Atmos. Chem. Phys. Discuss., 11, 30719–30755, 2011
www.atmos-chem-phys-discuss.net/11/30719/2011/
doi:10.5194/acpd-11-30719-2011

Atmospheric Chemistry and Physics Discussions

Characterization of near-highway submicron aerosols in New York City with a high-resolution time-of-flight aerosol mass spectrometer

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Received: 19 September 2011 – Accepted: 2 November 2011 – Published: 16 November 2011

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Abstract

Knowledge of the variations of mass concentration, chemical composition and size distributions of submicron aerosols near roadways is of importance for reducing exposure assessment uncertainties in health effects studies. The goal of this study is to deploy and evaluate an Atmospheric Sciences Research Center-Mobile Laboratory (ASRC-ML), equipped with a suite of rapid response instruments for characterization of traffic plumes, adjacent to the Long Island Expressway (LIE) – a high-traffic highway in the New York City Metropolitan Area. In total, four measurement periods, two in the morning and two in the evening were conducted at a location approximately 30 m south of the LIE. The mass concentrations and size distributions of non-refractory submicron aerosol (NR-PM_1) species were measured in situ at a time resolution of 1 min by an Aerodyne High-Resolution Time-of-Flight Aerosol Mass Spectrometer, along with rapid measurements (down to 1 Hz) of gaseous pollutants (e.g., HCHO, NO_2, NO, O_3, and CO_2, etc.), black carbon (BC), and particle number concentrations and size distributions. The particulate organics varied dramatically during periods with highest traffic influences from the nearby roadway. The variations were mainly observed in the hydrocarbon-like organic aerosol (HOA), a surrogate for primary OA from vehicle emissions. The inorganic species (sulfate, ammonium, and nitrate) and oxygenated OA (OOA) showed much smoother variations – with minor impacts from traffic emissions. The concentration and chemical composition of NR-PM_1 also varied differently on different days depending on meteorology, traffic intensity and vehicle types. Overall, organics dominated the traffic-related NR-PM_1 composition (> 60 %) with HOA being the major fraction of OA. The traffic-influenced organics showed two distinct modes in mass-weighted size distributions, peaking at ~ 120 nm and 500 nm (vacuum aerodynamic diameter, D_{va}), respectively. OOA and inorganic species appear to be internally mixed in the accumulation mode peaking at ~ 500–600 nm. The enhancement of organics in traffic emissions mainly occurred at ultrafine mode dominated by HOA, with little relation to the OOA-dominated accumulation mode. From Fast Mobility Particle

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Sizer (FMPS)measurements, a large increase in number concentration at ~ 10 nm (mobility number mean diameter, D_m) was also found due to traffic influence; though these particles typically contribute a minor fraction of total particle mass. Results here may have significant implications for near-highway air pollution characterization and exposure assessments. Our results suggest that exposure assessments must take into account the rapid variations of aerosol chemistry over short distances near roadways, and also that long-term monitoring of air pollutants throughout the day on different types of days is necessary to accurately gauge exposure to individuals.

1 Introduction

On-road vehicle emissions constitute a major source of ultrafine particle pollution and gaseous pollutants (e.g., CO, CO_2, NO_x, and volatile organic compounds (VOCs)) in urban environments (Rogge et al., 1993; Kirchstetter et al., 1999; Zhu et al., 2002a; Canagaratna et al., 2004; Kolb et al., 2004; Zavala et al., 2006; Thornhill et al., 2010). Of particular, the number concentrations of ultrafine particles (UFP) from vehicle emissions have been found to account for a major fraction of total number concentrations though they might contribute a small fraction of total volume and mass (Zhu et al., 2002b; Ban-Weiss et al., 2010). Growing evidence shows that people living or otherwise spending substantial time within ~ 300 m of highways are exposed to these pollutants more than persons living a greater distance. Exposure to the traffic-related air pollutants is associated with the adverse health effects including the prevalence of asthma and chronic obstructive pulmonary disease (COPD) diagnosis, reduced lung function in children, and potential cardiac and pulmonary mortality (Brunekreef et al., 1997; Brugge et al., 2007; Lindgren et al., 2009; Pope et al., 2009). Studies also suggest that the UFP measurements should be conducted in the vicinity of freeway for exposure experiments since UFP number concentration measured at 300 m downwind from the freeway was indistinguishable from upwind background concentration (Zhu et al., 2002a).

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The pollutant levels and aerosol properties vary rapidly as a function of traffic type, traffic flow, meteorology, atmospheric mixing conditions and chemical reactions over short distances near highways. The high variability of near-highway pollution levels remains a challenge for exposure assessment. In order to capture the rapid changes, mobile laboratories equipped with fast response systems (usually 1 s) are often deployed to measure gaseous and particulate pollutants (Canagaratna et al., 2004; Kolb et al., 2004; Herndon et al., 2005; Zavala et al., 2009; Canagaratna et al., 2010; Thornhill et al., 2010). Different driving modes, e.g., roadside stationary measurements, chase studies, and fleet average sampling have been conducted to investigate the variability of gases and particle emission ratios (Zavala et al., 2009). A recent study combining the fast on-road measurements of vehicle emissions and positive matrix factorization (PMF) receptor modeling within the Mexico City Metropolitan Area (MCMA) was able to distinguish the gasoline and diesel emission exhaust (Thornhill et al., 2010). Gasoline-powered vehicle emissions were found to dominate the contribution to CO, aromatic and carbonyl species, and ammonia, but contributed a small fraction of $PM_{2.5}$ and a minor fraction of BC.

Most of previous studies have been focused on particle number concentration and gaseous species (Morawska et al., 2008). Measurements of particle number concentration and number-weighted size distributions downwind of a freeway in Los Angeles showed three distinct ultrafine modes with geometric mean diameters of 13, 27, and 65 nm, respectively, within a distance of 30 m (Zhu et al., 2002b). The number distributions rapidly evolved to larger particles (> 10 nm) within 30–90 m downwind of freeways due to condensation and coagulation. The particle composition may also change dramatically because of size evolution (Zhang et al., 2004). The concentrations of primary emission tracers CO, BC, and hydrocarbon-like organic aerosol (HOA) also tracked the exponential decrease of particle numbers as the distance from the freeway increased (Zhu et al., 2002a; Canagaratna et al., 2010). Similarly, Roorda-Knape et al. (1998) also observed the curvilinear decrease of black smoke and NO_2 with distance from the motorway depending on wind direction and traffic intensity.

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Despite the extensive measurements of on-road vehicle emissions, investigations of particle composition are rather limited. Since particle composition is a factor determining particle toxicity, there is a need for characterization of fine particle chemistry in different environments. The measurements of elemental composition near a busy Southern California freeway found enriched toxic trace metals (e.g., Sb, Cu, Ba etc.) in $PM_{0.18}$ from the vehicles emissions (Ntziachristos et al., 2007). The enrichments of primary traffic emissions including BC and the toxic metals above were also observed by comparing the elements and PM components collected simultaneously at urban background, traffic and heavy traffic locations (Amato et al., 2011). In contrast, the secondary species sulfate and ammonium did not show consistent enrichments due to their low vehicle emissions.

The aerosol mass spectrometer (AMS) (Jayne et al., 2000; Jimenez et al., 2003; Drewnick et al., 2005; DeCarlo et al., 2006) allows us to measure non-refractory submicron aerosol ($NR\text{-}PM_1$) species (organics, sulfate, nitrate, ammonium, and chloride) with time resolution from seconds to minutes. A deployment of Quadrupole-AMS inside the Aerodyne mobile laboratory which involved chasing vehicles found that diesel aerosol particles show very similar spectral patterns to lubricating oil, and their mass-weighted size distributions peak at ~90 nm in vacuum aerodynamic diameters (D_{va}) (Canagaratna et al., 2004). Chemical composition measurements of individual ambient spikes during morning rush hours by a nano-aerosol mass spectrometer showed low O/C ratios (generally < 0.5), consistent with their hydrocarbon characteristics (Zordan et al., 2008). Durant et al. (2010) observed a similar downwind profile of organics to particle number concentration and NO with the highest concentration at 34 m and then a decrease of ~2 times within 100–250 m from the highway. Nitrate and sulfate, however showed little spatial variation with distance from the highway due to their minor contributions from vehicle emissions (Canagaratna et al., 2010).

The relatively newer version of AMS, i.e., High Resolution Time-of-Flight Aerosol Mass Spectrometer (HR-AMS) (DeCarlo et al., 2006) allows to resolve most ion fragments below $m/z < 100$ and determine the elemental composition (C, H, O, and N) and

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oxidation properties of organic aerosol (OA) (DeCarlo et al., 2006; Aiken et al., 2008). In addition, Positive Matrix Factorization (PMF; (Paatero and Tapper, 1994)) analysis of high resolution mass spectra can further deconvolve OA into different components corresponding to different sources and properties and playing different roles in atmospheric chemistry (Zhang et al., 2011).

Knowledge of the particle composition and size distributions, and the causes of their variations near roadway, is of importance for exposure assessment in health studies. Given that the pollutants may vary significantly in a short time near highways throughout the day, there is a need for multiple roadside measurements of gaseous and particle pollutants at different times and on different days to reflect these changes and reduce the errors of exposure estimates. In the present work, we conducted four roadside measurements, i.e., two in the morning and two in the evening, with a mobile laboratory equipped with a suite of fast response instruments during the summer 2009 Field Intensive Study at Queens College in New York (Sun et al., 2011). The objective of our study is to characterize the variations of mass concentrations and chemical composition of NR-PM_1 species, size distributions of NR-PM_1 species and OA components, and oxidation properties of OA near a highway in different days.

2 Methods

2.1 Sampling site and measurements

The roadside measurements were conducted at the parking Lot 15 on the campus of Queens College (Fig. 1, site C) with the state-of-the-art Atmospheric Sciences Research Center-Mobile Laboratory (ASRC-ML). The ASRC-ML was built upon a 2007 diesel powered Dodge 2500 Sprinter Van equipped with catalytic diesel filter trap emission control. During the roadside measurements, all the instruments were powered alternatively between a 4 kW gasoline generator and rechargeable Li ion batteries. A more detailed description of the ASRC-ML has been given in Lin et al. (2011). The

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ASRC-ML was situated ~ 30 m south of the Long Island Expressway (LIE, I-495), one of the busiest high-traffic highways in the NYC metropolitan area, and ~ 6 m from the Horace Harding Expressway (HHE), the frontage road of LIE. The LIE has three westbound lanes and three eastbound lanes with an additional lane exiting LIE to HHE. The Kissena Blvd with three northbound lanes and three southbound lanes is approximately 200 m east of our sampling site. Another high traffic road, Main Street (6 lanes in total), is approximately 600 m west of the sampling site. Additionally, a MTA bus stop is located approximately 5 m north of ASRC-ML. Two buses, i.e., Q88 and Q74, stop at the sampling site for ~ 1 min every ~ 7–15 min and ~ 15–20 min, respectively. The earliest daily arrival of Q88 and Q74 at the sampling site is ~ 6:14 a.m. and 7:23 a.m., respectively. In total, four measurement periods, two in the morning (03:41–08:49 a.m., 28 July; 04:24–10:06 a.m., 30 July) and two in the evening (2:50–5:12 p.m., 27 July; 5:09–10:00 p.m., 1 August), were conducted in this study. Except for the four roadside experiments, the ASRC-ML was situated at parking Lot 6 (Fig. 1, site B) for routine measurements of aerosols and gaseous species from 13 July–3 August (Sun et al., 2011). It should be noted that an Aerodyne-ML (Kolb et al., 2004) was deployed in parallel to the ASRC-ML in the morning of 28 July with a focus on characterizing the concentration gradients of aerosols and gaseous species in the vicinity of LIE and adjacent residential communities to improve our understanding of population exposures.

Size-resolved NR-PM_1 species (organics, sulfate, nitrate, ammonium, and chloride) were measured in-situ by an Aerodyne HR-AMS (DeCarlo et al., 2006) that is operated inside the ASRC-ML. In order to capture the fast variation of aerosol species, the HR-AMS was operated under the sensitive V-mode and the high mass resolution (~ 6000) W-mode alternatively every 1 min. Under V-mode operation, the AMS cycled through the mass spectrum (MS) mode and the particle time-of-flight (PToF) mode every 30 s. The parallel measurements inside ASRC-ML include absorption coefficient (B_{abs}) by a DMT single-wavelength (781 nm) Photoacoustic Soot Spectrometer (PASS-1), formaldehyde (HCHO) and NO_2 by an Aerodyne Quantum Cascade Laser (QCL) Spectrometer, CO_2 and H_2O by a Li-COR CO_2 analyzer, trace gases of O_3,

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NO, and NO_2 by 2B technologies analyzers, and volatile organic compounds (VOCs) by a BTEX analyzer, aerosol number concentrations by a water-based condensation particle counter (WCPC, TSI 3781) and size-resolved number concentrations by a TSI Fast Mobility Particle Sizer (FMPS, Model 3091, 5.6–560 nm) spectrometer. All the measurements were performed at a fast time resolution from 1 min down to 1 Hz. However, some collocated data were missed due to the malfunction of instruments or non-operating because of limited power supply. Collocated measurements of aerosols and gaseous species were also conducted in New York State Department of Environmental Conservation (DEC) Air Monitoring Building (Fig. 1, site A). A key instrument deployed at this site is an Aerosol Chemical Speciation Monitor (ACSM) recently developed by Aerodyne Research Inc. for long-term routine measurements of mass concentrations and chemical composition of ambient aerosols with low cost and maintenance (Ng et al., 2011). The non-refractory aerosol species were measured in-situ at a time resolution of 30 min from 16 July to 9 September. In addition, the meteorology data including wind direction, wind speed, relative humidity, and temperature measured at site A were used as a reference since the synchronous measurement of meteorology at Site C (Lot 15) was not available. Detailed descriptions of other collocated measurements are given in Sun et al. (2011) and Lin et al. (2011).

All the data in this study are reported at ambient temperature and pressure conditions in Eastern Standard Time (EST), which equals Coordinated Universal Time (UTC) minus 5 h or local time (i.e., East Daylight Time – EDT) minus 1 h.

2.2 AMS data analysis

The aerosol mass spectrometry data were analyzed for the mass concentrations and size distributions with the standard AMS data analysis software (SQUIRREL v1.51, Sueper, 2011) and the ion-speciated composition and elemental composition i.e., oxygen-to-carbon (O/C), hydrogen-to-carbon (H/C), nitrogen-to-carbon (N/C), and organic mass-to-organic carbon (OM/OC) ratios with the high resolution data analysis software (PIKA, v1.10) and APES (v 1.04A) (http://cires.colorado.edu/jimenez-group/

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ToFAMSResources/ToFSoftware/index.html), respectively. The same data analysis procedures have been detailed in Sun et al. (2011).

We applied positive matrix factorization (PMF) analysis to the high resolution mass spectra (HRMS) acquired near the roadway. The mass spectral and error matrices were prepared following the procedures described in DeCarlo et al. (2010). The mass spectral datasets from four experiments were combined into one single dataset. The PMF2.exe algorithm (v. 4.2) in robust mode (Paatero and Tapper, 1994) was run on the combined dataset to force the retrieved mass spectral profiles to be identical for all four experiments. The PMF2 solutions were then evaluated with an Igor Pro-based PMF Evaluation Tool (PET, v. 2.04) (Ulbrich et al., 2009). In addition, the combined dataset was also analyzed with PMF by excluding the dataset of 27 July when ambient aerosol particles were contaminated by the silicone from the ASRC-ML generator exhaust, and similar results were found. Four OA components were identified including a hydrocarbon-like OA (HOA) that represents primary OA from incomplete fossil fuel combustion given its low O/C ratio (O/C = 0.08) and good correlations with combustion tracers such as NO_x and BC (Aiken et al., 2009; Sun et al., 2011), a regional, oxidized low-volatility oxygenated OA (LV-OOA, O/C = 0.49), a less photo-chemically aged semi-volatile OOA (SV-OOA, O/C = 0.34), and a similar nitrogen-enriched OA (NOA) characterized by higher N/C ratio (= 0.08) than other OA components. Increase of the number of factors led to a further split of SV-OOA into two subtypes of OOA rather than identification of cooking-related OA (COA) that was observed at Lot 6, indicating the COA accounted for a minor fraction of OA during four roadside measurements.

A tracer-based method was used to derive the size distributions of HOA and OOA in this study. *m/z* 44 (mainly CO_2^+) that shows tight correlation with OOA (Zhang et al., 2005a,c) is often used as a tracer for OOA. The size distribution of OOA is thus derived by normalizing the integrated signals of *m/z* 44 between 30–1500 nm to the OOA concentrations (Zhang et al., 2005c). For Quadrupole-AMS measurements, the size distribution of HOA is derived from *m/z* 57 after subtracting contributions from OOA (Zhang et al., 2005c). HRMS show that *m/z* 57 at urban sites in summer mainly constitutes

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a hydrocarbon ion ($C_4H_9^+$) and an oxygenated ion ($C_3H_5O^+$). While $C_4H_9^+$ tightly correlates with HOA, $C_3H_5O^+$ shows good correlation with *m/z* 44 (Aiken et al., 2009; Sun et al., 2011), indicating that $C_3H_5O^+$ is primarily OOA and $C_4H_9^+$ is a better tracer for HOA in comparison to the total *m/z* 57 signal which includes contributions from both $C_4H_9^+$ and $C_3H_5O^+$. Thus we derived the size distribution of HOA using *m/z* 57 by subtracting the contribution of $C_3H_5O^+$, and then normalized the signals between 30–1500 nm to the HOA concentrations. This method is found to show similar results to those derived from the tracer-based method reported by Zhang et al. (2005c).

3 Results and discussion

3.1 Mass concentration and chemical composition

Figure 2 shows the time series of mass concentrations of NR-PM_1 species and OA components and meteorological variables during four measurements near highway, and Fig. 3 presents the average composition for each experiment. Aerosol particles on 27 July are found to have a large interference from the ASRC-ML generator exhaust with silicone contamination (see Supplement for details), thus our discussions will focus on the other three observations. The inorganic species (sulfate, nitrate, and ammonium) vary smoothly throughout the two mornings of 28 and 30 July. This is not surprising because vehicles are not direct emitters of nitrate aerosols (Gillies et al., 2001), and the introduction of ultra-low sulfur fuel (< 15 ppm S by weight) leads to very low emissions of sulfur. Their variations are thus mainly related to the meteorology, boundary layer height, and also likely photochemical reactions. Organics, however, show different behaviors between the early and late mornings. Organics show smooth variations in early mornings, e.g., before 5:30 a.m. on 28 July and 7:30 a.m. on 30 July, while vary dramatically with frequent spikes during late morning periods due to the penetration of roadway plumes. A further analysis of the variations of OA components (Fig. 2) indicates that the organic spikes are primarily caused by the HOA, a surrogate

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of primary emissions from vehicles. Note that the intensities of the spikes fluctuate minute to minute, which reflect the rapid temporal changes in traffic flow and traffic type, and also meteorology. The variation of LV-OOA is flat throughout the morning, which can be explained by its regional characteristics since photochemical production of secondary OA (SOA) would not play significant roles in the mornings. We also observed a dramatic decrease of SV-OOA from 2.0 to 0.8 $\mu g\,m^{-3}$ after 7:30 a.m. on 30 July, likely due to the dilution from HOA-dominated traffic plumes near highway. Compared to the two morning measurements, all aerosol species covary in the evening on 30 July, consistent with the internally mixed characteristics of aerosol particles (see Sect. 3.2). Note that the average mass concentration of NR-PM_1 is 20.7 $\mu g\,m^{-3}$ on 28 July, about twice as high as the 8.5 and 11.9 $\mu g\,m^{-3}$ measured on 30 July and 1 August, respectively, mainly due to the stagnant conditions associated with low wind speed ($< 2\,m\,s^{-1}$). This is consistent with the observation of high aerosol optical depth (AOD) values across the whole Northeast US on 28 July, while relatively low AOD on the other two days (Fig. S1). The aerosol composition shows differences between mornings and evenings, but overall, organics is the major component, accounting for > 55 % of total NR-PM_1 mass, with sulfate being the second most abundant species.

To better characterize the impact of traffic plumes on aerosol composition, each morning measurement was further classified into two events, i.e., less traffic (LT) and more traffic (MT) that were separated at 5:30 a.m. and 7:30 a.m. on 28 and 30 July, respectively. The NR-PM_1 shows very similar average bulk composition before and after 5:30 a.m. on 28 July regardless of the traffic influences, due to persistent wind from the direction of the campus of QC rather than from the LIE highway throughout the morning. However, the OA composition shows differences with ~ 12 % enhancement of HOA contribution to OA during the MT event. This is consistent with a synchronous elevation of ultrafine mode organics (Sect. 3.2) while the accumulation mode remains unchanged. Since the wind direction was from the north, the enhancements of HOA and ultrafine mode organics are likely due to MTA bus emissions at the bus stop rather than from LIE. Comparatively, 30 July shows significant differences in aerosol

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composition between the LT and MT events associated with a change in wind direction from the QC campus to LIE. The contribution of organics therefore elevates 18 %, accounting for 74 % of total NR-PM_1 mass during the MT event. The HOA contribution jumps from 27 % to 62 %, associated with a decrease of SV-OOA from 42 % to 13 % of OA. We didn't observe clear traffic influences on 1 August, consistent with the OA composition being dominated by LV-OOA (79 %) with a minor contribution of HOA (∼ 9 %). The significantly different composition might be also related to the low traffic flow with less diesel trucks (∼ 1.2 % of total vehicles) on Saturday.

We further compared the aerosol measurements near highway by HR-AMS and the site A by ACSM. The synchronous measurements in the same day at Lot 6 by the HR-AMS and at site A by the ACSM are also plotted as a comparison (Fig. 4 and Fig. S2). As shown in Fig. 4, sulfate near the roadway appears to be ∼ 10–15 % lower than campus site on both 28 and 30 July. Nitrate does not show significant differences between the two sites in both mornings. Organics show slightly higher concentration after 5:30 a.m. on 28 July due to traffic influences. Figure 4b further demonstrates that the slightly higher OA during MT is mainly caused by HOA rather than OOA. Given that the roadside and campus sites are both located upwind of LIE on 28 July (wind direction from S and SW), the sporadic traffic spikes observed might be mainly due to the influences of MTA bus emissions rather than the LIE traffic emissions. Comparatively, while the organics before 7:30 a.m. on 30 July are very close between the roadside and campus sites, it was almost twice elevated after 7:30 a.m. due to the influences of traffic plumes from LIE. The HOA near roadway is more than 3 times elevated in comparison to the campus site while OOA is very close between these two sites. These results overall suggest that traffic plumes show the biggest impact on the HOA component, but minor effects on inorganic species and the SOA components.

3.2 Size distributions

Figure 5 shows the average size distributions of NR-PM_1 species and OA components for the four case events. Organics present distinct bimodal mass-weighted distributions

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during two morning events which are characterized by an ultrafine mode peaking at ~ 120 nm, and a large accumulation mode peaking at ~ 500–600 nm. The inorganic species, however, show a single accumulation mode overlapping with that of organics. The ultrafine mode, also known as "traffic" mode, with dominant contribution by organics has been observed previously at the same site (Drewnick et al., 2004) and other urban sites (Allan et al., 2003; Zhang et al., 2005b), and also in vehicle exhausts from chase studies (Canagaratna et al., 2004). The ultrafine mode organics show good correlations with HOA and the tracers for primary emissions, e.g., BC, NO_x, and CO (Zhang et al., 2005b), demonstrating the dominant contribution of traffic emissions to this mode. Size distributions of OA components further confirm that the "traffic" mode is primarily contributed by HOA with only a minor contribution from OOA (Fig. 5b). A comparison of the size distributions of organics between LT and MT (Fig. 5a) show a significant enhancement of the ultrafine mode organics while the accumulation mode shows little change. In order to determine the enhancement, a log-normal fitting (Seinfeld and Pandis, 2006) was performed to the size distributions of organics on 28 and 30 July. Generally, 2 modes and sometimes 3 modes are needed to obtain the best log-normal fit. The fitting results including the mass concentration and mean diameter for each mode are shown in Table 1 and Fig. S3. The results show that the "traffic" mode during the period with more traffic influences is elevated by ~ 50 % from 4.5 to 6.6 $\mu g\,m^{-3}$ on 28 July, and 2.6 times from 1.0 to 2.6 $\mu g\,m^{-3}$ on 30 July. The accumulation modes, on the other hand, show little variations. The same comparisons applied to OA components suggest that the enhancement of "traffic" mode organics is primarily due to HOA. In fact, HOA during MT on 28 July shows very similar size distributions to BC measured by a Soot-Particle AMS (SP-AMS)(Massoli et al., 2010). This further demonstrates the primary characteristics of the "traffic" mode organics. The simultaneous measurements carried out at Lot 6 also presents similar bimodal distributions for the HOA tracer $C_4H_9^+$ (*m/z* 57) in the morning (Sun et al., 2011). All these results suggest the external mixing characteristics of "traffic" mode organics with secondary inorganic species. OOA, however, shows very similar size distributions to sulfate for all

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events despite the traffic influences, indicating that these two species are secondary in nature and often internally mixed. The aerosol species and OA components in the evening of 1 August also presents a very similar and single large accumulation mode, indicating that they are internally mixed, consistent with the tight correlations between organics and sulfate ($r^2 = 0.53$), and the overall aged OA (O/C = 0.41).

Figure 6 shows the evolution of the number distributions on 30 July measured by the FMPS. Due to the influences of traffic emissions, the number distributions show a dramatic change at 7:30 a.m. Before 7:30 a.m., the number-weighted concentrations show a bimodal structure, peaking at ~ 15 nm and ~ 40–50 nm (mobility diameter, D_m), respectively. In addition, the second mode is more significant than the first mode. After 7:30 a.m., the number concentrations are characterized by a burst of particles at D_m =~ 10 nm associated with a decrease of large particles due to the traffic influences from LIE. The distributions show approximate 3 modes, peaking at ~ 10, 30, and 50 nm, respectively, similar to those observed ~ 30 m downwind of a highway in Los Angeles (Zhu et al., 2002b). The significant enhancement of the number concentration of ultrafine particles near highway in comparison to hundreds of meters downwind has been observed widely (Kirchstetter et al., 1999; Zhu et al., 2002a; Zavala et al., 2009). It is important to capture the rapid changes of number concentrations to improve the accuracy of exposure estimates despite the fact that these particles might only contribute a small fraction of total mass.

3.3 Investigation of OA near roadway

The mass spectra and time series of the four OA components identified near roadway are shown in Figs. 7 and 2, respectively. The mass spectra of OA components show very similar spectral patterns to those identified at Lot 6 (Fig. S4). Briefly, LV-OOA is characterized by the high *m/z* 44 (mainly CO_2^+) and O/C ratio (0.49), showing overall resemblance tothose observed at other sites (Aiken et al., 2010; Allan et al., 2010; DeCarlo et al., 2010; Hildebrandt et al., 2010). SV-OOA with O/C of 0.34 represents a less oxidized component characterized by the high ratio of *m/z* 43 to 44. HOA on

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the other hand, shows the typical hydrocarbon ion series ($C_nH^+_{2n-1}$ and $C_nH^+_{2n+1}$) as previously reported (Zhang et al., 2005a). Similar to NOA observed at Lot 6, the NOA near roadway is also characterized by amine-related ion peaks, e.g.,$C_2H_6N^+$, $C_3H_8N^+$, and $C_4H_{10}N^+$ etc. But overall NOA is only a minor fraction of total OA (< 8 %). Note that LV-OOA and SV-OOA observed near roadway appear to be slightly less oxidized in comparison to those observed at Lot 6, which are indicated by their lower O/C ratios (0.63 and 0.38 for LV-OOA and SV-OOA, respectively at Lot 6). Figure 8 shows a comparison of the HRMS before and after 7:30 a.m. on 30 July. The difference spectrum (Fig. 8c) is characterized by prominent peaks of *m/z* 41 ($C_3H^+_5$), 43 ($C_3H^+_7$), 55 ($C_4H^+_7$), 57 ($C_4H^+_9$), 69 ($C_5H^+_9$), and 71 ($C_5H^+_{11}$) which are typical *m/z*'s of vehicle exhaust (Canagaratna et al., 2004), confirming the significant traffic influences after 7:30 a.m.

HOA correlates well with BC ($r^2 = 0.52$) and NO_x ($r^2 = 0.56$) on 30 July (Fig. 9). This is consistent with the conclusion from a number of studies that HOA is likely a surrogate for combustion POA associated with traffic emissions (Zhang et al., 2005c, 2007; Aiken et al., 2009; Ulbrich et al., 2009). The linear regression slope of HOA/NO_x (= 0.044 μg m^{-3} $ppbv^{-1}$) is close to the value observed at Lot 6 (0.045), while that of HOA/BC (1.02) is slightly lower than at Lot 6 (1.29). It's interesting to note that HOA does not correlate with BC on 28 July ($r^2 = 0.03$). A detailed analysis found that the HOA plumes did not correspond to a simultaneous increase of BC, suggesting the different impacts of traffic emissions on HOA and BC on 28 July. Indeed, the chase study conducted by the Aerodyne group on the same day shows that the emissions of organics, BC, CO_2, and NO_x strongly depend on the types of vehicles (Massoli et al., 2010). Heavy and medium duty trucks and the NYC Metropolitan Transit Authority (MTA) standard buses emit large quantities of both OA and BC, while MTA buses using clean technology such as compressed natural gas (CNG) and hybrid buses emit less OA and almost no BC (Massoli et al., 2010). A chase study conducted in 2000 during the $PM_{2.5}$ Technology Assessment and Characterization Study in NYC (PMTACS-NY) investigated particulate emissions from in-use NYC vehicles and showed that diesel buses have much larger emission ratios (0.10–0.23 g NR-PM_1/kg Fuel) than those fueled by

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CNG (0.034 g NR-PM_1/kg Fuel) (Canagaratna et al., 2004). These results might explain our observations of organic plumes with no simultaneous enhancement of BC, i.e., NR-PM_1 in the morning of 28 July were mainly influenced by the emissions from the nearby MTA CNG buses, which emit a large fraction of OA and minor amounts of BC. This also suggests that our sampling site was less affected by the high traffic flow (~ 10 000 vehicles per hour, of which ~ 12 % is diesel trucks based on our manual counting) on 28 July. Another possibility is that the relatively small silicone contamination from the generator exhaust tubing might have affected the properties of BC (Timko et al., 2009).

We further calculated the emission ratios (ER) of HOA and BC from LIE during the MT period on 30 July. The ER on 28 July was not calculated since the ASRC-ML was located upwind of LIE and did not capture the direct vehicle emissions from the highway. It should be noted that the ER calculated in this study is more representative of the average mixed emissions from all types of vehicles on LIE, which is different from those of individual vehicles from chase studies. The ER can be calculated as (1) ER = ΔSignal/ΔCO_2, where ΔCO_2 is the difference of CO_2 and background CO_2 or (2) by performing a linear fit to HOA or BC versus ΔCO_2 (Fig. 10). The background CO_2 (~ 410 ppm on 30 July) was calculated as the average of the lowest 5 % of data during the MT period. The ER calculated from the two methods are consistent, e.g., 0.20 vs. 0.18 $\mu g\,m^{-3}$ of HOA per ppm of CO_2. Given that the variations of NR-PM_1 after 7:30 a.m. on 30 July are overwhelmingly controlled by HOA, the ER of HOA would be also representative of the ER of NR-PM_1. The average ER of HOA agrees within the range of ERs obtained by chasing different types of vehicles in NYC in 2000 (Canagaratna et al., 2004). This implies that the vehicle emissions of organics are likely not improved, at least not significantly, during the last 10 yr. This conclusion is also supported by the observation that the mass concentrations of OA in 2009 (Sun et al., 2011) show a slight increase in comparison to those observed in the same month in 2001 (Weimer et al., 2006), though sulfate has been considerably reduced, likely due to the introduction of ultra-low sulfur fuel. BC shows comparable ER (0.19 $\mu g\,m^{-3}$/ppm CO_2)

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as HOA, consistent with the co-variations of these two species on 30 July (Fig. 9a). HOA and BC together contribute an average emission of $\sim 0.4\,\mu g\,m^{-3} PM_1/ppm\ CO_2$, corresponding to an emission index (EI) of $\sim 0.71\,g\,PM_1/kg$ fuel assuming that the weight fraction of carbon in diesel fuel is 0.87 (Kirchstetter et al., 1999). Note that the emission ratio calculated here represents an average value under mixed-traffic conditions (i.e., gasoline and diesel vehicles) on one day. It might vary significantly depending on traffic types and driving conditions on different days.

4 Conclusions and implications

We have characterized the mass concentrations, chemical composition and size distributions of submicron aerosol species in the vicinity of a major highway in NYC with an Aerodyne HR-AMS deployed inside the ASRC-ML. Four experiments were conducted on different days with two in the morning and two in the evening. Our results show that the organic aerosols vary dramatically due to influences from vehicle emissions near roadway, while inorganic species including sulfate and nitrate show relatively smooth variations. The enhancements of aerosol particle mass concentrations during traffic-influenced periods are therefore mainly attributed to organics. Also, the mass concentrations and chemical composition of submicron particles vary significantly from day to day, but overall organics account for a the major fraction (55–74 %) of the total mass. Our results suggest that people living in close proximity to the highways are regularly exposed to higher level of particle pollution than people living upwind or far away. Distinct mass-weighted bimodal distributions, peaking at ~ 120 nm and 550 nm (D_{va}), respectively, are observed for organics in the two morning measurements. However inorganic species (sulfate, ammonium, and nitrate) present a single large accumulation mode, peaking at ~ 550 nm. The different size distributions between organic and inorganic species suggest that fresh traffic emitted aerosol particles are externally mixed with more aged, secondary particles. Significant enhancements in ultrafine organic aerosol mass concentrations and particle number concentrations at ~ 10 nm (D_m) are

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frequently observed in traffic plumes. A further analysis of OA composition and size distributions suggests that the ultrafine mode organics are dominated by HOA from vehicle emissions near highway. OOA in the large accumulation mode, however, shows minor influences from traffic emissions. In comparison to the morning experiments, all NR-PM_1 species appear to be internally mixed at a broader accumulation mode with OA composition being dominated by OOA in the evening event, likely due to the low traffic flow on Saturday and consistent wind direction from upwind areas.

Our results are of importance for near-highway air pollution characterization and exposure assessments. The results confirm that the mass concentrations and chemical composition of submicron aerosol particles change rapidly over short distances near highways, strongly depending on wind direction, vehicle types and traffic flow. Also we demonstrate a large difference of aerosol particles between morning and evening in different days. Exposure assessments must take into account of these variations and differences. Further, our results suggest that a long-term measurement of air pollutants throughout the whole day on different days is necessary to gain accurate exposure information. It's also important to perform the same measurements in different seasons since the aerosol dynamics, photochemical reactions, and meteorology may vary significantly among seasons (Zhang et al., 2004).

Supplementary material related to this article is available online at: http://www.atmos-chem-phys-discuss.net/11/30719/2011/acpd-11-30719-2011-supplement.pdf.

Acknowledgements. This study was supported by the Office of Science (BER), US Department of Energy, Atmospheric Systems Research (ASR) Program (Grants No. DE-FG02-08ER64627, DE-SC0002191), the One Hundred Person Project of the Chinese Academy of Sciences, New York State Energy Research and Development Authority, New York State Department of Environmental Conservation, and New York State Office of Science, Technology and Academic Research. We thank the New York State Department of Environmental Conservation for use of their facility, and particularly Mike Christopherson, Ed Marion, and Dirk Felton. We thank the Queens College administration and staff, especially Wing Chan, for hosting this study.

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Table 1. Mass concentrations (C_i) and median diameters ($D_{va,i}$) of the modes calculated from lognormal fitting of average size distributions of organics during less traffic (LT) and more traffic (MT) periods on 28 July and 30 July, respectively.

		$D_{va,1}$ nm	C_1 $\mu g\,m^{-3}$	$D_{va,2}$ nm	C_2 $\mu g\,m^{-3}$	$D_{va,3}$ nm	C_3 $\mu g\,m^{-3}$	
28 Jul	LT	127	4.5	548	6.5	655	1.3	
	MT	120	6.6	567	7.7			
30 Jul	LT	119	1.0	386	2.2	622	1.5	
	MT	129	2.6			539	3.3	

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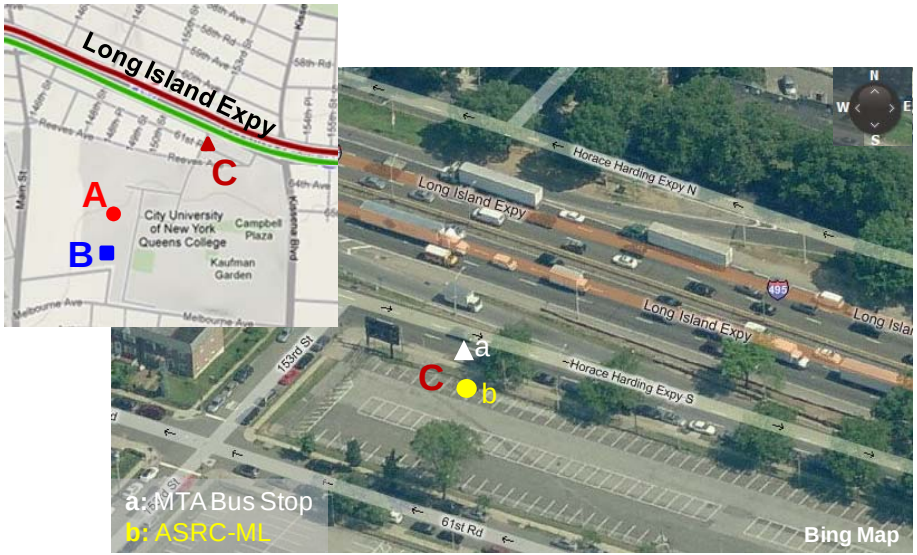

Fig. 1. Map of sampling sites of **(A)** DEC ambient monitoring station, **(B)** Parking Lot 6, and **(C)** Parking Lot 15. An MTA bus stop **(a)** is ~ 5 m north of ASRC-ML **(b)**.

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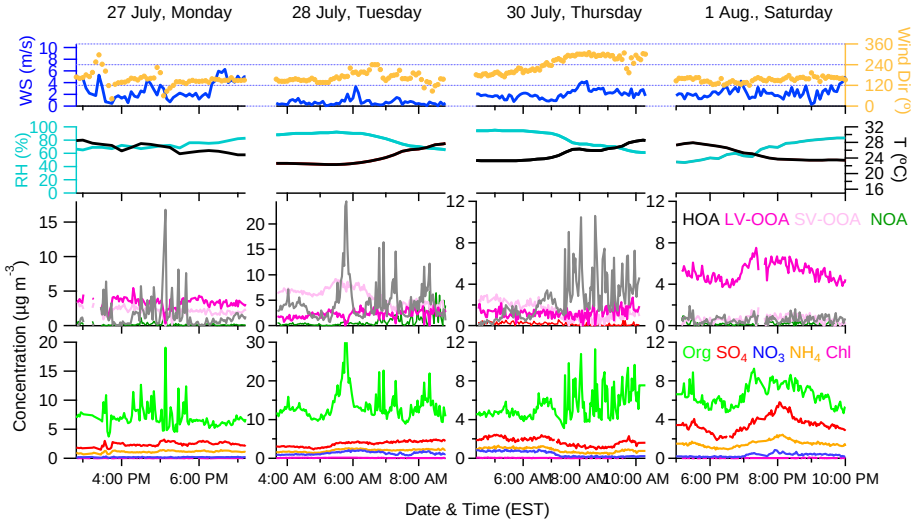

Fig. 2. Time series of mass concentrations of NR-PM_1 species (organics, sulfate, nitrate, ammonium, and chloride), OA components (LV-OOA, SV-OOA, HOA, and NOA) and meteorology during four roadside measurements.

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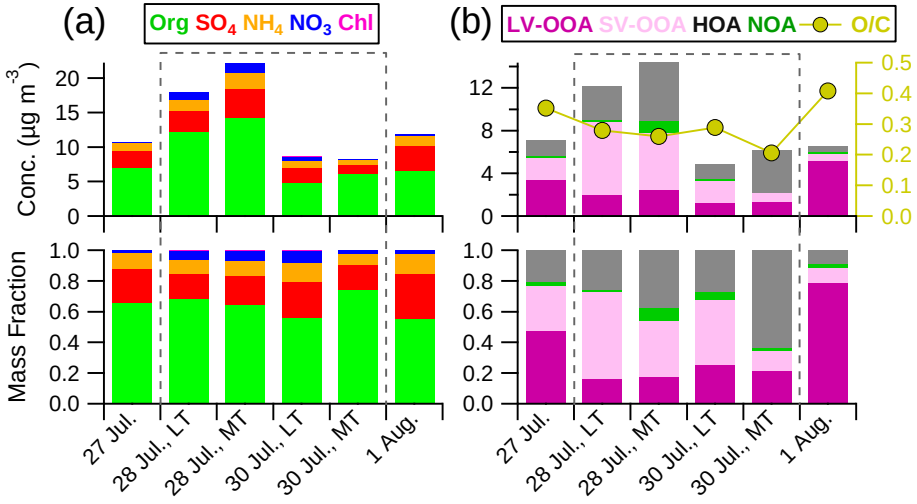

Fig. 3. Average composition of **(a)** NR-PM_1 and **(b)** OA for each roadside measurement. Each morning measurement (dash line regions) was further classified into two events with less traffic (LT) and more traffic (MT) influences, respectively. Details are described in the text. In addition, the O/C ratio for each event is also shown in **(b)**.

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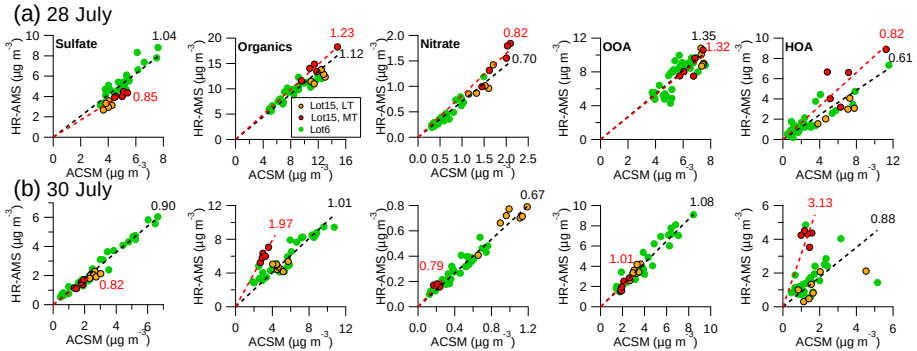

Fig. 4. Comparisons of mass concentrations of sulfate, organics, nitrate, OOA and HOA measured at Lot 15 by HR-AMS and DEC monitoring station by ACSM on **(a)** 28 July and **(b)** 30 July. The green solid circles show the comparisons of synchronous measurements at Lot 6 and DEC monitoring station in the same day. The numbers shown on the plots are linear regression slope with intercept forcing to zero.

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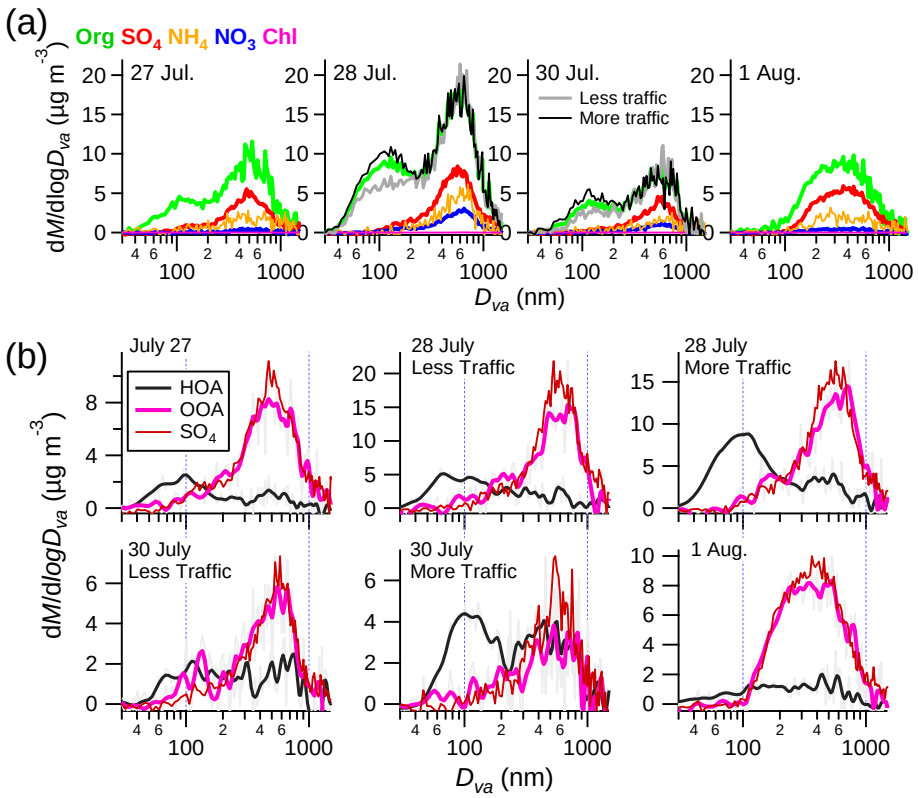

Fig. 5. Average size distributions of **(a)** NR-PM_1 species and **(b)** HOA and OOA. The size distributions of organics with less and more traffic influences in two mornings are also shown in **(a)**. The size distributions of sulfate that were scaled to the peak values are shown in **(b)** for a reference. Note that the size distributions of HOA and OOA (light gray lines) were smoothed with 3 points using binominal algorithm.

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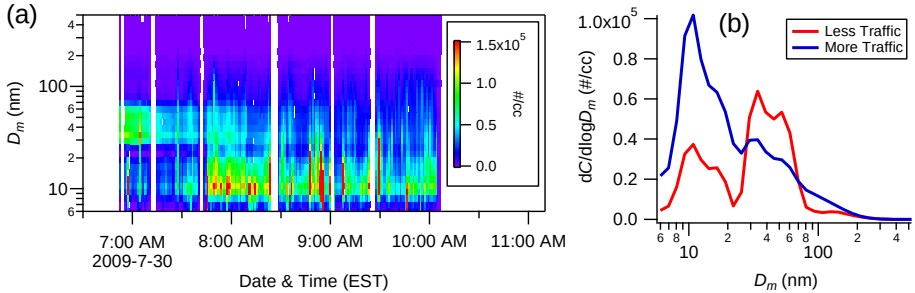

Fig. 6. **(a)** size-resolved number concentrations measured by a FMPS on 30 July. **(b)** shows the average size distributions of number concentrations before 7:30 a.m. (less traffic) and after 7:30 a.m. (more traffic), respectively.

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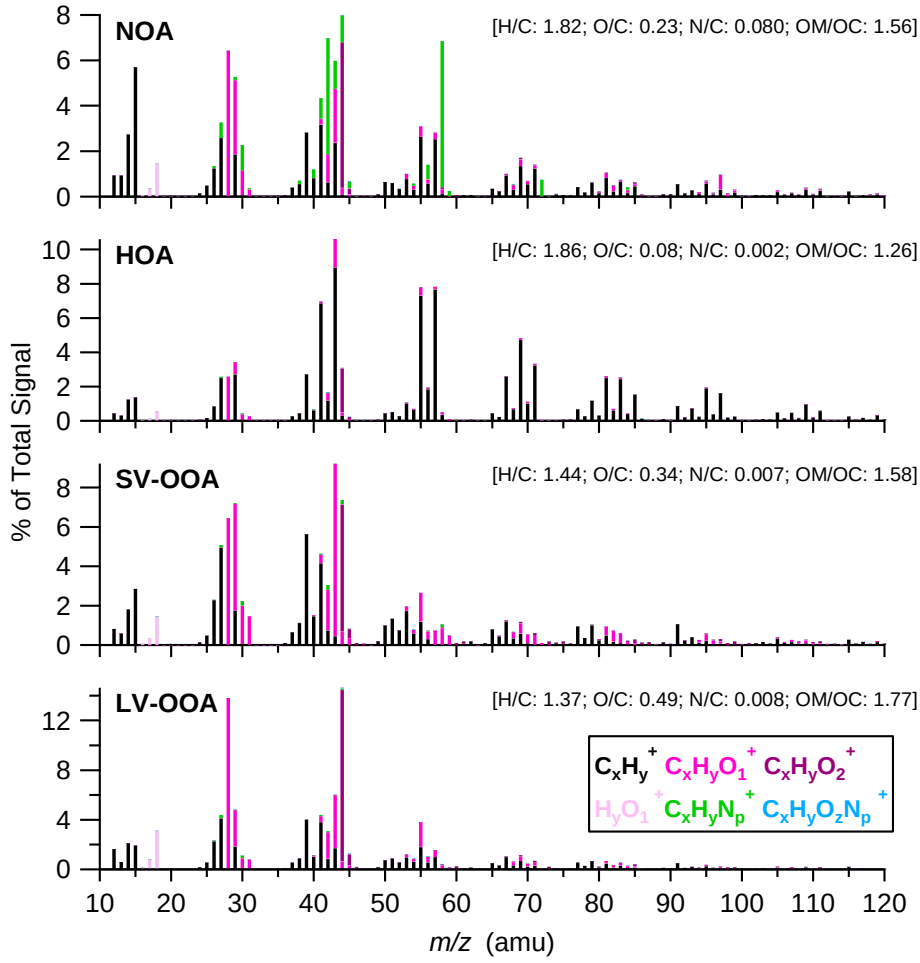

Fig. 7. High resolution mass spectra of OA components. The elemental ratios and OM/OC ratio of each component are also shown in the legends.

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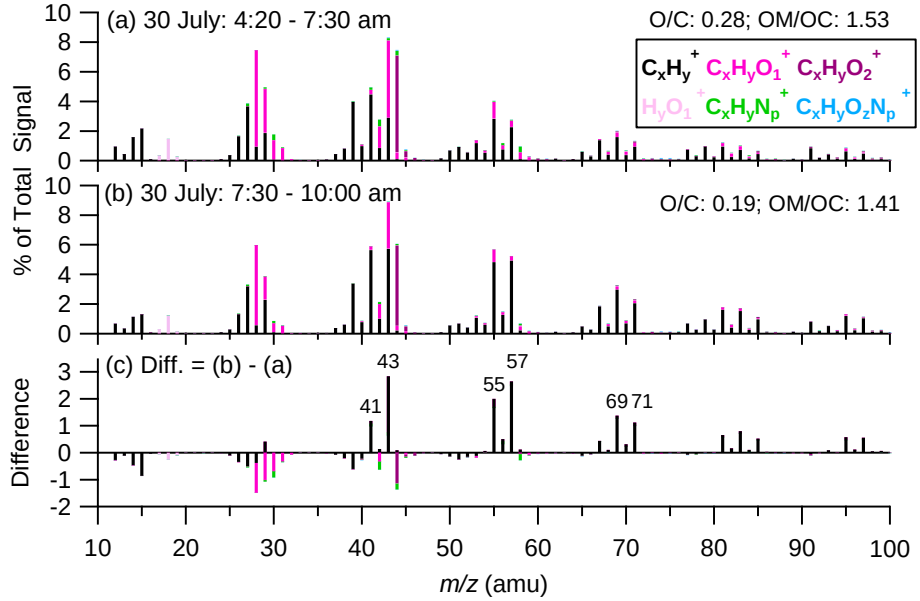

Fig. 8. Average high resolution mass spectra of OA **(a)** before and **(b)** after 7:30 a.m. on 30 July. **(c)** shows the difference spectra between **(b)** and **(a)**.

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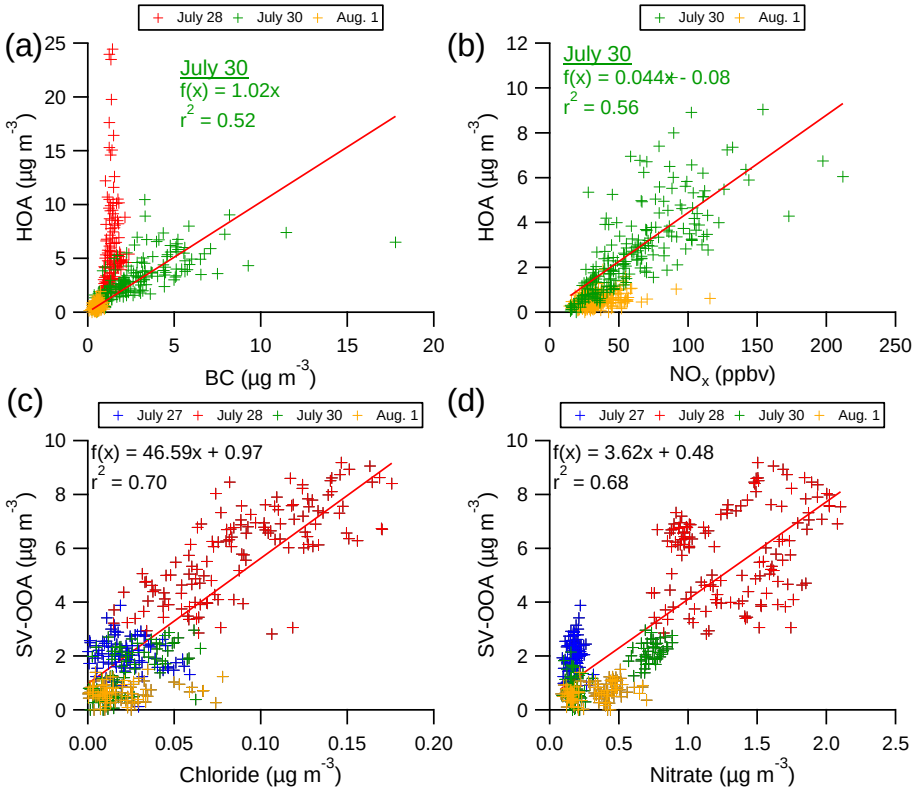

Fig. 9. Correlation plots of **(a)** HOA vs. BC, **(b)** HOA vs. NO_x ($NO + NO_2$), **(c)** SV-OOA vs. Chloride, **(d)** SV-OOA vs. nitrate. Missed BC and NO_x data are due to either the malfunction of instruments or non-operating because of limited power supply.

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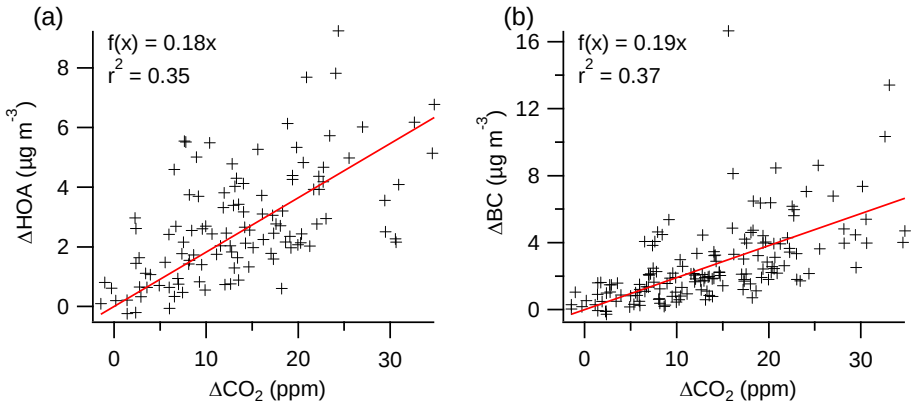

Fig. 10. Correlation plots of **(a)** ΔHOA vs. ΔCO_2, **(b)** ΔBC vs. ΔCO_2 during the period with more traffic influences, i.e., after 7:30 a.m. on 30 July.

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