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Vehicular emissions of organic particulate matter in Sao Paulo, Brazil

B. S. Oyama[1,2], M. F. Andrade[1], P. Herckes[3], U. Dusek[2,4], T. Röckmann[2], and R. Holzinger[2]

[1]Institute of Astronomy, Geophysics and Atmospheric Sciences, University of Sao Paulo, Sao Paulo, Brazil
[2]Institute for Marine and Atmospheric Research, University of Utrecht, Utrecht, the Netherlands
[3]School of Molecular Sciences, Arizona State University, Tempe, USA
[4]Center for Isotope Research, University of Groningen, Groningen, the Netherlands

Correspondence to: B. S. Oyama (beatriz.oyama@iag.usp.br)

ACPD

15, 33755–33788, 2015

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Abstract

Vehicular emissions have a strong impact on air pollution in big cities. Many factors affect these emissions: type of vehicle, type of fuel, cruising velocity, and brake use. This study focused on emissions of organic compounds by Light (LDV) and Heavy (HDV) duty vehicle exhaust. The study was performed in the city of Sao Paulo, Brazil, where vehicles run on different fuels: gasoline with 25 % ethanol (called gasohol), hydrated ethanol, and diesel (with 5 % of biodiesel). The vehicular emissions are an important source of pollutants and the principal contribution to fine particulate matter (smaller than 2.5 µm, $PM_{2.5}$) in Sao Paulo. The experiments were performed in two tunnels: Janio Quadros (TJQ) where 99 % of the vehicles are LDV, and Rodoanel Mario Covas (TRA) where up to 30 % of the fleet was HDV. The $PM_{2.5}$ samples were collected on quartz filters in May and July 2011 at TJQ and TRA, respectively, using two samplers operating in parallel. The samples were analyzed by Thermal-Desorption Proton-Transfer-Reaction Mass-Spectrometry (TD-PTR-MS), and by Thermal-Optical Transmittance (TOT). The organic aerosol (OA) desorbed at TD-PTR-MS represented around 30 % of the OA estimated by the TOT method, mainly due to the different desorption temperatures, with a maximum of 870 and 350 ˚C for TOT and TD-PTR-MS, respectively. Average emission factors (EF) organic aerosol (OA) and organic carbon (OC) were calculated for HDV and LDV fleet. We found that HDV emitted more OA and OC than LDV, and that OC emissions represented 36 and 43 % of total $PM_{2.5}$ emissions from LDV and HDV, respectively. More than 700 ions were identified by TD-PTR-MS and the EF profiles obtained from HDV and LDV exhibited distinct features. Nitrogen-containing compounds measured in the desorbed material up to 350 ˚C contributed around 20 % to the EF values for both types of vehicles, possibly associated with incomplete fuel burning. Additionally, 70 % of the organic compounds measured from the aerosol filters with TD-PTR-MS were oxygenated for LDV and HDV, suggesting that the oxygenation occurs during fuel combustion and that the oxygen content of the fuel itself contributes. The thermal desorption analysis showed that HDV emitted

compounds with higher volatility, mainly oxygenated (with up to 2 oxygen atoms) and longer chain hydrocarbons than LDV.

1 Introduction

The Metropolitan Area of Sao Paulo (MASP) is composed of 39 municipalities, with a fleet of more than 7 million vehicles (Cetesb, 2014), which nowadays run on three different types of fuel: diesel (with 5 % of biodiesel, shortly referred to as diesel afterwards), hydrated ethanol and gasohol (gasoline with 25 % of ethanol). The number of vehicles has grown more rapidly than the population in the last 15 years. In 2000, the population was around 10 million and the number of vehicles was 0.9 million in the city of Sao Paulo. In 2013, these values increased to 11.4 million and around 4.5 million, respectively (Infocidade, 2015; Cetesb, 2014). Figure 1 presents the evolution of initial registrations of new vehicles in Sao Paulo, classified by fuel usage over the past 40 years (Cetesb, 2014). In 2003, a new vehicle technology was introduced: flex fuel vehicles, which are able to operate on any proportion of ethanol and gasohol.

The implementation of the National Pro Alcohol Program (Proalcool) in Brazil during the 1980s had an important influence on the increase in vehicles running on hydrated ethanol. In the early 1970's, the ethanol production was not significantly higher than 1 million cubic meters in Brazil. However, due to the Proalcool, this value increased to more than 10 million cubic meters in the mid-1980's (Stattman et al., 2013). This program stimulated the use of alcohol from sugarcane as fuel in order to decrease the dependence on imported fuel and also to stimulate industrial and agricultural growth (Rico and Sauer, 2015; Stattman et al., 2013). Besides that, between 1973 and 1974 the addition of 10 % of ethanol to gasoline was legally mandated. Also at that time, the hydrated alcohol price was significantly lower than the price for gasoline (64.5 % less) due to governmental incentives (Stattman et al., 2013). Following a governmental change in 1985, the subsidy for alcohol decreased dramatically, thus the alcohol price increased, followed by a fall in sales of ethanol fueled vehicles (Fig. 1).

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In the early 1990s the number of vehicles increased substantially due to a political decision of increasing the sales of vehicles to stimulate the economy. Following international regulations for vehicular emissions, the Program for Controlling Vehicular Emission (PROCONVE) was implemented in the late 1980's. This program established emission standards for new vehicles with the aim of reducing these emissions (Szwarcfiter et al., 2005). Despite an increase in the number of vehicles, the program resulted in an improved air quality with lower concentrations of carbon monoxide (CO), sulfur dioxide (SO_2) and coarse particles (with diameters between 2.5 and 10 µm), as shown by (Carvalho et al., 2015). Pérez-Martínez et al. (2014) did not observe a decreasing trend on fine particles ($PM_{2.5}$) and ozone (O_3). On the other hand, Salvo and Geiger (2014) demonstrated that the ozone levels have been decreased by replacing ethanol with gasoline.

In 2004, the National Program of Production and Usage of Biodiesel (PNPB) was created in order to stimulate the use of biofuels as well as the associated agricultural activities for its production. The main motivation was to decrease the dependence on imported diesel (Stattman et al., 2013), similar to Proalcool. In the same year, the addition of 2 % of biodiesel to conventional diesel fuel was authorized, but only since 2008 this addition has become mandatory. Until 2010, the percentage has gradually increased to the current 5 % (MME, 2015). Rico and Sauer (2015) and Stattman et al. (2013) discussed in detail the impact of the biodiesel production on agricultural and economical activities. Nowadays, 74.7 % of the biodiesel produced in Brazil is made from soybean oil, 20.4 % from animal fat (mainly bovine), and 4.9 % from other sources (ANP, 2015).

The burning of biofuels and fossil fuels causes substantial emissions of Volatile Organic Compounds (VOC) – important precursors of ozone and organic fine particles and Black Carbon (BC) – mainly emitted from the burning of diesel. Andrade et al. (2012) presented the fraction of BC in $PM_{2.5}$ for six Brazilian cities and the values ranged from 15 % in coastal regions to 30 % in urban areas.

Due to its density population, political and economic importance, the MASP has been in the focus of several studies that investigated the impact of vehicular emissions on

the concentration and composition of particulate matter (Albuquerque et al., 2012; Andrade et al., 2012; Miranda and Andrade, 2005; Miranda et al., 2002). The distinction between contributions from light duty vehicles (LDV) and heavy duty vehicles (HDV) is still a challenge. Different methods can be used in order to estimate the emissions from the vehicular fleet. Emission factors (EF) for gaseous and particulate compounds have been calculated based on tunnel measurements, and recent results were presented by Pérez-Martínez et al. (2014). The analysis of fine particulate matter ($PM_{2.5}$) in tunnels was described by Brito et al. (2013). They performed a chemical characterization of $PM_{2.5}$ by separating the total mass into organic carbon, elemental carbon, and contributions from other trace elements. They concluded that the organic aerosol fraction estimated from OC measurements represented around 40 % of $PM_{2.5}$ emitted by LDV and HDV.

In spite of all the development and studies concerning the composition and sources of aerosols in the area, very few studies have analyzed the organic composition of particulate matter in Sao Paulo. Previous studies estimated the contribution of OC present within the particulate matter in the city of Sao Paulo, as described in Castanho and Artaxo (2001), and Miranda and Andrade (2005). In a more recent study, Albuquerque et al. (2012) attributed a part of the non-explained mass obtained from the mass balance model to OA. In a study performed in 2008, Souza et al. (2014) estimated from OC measurements that around 26 % of the $PM_{2.5}$ was composed of particulate organic matter. Recently, Brito et al. (2013) discussed the aerosol composition including the OC and PAH.

Here, we discuss the composition of OA and EF of condensed organics from LDV and HDV, obtained from aerosol filter samples ($PM_{2.5}$) collected in traffic tunnels. For the first time, TD-PTR-MS was applied to samples from Sao Paulo, where hundreds of organic compounds were identified to contribute to OA.

2 Methods

2.1 Field campaigns

The field campaigns were performed at two different tunnels: the first campaign took place in the Janio Quadros tunnel (TJQ), from 4 to 13 May 2011 and a second campaign was performed in the Rodoanel Mario Covas tunnel (TRA), from 6 to 17 July 2011. In a third campaign, daily ambient particle samples were collected during the Southern Hemisphere Winter from 8 August to 9 September 2012, on the roof of a building on the University of Sao Paulo campus

TJQ is a two-lane tunnel located in the Center of Sao Paulo and characterized mainly by light-duty vehicle (LDV) traffic. The direction of the car traffic in this tunnel alternated twice a day at 6 a.m. and 9 a.m. LT TJQ has a length of 1.9 km, speed limit of 60 km h^{-1}, and a natural wind flow velocity ranging from 1.0 to 4.9 m s^{-1} during congested and normal traffic conditions, respectively as described by (Pérez-Martínez et al., 2014). TRA is located on the outskirts of the city on a highway ring. This tunnel is an important alternative route for heavy-duty vehicles (HDV) due to traffic restrictions in the center of Sao Paulo. With a length of 1.7 km and a speed limit of 70 km h^{-1}, the traffic flow is always on four lanes in one direction. Pérez-Martínez et al. (2014) described that the natural flow velocity ranged from 1.0 to 6.1 m s^{-1} during congested and normal traffic conditions, respectively.

In TJQ, the traffic of vehicles was monitored by cameras and vehicle numbers were obtained by counting from recorded videos. The fleet was classified into four different groups: HDV, LDV, motorcycles and taxis. For this study, the motorcycles and the taxis were considered as LDV, since they use hydrated ethanol or gasohol (see Table 1). The TRA campaign had an automated counting system by weighing vehicles, which sorts the fleet into the two categories LDV and HDV. The other two kinds of vehicles were excluded mainly due to the fact that motorcycles hardly circulate on highways with high speed limit and taxi traffic is very limited far from the city center. A detailed discussion

about the traffic of the vehicles during these experiments is shown by Brito et al. (2013) and Pérez-Martínez et al. (2014).

Filter samples were collected at the midpoint of both tunnels. Two samplers were deployed in parallel: a low-volume sampler (Partisol Dichotomous Ambient Particle Sampler, with the sampling rate of $16.6\,L\,min^{-1}$) collected simultaneously $PM_{2.5}$ and $PM_{2.5-10}$ on two different filters (coarse particles, comprising PM_{10}) and a mini-volume sampler (Airmetrics, with a sampling rate of $5\,L\,min^{-1}$), sampled only the $PM_{2.5}$ fraction. These samples were collected on pre-heated quartz fiber filters (800 °C, for 12 h), subsequently wrapped in aluminum foil (pre-cleaned at 550 °C, for 8 h) and stored inside polyethylene bags in a freezer at −18 °C until analysis.

Measurements of carbon monoxide (CO) and carbon dioxide (CO_2) were performed inside and outside the tunnels during the whole campaigns. CO measurements were done with non-dispersive infrared photometry equipment (Thermo Electron 48B). CO_2 was measured using a LICOR-6262 instrument inside and a Picarro-G1301 instrument outside the tunnels, as described in detail elsewhere (Pérez-Martínez et al., 2014). Trace gas concentrations were averaged to the filter sampling times. These values as well as the information regarding the samples are summarized in Table 1 and 2. The gaseous concentration was obtained on a hourly base and the average value was calculated for the same period of particulate sample.

In order to calculate emission factors according to Kirchstetter et al. (1999) and Pérez-Martínez et al. (2014), ambient samples were used to determine background concentrations that were subtracted from the inside tunnel concentrations. The ventilation system in the tunnels brings the air from the outside to the interior, by ventilation fans on the roof of the tunnel operating continuously to provide fresh air inside. The ambient samples were collected on the roof of the Institute of Astronomy, Geophysics and Atmospheric Sciences building, located on the campus of the University of Sao Paulo. Previous studies were already performed at this point (Miranda et al., 2002; Sánchez-Ccoyllo and Andrade, 2002; Ynoue and Andrade, 2004). From 8 August to 9 September 2012 (winter time), daily $PM_{2.5}$ samples were taken at 9 a.m. by using

a high volume sampler ($1.13 \, \text{m}^3 \, \text{min}^{-1}$) for 24 h. 31 filter samples were obtained in total. The analytical methods and data treatment used for these measurements were the same as for the tunnel samples. In order to minimize the effect of meteorological conditions, the average concentration over the sampled period was used as the background concentration for both tunnel campaigns.

Many studies have been performed concerning the identification of the sources of atmospheric aerosols in Sao Paulo and they have shown that the dominant source of $PM_{2.5}$ is vehicular emission (Albuquerque et al., 2012; Andrade et al., 2012). These studies, performed during the Southern Hemisphere wintertime, showed similar behavior in different years of analysis from 2010 to 2014, in terms of concentration and composition of the $PM_{2.5}$. The authors performed the identification of these sources using a multivariate analysis and found that the vehicular emissions explained 60 % of the $PM_{2.5}$. Furthermore, $PM_{2.5}$ concentrations from different stations in the city of Sao Paulo showed similar yearly averages in 2011 and 2012 (Cetesb, 2012, 2013): $25 \pm 19 \, \mu\text{g m}^{-3}$. Therefore, the ambient data is considered an adequate background concentration for the EF study.

2.2 Analytical methods

A Proton-Transfer-Reaction Time of Flight Mass-Spectrometer (PTR-ToF-MS, model PTR-TOF8000, Ionicon Analytik GmbH, Austria, referred to as PTR-MS hereafter) was used to perform the analysis of organic compounds on the filters (collected by the low volume sampler, Partisol). Briefly, the PTR-MS uses a soft chemical ionization technique, reducing the fragmentation compared to electron impact ionization. Reactions between protonated water (H_3O^+) and organic species in the sample lead to mostly non-dissociative proton transfers, with the advantage that most organic compounds can be detected quantitatively. A detailed discussion on the system, using a quadrupole detector, can be found in Hansel et al. (1995) and Lindinger et al. (1998), while Graus

et al. (2010) and Jordan et al. (2009) describe the PTR-MS using the Time of Flight Mass Spectrometer.

The PTR-ToF-MS used in this study operated with the following settings: drift tube temperature at 120 °C; inlet tube temperature at 180 °C; and ion source voltages of Us = 140 V, Uso = 92 V, E/N 130 Td. The extraction voltage at the end of the drift tube (Udx) was 28 V.

A thermal desorption system was used for the filter sample analysis, as described by Timkovsky et al. (2015). In short, the setup consisted of a cylindrical quartz glass tube surrounded by two ovens: the first oven, where the sample was inserted using a filter holder, can be controlled over a temperature range of 50 to 350 °C. The second oven worked at a constant temperature of 180 °C. A piece of $0.20 \, \text{cm}^2$ area from each filter was introduced to the first oven at 50 °C and heated in temperature steps of 50 °C from 100 to 350 °C, allowing 3 min for the measurement at each temperature. The N_2 flow rate (ultrapure nitrogen, 5.7 purity, Airproducts) was usually adjusted by a thermal mass-flow controller (MKS Instruments, Germany) at $100 \, \text{mL} \, \text{min}^{-1}$, except for a few tunnel samples, which were measured at a flow rate of $50 \, \text{mL} \, \text{min}^{-1}$. Pure N_2 was used as carrier gas and transported organic molecules desorbed from the sample to the PTR-MS. The heating steps were performed under inert atmosphere, where no other gas besides N_2 was present in the oven system, in order to exclude oxidation during desorption. Each filter was measured three times and unless otherwise mentioned the average of the three replicas is presented and discussed hereafter.

The quartz filters were collected by the mini-volume sampler and were used for the quantification of Total Carbon (TC) separated in Organic (OC) and elemental (EC) carbon using Thermal-Optical Transmittance (TOT) with a Sunset Laboratory Inc. instrument (Sunset labs, Tigard, USA) as described by Brito et al. (2013). The evaluation of OC occurred at temperature steps of 310, 475, 615, and 870 °C, with heating times ranging from 60 to 200s. Here, the discussion focused on particulate organic matter. Thus, the EC and TC values are not presented.

Pérez-Martínez et al. (2014) presented emission factors of the total PM$_{2.5}$ mass concentration, for the same tunnels campaigns described here. Briefly, PM$_{2.5}$ was sampled on polycarbonate filter by a dichotomous sampler, and its mass concentration was gravimetrically determined, using an electronic microbalance with a sensitivity of 1 µg under controlled conditions.

2.3 TD-PTR-MS data treatment

The TD-PTR-MS data evaluation was performed with custom routines described in Holzinger et al. (2010) by implementing the widget-tool, using Interactive Data Language (IDL, version 7.0, ITT Visual Information Solutions), described in Holzinger (2015). In total, 762 ions were detected in the mass spectra. In order to avoid primary ions and inorganic ions, all ions with $m/z < 40$ Da were excluded, except m/z 31.077 (CH_2OH^+) and 33.033 (CH_4OH^+). Additionally, ions associated with the inorganic ion NO_2^+ and higher water clusters (($H_2O)_2H_3O^+$) were removed. After this screening, the final mass list contained 712 ions that were attributed to organic molecules.

The data (volume mixing ratios, VMR, in nmol mol^{-1}) had a temporal resolution of 5 s. Similar to the procedure described by Timkovsky et al. (2015), the instrument background (VMR$_{i,\text{instrbgd}}$), identified in Fig. 2 by the first horizontal gray line, was subtracted from the measured volume mixing ratio (VMR$_{i,\text{measeured}}$) for an ion "i" at each temperature step:

$$VMR_i = VMR_{i,\text{measured}} - VMR_{i,\text{instrbgd}} \qquad (1)$$

Where: VMR$_i$ is the volume mixing ratio corrected by the background. This calculation was done for all filters samples and all field blanks. Figure 2 presents an example of this procedure: the sum of the volume mixing ratios for all $m/z > 50$ Da per time interval of 5 s (also called cycles). The different temperature plateaus are separated by the vertical gray lines. The background is calculated by averaging the first eight cycles before heating starts as indicated by the first short horizontal line (close to zero). All other short horizontal lines represent the averages of each temperature step.

All filter samples were measured three times. From these measurements, the average of the VMR per filter was calculated for each ion i at each temperature step ($\overline{VMR_i}$). Note that all VMR_i values have been normalized to a N_2 carrier gas flow of $100\,mL\,min^{-1}$.

A t test was performed in order to confirm the statistical significance of the ion signals compared to the blank filters. After this test, 605 (TJQ), 627 (TRA) and 440 (winter) ion masses were kept in the database as their signal was significantly above the signal of the blank filters.

For the remaining masses, the median VMR of the field blanks (fb) was subtracted from the average VMR of the sampled filters ($\left(\overline{VMR_{i,\text{sampled}}}\right)$) for each ion "$i$" and each temperature step.

$$VMR_{i,\text{final}} = \left(\overline{VMR_{i,\text{sampled}}}\right) - \left(\overline{VMR_{i,\text{fb}}}\right)_{\text{MED}} \tag{2}$$

The $VMR_{i,\text{final}}$ was used to calculate the concentration ($ng\,m^{-3}$) for a specific ion "i", at a specific temperature step (C_i), according to Timkovsky et al. (2015):

$$C_i = \frac{VMR_{i,\text{final}} \cdot M_i \cdot V_{\text{Nitrogen}}}{V_{\text{samp}} \cdot f} \tag{3}$$

Where: M_i is the molecular weight of the ion "i" (minus one atomic mass unit, once TD-PTR-MS measures protonated ions), V_{Nitrogen} is the amount of N_2 carrier gas (in mol), V_{samp} is the volume of air during sampling (in m^3), and f is the area of the measured filter aliquot divided by the area of the whole filter (Timkovsky et al., 2015).

2.4 Vehicular Emission Factors of organic species

Emission factors (EF) in units of mg of pollutant per kg of burned fuel were calculated according to Eq. (4) (Martins et al., 2006; Kirchstetter et al., 1999; Miguel et al., 1998),

assuming that under normal driving conditions the fuel is converted to CO and CO_2 while contributions from other carbon compounds are negligible:

$$EF_P = 10^3 \left(\frac{\Delta[P]}{\Delta[CO_2] + \Delta[CO]} \right) \omega_c \qquad (4)$$

Where: EF_P is the emission factor of pollutant P (mg of P per kg of burned fuel); $\Delta[P]$ is the increase of $[P]$ above the background levels (in $ng\,m^{-3}$); $\Delta[CO_2]$ and $\Delta[CO]$ are the increases of the CO_2 and CO concentrations, respectively, above the background levels [µg of carbon m^{-3}]. The ω_c term is the fuel carbon weight fraction (in g of C g^{-1} of fuel) for a fuel $c - \omega_G = 0.757$ for gasohol (26.5 % ethanol, 73.5 % gasoline) and $\omega_D = 0.818$ for diesel (5 % biodiesel, and 95 % diesel).

The emission factors for LDV were directly calculated from the filters sampled in the TJQ tunnel due to the fact that LDV dominated the emissions in the TJQ tunnel. However, the HDV EF just can be estimated after subtracting LDV emissions from the samples collected in the TRA. Previous studies, also performed in tunnels, have shown that HDV and LDV emit comparable amounts of CO per travelled distance (Kirchstetter et al., 1999; Miguel et al., 1998; Pierson et al., 1996). The CO_2 emissions from the diesel burning could be estimated according to the following equation:

$$\frac{\Delta[CO_2]_D}{\Delta[CO_2]} = \frac{f_D U_D \rho_D \omega_D}{f_D U_D \rho_D \omega_D + ((1 - f_D).U_G \rho_G \omega_G)} \qquad (5)$$

Where $\Delta[CO_2]_D$ is the component of $\Delta[CO_2]$ related to the emissions from diesel vehicles (equal to HDV), f_D is the fraction of HDV, U is the average fuel consumption rate in $g\,km^{-1}$ ($75\,g\,km^{-1}$ for gasohol and $251\,g\,km^{-1}$ for diesel), ρ is the fuel density ($765\,g\,L^{-1}$ for gasohol, $854\,g\,L^{-1}$ for biodiesel). The subscripts G and D denote gasohol and diesel, respectively.

The contribution of HDV to the concentration of a pollutant P can be estimated by the equation:

$$\Delta[P]_{HDV} = \Delta[P] - \Delta[CO](1 - f_D)\left(\frac{\Delta[P]_{LDV}}{\Delta[CO]_{LDV}}\right)_{TJQ} \tag{6}$$

Where $\Delta[P]_{HDV}$ is the contribution of $\Delta[P]$, related to HDV emissions, $\Delta[CO](1 - f_D)$ is the fraction of $\Delta[CO]$ attributed to the LDV emissions. The last term in Eq. (6) was calculated from the measurements in the TJQ campaign.

The presented EF's are the averages of several filters. The HDV emission factors are averages from all filters collected in the TRA tunnel, and the LDV emission factors are averages of all afternoon and 12 h weekday samples from the TJQ tunnel, as these samples were less impacted by background ambient aerosol (see discussion below).

3 Results and discussion

Table 3 shows EFs (in mg of pollutant per kg of burned fuel) for OC, OA, and total PM$_{2.5}$, as obtained by TOT, TD-PTR-MS, and gravimetrical analyses (Pérez-Martínez et al., 2014), respectively. All EF's were higher for HDV than for LDV.

The EF of OC represented 36 and 43 % of the EF of PM$_{2.5}$ for LDV and HDV, respectively. Brito et al. (2013) used OA/OC ratios of 1.6 and 1.5 for the TJQ and TRA campaigns, respectively. Using these ratios and measured OC (TOT, up to 310 °C) and OA (TD-PTR-MS, up to 300 °C) we infer that TD-PTR-MS quantified ∼ 90 and ∼ 75 % of LDV and HDV emissions, respectively, which is in line with known loss processes in TD-PTR-MS discussed by Holzinger et al. (2010 and 2013). It is difficult to compare the OA measured by TD-PTR-MS and TOT, respectively, because of different desorption temperatures. Overall we estimate that OA as measured by TD-PTR-MS accounts for 30 % or less for the total organic matter measured by TOT analyzer over all thermal fractions (up to 870 °C).

Table 3 also presents the EF of compounds containing oxygen (O) for LDV and HDV. We found high contributions from oxygenated compounds of around 70 % for both, LDV and HDV. This indicates that the fraction of oxygenated compounds in particulate matter is substantially higher than in the fuel. This can be associated to significant oxidation during the combustion, since photochemical processes are negligible inside tunnels due to the absence of sunlight.

Figure 3 shows the average EF (in mg kg^{-1} of fuel) profiles for LDV and HDV, obtained from the TD-PTR-MS. As discussed above, HDV emitted higher concentrations of organic particulate compounds than the vehicles using gasohol. Differences between LDV and HDV are also seen from the chemical composition of the emitted particles. Several ions above 475 Da were detected from LDV emissions with the TD-PTR-MS, and only two compounds exceeded EF's of 0.250 mg kg^{-1} of fuel. In contrast, many compounds emitted by HDV exceeded 0.250 mg kg^{-1} of fuel, especially at m/z's at around 200 Da, however, no ions above 475 Da were detected.

Table 4 and 5 show the ten highest average EF values for both types of vehicles, as well as their m/z, their estimated empirical formula, the median, maximum and minimum EF values. The complete list of all compounds is shown in the Supplement Material. Using improved routines described in Holzinger et al. (2010), it was possible to attribute empirical formulas to the m/z identified by the TD-PTR-MS, namely compounds with up to 16 atoms of oxygen and 2 atoms of nitrogen.

The highest average EF was found for m/z 149.024 for the LDV with the value of 5.6 mg kg^{-1} of fuel. This compound was identified as $C_8H_4O_3$, tentatively attributed to phthalic anhydride. This compound is known for its use as plasticizers (responsible for the flexibility, resilience and transparency of the plastic) and it is also present in the plastic bags in which the filters (wrapped in aluminum foil) have been stored. Therefore, this peak potentially indicates a positive artifact due to the handling of the filters, however the blank filters that were also stored in plastic bags did not show a significant signal on this mass. Decarlo et al. (2006), using the High-Resolution Time-of-Flight Aerosol Mass Spectrometer (HR-ToF-AMS), stated that the m/z 149 (phthalates) peak

showed only little influence on real AMS measurements. Although these considerations indicate the m/z 149.024 as a possible contamination/artifact, it is important to point out that the instrumental background, field blank, and ambient air background subtractions were performed before calculating the emission factors. Therefore this ion is most likely originating from the collected aerosol on the filters. Furthermore, phthalic anhydride ($C_8H_4O_3$, detected on m/z 149.024) has been positively identified in the atmosphere (Chan et al., 2009; Samy and Zielinska, 2010). Another possibility would be that this compound is produced from octane present in gasoline. Higher values of octane in the fuel results in a higher resistance to auto ignition and consequently a lower chance for engine knocking (Cerri et al., 2013; Westbrook et al., 2011). However, this dataset does not suggest that m/z 149.024 might be a unique tracer for gasohol because this compound was also substantially emitted from HDV ($1.363\,\mathrm{mg\,g^{-1}}$ of fuel, see Table 5). This can be due to the procedure used for the calculation of the HDV EF, which considers the subtraction of the LDV EF. It can be cautiously argued that m/z 149.024 may be a general tracer for aerosol from vehicles engine exhaust. However, more research is necessary to clarify the origin of this compound.

The ion detected at m/z 149.131 ($C_{11}H_{16}H^+$), as presented in Table 4, was tentatively attributed to pentyl benzene. Pentyl benzene is a potential unique tracer for gasoline, as this compound is a known constituent of gasoline, e.g. Ramadhan and Al-Hyali (1999) used pentyl benzene to calculate the octane number in the fuel. For HDV emissions, m/z 299.289 is a potentially unique tracer for this source. This ion was attributed to the formula $C_{19}H_{38}O_2H^+$, and tentatively attributed to methyl stearate, which is one of the main components found in biodiesel (Naik et al., 2011). The emission factor for LDV was approximately a factor of 6 lower (see the Supplement) than for HDV and this signal might originate from the low number of diesel fueled vehicles moving in the TJQ tunnel.

Figure 4 shows the average EF for LDV and HDV divided in groups containing: CH, CHO, CHON, and CHN. The hydrocarbon group (CH) presented an important contribution to the total EF: for the LDV close to a quarter and for the HDV the contribution was

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around a third. Oxygenated hydrocarbons (CHO) showed highest contribution to emissions for both vehicle types, where LDV exhibited a slightly larger fraction than HDV. The nitrogen-containing groups contributed above 20 % to the measured OA. Since the presence of nitrogen in the fuels is significantly lower than in the air, such a high percentage in the aerosol can be attributed to NO_x chemistry during the combustion process (thermal effect).

Figure 5 shows the relation between the atomic ratios H/C and O/C (Van Krevelen Diagram). The average O/C ratio calculated from the ambient air samples (winter campaign) was higher than that measured in the tunnels. This can be associated to photochemical reactions in presence of sunlight producing oxygenated aerosol. The high H/C ratios found for tunnel samples indicated that fresh aerosols were collected on the filters due to primary emission from vehicle exhausts.

The O/C and H/C ratios varied more for the samples collected during the TJQ campaign than for the samples collected in TRA, possibly due to the different sampling times (see Table 1). In general, the samples collected during the morning (for 6 h) and at night (for 12 h) were more oxidized than the others. This can be related to a smaller number of cars and consequently to less POA emissions. In addition, the contribution of external air was more significant during these times. The afternoon samples (sampled for 3 h) were collected during the traffic congestion periods (between 5 and 8 p.m. – Brito et al., 2013) suggesting that POA dominated the burden sampled on the filters. Samples collected during the day (for 12 h) were mainly dominated by afternoon traffic congestion profile. Consequently, we used the 12 h day samples and the afternoon samples from the TJQ tunnel to calculate LDV emission factors.

The O/C ratios considered for EF calculation ranged between 0.16 and 0.20 (O/C), indicating a higher amount of oxygen in POA for the OA desorbed up to 350 °C than reported in previous studies. Chirico et al. (2011) found O/C ratio ranging between 0.073 (workday) and 0.199 (weekend). Collier et al. (2015) estimated O/C ratio around 0.19 for low particulate matter concentrations, measured in vehicles in a dynamometer. Given the fact that O/C ratios measured with the TD-PTR-MS are biased low

(Holzinger et al., 2013), the values found here indicate a more oxidized aerosol originated from the fuels used in Brazil, which may be related to the use of ethanol.

The distribution of the total emissions over the different desorption temperatures is presented in Fig. 6. This analysis indicated that OA produced from HDV were more volatile than OA from LDV. This can be seen by the higher amounts of HC and HCO ions derived from HDV up to 200 °C.

Hydrocarbons (HC) represented the most volatile group. Their volatility was related to the number of carbons present in molecules: short-chain hydrocarbons (up to 9 carbon atoms) were more volatile than the long-chain ones (more than 9 carbon atoms). The short-chain HC contribution was substantially low at 250 °C and higher temperatures while the long-chain HC contribution was still significant at 350 °C.

HDV emitted more volatile nitrogen compounds than LDV. Such distinction between the two categories of vehicular fleet was not observed in previous studies.

The oxygenated hydrocarbon compounds containing up to 2 oxygen atoms emitted by HDV were more volatile, as can be seen by the histogram in the 150–200 °C temperature steps. LDV emitted more volatile compounds containing three oxygen atoms due to the high contribution of phthalic anhydride ($C_8H_4O_3$), as presented in Table 4. Compounds containing more than 4 oxygen atoms were less volatile than compounds from other groups.

4 Conclusions

The main objective was the characterization of average emission factors of organic particulate compounds for Light (LDV) and Heavy (HDV) duty vehicles. The study was performed in the city of Sao Paulo, Brazil. Its atmosphere is impacted by the burning of different fuels: gasohol (gasoline with 25 % of ethanol), ethanol, and diesel (95 % diesel and 5 % biodiesel). The organic aerosol has an important contribution to the fine particle concentrations and previous studies showed that the main sources of these particles are vehicular emissions. In this study, two campaigns in traffic tunnels

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and one campaign in ambient air were performed in the city of Sao Paulo, collecting aerosol samples on quartz filters. The quantification and identification of the organic compounds was performed by TD-PTR-MS and TOT. Additional data from previous studies in this area were used for comparison and interpretation.

5   We observed, with all methods, that HDV emitted more fine particles than LDV (per kg fuel burned). OC represented a significant fraction of emitted $PM_{2.5}$: 36 % of LDV and 43 % of HDV, respectively. The amount of oxygen found in the desorbed aerosol up to 350 °C samples was higher than that found in the fuels. The emission of oxygenated compounds represented around 70 % of total organic aerosol for both types of vehicles
10 measured by the TD-PTR-MS.

A comparison between EF's of organic compounds (obtained by the TD-PTR-MS) from LDV and HDV showed distinct spectrum profiles. The m/z 149.024 ($C_8H_4O_3H^+$) may be a tracer for aerosol formed in the exhaust from vehicle engines. However, possible contamination could not be completely excluded. Furthermore, m/z 149.131
15 ($C_{11}H_{16}H^+$) tentatively attributed to pentylbenzene may be a unique tracer for gasoline, and, m/z 299.289 ($C_{19}H_{38}O_2H^+$) tentatively attributed to methyl stearate, may be a unique tracer for aerosols originating from biodiesel combustion.

A comparison among chemical groups (CH, CHO, CHON, and CHN) did show differences between LDV and HDV emissions. The nitrogen-containing compound found
20 in the particulate phase contributed around 20 % to the total OA emissions, probably related to NO_x chemistry during fuel combustion. The thermal desorption analysis showed that HDV emitted more volatile compounds for the aerosol desorbed up to 350 °C, mainly oxygenated hydrocarbons containing up to two oxygen atoms and long-chain hydrocarbons, than LDV.

25 Our results show that OA emission from LDV and HDV is a complex process involving oxidation of fuel constituents, NO_x chemistry, and condensation of unburned fuel hydrocarbons on new or existing particles. The obtained emission patterns can be used to study processing of young aerosol in ambient air. If chemically stable, the

found markers may prove useful to constrain the contribution of traffic to the OA burden at different locations in Brazil.

The Supplement related to this article is available online at doi:10.5194/acpd-15-33755-2015-supplement.

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Table 1. Filter identification, sampling time start, sampling duration, volume sampled (for OA samples), vehicle counts, OC and OA concentrations, and average CO and CO_2 concentrations during sampling in the TJQ tunnel in the year 2011.

Filter #	Start Sampling	Sampling duration (h)	Volume sampled (m^3)	# vehicles		OC[a] ($\mu g\,m^{-3}$)	OA[b] ($\mu g\,m^{-3}$)	Inside		Outside	
				LDV	HDV			CO_2	CO	CO_2 (ppm)	CO
TJQ 01	4 May 08:16	6	5	13 920	29	17.6	4.7	513.6	5.10	403.2	1.33
TJQ 02	4 May 17:00	3	3	12 856	34	–	4.2	526.3	6.15	401.1	1.14
TJQ 03	4 May 20:28	12	11	13 584	36	10.2	1.9	456.0	2.66	416.2	1.09
TJQ 04	5 May 08:22	5	5	14 759	49	14.7	4.0	513.6	5.47	403.2	1.33
TJQ 05	5 May 17:00	3	3	12 252	6	–	4.4	526.3	7.06	401.1	1.14
TJQ 06	5 May 20:10	12	11	13 538	18	20.7	4.2	456.0	4.42	416.2	1.09
TJQ 08	6 May 08:13	6	5	13 338	19	18.0	4.9	513.6	7.25	403.2	1.33
TJQ 09	6 May 17:00	3	2	12 660	6	–	5.8	526.3	7.37	401.1	1.14
TJQ 10	6 May 20:15	12	11	12 363	43	12.9	2.6	456.0	3.58	405.1	1.09
TJQ 11	7 May 08:05	12	11	24 510	272	12.8	2.4	510.5	3.47	400.4	1.24
TJQ 12	9 May 08:10	12	11	25 067	387	10.5	2.2	511.0	5.04	394.5	1.26
TJQ 13	9 May 20:10	12	11	11 546	36	8.2	1.8	425.9	2.05	390.5	0.75
TJQ 14	10 May 08:11	12	11	31 258	79	12.5	2.7	498.9	5.41	405.4	1.45
TJQ 15	10 May 20:15	12	11	13 113	111	8.3	2.1	437.5	2.50	392.5	0.49
TJQ 16	11 May 08:22	12	11	36 288	1223	14.7	2.9	507.3	5.45	395.7	0.73
TJQ 17	11 May 20:33	12	11	13 274	86	15.2	3.6	488.1	3.32	458.5	1.88
TJQ 18	12 May 08:37	11	10	32 800	283	15.3	3.2	512.2	5.79	393.9	1.29
TJQ 19	12 May 19:45	13	12	14 209	35	8.3	2.1	436.3	2.40	393.2	0.76
TJQ 20	13 May 08:25	12	11	27 162	87	12.3	2.4	510.0	5.35	403.1	1.35

[a] measured by TOT
[b] measured by TD-PTR-MS

Table 2. Filter identification, sampling time start, sampling duration, volume sampled (for OA samples), vehicle counts, OC and OA concentration, and average CO and CO_2 concentrations during sampling in the TRA tunnel in the year 2011.

Filter #	Start Sampling	Sampling duration (h)	Volume sampled (m^3)	# vehicles		OC^a ($\mu g\,m^{-3}$)	OA^b ($\mu g\,m^{-3}$)	Inside		Outside	
				LDV	HDV			CO_2	CO	CO_2 (ppm)	CO
TRA 01	7 Jul 16:30	6	6	10 497	4189	32.5	10.3	671.5	3.90	405.7	0.78
TRA 02	8 Jul 08:45	6	5	8406	4401	57.9	11.2	681.7	3.49	415.5	0.83
TRA 03	8 Jul 14:20	6	6	14 432	5171	54.3	10.5	661.9	3.91	416.8	0.74
TRA 04	11 Jul 08:53	5	5	7675	3960	71.4	11.4	678.1	4.56	417.1	1.49
TRA 05	11 Jul 14:26	7	6	10 807	4865	57.8	9.6	689.4	3.91	416.8	0.91
TRA 06	12 Jul 08:18	6	5	9836	5030	98.1	12.1	746.5	5.35	417.6	2.09
TRA 07	12 Jul 14:19	6	6	12 860	5441	54.1	11.5	679.1	3.85	416.8	0.96
TRA 08	13 Jul 08:10	6	5	10 585	5426	60.2	14.8	696.1	4.79	417.6	1.01
TRA 09	13 Jul 14:10	7	8	11 739	5311	63.9	8.9	678.8	4.62	416.8	1.04
TRA 10	14 Jul 08:28	6	5	10 751	5386	68.2	13.6	754.1	6.68	417.6	2.43
TRA 11	14 Jul 14:28	6	5	11 795	5112	70.0	11.5	683.5	4.31	416.8	1.15
TRA 15	15 Jul 08:10	6	5	10 400	5354	54.2	15.1	694.4	4.83	417.6	1.15
TRA 12	15 Jul 14:10	5	6	14 351	5142	47.8	11.6	689.0	3.62	416.8	1.00

[a] measured by TOT
[b] measured by TD-PTR-MS

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Table 3. OA (TD-PTR-MS), OC (TOT) and $PM_{2.5}$ averages emission factors ($mg\,kg^{-1}$ of burned fuel) and SD of the filters, for LDV and HDV.

	PTR-MS up to 300°C	Total[a]		TOT at 310°C	From 310–870°C	Gravimetry[b] $PM_{2.5}$
		All compounds	Compounds with O			
LDV	27.4 ± 10.4	30.9 ± 12.2	21.0 ± 8.8	28.0 ± 7.9	108.3 ± 35.7	300 ± 100[a]
HDV	69.1 ± 15.0	74.5 ± 15.0	50.0 ± 11.0	58.6 ± 8.9	304.0 ± 81.4	700 ± 300[a]

[a] The sum of all EF per temperature step (from 100 until 350°C)
[b] Values obtained from Pérez-Martínez et al. (2014)

Table 4. The ten highest EFs ($mg\,kg^{-1}$ of fuel) for LDV.

m/z	Empirical Formula	Average ± SD	Med (Min, Max)
149.024	$C_8H_4O_3H^+$	3.403 ± 0.861	3.221 (2.252, 4.500)
399.391	$C_{25}H_{50}O_3H^+$	0.255 ± 0.043	0.261 (0.170, 0.305)
397.377	$C_{29}H_{48}H^+$	0.231 ± 0.038	0.234 (0.154, 0.277)
413.405	$C_{26}H_{52}O_3H^+$	0.231 ± 0.040	0.237 (0.155, 0.283)
411.39	$C_{26}H_{50}O_3H^+$	0.230 ± 0.054	0.226 (0.143, 0.327)
253.102	$C_{13}H_{16}O_5H^+$	0.227 ± 0.066	0.218 (0.128, 0.355)
114.091	$C_6H_{11}ONH^+$	0.223 ± 0.224	0.104 (0.046, 0.603)
177.055	$C_{10}H_8O_3H^+$	0.208 ± 0.174	0.173 (0.039, 0.586)
385.375	$C_{24}H_{48}O_3H^+$	0.206 ± 0.038	0.210 (0.133, 0.255)
149.131	$C_{11}H_{16}H^+$	0.187 ± 0.053	0.164 (0.119, 0.257)

Table 5. The ten highest EFs ($mg\,kg^{-1}$ of fuel) for HDV.

m/z	Empirical Formula	Average ± SD	Med (Min, Max)
199.041	$C_{12}H_6O_3H^+$	2.035 ± 0.351	2.013 (1.558, 2.780)
149.024	$C_8H_4O_3H^+$	1.363 ± 0.493	1.181 (0.902, 2.578)
165.02	$C_8H_4O_4H^+$	0.990 ± 0.210	0.965 (0.674, 1.398)
203.087	$C_9H_{14}O_5H^+$	0.947 ± 0.181	0.905 (0.761, 1.424)
299.289	$C_{19}H_{38}O_2H^+$	0.938 ± 0.242	0.884 (0.691, 1.538)
181.08	$C_5H_{12}O_5N_2H^+$	0.722 ± 0.144	0.693 (0.557, 1.076)
207.117	$C_{16}H_{14}H^+$	0.706 ± 0.144	0.684 (0.523, 1.030)
257.246	$C_{16}H_{32}O_2H^+$	0.678 ± 0.474	0.475 (0.128, 1.559)
163.04	$C_9H_6O_3H^+$	0.641 ± 0.137	0.630 (0.449, 0.920)
213.06	$C_6H_{12}O_8H^+$	0.607 ± 0.108	0.613 (0.476, 0.851)
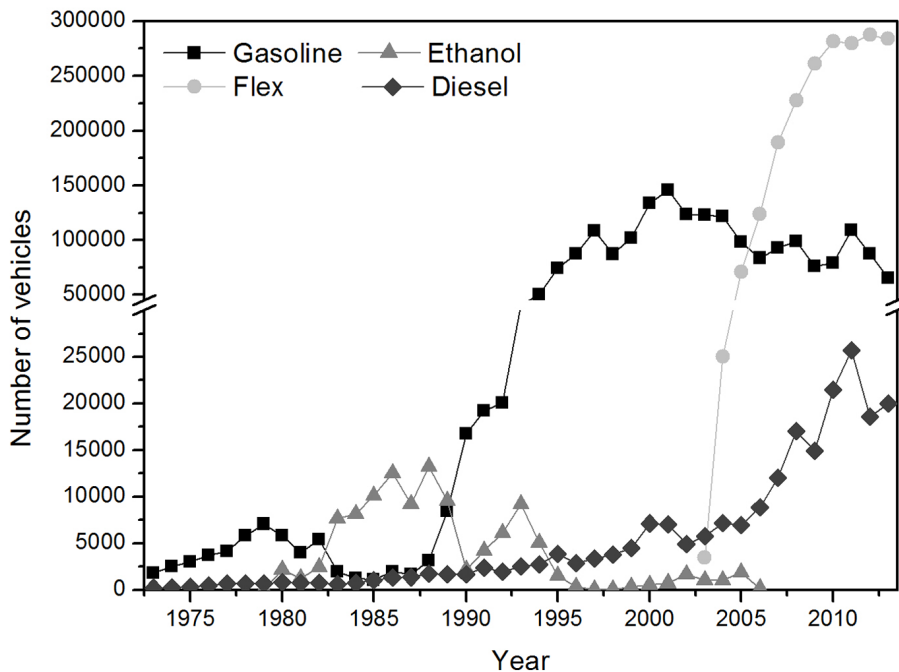
Figure 1. Annual registrations of new vehicles in the city of Sao Paulo.
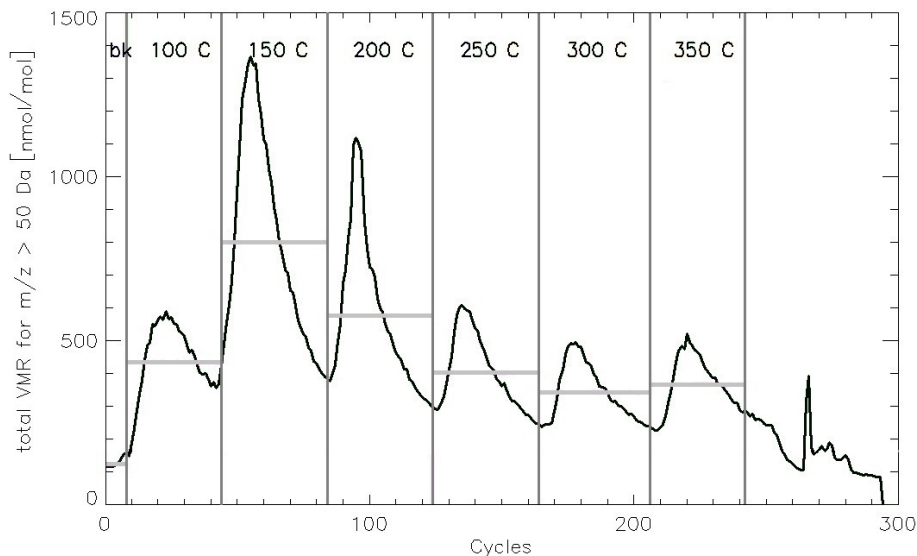
Figure 2. Result of an analysis of filter TRA 10 by TD-PTR-MS. The figure shows the total volume mixing ratios (VMR) of all ions above 50 Da (in nmol mol^{-1}) with a temporal resolution of 5 s. The vertical lines represent the heating steps as indicated on the top of the figure. The horizontal gray lines between these vertical lines are the concentration averages at each temperature step, and the background level (the first short horizontal line) is subtracted from these values before further analysis.

Discussion Paper | Discussion Paper | Discussion Paper | Discussion Paper | Discussion Paper
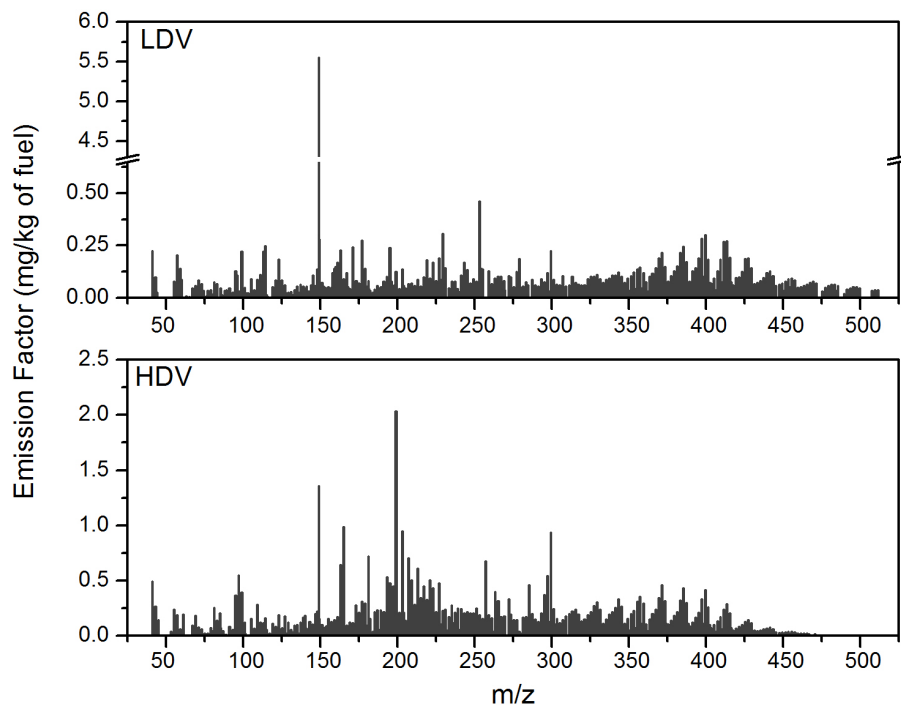
Figure 3. Average emission factor (mg kg^{-1} of fuel burned) mass spectra identified by the TDPTR-MS for LDV and HDV, which are identified on the left top of each figure.

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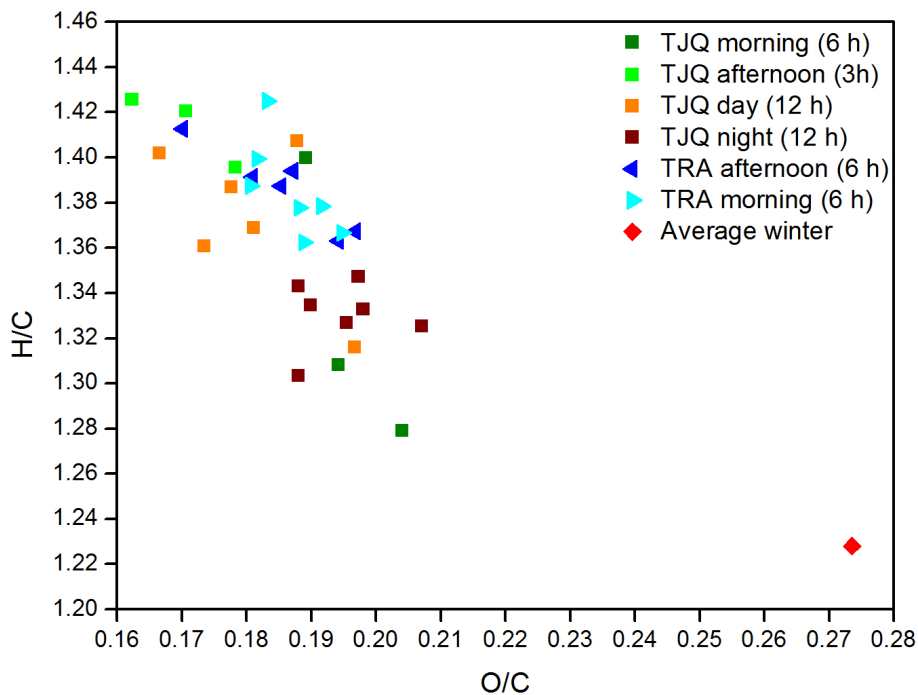Full Screen / Esc

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Interactive Discussion
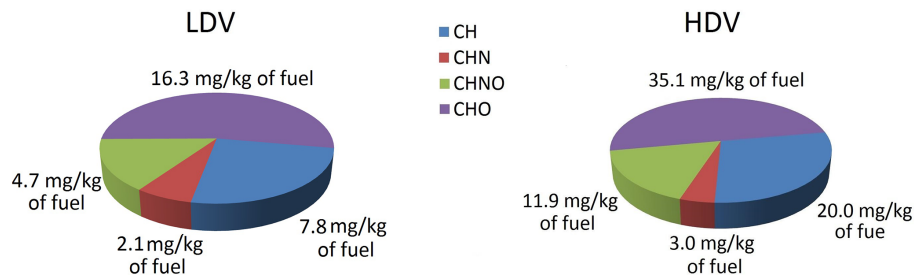
Figure 4. Total average emission factors calculated for LDV and HDV divided in groups containing CH, CHO, CHN, and CHON.

Figure 5. Scatter plot of atomic ratios O/C and H/C (van Krevelen diagram) of TD-PTR-MS data for the TRA, TJQ and winter campaigns.
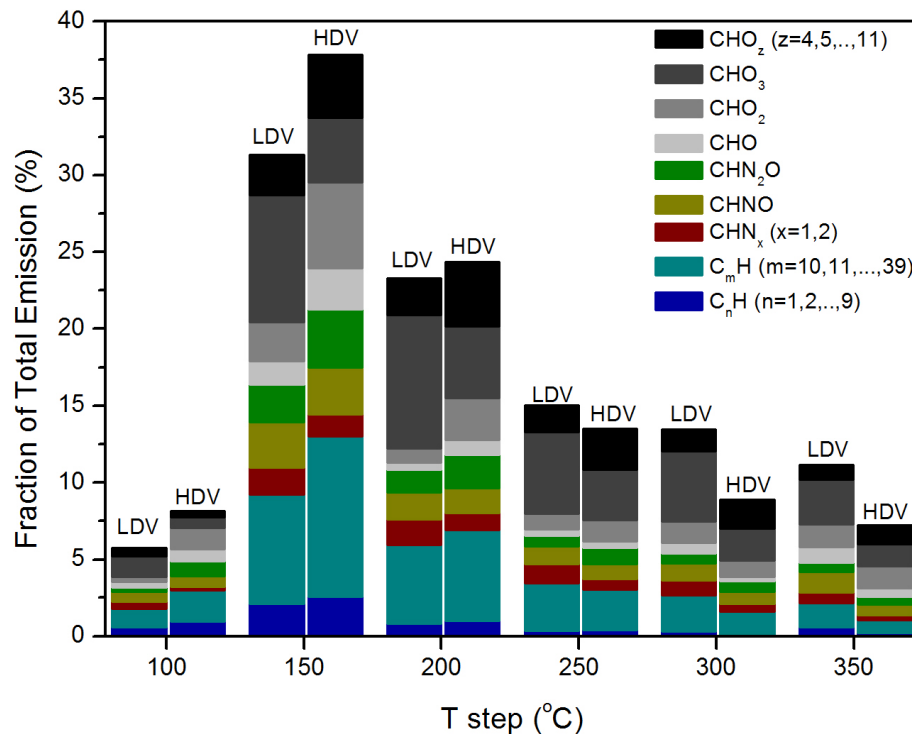
Figure 6. Fraction of total average emission (in %) divided into groups containing CH, CHO, CHON, and CHN, considering different numbers of carbon and oxygen atoms in the compounds, for LDV and HDV at each temperature step.