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Size-segregated composition of particulate matter (PM) in major roadways and surface streets

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ABSTRACT

A sampling campaign was conducted to assess on-road particulate matter (PM) composition for three size fractions ($PM_{10-2.5}$, $PM_{2.5-0.25}$, and $PM_{0.25}$) on three representative roadways in Los Angeles: 1) the I-110, a high-traffic freeway composed mostly of light-duty vehicles (LDVs), 2) the I-710, a major freeway for heavy-duty vehicles (HDVs) traveling to and from the Ports of Los Angeles and Long Beach, and 3) Wilshire/Sunset Blvd, two major surface streets. Concurrent sampling was conducted at the University of Southern California (USC), which was used as an urban background site. Two sets of PM samples were collected for each roadway, with a sampling duration of approximately 50 h for each set. The samples were analyzed for inorganic ions, elemental carbon (EC), organic carbon (OC), water-soluble OC (WSOC), and trace elements and metals. Results showed that the $PM_{0.25}$ fraction is heavily influenced by on-road vehicular emissions, as indicated by average roadway PM concentrations that were $48.0 \pm 9.4\%$ higher than those observed at USC ($p < 0.05$), while the $PM_{10-2.5}$ fraction is mostly influenced by resuspension of road dust and the $PM_{2.5-0.25}$ fraction is mainly composed of secondary species. Overall, the composition of inorganic ions (%) was relatively consistent across the three roadway environments. With very low EC levels in $PM_{10-2.5}$, the most notable difference among the three roadway environments was the $PM_{2.5}$ EC levels observed on the I-710, which are 2.0 ± 0.2 μg m^{-3} and 4.1 times greater than USC, while levels on the I-110 and Wilshire/Sunset were 1.0 ± 0.2 μg m^{-3} and 0.6 ± 0.01 μg m^{-3} and 2.1 and 1.2 times greater, respectively. $PM_{2.5}$ OC and WSOC concentrations were observed to be 1.6, 2.0, and 1.7 times greater on the I-110, I-710, and Wilshire/Sunset than corresponding levels at USC, respectively. Results from this study may have major public health implications for passengers who commute frequently on high-traffic roadways. Finally, a comparison of EC levels to previous studies conducted at fixed sites near the I-110 and I-710 showed substantial decreases in EC concentrations over the past years, which may be a result of the recent Port of Los Angeles Clean Truck Program.

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1. Introduction

The association between exposure to particulate matter (PM), especially fine PM or $PM_{2.5}$ (aerodynamic diameter less than 2.5 μm), and adverse health effects has been well established (Samet et al., 2000; Pope and Dockery, 2006). Numerous studies have shown that high concentrations of PM may be linked to cardiovascular disease outcomes (Pope et al., 2004; Delfino et al., 2010, 2011), respiratory disease outcomes (Li et al., 2003; Dominici et al., 2006), adverse birth outcomes (Ritz et al., 2002; Wilhelm and Ritz, 2005; Wu et al., 2009), and neurodegenerative disorders (Campbell et al., 2005; Morgan et al., 2011).

In major metropolitan areas, the major source of PM is vehicular emissions (Schauer et al., 1996; Querol et al., 2001). Populations in the proximity of trafficked roadways are most susceptible to PM-related health effects (Tonne et al., 2007), with the most sensitive demographic being children (Brunekreef et al., 1997; Dales et al., 2009; Delfino et al., 2009) and the elderly (Liao et al., 1999; Creason et al., 2001). Although the underlying physiological pathways remain largely uncertain, several studies have postulated that certain PM components, including elemental carbon (EC), organic carbon (OC), and trace metals (Metzger et al., 2004; Ostro et al., 2008; Verma et al., 2010) may play a role in PM toxicity.

It is therefore important to characterize PM in major roadway environments, where elevated levels of PM have been observed (Zhu et al., 2002). Various methodologies have been used to assess the impact of vehicular emissions on ambient air. Chassis

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Fig. 1. Map of the three sampling routes: 1) I-110 (blue), 2) I-710 (red), and Wilshire/Sunset (purple). The USC background site is denoted by the red star.

dynamometer studies can measure the emissions of a target vehicle in a controlled environment, but cannot account for particle aging effects and cannot capture non-tailpipe emissions such as brake and tire wear (Schauer et al., 1999; Yanowitz et al., 1999). Another method is roadside sampling, where continuous and time-integrated instruments are used to measure physical and chemical components of PM at designated sites downwind of roadways (Kuhn et al., 2005b; Ning et al., 2010). Several recent studies have conducted on-road sampling, in which a mobile laboratory (typically a hybrid or electric vehicle) equipped with various continuous instruments have been used to measure black carbon (BC) (Fruin et al., 2004), particle size distribution (Gouriou et al., 2004; Westerdahl et al., 2005; Weimer et al., 2009), $PM_{2.5}$, particle-bound PAH, and gaseous pollutants including NO_x, CO, ozone, and hydrocarbons (Bukowiecki et al., 2002; Ning and Chan, 2007; Weiss et al., 2011). However, there are no on-road studies that have reported detailed time-integrated chemical data, which would substantially enhance the current knowledge base of on-road PM, and thus a more accurate estimate of the health risks associated with exposure to these particles.

The novelty of this study lies in the sampling instrumentation used to collect on-road PM. The use of portable, lightweight battery-operated pumps, which operate at relatively high flow rates coupled with cascade impactors made it possible to collect size-fractionated PM. A quasi-isokinetic inlet was deployed to collect time-integrated samples along three routes in Los Angeles: a major roadway dominated by light-duty vehicles (LDVs), a major roadway with a higher fraction of heavy-duty vehicles (HDVs), and two major surface streets. Concurrent samples were collected at a fixed site at the University of Southern California (USC), representing an urban background site. Other studies have provided measures of roadway ambient air pollutants which may be representative of a busy traffic area, but the current study focuses on assessing private commuter exposure by selecting three distinct commute environments which encompass various traffic volumes, traffic composition, and driving conditions. Chemical analysis has been performed for three size fractions of PM, including $PM_{10-2.5}$, $PM_{2.5-0.25}$, and $PM_{0.25}$. The objectives of this study are: 1) provide a chemical comparison of the three roadway environments and USC background site, 2) discuss factors that may contribute to the differences in chemical composition of the roadway environments, and 3) compare results to previous studies that have been conducted at fixed sites near the same roadways.

2. Experimental methodology

The sampling campaign was undertaken in Los Angeles in March–April 2011. Sampling was conducted for 11 h per day on Monday–Friday, from 6:00 a.m. to 5:00 p.m. Fig. 1 shows the three sampling routes that were selected to each represent a distinct roadway environment. The I-110 is a high-traffic freeway that runs 51-km from the Port of Los Angeles through downtown Los Angeles to Pasadena and is composed mostly of light-duty vehicles (LDVs); the I-710 is a 43-km freeway and has a higher heavy-duty vehicle (HDV) composition than the I-110 because it serves as the main corridor for HDVs traveling to and from the Ports of Los Angeles and Long Beach; Wilshire/Sunset Boulevards is a 48-km major surface street route that traverses downtown Los Angeles, Koreatown, Miracle Mile, Beverly Hills, and Hollywood. A summary of the traffic data is shown in Table 1, which is taken from the CalTrans Performance Measurement System (PeMS) database. The total vehicle flow for the I-110 (6378 vehicles h^{-1}) is approximately 1.5 times higher than total flow for the I-710 (4247 vehicles h^{-1}). However, the I-110 truck flow (243 trucks h^{-1}) is approximately half of the I-710 truck flow (470 trucks h^{-1}), yielding a truck composition of 3.9% and 11.3% for the I-110 and I-710, respectively. In addition, the northern section of the I-110, which is approximately 12-km, is limited to LDVs only. It is important to note that even though traffic flows may differ for various parts of the freeway, the traffic sites were carefully selected to be located in the center of the freeway to characterize the entire freeway. The Wilshire/Sunset route had a total flow of 1839 vehicles h^{-1} with a negligible truck flow. Concurrent sampling was conducted at University of Southern California (USC) and served as our background site (Moore et al., 2007; Ning et al., 2007). Two samples were collected for the three routes and for the USC background site.

Table 1
Summary of meteorological parameters from nearby air quality monitoring sites (South Coast Air Quality Management District (SCAQMD)). Traffic data is from the CalTrans database.

Route	Dates of sampling	Temp (deg C)	±	RH (%)	±	Prevailing wind direction	Wind speed (m s^{-1})	±	Total/truck flow (vehicle h^{-1})	Truck composition (%)
110 S1	3/1–3/8/11	17.8	3.8	54.2	17.0	W	3.2	0.9	6378/243	3.9
110 S2	4/11–4/18/11	18.7	2.5	60.1	13.1	SW	3.1	0.8		
710 S1	3/17–3/25/11	15.8	3.2	55.3	16.2	W	3.6	0.9	4247/470	11.3
710 S2	4/19–4/25/11	18.7	1.7	64.5	8.3	W	3.4	0.9		
WS S1	3/9–3/16/11	21.7	3.8	48.3	16.0	SW	2.9	1.2	1839/NA	NA
WS S2	4/26–5/2/11	25.8	4.2	35.6	13.4	SW	3.7	1.0		

2.1. Sampling instrumentation

The sampling vehicle (Honda Insight Hybrid 2011) was equipped with six Personal Cascade Impactor Samplers (PCIS) (Misra et al., 2002; Singh et al., 2003), each operated individually with a battery-powered Leland Legacy pump (SKC Inc., Eighty-Four, PA) at a flow rate of 9 liters per minute (lpm). The pumps were calibrated with a Gilian Gilibrator-2 Air Flow Calibrator (Sensidyne Inc., Clearwater, FL) before and after sampling, and pump flows were checked regularly with flow meters throughout the sampling campaign. Two PCIS units were operated concurrently at the USC background site. The inlet for roadway air was designed to have a 90° bend that is characterized by a 50% cut point of 10 μm (Peters and Leith, 2004). Each PCIS had two impaction stages – the first with a cut point of 2.5 μm to collect $PM_{10-2.5}$ particles and the second with a cut point of 0.25 μm to collect $PM_{2.5-0.25}$ particles – and an after-filter stage to collect $PM_{0.25}$. For the purpose of conducting comprehensive chemical analysis, three PCIS were loaded with PTFE (Teflon) filters and three were loaded with quartz filters. In the Teflon units, 25-mm Zefluor-supported PTFE filters (Pall Life Sciences, Ann Arbor, MI) were used as the impaction substrates and 37-mm PTFE membrane filter with PMP ring (Pall Life Sciences, Ann Arbor, MI) were used as after-filters; in the quartz units, quartz microfiber filters (Whatman International Ltd, Maidstone, England) were used as both the impaction substrates and after-filters. Two DustTrak (Model 8520, TSI Inc., Shoreview, MN) were also deployed to measure continuous $PM_{2.5}$ and PM_{10} mass concentrations. However, DustTrak results will not be presented in this paper.

Roadway air was supplied to the PCIS units and DustTrak monitors by a custom-designed, stainless steel inlet with an inner diameter of 0.95 cm (3/8 inch). The curved PM_{10} inlet directed roadway air into the vehicle window to a manifold with six branches (one for each PCIS) with the two DustTrak connected to the end (Fig. 2). Total flow rate through the inlet was 57.4 lpm (6 PCIS*9 lpm + 2 DustTrak*1.7 lpm), yielding a velocity of 13.4 m s^{-1} (or 30 mph) at the inlet. Hence, isokinetic sampling was achieved when the vehicle was moving at 13.4 m s^{-1}. Anisokinetic sampling may result in the overestimation or underestimation of relatively larger particles (i.e. $PM_{10-2.5}$) and can be calculated based on the following equation (Belyaev and Levin, 1974):

$$\frac{C}{C_o} = 1 + \left(\frac{U_o}{U} - 1\right)\left(1 - \frac{1}{1 + \left(2 + \frac{0.62U}{U_o}\right)\mathrm{St}}\right)$$

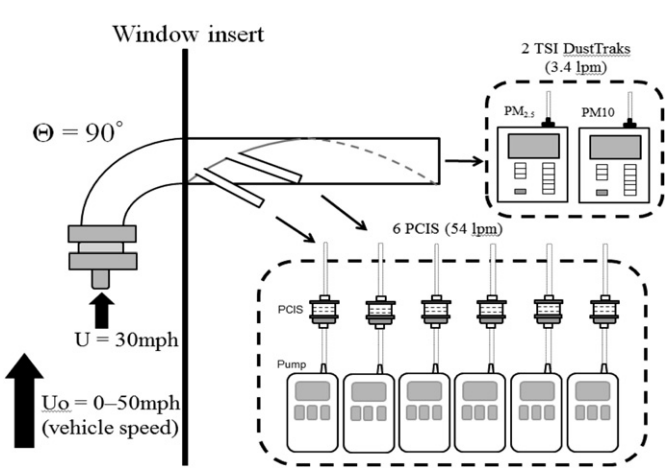

Fig. 2. Sampling schematic of the inlet into the vehicle and the instrumental set up.

where C is the estimated PM concentration, C_o is the actual PM concentration, U_o is the free stream velocity, or vehicle speed, U is the inlet velocity, and St is Stokes number. When the vehicle speed is above 13.4 m s^{-1} or $U_o > U$, sub-isokinetic sampling occurs; conversely, when vehicle speed is below 13.4 m s^{-1} or $U_o < U$, super-isokinetic sampling occurs. Considering the two most extreme cases for $d_p = 10$ μm, when the vehicle speed is 22.3 m s^{-1} (or 50 mph), $C/C_o = 1.34$, and when the vehicle speed is 4.5 m s^{-1} (or 10 mph), $C/C_o = 0.58$. For particles smaller than 5 μm, the resulting over- or under- estimation of concentration in these two extreme cases of vehicle speed is less than 20%, and decreases rapidly with decreasing particle size. $PM_{2.5}$ is virtually unaffected by anisokinetic sampling.

2.2. Sample analysis

After completion of sampling, Teflon filters were analyzed gravimetrically and chemically while quartz filters were only analyzed chemically. The Teflon filters were equilibrated for 24 h, then pre- and post-weighed in a temperature and relative humidity-controlled room using a MT5 Microbalance (Mettler-Toledo Inc., Columbus, OH) to determine gravimetric mass concentrations. The Teflon filters were analyzed by magnetic-sector Inductively Coupled Plasma Mass Spectroscopy (SF-ICPMS) using acid extraction to determine total elemental composition (Zhang et al., 2008) and ion chromatography (IC) to determine the PM concentrations of inorganic ions (Kerr et al., 2004). The quartz substrates were prebaked at 550 °C for 12 h and stored in baked aluminum foil prior to sampling. Elemental and organic carbon (EC/OC) content was determined using the Thermal Evolution/Optical Transmittance analysis (Birch and Cary, 1996). Water extracts of OC yielded WSOC. Organic speciation analysis was conducted with gas chromatography mass spectroscopy (GC/MS) (Schauer et al., 1999). However, organics and metals speciation results are not discussed here and will be the topic of upcoming manuscripts.

3. Results and discussion

3.1. Overview of campaign

Table 1 provides the dates of sampling, a summary of the meteorological conditions, and the traffic flows on the sampled roadways. Meteorological data are obtained from the nearby Downtown Los Angeles and Long Beach air quality monitoring sites that are maintained by the South Coast Air Quality Management District (SCAQMD). Data presented are for the corresponding dates and times of sampling. Variation in both temperatures (°C) and relative humidities (%) were expected considering the daily sampling duration (6 a.m.–5 p.m.). The prevailing wind direction during sampling hours was consistent across all samples with an onshore breeze from W or SW. Average wind speed (m s^{-1}) was also relatively consistent.

Fig. 3 shows the size-fractionated PM mass concentrations of the two samples collected for each route and for USC background site. In terms of PM size composition, no PM mode is dominant and $PM_{10-2.5}$, $PM_{2.5-0.25}$, and $PM_{0.25}$ account for an average of 37.2 ± 4.1%, 28.3 ± 3.9%, and 34.6 ± 3.6% of total PM mass, respectively, across all sites. Although there is some variation in total mass concentrations between the two sets of samples, the USC background site has the lowest levels of 24.1 ± 2.8 μg m^{-3} while the three sampled roadways exhibited comparable levels of 32.2 ± 3.32 μg m^{-3}.

3.2. Mass balance

Fig. 4a–c shows the mass balance for each site (I-110, I-710, Wilshire/Sunset, and USC) and each size fraction. Gravimetric mass concentrations are shown with error bars representing one

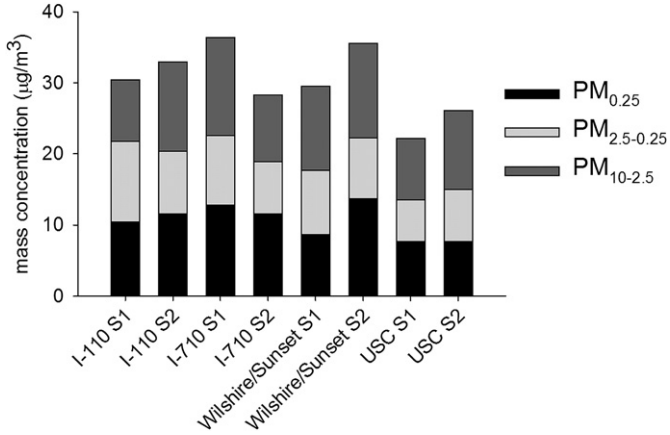

Fig. 3. Size-fractionated mass summary the three roadways and USC background site. S1 and S2 represent the two sets of samples collected, with a sampling duration of approximately 50 h for each set. Sampling dates are shown in Table 1.

standard deviation. The mass balance was constructed based on 5 categories: inorganic ions, organic matter (OM), elemental carbon (EC), crustal metals, and trace metals. Inorganic ions consist of chloride, nitrate, phosphate, sulfate, sodium, ammonium, and potassium. Organic matter is calculated by multiplying OC by a correction factor of 1.8 (Turpin and Lim, 2001). Crustal metals include Mg, Al, K, Ca, Ti, and Fe multiplied by a corresponding factor to account for oxide forms, with the exception of Si which is derived from Al (Chow et al., 1994; Marcazzan et al., 2001; Hueglin et al., 2005). Trace metals include the remaining measured elements. A detailed discussion of metals will be discussed in a separate manuscript, however, individual metal mass concentrations (ng m^{-3}) for the three roadway environments and for USC background site are shown in Table S1.

3.2.1. $PM_{10-2.5}$

In $PM_{10-2.5}$, USC exhibited the lowest gravimetric and reconstructed mass concentrations while Wilshire/Sunset exhibited the highest in both (Fig. 4a). In spite of the PM mass differences, the composition of the five designated PM components are relatively consistent across all routes and USC, with crustal metals accounting for 40–50% of reconstructed mass, ions for 30–40%, OM for 15–25%, trace metals for 3%, and EC for 1%. This consistency demonstrates that the differential microenvironment of each roadway does not play a substantial role in the composition of $PM_{10-2.5}$. This can also be explained by the fact that the major sources of $PM_{10-2.5}$ are not from traffic sources (i.e. vehicular combustion), but rather from resuspension of road dust, large sea salt particles, mechanically generated particles, and biogenic particles (i.e. pollen, fungal spores).

The unidentified mass in this mode is the largest of the three PM size fractions, with I-110 having the lowest of 26% unidentified mass and USC site having the highest of 41%. This underestimation of reconstructed mass calculations can be attributed to the uncertainty in the OC multiplication factor and other mineral compounds that may exist in oxide form. Previous studies of this size fraction in urban areas of Los Angeles have also found that crustal metals and inorganic ions account for the majority of the mass balance (Sardar et al., 2005; Arhami et al., 2009) and that $PM_{10-2.5}$ may be characterized by a relatively high percentage of unidentified mass (Cheung et al., 2011).

3.2.2. $PM_{2.5-0.25}$

Fig. 4b shows the PM composition for $PM_{2.5-0.25}$ for the 3 roadways and USC background site. Contrary to the $PM_{10-2.5}$ composition, there is more variability in some of the PM components,

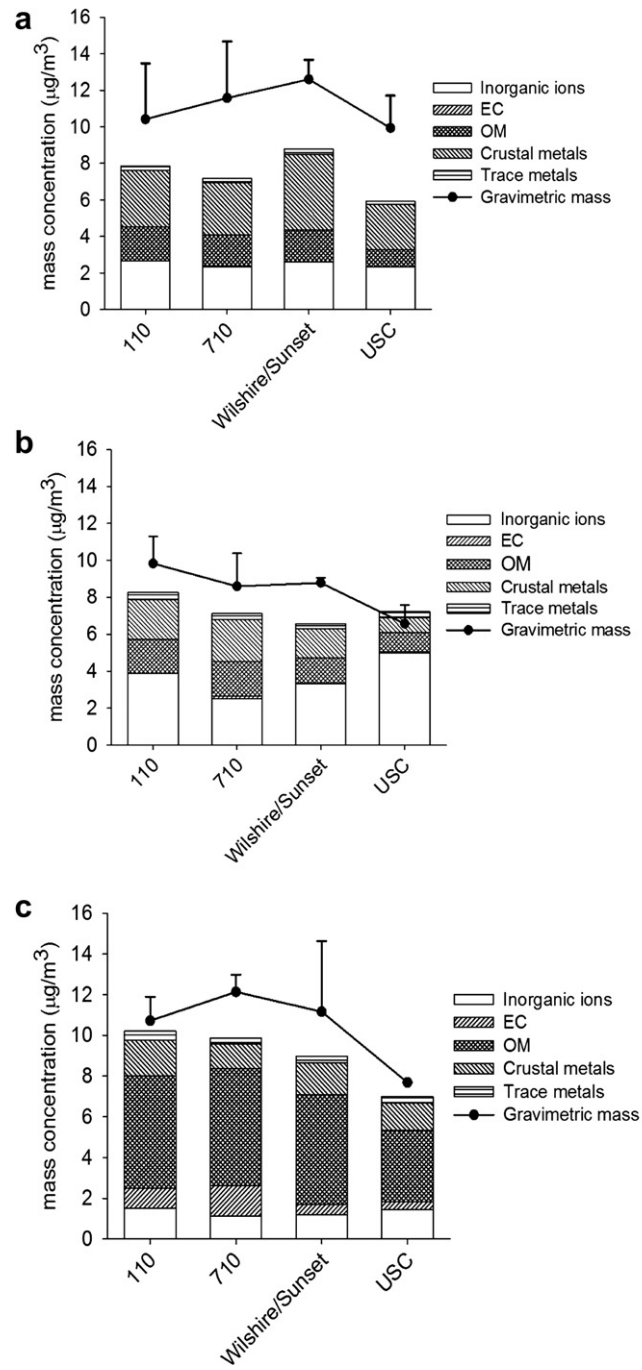

Fig. 4. Mass balance constructed based on five identified categories for a) $PM_{10-2.5}$, b) $PM_{2.5-0.25}$, and c) $PM_{0.25}$. Error bars represent one positive standard deviation.

notably the inorganic ions, which account for 35% of reconstructed mass at I-710 and 69% at USC background site. Crustal metals also exhibited variability across the sites, with 11% for USC and 32% for I-710, and OM ranged from 14 to 26% with the lowest fraction at USC. This variability in composition suggests that this mode may be more influenced by sources in the immediate environment (i.e. vehicular resuspension, tire and brake wear). Inorganic ions are primarily formed in the atmosphere in the presence of gaseous precursors (SO_2, NO_2), and thus secondary in nature (Seinfeld and Pandis, 2006). Previous studies have also found that PM in $PM_{2.5-0.25}$ is dominated by inorganic ions (primarily sulfate and nitrate) in various regions of Los Angeles (Sardar et al., 2005; Arhami et al.,

2009). Although there appears to be a greater difference in inorganic ions between the various roadways and USC background site, statistical analysis showed that the differences are not statistically significant ($p = 0.17$). EC and trace metals are low contributors in this mode, accounting for 1–2% and 4–5%, respectively. Finally, 15–25% of gravimetric mass concentrations were unidentified for the roadway sites while USC exhibited an overestimation of 10% of mass.

3.2.3. $PM_{0.25}$

In $PM_{0.25}$, USC exhibits the lowest total PM mass concentrations (Fig. 4c). On average, the three roadway environments have gravimetric PM concentrations that are 48.0 ± 9.4% higher than levels observed at USC ($p < 0.05$), which strongly suggests that vehicular emissions from both LDVs and HDVs are major contributors to PM in this mode. OM is the dominant component and its contribution is consistent across all sites, accounting for 50–60% of reconstructed mass. A previous study in Los Angeles also determined OM to be the dominant contributor of $PM_{0.25}$ (Arhami et al., 2009). Contrary to the larger size fractions, EC exhibited substantial variation across the three roadway environments, accounting for 15% for the I-710, 10% for the I-110, 6% for Wilshire/Sunset and 6% for USC. This observation is consistent with the application of using EC as a surrogate for primary emissions and as a tracer of diesel fuel combustion (Schauer, 2003). The significantly higher contribution of EC in the two freeway environments relative to Wilshire/Sunset and USC ($p < 0.05$) can be attributed to the fleet fraction of HDVs, of which the I-710 has the highest of 11.3%, the I-110 at 3.9%, and Wilshire/Sunset with a negligible HDV fraction. Of the three size fractions, $PM_{0.25}$ appears to be most heavily influenced by traffic emissions. Inorganic ions' contribution exhibited slight variation, with the I-710 at a low of 11% and USC at a high of 21%; crustal metals' contribution ranged from 12% at I-710 and 19% at USC; trace metals' contribution were consistently low at 3–5% at all sites. $PM_{0.25}$ is characterized by the lowest fraction of unidentified mass, with 6% for the I-110 and 19% for both the I-710 and Wilshire/Sunset.

The authors acknowledge that quartz filters are subject to both positive (adsorption) and negative (volatility) artifacts of OC, especially for particles collected through filtration (i.e. $PM_{0.25}$) (Turpin et al., 2000). However, significant organic adsorption and volatility artifacts are not expected in this study due to the very high PM mass loadings (Kim et al., 2001) and the low pressure drop of the PCIS (Misra et al., 2002). Particles in $PM_{10-2.5}$ and $PM_{2.5-0.25}$ are collected by impaction and are thus less susceptible to sampling artifacts (Zhang and McMurry, 1987).

3.3. Inorganic ions

Fig. 5 shows the inorganic ions concentrations for five inorganic ions (nitrate, sulfate, sodium, chloride, and ammonium). Ion balance calculations showed that particles in $PM_{2.5-0.25}$ and $PM_{0.25}$ were almost fully neutralized; however, the calculation was not possible for $PM_{10-2.5}$ without information for calcium and carbonate.

3.3.1. $PM_{10-2.5}$

In $PM_{10-2.5}$, the average of total inorganic ion concentrations of the four sites is 2.5 ± 0.2 μg m^{-3} (Fig. 5a). Nitrate is the dominant component and its contribution to total ions ranges from 31.9% on the I-710 to 50.1% for the I-110. A previous study in Los Angeles in this size fraction also found nitrate to be the major component of inorganic ions (Cheung et al., 2011). Given the southwesterly sea breeze from the Pacific Ocean, sea salt is considered to be a contributor to $PM_{10-2.5}$ and its primary components, sodium and chloride, have concentrations of 0.9–1.2 μg m^{-3} and make up 37–49% of total inorganic ions. On average, sea salt levels are 27.7 ± 11.0% higher on roadways relative to USC levels, however, the difference is not statistically significant ($p = 0.43$). Sulfate concentrations are relatively low (0.27–0.29 μg m^{-3}) and constitute 10–12% of total ions across all sites.

3.3.2. $PM_{2.5-0.25}$

It is clear from the mass balance that inorganic ions dominate the $PM_{2.5-0.25}$ mode (Fig. 4b) and that its concentrations are highest in this mode ($p < 0.05$) (Fig. 5b). The I-110, I-710, Wilshire/Sunset, and USC sites have total inorganic ions concentrations of 3.9 ± 0.5 μg m^{-3}, 2.4 ± 1.6 μg m^{-3}, 3.3 ± 0.1 μg m^{-3}, and 5.0 ± 1.4 μg m^{-3}, respectively. However, the differences in inorganic ions concentrations are not statistically significant ($p = 0.17$). With the exception of chloride, the concentrations of inorganic ions are comparable to or lower than USC levels. Although the total concentrations vary, the individual inorganic ion contributions are relatively consistent across all sites, with nitrate dominating and accounting for 44–52%, followed by sulfate (17–29%) and sodium (10–18%).

3.3.3. $PM_{0.25}$

Of the three size fractions, the $PM_{0.25}$ has the lowest total inorganic ion concentrations, with an average of 1.29 ± 0.14 μg m^{-3}

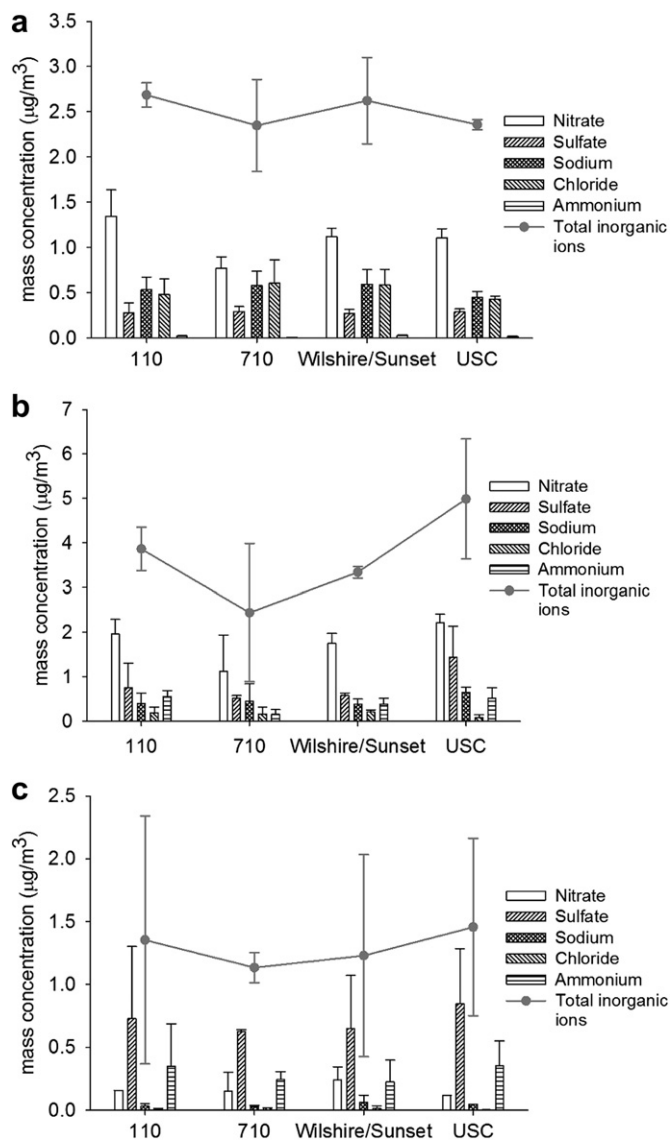

Fig. 5. Inorganic ions concentrations for a) $PM_{10-2.5}$, b) $PM_{2.5-0.25}$, and c) $PM_{0.25}$. Error bars represent one standard deviation.

across the four sites (Fig. 5c). Overall, there is not a substantial amount of variation in concentration and composition among the three roadway environments. Sulfate is the dominant component and contributes 52–58% of total inorganic compounds across all sites, followed by ammonium (18–29%) and nitrate (8–19%). Previous studies in the Los Angeles basin also found sulfate to be the major inorganic component in $PM_{0.25}$ (Minguillon et al., 2008; Arhami et al., 2009). Similar to $PM_{10-2.5}$ and $PM_{2.5-0.25}$, the inorganic ions concentrations in $PM_{0.25}$ at the roadway environments are generally comparable or less than USC background levels.

3.4. EC and OC

Fig. 6 shows the average total carbon (TC), EC, OC, and water-soluble OC (WSOC) concentrations for the four sites. TC is the sum of EC and OC (Fig. 6a). $PM_{0.25}$, $PM_{2.5-0.25}$, and $PM_{10-2.5}$ constitute 67–71%, 16–19%, and 11–15% of total TC, respectively. The I-710 exhibits the greatest TC concentration of 9.3 ± 2.2 μg m^{-3} and USC has the lowest of 4.1 ± 0.2 μg m^{-3}. In terms of enrichment ratios relative to USC, the I-710, I-110, and Wilshire/Sunset are 2.2 ± 0.4, 1.7 ± 0.2, and 1.7 ± 0.1, respectively. Of TC, OC accounts for 78–91% and EC accounts for 9–22%.

EC concentrations are significantly higher in $PM_{0.25}$ relative to the other two size fractions ($p < 0.05$), and 80–95% of total EC is accounted for in this mode for all four sites (Fig. 6b). The most substantial difference among the three roadway environments is the EC levels observed on the I-710, of which EC concentrations are 2.1 ± 0.2 μg m^{-3} and 4.1 times greater than USC, while levels on the I-110 and Wilshire/Sunset are 1.1 ± 0.2 μg m^{-3} and 0.6 ± 0.02 μg m^{-3} and 2.1 and 1.3 times greater, respectively. Given that EC is a primary pollutant and can be used as a tracer for diesel emissions at least in the Los Angeles Basin, the differences in EC concentrations may be explained by the truck density in each roadway. The I-710 and I-110 had truck flows of 470 h^{-1} and 243 h^{-1}, respectively, for the periods of sampling (CalTrans). Although the I-110 has a greater total vehicle flow than the I-710, the near two-fold difference in truck flows highlights the significant contribution of HDVs to EC. The Wilshire/Sunset traffic flow consists mainly of passenger cars and few compressed natural gas (CNG) buses, which emit lower levels of PM and gaseous pollutants than conventional diesel buses (Hesterberg et al., 2008). The negligible HDV flow is evident in the comparable levels of EC on Wilshire/Sunset to the USC background site.

Similar to EC, OC is significantly higher in $PM_{0.25}$ ($p < 0.05$), of which 62–67% of total OC is accounted for in all 4 sites, while in $PM_{2.5-0.25}$ and $PM_{10-2.5}$, OC accounts for 17–21% and 13–17%, respectively (Fig. 6c). Previous studies of ultrafine PM, $PM_{0.18}$, in Los Angeles also found OC to be the dominant PM component (Hughes et al., 1998; Arhami et al., 2009). Total OC concentrations for the I-110, I-710, Wilshire/Sunset, and USC are 6.1 ± 0.8 μg m^{-3}, 7.3 ± 2.0 μg m^{-3}, 6.2 ± 0.1 μg m^{-3}, and 3.6 ± 0.04 μg m^{-3}, respectively; enrichment ratios for the roadways relative to USC are 1.7 ± 0.2, 2.0 ± 0.5, and 1.7 ± 0.1, respectively. Organic mass originates from a mix of both primary (vehicular emissions) and secondary sources (photochemical reactions) (Kim et al., 2002). The more than two-fold difference in OC concentrations observed on the three roadway environments shows the significant contribution of vehicular traffic to OC.

Fig. 6d shows WSOC concentrations, which are also significantly higher in $PM_{0.25}$ ($p < 0.05$). Total WSOC concentrations for the I-110, I-710, Wilshire/Sunset, and USC are 1.8 ± 0.02 μg m^{-3},

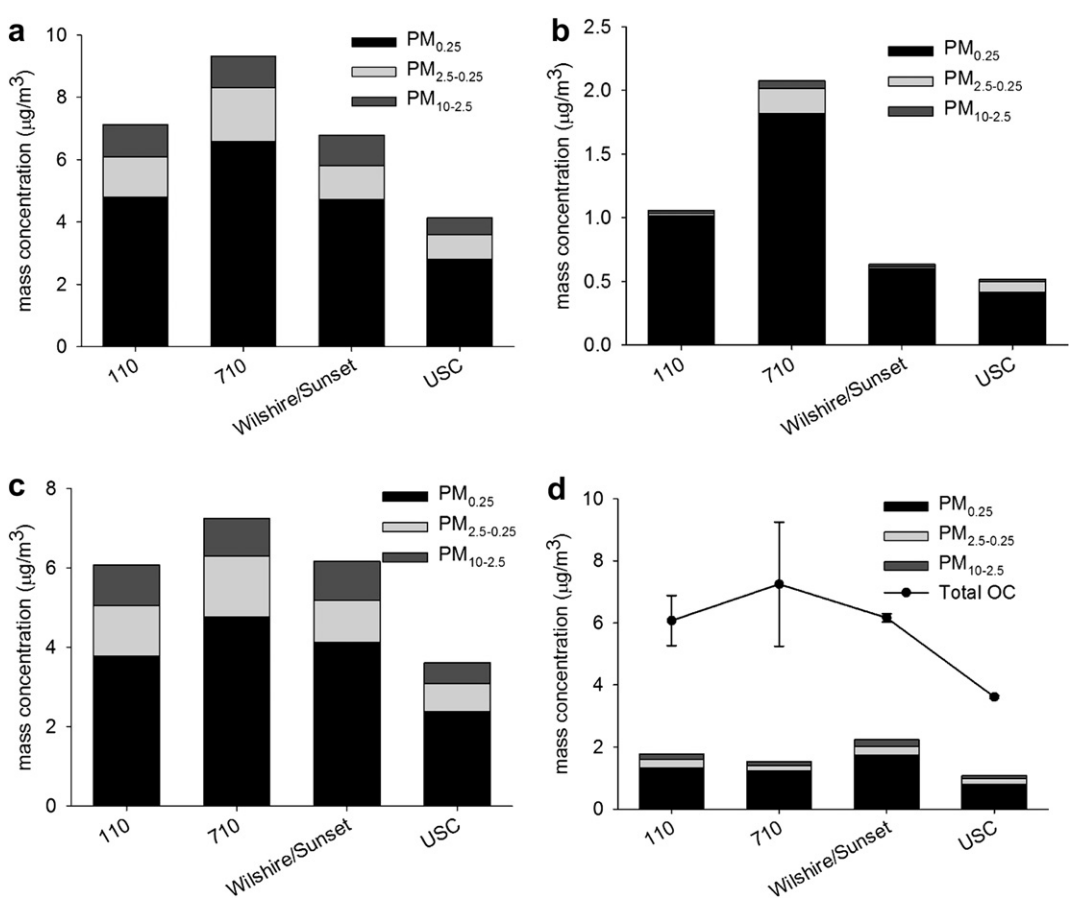

Fig. 6. Size-segregated concentrations of a) total carbon (TC), b) elemental carbon (EC), c) organic carbon (OC), and d) water-soluble OC (WSOC).

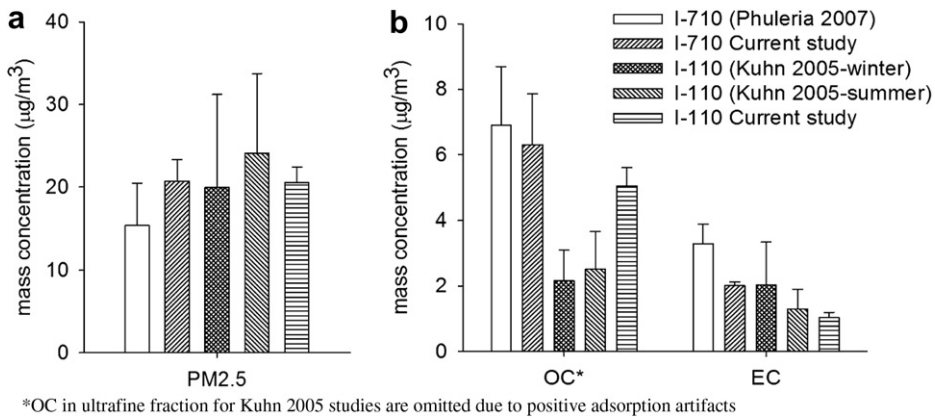

Fig. 7. Comparison of $PM_{2.5}$ concentrations of a) mass and b) OC and EC to previous studies conducted at fixed sites in the vicinity of the I-110 and I-710.

1.5 ± 0.1 μg m^{-3}, 2.2 ± 0.2 μg m^{-3}, and 1.1 ± 0.03 μg m^{-3}, and accounts for 29.4 ± 3.8%, 21.9 ± 5.6%, 36.3 ± 3.1%, and 29.8 ± 0.8% of total OC. The relatively low WSOC fractions observed are consistent with a previous study that showed OC in urban settings is less oxidized than OC in rural settings, and thus less water-soluble (Salma et al., 2007).

3.5. Comparison to previous studies in Los Angeles

Fig. 7 shows a comparison of $PM_{2.5}$ mass, OC, and EC concentrations from the current study to previous studies conducted at fixed sites near the I-710 and I-110 (Kuhn et al., 2005a, 2005b; Phuleria et al., 2007). In Phuleria et al. (2007), the I-710 study was conducted directly adjacent to the roadway, at approximately 10 m from the centerline of the freeway and sampling took place in February and March 2006 from 11 a.m. to 7 p.m. Kuhn et al. (2005a) was conducted in winter 2005 (January) and Kuhn et al. (2005b) was conducted in summer 2004 (May). However, the sampling site for these two studies was in the northern "gasoline-only" portion of the I-110 where HDVs were not allowed, while results from the current study are based on a 3.9% HDV fraction. OC concentrations in the ultrafine fraction were omitted due to positive adsorption artifacts from the Kuhn et al. (2005a,b) studies. Differences in PM mass and OC concentrations are not substantial for either roadway comparisons. However, average EC concentrations seem to have decreased by approximately 50% for both roadways in the last 5 years.

This improvement may be partially explained by differences in sampling conditions (i.e. time of year), but is most likely the result of the Port of Los Angeles Clean Truck Program, which calls for a progressive ban on older polluting drayage trucks (San Pedro Bay Ports Clean Air Action Plan (CAAP)). In October 2008, all pre-1989 drayage trucks were banned from entering the Port and in January 2010, all 1989–1993 drayage trucks were banned in addition to 1994–2003 drayage trucks that were not retrofitted. Finally, in January 2012, drayage trucks that do not meet the 2007 Federal Clean Truck Emission Standards will be banned. The impact of the program has been regional, and its effectiveness is illustrated in the decrease in EC levels of the current I-110 study (with 3.9% HDVs) in comparison to the previous I-110 study (no HDVs). This is consistent with a study that observed a reduction in BC emission factors after the implementation of diesel particle filter (DPF) retrofit and truck replacement program in 2010 at the Port of Oakland (Dallmann et al., 2011).

4. Concluding remarks

A sampling campaign was conducted to assess the on-road chemical composition of PM in three roadway environments (I-110, I-710, and Wilshire/Sunset) for three size fractions ($PM_{10-2.5}$, $PM_{2.5-0.25}$, and $PM_{0.25}$). Based on average PM concentrations, $PM_{0.25}$ is heavily influenced by vehicular emissions, which is evident in its substantial contribution to TC, including both EC and OC components, while $PM_{2.5-0.25}$ and $PM_{10-2.5}$ are less impacted by on-road sources. Inorganic ions compositions (%) were found to be relatively consistent across the three roadways. Although concentrations in $PM_{2.5-0.25}$ and $PM_{0.25}$ at USC were higher than corresponding levels at roadways, the differences were not significant ($p = 0.17$). The most notable finding from this study is the elevated levels of EC on the I-710, which were 4.0 times greater than the USC ambient site, while the I-110 and Wilshire/Sunset roadways were approximately 2.1 and 1.2 times greater, respectively. In comparison to previous studies, EC levels appear to have decreased substantially on both the I-110 and I-710, which may be explained by the effectiveness of the Port of Los Angeles Clean Truck Program that began in 2008.

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Appendix. Supplementary material

Supplementary data related to this article can be found online at doi:10.1016/j.atmosenv.2012.03.028.

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