Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2017-432
Manuscript under review for journal Atmos. Chem. Phys.
Discussion started: 27 June 2017

Atmospheric Chemistry and Physics Discussions

Evaluation of traffic exhaust contributions to ambient carbonaceous submicron particulate matter in an urban roadside environment in Hong Kong

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Abstract. Road traffic has significant impacts on local air quality particularly in densely urbanized and populated areas where vehicle emissions are a major local source of ambient particulate matter. Characterization studies on road traffic emissions in Hong Kong are sparse due to the complexity of the urban built environment and the encountered transient engine loads which make emission factor and dispersion modeling approaches difficult to implement. This study provides an estimation of the contribution of vehicles powered by different fuels (gasoline, diesel, LPG) to carbonaceous aerosol based on ambient aerosol mass spectrometer (AMS) and elemental carbon (EC) measurements and real traffic data in an urban inner city environment with the aim to gauge the importance of different vehicle types to particulate matter burdens in a typical urban street canyon. On an average per-vehicle basis, contributions of diesel and gasoline vehicles to carbonaceous PM_1 were similar, contrary to previous studies which attributed higher particulate matter emissions to diesel vehicles. This clear reduction is likely due to recent control strategies targeted at commercial vehicles and buses. LPG vehicles were found to be a negligible source of elemental carbon and only small contributor to organic particulate mass despite their high abundance in the traffic mix. Gasoline vehicle exhaust contained similar amounts of elemental carbon and organic species, while diesel vehicle exhaust was dominated by elemental carbon.

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1. Introduction

1.1. Primary particulate matter from motor vehicles in urban areas

Primary emissions from on-road motor vehicles comprise gas-phase species, such as CO, NOx and volatile organic compounds, as well particulate components predominantly in the fine ($PM_{2.5}$) and ultrafine particle size range ($PM_{0.1}$) and mostly as carbonaceous species, i.e. organic matter and elemental carbon (Giechaskiel et al., 2014). Increased acute occurrence and risk of chronic development of cardiovascular and pulmonary diseases are important epidemiological effects of particulate matter inhalation (Davidson et al., 2005;Pope, 2007;Valavanidis et al., 2008;WHO, 2011). In urban areas with high population and building densities, proximity to vehicle emissions poses a significant public health risk and renders paramount importance to the characterization and quantification of vehicle emissions in such areas (Kumar et al., 2014;Uherek et al., 2010). Contributions of vehicle emissions to ambient particulate matter levels vary widely and are dependent on a complex set of parameters, including dispersion characteristics of the sampling site, traffic flow, local meteorology and influence of other aerosol emission and formation sources. Vehicle technology, such as engine type and fitted exhaust control devices, have also been noted to significantly affect measured emission rates and species distribution across tested vehicles (Alves et al., 2015;Franco et al., 2013;Jang et al., 2016;Kam et al., 2012;Karjalainen et al., 2014;Kwak et al., 2014). Investigations on the impacts of different vehicle groups on ambient air pollution and related effects such as health implications (Kheirbek et al., 2016;Zhang and Batterman, 2013;Levy et al., 2010) typically rely on combinations of source inventories with dispersion modelling and combined physical-chemical models with significant uncertainties arising from the complexity of the urban built environment (Kumar et al., 2011;Belcher et al., 2013), accuracy of emission factors and inventory currentness (Simon et al., 2008;Fuzzi et al., 2015).

In this study, we take a different approach to evaluating contributions of the three major engine-type vehicle groups (gasoline, diesel, LPG) in Hong Kong to carbonaceous aerosol by combining time-resolved ambient measurements by aerosol mass spectrometry (AMS) and ECOC analysis with vehicle count data. Measurements were undertaken within a street canyon at a typical inner-city location where urban driving patterns with transient engine loads and frequent stop-and-go traffic are prevalent, which may not be adequately reflected in dynamometer or cruising speed chase studies, but are more representative of pedestrian exposure levels particularly in view of growing concerns about exposure to air pollutants and their public health impacts in densely populated and built-up environments in Hong Kong and similar megacities across East and Southeast Asia.

1.2. Background of vehicle emission studies in Hong Kong

Despite a low vehicle-to-population ratio (<10%), private and public road transport of passengers and goods is extensive throughout Hong Kong. In the year of this study (2013) 680,914 vehicles were registered in the Hong Kong Special Administrative Region (HKSAR) which accounted for an average of 35.17 million vehicle kilometers per day across all modes of road transport such as heavy goods haulage, commercial transport, private and public transportation. Passenger journeys on

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Hong Kong's three major franchised bus companies in 2013 were in excess of 1.1 billion (Transport Department, 2014). Road traffic has been recognized as a major local emission source and subjected to various regulatory efforts over the years, such as a large-scale fuel switch of taxis to a virtually all-LPG fleet, partial conversion of minibuses to LPG engines, ex-gratia incentive schemes for vehicle replacement or control device retrofitting and increased stringency in new-vehicle imports (Environmental Protection Department, 2013;Lyu et al., 2017;Ning et al., 2012).

Characterization studies on particle-phase species associated with traffic emissions in Hong Kong have mainly focused on semi-continuous online and offline filter analysis with carbonaceous components (sum of elemental carbon and organic matter) typically constituting the bulk (45-70%) of particulate mass in $PM_{2.5}$ at roadside sampling sites and up to 82% in road tunnel environments (Cheng et al., 2010;Huang et al., 2014;Lee et al., 2006;Louie et al., 2005;Research Centre of Environmental Technology and Management, 2005). Among major primary and secondary aerosol sources of ambient particulate matter which were identified from speciated long-term filter samples (1998-2008) of $PM_{2.5}$ by source apportionment analysis utilizing positive matrix factorization, vehicle emission exhibited substantial contributions: at general measurement sites (urban, rooftop), vehicle emissions accounted for 8-9 μg m^{-3} equivalent to 11-25% of total $PM_{2.5}$ with lower fractions in the fall and winter seasons primarily due to the masking influence of regional and long-range transport. Higher fractions (22-47%) and concentrations (19-23 μg m^{-3}) were resolved from roadside samples (street level) and with seasonal variations similar to those at the general sites attributed to similar effects of non-local pollution sources (Yuan et al., 2013).

Generally, low overall organic carbon (OC) to elemental carbon (EC) ratios (0.6-0.8) which are typical for locations in direct proximity to primary combustion sources were observed whereas in comparison samples from urban rooftop sites exhibited lower contributions of carbonaceous constituents (<50%) and greater impacts of oxidized secondary organic species with correspondingly higher overall OC/EC ratios (~1.9) (Louie et al., 2005;Cheng et al., 2010;Lee et al., 2006). Impacts of long-range transport of continental aerosol were evident in both higher total PM and higher OC concentrations in the winter months. By contrast, seasonal variations of EC concentrations were weak. Higher EC concentrations were typically associated with rush hour traffic and confirm the local nature of EC and its relation to mainly on-road traffic (Lee et al., 2006;Cheng et al., 2010;Huang et al., 2014;Louie et al., 2005). While earlier studies (*samples dated pre-2005*) reported EC concentrations in the range of 11-25 μg C m^{-3} in $PM_{2.5}$ at the open roadside (Louie et al., 2005;Cheng et al., 2010;Lee et al., 2006), more recent measurements (*2012-2013*) indicate a significant reduction in overall roadside EC burdens with concentrations ~ 5 μg C m^{-3} (Huang et al., 2014;Sun et al., 2016;Lee et al., 2015). Vehicle-related OC and organic matter (OM) concentrations at a roadside measurement site were estimated to ~2 μg C m^{-3} and ~7 μg m^{-3} respectively in 2012, accounting for one-third of total OC in $PM_{2.5}$ and one-quarter of total $PM_{2.5}$ (Huang et al., 2014).

Gas-phase species contributions were evaluated utilizing VOC canister samples collected in locations with different dominant-vehicle types in Hong Kong in 2003 (Ho et al., 2013). Propane, n- and i-butane accounted for over 80% of identified species in the LPG vehicle dominated samples, while toluene was the most abundant species in the gasoline vehicle dominated samples. Ethene and ethyne were enriched in diesel exhaust dominated samples. Contributions of vehicle-related VOCs to ozone formation were evaluated from the maximum incremental reactivity, with toluene (15-17%) and propene (7-8%)

accounting for the largest shares (Ho et al., 2013). Vehicle emission factors were estimated by a mass-balance model with differential measurements near the entrance and exit of a tunnel bore in 2003 and manual vehicle counts. Diesel vehicles were found to contribute substantially more to NO_x, $PM_{2.5,}$ and PAH than gasoline vehicles which dominated CO emissions. Diesel and LPG-fueled vehicles dominated total measured VOCs and total measured carbonyl compounds. EC emission factors of diesel vehicles (131 mg veh^{-1} km^{-1}) were ~40 times higher than those of non-diesel (i.e. gasoline and LPG-fueled) vehicles (3.2 mg veh^{-1} km^{-1}). For OC, the difference amounted to a smaller factor of ~8 with emission factors of 67.9 mg veh^{-1} km^{-1} and 8.5 mg veh^{-1} km^{-1} for diesel and non-diesel vehicles respectively. In terms of fractional contribution, OC made up 51% of $PM_{2.5}$ in non-diesel emissions, while EC made up 51% of $PM_{2.5}$ in diesel emissions. Contributions of inorganic species including ions and trace metals in traffic emissions were minor amounting to only ~10% (Cheng et al., 2010;Research Centre of Environmental Technology and Management, 2005). While these emission factors compared fairly well with those from similar studies undertaken in the 1990s (Gertler et al., 2001;Lowenthal et al., 1994;W. Kirchstetter et al., 1999) in other parts of the world, they are unlikely to reflect the properties of contemporary mobile road traffic emissions in Hong Kong with substantial changes in vehicle fleet composition and the emergence of more advanced engine and emission control technologies over the last 15 years. A mobile measurement platform with an array of on-board PM and gas monitors was deployed in early 2012 for a more up-to-date characterization of fuel-based emission factors of PM, $NO_{x,}$ and butane by chasing vehicle plumes on major roadways and highways. Measurements focused on the evaluation of heavy duty diesel trucks (HDDV), franchised diesel buses (DB) and LPG fueled light buses (LB) with plumes sampled at cruise speed to mitigate biases from engine load-dependent emission variability. HDDVs were the highest emitters of BC (1.6 g kg^{-1} of fuel) followed by diesel buses (1.1 g kg^{-1} of fuel) and LPG light buses (0.1 g kg^{-1} of fuel). Analogously, average particle number emission factors were 3.1 x 10^{15} kg^{-1} of fuel, 3.1 x 10^{15} kg^{-1} of fuel and 0.9 x 10^{15} kg^{-1} of fuel for HDDVs, diesel buses and LPG light buses respectively (Ning et al., 2012). On-road remote sensing measurements of gas-phase emissions showed that gasoline vehicles had higher CO and HC emissions and lower NO emissions compared to diesel vehicles, while LPG vehicles overall emitted more gaseous pollutants than their light-duty petrol and diesel powered vehicle counterparts. The higher LPG vehicle emission factors were attributed to the higher usage rate of mostly LPG-powered taxis and light buses combined with insufficient vehicle maintenance, imploring a gap between tightened regulations and effectiveness in the reduction of on-road emissions. Overall, lower emission factors in newer vehicles within the same engine category were attributed to the efficacy of fitted emission control technologies (Lau et al., 2012).

Despite road traffic representing a major local source of ambient particulate matter in Hong Kong, characterization studies on vehicle emissions in Hong Kong remain sparse. While most previous studies evaluated traffic exhaust contributions in confined environments (tunnels), focal locations (e.g. bus terminus, taxi stand) or by plume chase, this work aims to provide a quantitative estimation of vehicle exhaust related carbonaceous aerosol contributions and their relationship to traffic flow characteristics from ambient measurements in a more complex urban environment. Traffic-related organic aerosol resolved by factor analysis of aerosol mass spectrometry (AMS) data were employed to complement past studies that were predominantly

based on estimations from both online and offline ECOC measurements at different time resolutions ranging from hourly to 24h samples.

2. Methodology

Sampling of ambient particulate matter took place in spring 2013 (7 March 2013 to 15 May 2013) and summer 2013 (16 May 2013 to 19 July 2013). A ground shelter housing a high-resolution time-of-flight aerosol mass spectrometer (HR-ToF-AMS, Aerodyne Inc.), a fast mobility particle sizer (FMPS, TSI Inc.) and an aethalometer (Magee Scientific Inc.) was located on a pedestrian island in the center of Lai Chi Kok Road, a bidirectional urban main road branching off the north-south Nathan Road corridor at the south-east end of the sampling site. Located in the Mong Kok (MK) district in the densely populated and built-up Kowloon peninsula, the measurement site represents an inner-city environment typical for the central city areas of Hong Kong with dense and relatively slow moving traffic and tall bordering buildings. The sampling inlet on top of the shelter at a height of ~3m was equipped with a $PM_{2.5}$ cyclone (flow rate: 16.67 L min^{-1}). A four-way sampling port supplied the HR-ToF-AMS at a flow rate of 0.08 L min^{-1} while the remaining sampling volume was distributed among co-sampling instruments and an auxiliary pump. The AMS sampling stream passed through a diffusion drier (BMI, San Francisco CA, USA, length 1m, silica gel as drying agent) for the removal of gas- and particle-phase water prior to entering the instrument. The Environmental Protection Department (EPD) of the HKSAR Government operates an air quality monitoring site (AQMS) on the same road divider island and provided additional data, such as meteorological data (wind, temperature, relative humidity, solar irradiation) and concentrations of volatile organic compounds (VOCs), standard trace gases such as NO_x, SO_2, and O_3, elemental and organic carbon (EC, OC). Details on employed instrument model and sampling methodologies are available in other dedicated publications (Lee et al., 2015;Environmental Protection Department, 2016;Sun et al., 2016). The AMS data were treated according to general AMS data treatment principles (DeCarlo et al., 2006;Jimenez et al., 2003) with standard software packages (SQUIRREL v1.53G, PIKA v1.12G). Positive Matrix Factorization (PMF) was used to deconvolute high-resolution organic mass spectra following recommended PMF guidelines for AMS data (Zhang et al., 2011) with the AMS PMF analysis toolkit (Ulbrich et al., 2009). An overview of the characteristics of submicron particulate matter from this measurement campaign has been published previously and offers detailed discussions on instrument operation and calibration, data analysis and PMF (Lee et al., 2015). Traffic data were obtained from the Hong Kong Government which were assessed during a counting exercise over three weekdays (noon 28 May 2013 to noon 31 May 2013, Tue to Fri) using automated license plate recognition (ALPR) with four infrared cameras on-site. Traffic along Lai Chi Kok road was monitored with three cameras monitoring all three lanes in one direction (out- or inbound) and the remaining camera monitoring one lane of the opposite direction. Camera positions and the monitored single lane were swapped in 2-3h intervals. Non-personalized data on registered vehicles were obtained, including license class of (*vehicle type*), year of manufacture (*vehicle age*) and engine type (*gasoline, diesel, LPG, others*).

Vehicle count data were pooled per engine type and measured HOA and EC during the traffic counting period decomposed by multilinear regression based on the time series of the engine count data. To reduce the impact of scattered spikes in vehicle count number, HOA and EC concentrations, the time series were subjected to three-point box smoothing prior to regression analysis. Multiple linear regression was performed for two and three factor solutions (see Section 3.3.1) and with a constrained 0-intercept, i.e. assuming negligible impacts of transport on measured traffic-related carbonaceous constituents. Solutions were assessed per statistical significance of resolved factors, adjusted R^2 of the regression and the distribution of residuals.

3. Results

3.1. Chemical and temporal characteristics of traffic-related carbonaceous species

Organic aerosol components were resolved by PMF from the organic part of the measured high-resolution mass spectra acquired during the measurement campaign and scaled to the measured total organic species concentrations based on the unit-mass resolution acquisition mode (Lee et al., 2015). Hydrocarbon-like organic aerosol (HOA) was resolved and identified as the traffic exhaust related factor, exhibiting chemical characteristics typically associated with freshly emitted primary organic aerosol from fossil fuel combustion. Its mass spectrum (Figure S1a in the Supporting Material) is dominated by ions of saturated hydrocarbons (C_nH_{2n+1} series) and its elemental composition is largely void of oxygenated components with correspondingly low O/C ratio of 0.066 and a high H/C ratio of 2.073. These findings are in line with most ambient studies that have identified a similar factor, e.g. (Sun et al., 2012;Sun et al., 2011;Mohr et al., 2012;Lanz et al., 2007;Huang et al., 2010;Sun et al., 2010;Aiken et al., 2009;Setyan et al., 2012). Over the whole sampling period, HOA correlated appreciably with NO_x (R_{pr}=0.64) as well as i- and n-Pentane (R_{pr}=0.66-0.67). The correlation with CO was much weaker (R_{pr}=0.37) indicating the presence of other significant, non-traffic related sources of CO in the vicinity of the Mong Kok measurement site. The highest fractions of HOA among total organic particulate matter in PM_1 were observed with southeasterly and northwesterly surface winds following the street canyon axis along Lai Chi Kok Road (Figure S2a in the Supporting Material). Average HOA mass concentrations varied between spring (3.5 µg m^{-3}) and summer (2.0 µg m^{-3}), with an overall campaign average of 2.8 µg m^{-3}. Diurnal variations of HOA were substantial, with mass concentrations rising sharply in the early morning at 06:00, increasing almost linearly during the morning rush hour at rates between 0.6 and 0.8 µg m^{-3} h^{-1} and leveling off beyond 09:00 (Figure 1a). 90% of the daily HOA was is accumulated between the start of the rush hour and midnight. Minimum HOA concentrations in the low traffic period (00:00 to 06:00) amounted to ~1.7 µg m^{-3} in spring and ~0.7 µg m^{-3} in summer. Average post rush-hour concentrations (09:00 to 00:00) were 4.1 µg m^{-3} and 2.6 µg m^{-3} in spring and summer respectively. Elemental carbon (EC) and organic carbon (OC) were measured semi-continuously at the adjacent AQMS following Huang et al. (Huang et al., 2014). Concentrations of EC and OC in PM_1 were estimated by converting the raw $PM_{2.5}$ concentrations using a PM_1 to $PM_{2.5}$ ratio of 0.8 representing the overall average of PM_1 to $PM_{2.5}$ ratios from previous roadside sampling studies (0.75-0.85) in Hong Kong (Cheng et al., 2006;Lee et al., 2006). Diurnal variations of EC were similar to those of HOA, however, nominal concentrations were not affected by the seasonal transition. This led to significantly different EC/HOA

ratios of 0.86 in spring and 1.78 in summer (Figure S1b in the Supporting Material). As the measurement location falls within the Kowloon urban area, which is characterized by uniform annual traffic flows (Transport Department, 2014), the observed decrease in HOA concentrations was more likely due to significant amounts of HOA being semi-volatile and partitioning in the gas-phase portion of the exhaust emissions in summer than changes in traffic flows. This is also consistent with the trend in relative diurnal variation of HOA (depicted cumulatively in Figure 1b) which remained constant across seasons despite the seasonality in nominal concentrations, and the overall negative correlation of HOA mass concentration and temperature (Figure S2b in the Supporting Material). Both HOA and EC exhibited significant reductions in overall mass concentrations on Sundays between 16% and 36%, compared to the rest of the week (Monday to Saturday) as shown in Figure 1d. Mean reductions in nominal mass concentrations were generally quite similar in the range of 0.8 – 1.0 μg m^{-3} for EC and ~0.5 μg m^{-3} for HOA. The greater overall reduction in EC indicates a greater reduction in the number of diesel vehicles on Sundays, owing to reduced commercial traffic and lower bus frequency. Contributions of vehicle emissions to ambient organic aerosol have been estimated from ECOC measurements at the same site by deriving a characteristic $(OC/EC)_{vehicle}$ ratio during times in which vehicle emissions were dominant. Monthly average primary organic matter concentrations from traffic in $PM_{2.5}$ ranged between 2.7 – 3.4 μg m^{-3} with little seasonal variation, as vehicle-related organics were directly tied to EC concentrations, which did not exhibit a strong seasonal behavior (Huang et al., 2014). Using the same average ratio of $PM_1/PM_{2.5}$ of 0.8 as previously mentioned, this converts into an approximate 2.2 – 2.7 μg m^{-3} of traffic-related primary organics in PM_1 and compares well with the average concentration of traffic-related HOA in this study which amounted to 2.8 μg m^{-3} considering the whole sampling period. However, we observed significantly different concentrations depending on the season with much higher concentrations (3.5 μg m^{-3}) in spring than in summer (2.0 μg m^{-3}). Thus, while the long-term average primary organic aerosol contribution from vehicles is likely well-approximated with the OC/EC approach, its direct dependence on the variation of EC concentrations may lead to over- and underestimation of actual organic concentrations in shorter time frames, e.g. different seasons and different times of the day, as illustrated by the AMS measurement results of this study.

3.2. Traffic and vehicle flow characteristics

During the three-day counting exercise, a total of 21,048 vehicles were registered (~7016 vehicles per day). This accounts for approximately 18% of the annual average daily traffic (A.A.D.T.) of 38,220 vehicles estimated in the 2013 Annual Traffic Census (Transport Department, 2014). The diurnal variation of the counted vehicle number, resolved by broad vehicle classes, and their varying contribution to the vehicle mix during the day are depicted in Figure S2a in the Supporting Material. The maximum hourly vehicle number occurred towards the end of the rush-hour (~9:00) for most vehicle classes (except "*other vehicles*", which mostly comprised motorcycles). For the evening rush-hour (17:00-19:00), only the private car category exhibited a peak in vehicle number. Overall, the post rush-hour total vehicle count remained stable throughout the day, and only fell off after 19:00, largely due to a strong decrease in the number of goods and private vehicles. The variation in the fractional contribution of different vehicles types over the day resembles that assessed by the Transport Department (Transport

Department, 2014) at the closest core traffic counting station at Nathan Road (Figure S2c in the Supporting Material) and affirms that the measured traffic composition during the 72h counting period at Mong Kok was largely representative. At the Mong Kok site, smaller vehicles (*cars and taxis*) accounted for about 60% of total registered vehicles, while heavier vehicles (*buses, vans, trucks*) made up most of the remainder. Total HOA concentrations showed good correlations (R_{pr}>0.6) with most of the measured vehicle-related VOCs, NO_x and EC concentrations as well as the total number of passing vehicles during the counting period (Figure 2). As with the overall campaign data, CO did not correlate with either HOA or EC, indicating the impact of significant non-traffic-related CO sources in the Mong Kok area. Among the counted buses, light buses and goods vehicle, over 96% were running on diesel engines, while 99.9% of counted taxis utilized LPG engines. Private vehicles were almost exclusively powered by gasoline engines (99.4%) due to government restrictions on the import and use of diesel-powered private vehicles at the time of this study.

3.3. Estimation of engine-type contributions

3.3.1. Multiple Linear Regression of HOA and EC

Utilizing the detailed information on average daily traffic composition at the measurement site from the counting exercise, contributions of exhaust from different engine types to overall ambient HOA and EC concentrations can be evaluated. Two factor solutions (diesel + gasoline), as well as three factor solutions (diesel + gasoline + LPG), were considered, as LPG vehicles are expected to contribute less to particle-phase and more to gas-phase emissions (Faiz, 1996). Key statistical parameters of the multilinear regression analysis for HOA and EC for two and three factor models are presented in the Table S1 in the Supporting Material. For HOA, both two and three factor models yielded acceptable results with all resolved coefficients statistically significant at the 95% confidence level ($p<0.05$). Exclusion of LPG vehicles (two factor model) led to additional apportionment of HOA to both gasoline (+25%) and diesel (+18%) vehicles. Overall model performance improved only slightly when moving from the two factor solution (R^2_{adj}=0.86) to the three factor solution (R^2_{adj}=0.90). Comparative studies on particulate vehicle emissions have reported non-negligible particle mass contributions of LPG vehicles. Estimated particle mass emission factors from LPG passenger vehicles were similar (Chan et al., 2007) or ~30% lower (Ristovski et al., 2005) compared to gasoline powered models in chassis dynamometer runs. In on-road environments, absolute particle number concentrations in bus exhaust plumes were lower in samples from CNG and LPG fueled buses compared to diesel and DME (dimethyl ether) fueled buses, but still 10 times higher than typical ambient background particle concentrations (Kwak et al., 2014). Evaluating HOA concentrations measured between 0:00 and 5:00 when LPG vehicles dominated the total vehicle population (45-60% of total counted vehicles) in our study shows a clear positive relationship between ambient HOA and LPG vehicle count (Figure S3a in the Supporting Material). The two factor MLR model tends to underestimate measured HOA mass concentrations with the distribution of absolute residuals (*difference of reconstructed and measured HOA mass concentration*) biased to negative values whereas the three factor model yielded more normally distributed residuals (Figure S3b, c in the Supporting Material). We thus consider the three factor solution including LPG vehicles as a more appropriate

representation for the deconvolution of the ambient HOA mix from our measurements. For EC, a three factor representation could not resolve variable coefficients that were all statistically significant at the 95% confidence level, $p>0.05$ for the gasoline vehicle factor. While both diesel and gasoline vehicle number correlated appreciably with EC (Figure S4c in the Supporting Material), the number of LPG vehicles lacked a corresponding relation and stayed almost constant over the range of measured EC concentrations, rendering the two factor model the more appropriate representation in deconvoluting measured ambient EC.

3.3.2. Analysis of engine-type reconstructed carbonaceous components

The time series of measured and reconstructed HOA and EC concentrations are depicted in Figure S5a and S5c in the Supporting Material respectively. Gasoline vehicles accounted for more than 45% of total HOA, while diesel and LPG-fueled vehicles were responsible for similar shares of 25-29% (Figure S5b in the Supporting Material). Over 60% of total EC in PM_1 was accounted for by diesel vehicles (Figure S5d in the Supporting Material). The sum of HOA and EC in PM_1 represent approximately the total submicron primary carbonaceous aerosol contributions from road traffic. Despite the limited time frame of the counting exercise, the MLR factors adequately resolved the overall trend in EC and HOA concentration (Figure 3a) and diurnal variation (Figure 3b). Relative residuals from the reconstructed sum of HOA and EC were ≤25% with overestimation ($Residuals < 0$) predominant in the later afternoon hours between 14:00 and 18:00, while significant underestimation ($Residuals > 0$) was observed mostly in the late evening hours between 19:00 and 0:00. The semi-volatile character of HOA would contribute to the observed reduced afternoon particle-phase concentration and conversely enhanced nighttime particle-phase concentrations. Averaged over the whole 72h period, measured and reconstructed carbonaceous submicron PM_1 differed by only 4% indicating that the overall reconstruction was not affected considerably by these diurnal trends in residuals. While vehicle emission factors are typically based on the concentration of emitted species per unit of consumed fuel or per driven distance, we can approximate the impacts of different engine types to ambient PM concentrations by normalizing the resolved engine-specific carbonaceous primary aerosol concentrations by the total number of vehicles in each category (Figure 3b). Gasoline and diesel vehicles emitted similar total amounts of primary carbonaceous PM_1 on an average per-vehicle basis and together 75-85% more than LPG powered vehicles which despite making up ~30% of total counted vehicle accounted for less than 13% of traffic-related PM_1 (Figure 3e).

The individual shares of diesel and gasoline vehicles in ambient HOA and EC, however, varied substantially, with diesel vehicles emitting almost three times as much EC as HOA (EC/HOA=2.85), while gasoline vehicles contributed similar mass concentrations to both HOA and EC (EC/HOA=1.02). This led to significant diurnal variation in the EC/HOA ratio (Figure S1c in the Supporting Material) with low values in the nighttime hours, where LPG- and gasoline-fueled vehicles were more dominant and highest values occurring at the tail of the morning rush-hour where fractions of goods vehicles and buses among overall traffic were highest.

Gasoline vehicles, therefore, accounted for 78% more ambient HOA (75% on per vehicle basis) than diesel vehicles and 56% more ambient HOA (93% on per vehicle basis) than LPG-fueled vehicles. As opposed diesel vehicles accounted for 62% more ambient EC than gasoline-powered vehicles (45% on a per vehicle basis). It must be noted that these data represent the total average of the encountered diesel, gasoline and LPG vehicle fleet, notwithstanding that each of these broad classes is inhomogeneous consisting of a wide variety of vehicles of different size, engine power and age, and thus different individual emission characteristics. Previous measurements of vehicle emissions in a highway road tunnel in the San Francisco Bay Area (Dallmann et al., 2014) employing a soot-particle aerosol mass spectrometer (SP-AMS) yielded a similar characteristic ratio of black carbon to organic aerosol (BC/OA~2.6) for diesel truck plumes and a smaller ratio of BC/OA<0.1 for gasoline vehicle plumes, while filter samples at the same location from light duty vehicles location exhibited BC/OA ratios of ~0.7 for light-duty vehicles and ~2.1 for medium and heavy diesel trucks and (Ban-Weiss et al., 2008). Reported ratios of EC/OC for gasoline powered vehicles from dynamometer studies were typically <1 (Alves et al., 2015;Geller et al., 2006) indicating a greater importance of particulate organics. The relatively high fraction of EC in gasoline engine related PM in our work is likely due to characteristics of inner-city urban road traffic and the proximity to both a road junction and pedestrian crossing. Sampled emissions thus include a considerable fraction of variable and higher engine loads during the acceleration phase whereas road tunnel environments are characterized by largely constant engine loads and traveling speeds. As gasoline vehicles are typically not equipped with particle filters, they have been shown to emit significant amounts of EC under unstable engine loads (Karjalainen et al., 2014). These specific characteristics of the Mong Kok measurement site are not represented well in typical dynamometer driving cycles and tunnel studies and are expected to have at least partially contributed to observed difference compared to the EC/HOA ratios in this study. $PM_{2.5}$ emission factors determined from dynamometer test runs of various vehicle types in Hong Kong were generally higher for diesel vehicles compared to gasoline and LPG vehicles (Chan et al., 2007), while we observed similar total particle mass emission on a per-vehicle basis for diesel and gasoline vehicles in this study. The dynamometer tests were conducted on relatively old vehicles (*newest date of manufacture: 2001*) and are unlikely to adequately reflect the ambient vehicle mix in our study, particularly with regard to the implementation of various control schemes in recent years targeting especially diesel vehicle emissions in Hong Kong. These included inter alia an incentive scheme in 2010 for the replacement of diesel commercial vehicles, the retrofitting of diesel particulate filters (DPF) on pre-Euro IV buses and subsequent replacement of older buses with Euro IV, V and VI standard models (Environment Bureau, 2013;Environmental Protection Department, 2013). New engine technologies for diesel vehicles, such as DPFs, have been shown to greatly reduce both EC and OC emissions (Alves et al., 2015) with vehicles employing newest emission control standards generally emitting little total particle mass but having been found to emit greater fractions of particles in the ultrafine mode (Giechaskiel et al., 2012). The Euro III, IV and V standards for trucks and buses were introduced in late 2000, late 2005 and late 2008 respectively. While the year of manufacture does not directly infer a specific emission standard, an approximate number of vehicles fulfilling a certain standard can be estimated assuming that vehicles produced between 2001 and 2005, between 2006 and 2008 and between 2009 and 2013 very likely comply with the Euro III, IV and V standards respectively, i.e. standards were immediately or had already been adopted in vehicle models in the corresponding year of manufacture.

Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2017-432
Manuscript under review for journal Atmos. Chem. Phys.
Discussion started: 27 June 2017

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Figure S6 in the Supporting Material depicts the number and proportion of vehicles of certain years of manufacture and their assumed Euro standard. For goods vehicles, 52% of counted vehicles were built between 2005 and 2013 (i.e. likely fulfilling
315 Euro IV and V), while for buses the proportion was slightly lower at 33%. With these two vehicle groups representing the bulk of diesel powered vehicles, an estimated 40% of diesel vehicles complied with Euro IV and Euro V standards during the time of our ambient measurements.

4. Conclusion

Primary submicron carbonaceous aerosol was measured by combined HR-ToF-AMS and ECOC measurements, supplemented by various VOCs and other gas-phase species, at an inner-city urban roadside sampling site in the Mong Kok District in Hong Kong. Organic species concentrations (HOA) were of similar magnitude as traffic-related organic matter estimated previously, but with strong seasonal dependency with on average 43% lower concentrations in summer (2.0 μg/m^3) compared to spring (3.5 μg/m^3) likely due to greater fractions of semi-volatile species remaining in the gas-phase in the warmer season. EC concentrations remained at similar levels throughout the sampling period, leading to significantly different average EC/HOA ratios in spring (0.86) and summer (1.78). Sunday concentrations of both HOA and EC were 16-36% lower than during the rest of the week (Mon-Sat) reflecting significant reductions in traffic volume on Sundays. Larger relative reductions in EC compared to HOA indicate a greater reduction in the number of diesel vehicles, e.g. commercial trucks and buses. Detailed vehicle counting data acquired during a 72h counting exercise in late May 2013 were utilized to decompose HOA and EC concentrations into vehicle-type factors (gasoline-, diesel- and LPG-powered vehicles) by multilinear regression analysis. Gasoline vehicles contributed similar amounts of EC and HOA, while diesel vehicles emitted predominantly EC and to a lesser extent HOA. On an average per-vehicle basis, contributions of diesel and gasoline vehicles to carbonaceous PM_1 were similar, contrary to previous studies which attributed higher particulate matter emissions to diesel vehicles. This clear reduction is likely due to recent control strategies targeted at commercial vehicles and buses, which represent the bulk of diesel powered vehicles at the measurement site. This becomes especially important in view of the growing number of higher Euro standard diesel vehicles which, while effectively reducing overall emitted particle mass may emit similar number concentrations of particles with particle sizes having been shown to shift more into the ultrafine region (Tartakovsky et al., 2015). The number of LPG-vehicles did not exhibit a significant correlation with EC concentrations and was thus considered to be a negligible EC source. Its contributions to HOA were small (13%) despite representing about one-third of total counted vehicles. While this study has focused on primary emissions, gas-phase emissions from the tailpipe can lead to subsequent condensation of organics or atmospheric oxidation to form secondary organic aerosol, significantly enhancing post-emission particulate matter concentrations (Gentner et al., 2012;Platt et al., 2013) and should be subject to further future investigation.

Acknowledgments

This work was supported by the Environment and Conservation Fund of Hong Kong (project number ECWW09EG04). Chak K. Chan gratefully acknowledges the startup fund of the City University of Hong Kong.

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The opinions expressed in this paper are those of the author and do not necessarily reflect the views or policies of the Government of the Hong Kong Special Administrative Region, nor does mention of trade names or commercial products constitute an endorsement or recommendation of their use.

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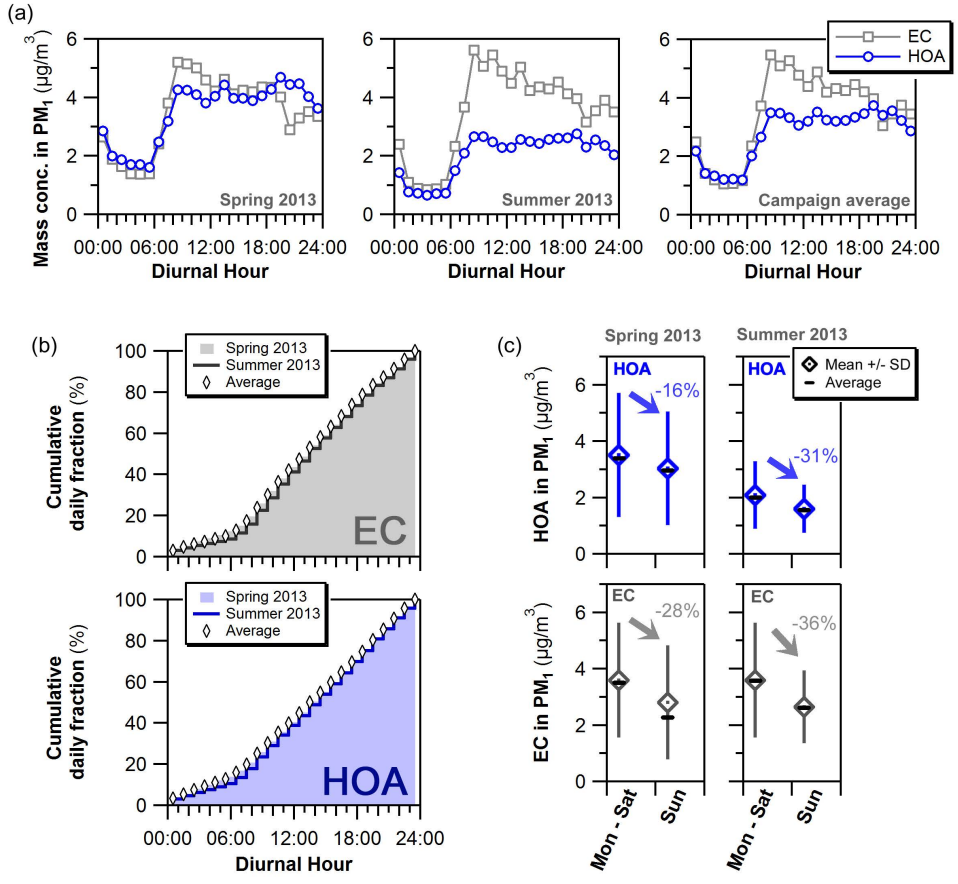

Figure 1.

(a) Diurnal variation of HOA and EC mass concentrations in spring 2013 (7-3-2013 to 15-5-2013), summer 2013 (16-5-2013 to 19-7-2013) and averaged over the entire sampling campaign (7-3-2013 to 19-7-2013)

(b) Diurnal variation of the cumulative fraction of total daily HOA and EC mass concentrations in spring 2013 (7-3-2013 to 15-5-2013), summer 2013 (16-5-2013 to 19-7-2013) and averaged over the entire sampling campaign (7-3-2013 to 19-7-2013)

(c) Mean HOA and EC concentrations from Monday through Saturday and on Sunday in spring (left) and summer (right) 2013, *bar as standard deviation and black hash as median*

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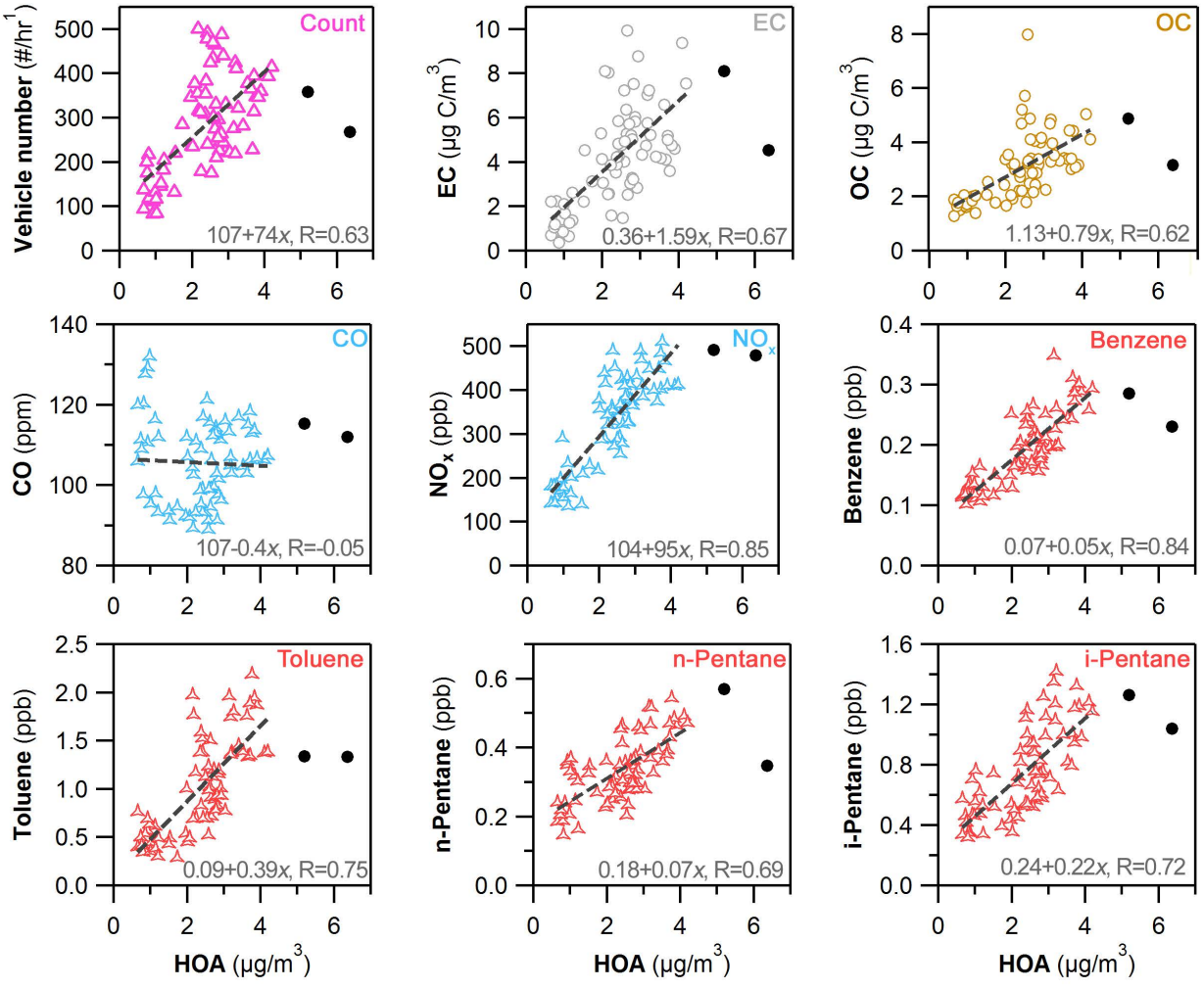

Figure 2.

Scatter plot of vehicle count, mass concentration of EC, OC and gas-phase concentrations of various VOCs, NO_x, and CO against HOA between May 28 and May 31, 2013, *linear least squares fits with equations and Pearson's R values in grey, black dots signify outlier values excluded from the curve fits*

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Manuscript under review for journal Atmos. Chem. Phys.
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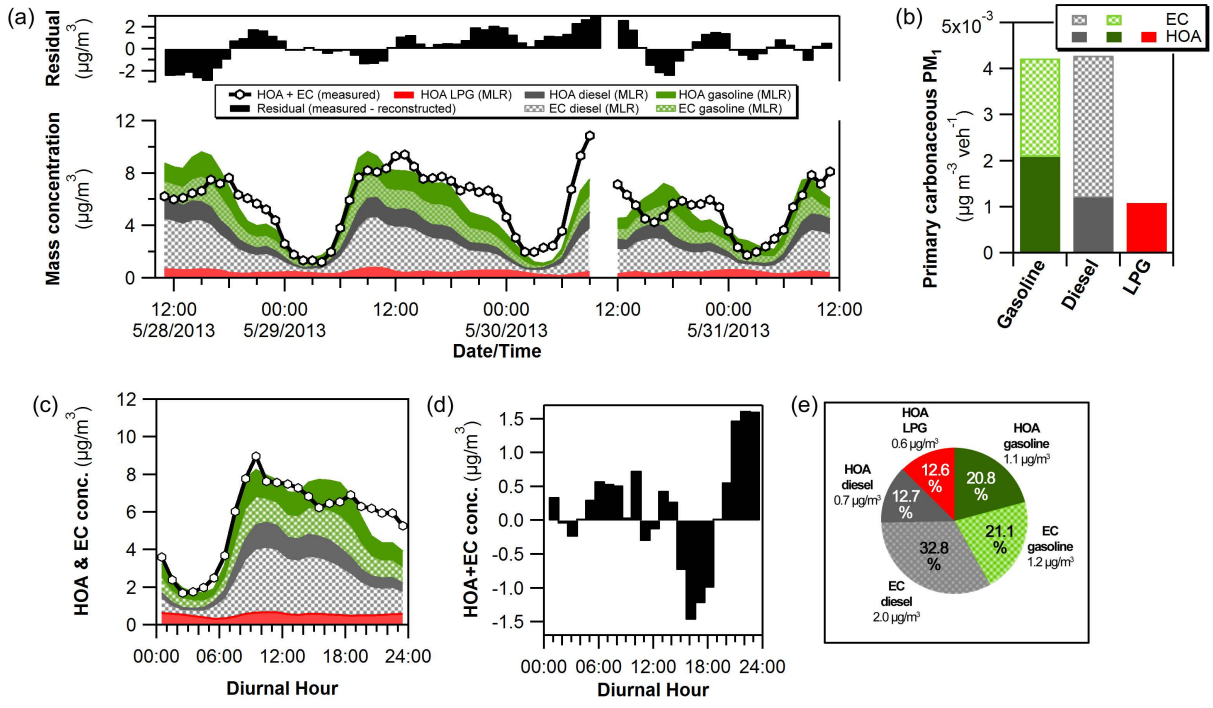

Figure 3.

(a) Time series of engine-type separated HOA and EC concentrations, sum of actual measured HOA and EC in PM_1, as well as residuals as the difference between resolved HOA+EC and measured HOA+EC

555 (b) Contribution of engine-type separated HOA and EC normalized by the total number of vehicles per engine category

(c) Diurnal variation of vehicle-type separated HOA and EC concentrations as well as sum of actual measured HOA and EC in PM_1

(d) Diurnal variation residuals as the difference between resolved HOA+EC and measured HOA+EC

(e) Average contribution of engine-type separated HOA and EC in total reconstructed HOA+EC in PM_1

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