicated possible secondary aerosol contributions, comprising lowest proportion of carbonaceous aerosols (~48% of $PM_{2.5}$), with the highest average OC/EC ratio of 1.9 ± 0.7. OC and EC had the highest concentrations in the poor-dispersion tunnel and the lowest in ambient air. The spatial distributions of EC concentrations at the three roadside sites, ranging from 44 ± 21 μg m^{-3} at the LMC cross boundary roadside site to 28 ± 3 and 20 ± 4 μg m^{-3} at the MK and PU urban roadside sites, corresponded to the abundances of diesel-fueled vehicles, which is ~80%, ~51%, and ~38%, respectively. $PM_{2.5}$ $SO_4^=$ and NH_4^+ concentrations were similar at outdoor sites, consistent with regional levels found in other studies. Highest NO_3^- concentration was found at the cross boundary roadside site, most likely resulting from the oxidization of NO_x emissions from the mainland diesel-fueled engines.

Higher $PM_{2.5}$ emission rate were found with large fraction of diesel-fueled vehicles in the tunnel. EC constitutes ~51% of $PM_{2.5}$ in diesel emissions, followed by OC (~26%). In contrast, OC composed a larger fraction of ~51% in gasoline and LPG emissions, followed by EC (~19%). For species such as V, Br, Sb, and Ba, gasoline and LPG engines showed higher emission rates than did the diesel engine.

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