Chemical characterization of organic particulate matter from on-road traffic in Sao Paulo, Brazil

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

[1] Institute of Astronomy, Geophysics and Atmospheric Sciences, University of Sao Paulo, Sao Paulo, Brazil

[2] Institute for Marine and Atmospheric Research, Utrecht (IMAU), Utrecht University, the Netherlands

[3] School of Molecular Sciences, Arizona State University, Tempe, United States

[4] Center for Isotope Research, University of Groningen, Groningen, the Netherlands

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

Abstract

This study reports emission of organic particulate matter by Light (LDV) and Heavy (HDV) duty vehicles in the city of Sao Paulo, Brazil, where vehicles run on three different fuel types: gasoline with 25% ethanol (called gasohol, E25), hydrated ethanol (E100), and diesel (with 5% of biodiesel). 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. Fine particulate matter ($PM_{2.5}$) samples were collected on quartz filters in May and July 2011 at TJQ and TRA, respectively. The samples were analyzed by Thermal-Desorption Proton-Transfer-Reaction Mass-Spectrometry (TD-PTR-MS), and by Thermal-Optical Transmittance (TOT). Emission factors (EF) for organic aerosol (OA) and organic carbon (OC) were calculated for the HDV and the LDV fleet. We found that HDV emitted more $PM_{2.5}$ than LDV, with OC emission factors of 108 and 523 mg kg^{-1}burned fuel for 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. Unique organic tracers for gasoline, biodiesel, and tire wear have been tentatively identified. Nitrogen-containing compounds contributed around 20% to the EF values for both types of vehicles, possibly associated with incomplete fuel burning or fast secondary production. Additionally, 70% and 65% of the emitted mass (OA) originates from oxygenated compounds for LDV and HDV, respectively. This may be a consequence of the high oxygen content of the fuel. On the other hand additional oxygenation may occur during fuel combustion. The high fractions of nitrogen and oxygen containing compounds show that chemical processing close to the engine/tailpipe region is an important factor influencing

primary organic aerosol emission. The thermal desorption analysis showed that HDV emitted compounds with higher volatility, mainly oxygenated 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, henceforth referred to as diesel), hydrated ethanol (E100) and gasohol (gasoline with 25% of ethanol, E25). 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 E100 and E25.

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 E100. The production of ethanol increased from 1 million cubic meter (1970's) to more than 10 million (in the mid-1980's), (Stattman et al., 2013). The 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. 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 (Figure 1).

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). Regarding the emission of fine particles ($PM_{2.5}$) and ozone (O_3), Pérez-Martínez et al. (2014) did not observe a decreasing trend. On the other hand, Salvo and Geiger (2014) attributed lower ozone levels to a shift in fuel use from ethanol to gasoline, while CO and NO_x exhibited an increasing trend.

The usage of ethanol blends on flex-fuel vehicles has been widely discussed. Some advantages on increasing the ethanol blend in gasoline by flex-fuels vehicles were discussed by Karavalakis et al. (2014). They showed a significant reduction in the emission of particulate matter (PM) mass including soot, and particle number but a sharp increase of acetaldehyde. Besides, they also discussed that the way the gasoline injection is performed in the vehicle has a significant impact on soot emissions, e.g. gasoline direct injection vehicles emitted more soot than port-fuel injection. In an investigation of the size distribution of soot formed from ethanol/gasoline blend diffusion flames, Matti Maricq (2012) found that the addition of small amounts of ethanol insignificantly changed the size distribution . Furthermore, they found that high amounts of ethanol in the fuel (E85) lead to a significant reduction of semi volatile organic compound formation.

In a comparison between ethanol fuel contents (E85 and E75, 85 and 75% of ethanol in gasoline respectively) in two different studies, Suarez-Bertoa et al. (2015a) and Suarez-Bertoa et al. (2015) concluded that a higher amount of ethanol resulted in a reduction of nitrogen oxides ($NO+NO_2=NO_x$) emissions, however, it increased acetaldehyde and ethanol emissions, which leads to a significant increase of ozone formation potential (OFP). Based on observations of road traffic levels, meteorological conditions and pollutant concentrations associated to a consumer demand model (for ethanol and gasoline), Salvo and Geiger (2014) concluded that ozone ambient levels increased with increased ethanol amounts in fuel.

Regarding the use of biodiesel, 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. 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). 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 emissions due to the use of diesel and bio-diesel have many important differences that affect the formation of secondary organic aerosol and the formation of fine particles. The use of biodiesel is associated with an increase in NO_x emission (Hoekman and Robbins, 2012), carbonyl compounds (Machado Corrêa and Arbilla, 2008) and also some poly aromatic hydrocarbons (PAHs) (Karavalakis et al., 2011). The number and size distribution of particles are also affected by the use of biodiesel. The ambient air in Sao Paulo city is highly affected by policy decisions concerning the use of different fuels. Therefore, the effects of specific fuels on ozone formation and fine particle concentrations need to be better understood in order to comply with air quality standards (Cetesb, 2014).

Due to its dense population, political and economic importance, the MASP has been 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), although only few publications focused on the organic part of the aerosols. In a study performed in 2008, Souza et al. (2014) estimated from OC measurements that approximately 26% of the $PM_{2.5}$ was composed of particulate organic matter. Recently, Brito et al. (2013) discussed the aerosol composition including OC and PAH in a tunnel study. 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 both light duty vehicles (LDV) and heavy duty vehicles (HDV).

Since the vehicular emission in Sao Paulo city is the main source for $PM_{2.5}$, it is of importance to distinguish the contributions from LDV and HDV. Different methods can be used in order to estimate the emissions from the vehicular fleet. Emission factors (EF) for gaseous and total $PM_{2.5}$ have been calculated based on tunnel measurements by Pérez-Martínez et al. (2014), showing that LDV emitted similar levels of CO than HDV, but much lower amounts of NO_x and $PM_{2.5}$ ($EF_{PM2.5}$ of 20 and 277 mg km^{-1} for LDV and HDV, respectively). Nevertheless, no publication so far has discussed the organic composition of aerosols formed from vehicular emissions.

The main contribution of this work is to analyze the composition of organic compounds found in fine particles emitted by the transport sector in Sao Paulo, which has the unique characteristic of using bio-fuels on a large scale. 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, the TD-PTR-MS was applied to filter 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 4th to 13rd May 2011 and a second campaign was performed in the Rodoanel Mario Covas tunnel (TRA), from 6th to 17th July 2011.

TJQ is a two-lane tunnel located in the Center of Sao Paulo and characterized mainly by light-duty vehicle traffic. The direction of the traffic in this tunnel alternated twice a day at 6 AM and 9 AM. 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 (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 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, 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 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 E100 or E25 (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 ^{o}C, for 12 hours), subsequently wrapped in aluminum foil (pre-cleaned at 550 ^{o}C, for 8 hours) and stored inside polyethylene bags in a freezer at -18 ^{o}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 Table 2. The gaseous concentration was obtained on an hourly base and the average value was calculated to match the period of filter sampling.

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 PTR-MS using a 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 = 140V, Uso= 92V, E/N 130 Td. The extraction voltage at the end of the drift tube (Udx) was 28V. We assumed a reaction rate constant of 3×10^{-9} $cm^3 s^{-1}$, which implies the same sensitivity for all compounds. This is a standard method for PTR-MS when complex mixtures of unknown composition are measured. Typical errors in the order of ~40% apply for individual species as discussed in Holzinger et al. (2010) and Timkovsky et al. (2015). The mass resolving power of the TOF was in the range of 3000-4000 (FWHM) for all measurements and the peak shape was near Gaussian. For instance, the peaks detected at 149.024 Da and 149.131 Da were well separated by more than 5 sigma of the normal distribution.

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^{o}C. A piece of 0.20 cm^2 area from each filter was introduced to the first oven at 50 ^{o}C and heated in temperature steps of 50^{o}C from 100 to 350^{o}C, allowing 3 minutes 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 ml min^{-1}, except for a few tunnel samples, which were measured at a flow rate of 50 ml 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 an inert atmosphere, where no other gas besides N_2 was present in the oven system, in order to exclude oxidation during desorption. Three replicas were measured from each filter 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^{o}C, with heating times ranging from 60 to 200s. Here, the discussion focus is 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 tunnel 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 5s. Similar to the procedure described by Timkovsky et al. (2015), the instrument background ($VMR_{i,instrbgd}$), identified in Figure 2 by the first horizontal gray line, was subtracted from the measured volume mixing ratio ($VMR_{i,measeured}$) for an ion 'i' at each temperature step:

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

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 ($\overline{VMR_{\imath}}$). 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. These blank filters were treated exactly like the aerosol sample filters (preparation, storage and analysis), except that no particles were collected on them. For TJQ campaign, 18 blank filters were analyzed, and for TRA, 14 blank filters. After this test, 605 (TJQ) and 627 (TRA) 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 ($\left(\overline{VMR_{\imath,sampled}}\right)$) for each ion '$i$' and each temperature step.

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

The $VMR_{i,final}$ 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):

$$C_i = \frac{VMR_{i,final} * M_i * V_{Nitrogen}}{V_{samp} * f} \qquad (3)$$

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); Δ[P] is the increase of [P] above the background levels (in ng m^{-3}); $\Delta[CO_2]$ and Δ[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 Carbon per g of fuel) for a fuel *c* - ω_G = 0.757 for E25 and ω_D = 0.818 for 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 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 E25and 251 g km^{-1} for diesel), ρ is the fuel density (765 g l^{-1} for E25, 854 g l^{-1} for diesel). The subscripts *G* and *D* denote gasohol (E25) and diesel, respectively.

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

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

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 equation (6) was calculated from the measurements in the TJQ campaign.

The ventilation system in the tunnels brings the air from the outside to the interior by ventilation fans on the roof of the tunnels operating according to the CO level in order to provide fresh air inside. This air already contains some urban background aerosol and hence a subtraction of this background is necessary to remove any contribution not originating from the traffic inside the tunnel itself. Considering that the difference of CO between inside and outside (ΔCO) is directly related to the vehicular emission (for Sao Paulo, more than 90% of CO comes from vehicular emissions), a linear relation between ΔCO and the pollutant, P, from the same source is expected. The background concentration can therefore be calculated as the intercept of a linear fit between ΔCO and P. A linear relation between ΔCO and OA (and OC) was mainly observed for the TJQ campaign. For the TRA campaign, the linear relation was not as evident as for the TJQ campaign. This is mainly because our measurements show that most OA originated from HDV, while most CO originated from LDV. Thus the sources of OA and CO were decoupled in the TRA tunnel. Moreover, ΔCO did not vary strongly in the TRA tunnel, which made a linear fit unreliable. We considered the background air near the tunnels was the same for both tunnels, and consequently subtracted the background estimates obtained for TJQ. Due to the high concentrations in the TRA tunnel, any type of background subtraction will have an insignificant effect on the final results. More details about the background correction can be found in the supplement.

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 EFs were higher for HDV than for LDV.

The EF of OC represented 28% and 60% 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 ^{o}C) and OA (TD-PTR-MS, up to 300^{o}C) we infer that TD-PTR-MS quantified ~70% and ~55% 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^{o}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% and 65% for LDV and HDV, respectively. 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.

The EF(OA) values presented here were lower than the ones found in other studies. Chirico et al.(2011) found 33.7 (HDV) 5.6 (LDV) mg km^{-1}, and another study in the ZhujiangTunnel in Guangzhou, China (He et al., 2008) found 76 (HDV) and 19 (LDV) mg km^{-1}. The observed differences are mostly due to the fact that in our study a large fraction of OA is missed due to the 350^{o}C limit for thermal desorption. Additional effects could be due to the different fuel composition used in Brazil, since the Brazilian gasoline includes 25% of ethanol. It has been shown that an increased percentage of biofuel can lead to the reduction of the particulate matter emission (Karavalakis et al., 2014; Mamakos et al., 2013). This may explain the larger difference observed for LDV as compared to HDV.

Regarding the EF (OC), most of the references found did not distinguish between the contribution of LDV and HDV for EF calculations. In a study conducted in China (Cheng et al., 2010) in Shing Mun Tunnel for diesel emission characterization found an emission factor of 67.9 mg km^{-1} for OC. Zhang et al. (2015) found 19.2 mg km^{-1} ,12% HDV and 27% liquefied petroleum gas vehicles. Hung-Lung and Yao-Sheng (2009) and Handler et al. (2008) found 4.7 (~15% HDV) and 2.3 (~10% HDV) mg km^{-1}, respectively. These values, although comparable, were lower than EF (OC) considering only LDV. In conclusion, we can affirm that the vehicles in Sao Paulo city emit more OC/km than in several other cities.

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 E25. 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 one compound exceeded EF's of 0.100 mg kg^{-1} of fuel. In contrast, many compounds emitted by HDV exceeded 0.100 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 Table 5 show the ten highest average EF values for both types of vehicles, as well as their m/z, their tentative empirical formula, the median, maximum and minimum EF values. The complete list of all compounds is shown in the Supplementary Material (Table S2). 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 both LDV and HDV with the value of 4.9 and 3.1 mg/kg of fuel, respectively. 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 is potentially prone to positive artifacts caused by the handling of the filters, however the blank filters that were also stored in plastic bags did not show a significant signal at this mass. It is important to point out that the instrumental background, field blank, and ambient air background subtractions were performed before calculating the emission factors and give no indication of an artifact. 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). We suggest that this species may be produced from tire wear. This is also supported by the fact that measured concentrations of m/z 149.024 do not correlate with excess CO (see supplemental information), a behavior which was observed for most ions and indicates that the emission is associated with fuel combustion.

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 Supplementary Material) 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 around a third. Oxygenated hydrocarbons (CHO) showed highest contribution to emissions for both vehicle types, where LDV (60%) exhibited a larger fraction than HDV (48%). The high fraction of oxygen containing compounds shows that chemical processing close to the engine/tailpipe region is an important factor influencing primary organic aerosol emission. Our findings are in line with Collier et al. (2015) who measured high O/C ratios in primary organic aerosol from gasoline and diesel engines. The nitrogen-containing groups contributed around 20% to the measured OA. Such a high percentage in the aerosol may be due to NO_x chemistry during the combustion process (thermal effect). Another production pathway for CHON compounds is facilitated by the absence of sunlight in the tunnels, which mimics nighttime chemistry. Several studies have shown that most nighttime secondary OA is due to NO_3 radicals formed by anthropogenic NO_x emissions (e.g. Rollins et al., 2011)). It is an open question to what extent the production of CHON compounds can be attributed to the use of bio-diesel, however, it is worthwhile to note that Hoekman and Robbins (2012) associated bio-diesel use with higher NO_x emissions.

Figure 5 shows the relation between the atomic ratios H/C and O/C (Van Krevelen Diagram), calculated from the mass concentration, corrected for ambient background as used for the EF calculation. Besides the ratios from the tunnel campaigns discussed here, Figure 5 also present the average ratios from an ambient campaign performed in the Sao Paulo city (5 km away from TJQ and 15 km from TRA) during the Southern Hemisphere winter, between August and September 2012 (yet unpublished results). The average ambient O/C was higher than measured in the tunnels, which is associated with photochemical reactions in presence of sunlight producing more oxygenated aerosol. The high H/C ratios found for the tunnels samples indicated that fresh aerosol were collected on the filters due to primary emission from vehicle exhaust.

The O/C and H/C ratios presented more variation for the samples collected during the TJQ campaign than for the samples collected in TRA; possibly due to the differences in the traffic and congestion (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. The afternoon samples (sampled for 3 h) were collected during the traffic congestion periods (between 5 and 8 pm, 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.

The O/C ratios ranged between 0.14 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. The ratios found here were significantly higher than the ratio found for gasoline and diesel (around 0.04), measured on POA formed under controlled conditions (Aiken et al., 2008). In a different tunnel study, Chirico et al. (2011) also found significant differences, the O/C ratios ranged between 0.073 (workday) and 0.199 (weekend). Collier et al. (2015) estimated O/C ratios around 0.19 for low particulate matter concentrations, measured in vehicles using a dynamometer, and they found higher O/C values for diesel engines. 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 and bio-diesel.

Chirico et al. (2011) found H/C ratios ranging between 1.84 and 1.71, for working and weekend days, respectively. These values were higher than 1.62, found by Aiken et al. (2008), in ambient measurements performed in Mexico City. In both studies the H/C ratio was higher than found here, ranging between 1.25 and 1.47. This is in agreement with the higher O/C ratio found in this study, showing a higher oxygenation state of the particulate compounds sampled in the tunnels comparing to results from Mexico City or Switzerland. It is important to highlight here that it may also be due to differences in the applied techniques: the AMS operates at high vaporization temperatures (usually constantly at 600°C), measuring smaller particles (PM1) than discussed here, and uses a different method of ionization, namely electron impact ionization.

The distribution of the total emissions over the different desorption temperatures is presented in Figure 6. This analysis indicated that OA produced from HDV were more volatile than OA from LDV. As expected, 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 very 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 were the most significant group in the aerosol composition. The group containing up to 3 oxygen atoms was predominant due to m/z 149.024, mainly at 150 and 200°C, for LDV emission. The relative contribution from oxygenated compounds to the total OA increased during the last temperature steps.

In addition, the fraction of ions with at least one oxygen atom is higher than reported by Chirico et al. (2011) in a tunnel in Switzerland. Chirico et al. (2011) showed that CH-ions largely dominated the average OA mass spectra from online AMS measurements sampled during rush hours on working days. The difference to this study can be explained by both the different analytical techniques and the use of ethanol and biodiesel in Brazilian fuels, which have a higher oxygen content than the fuels used in Switzerland.

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 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.

We observed, with all methods, that HDV emitted more fine particles than LDV (per kg fuel burned). OC represented a significant fraction of emitted $PM_{2.5}$: factors of 108 and 523 mg kg^{-1} burned fuel for LDV and HDV, respectively. The amount of oxygen found in the desorbed aerosol up to 350°C samples was higher than that found in the unburned fuels. The emission of oxygenated compounds represented around 70% of total organic aerosol for both types of vehicles measured by the TD-PTR-MS.

A comparison between EFs 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 tire wear. However, possible contamination could not be completely excluded. Furthermore, m/z 149.131 ($C_{11}H_{16}H^+$) 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 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, mainly oxygenated hydrocarbons containing up to two oxygen atoms and long-chain hydrocarbons, than LDV.

Acknowledgements

The collection and analysis of tunnel samples from Brazil has been funded by the Foundation for Research Support of the São Paulo State, (projects: 2011/17754-2 and 2012/21456-0), Improvement of Higher Education Personnel (CAPES) and National Council for Scientific and Technological Development (CNPq). The TD-PTR-MS has been funded by the Netherlands Organization for Scientific Research (NWO) under the ALW-Middelgroot program (Grant 834.08.002). U. Dusek acknowledges funding by the Netherlands Organization for Scientific Research (NWO), Grant no. 820.01.001. We thank Emilia Brasilio for implementing improvements on the EF calculation.

5. References

Aiken, A. C., Decarlo, P. F., Kroll, J. H., Worsnop, D. R., Huffman, J. A., Docherty, K. S., Ulbrich, I. M., Mohr, C., Kimmel, J. R., Sueper, D., Sun, Y., Zhang, Q., Trimborn, A., Northway, M., Ziemann, P. J., Canagaratna, M. R., Onasch, T. B., Alfarra, M. R., Prevot, A. S. H., Dommen, J., Duplissy, J., Metzger, A., Baltensperger, U. and Jimenez, J. L.: O / C and OM / OC Ratios of Primary , Secondary , and Ambient Organic Aerosols with High Resolution Time-of-Flight Aerosol Mass Spectrometry, Environ. Sci. Technol., 42(12), 4478–4485, 2008.

Albuquerque, T. A., Andrade, M. F. and Ynoue, R. Y.: Characterization of atmospheric aerosols in the city of Sao Paulo, Brazil: Comparisons between polluted and unpolluted periods, Environ. Monit. Assess., 184(2), 969–984, doi:10.1007/s10661-011-2013-y, 2012.

Andrade, M. F., Miranda, R. M., Fornaro, A., Kerr, A., Oyama, B., Andre, P. A. and Saldiva, P.: Vehicle emissions and PM2.5 mass concentrations in six Brazilian cities, Air Qual. Atmos. Heal., 5(1), 79–88, doi:10.1007/s11869-010-0104-5, 2012.

ANP: Boletim Mensal do Biodiesel- Fevereiro 2015 Agência Nacional do Petróleo, Gás Natural e Biocombustíveis., , 22, 2015.

Brito, J., Rizzo, L. V., Herckes, P., Vasconcellos, P. C., Caumo, S. E. S., Fornaro, A., Ynoue, R. Y., Artaxo, P. and Andrade, M. F.: Physical–chemical characterisation of the particulate matter inside two road tunnels in the São Paulo Metropolitan Area, Atmos. Chem. Phys., 13(24), 12199–12213, doi:10.5194/acp-13-12199-2013, 2013.

Carvalho, V. S. B., Freitas, E. D., Martins, L. D., Martins, J. A., Mazzoli, C. R. and Andrade, M. F.: Air quality status and trends over the Metropolitan Area of São Paulo, Brazil as a result of emission control policies, Environ. Sci. Policy, 47, 68–79, doi:10.1016/j.envsci.2014.11.001, 2015.

Cetesb: Relatório de Qualidade do Ar no Estado de São Paulo 2013., , 110 [online] Available from: http://ar.cetesb.sp.gov.br/publicacoes-relatorios/, 2014.

Chan, a. W. H., Kautzman, K. E., Chhabra, P. S., Surratt, J. D., Chan, M. N., Crounse, J. D., Kürten, a., Wennberg, P. O., Flagan, R. C. and Seinfeld, J. H.: Secondary organic aerosol formation from photooxidation of naphthalene and alkylnaphthalenes: Implications for oxidation of intermediate volatility organic compounds (IVOCs), Atmos. Chem. Phys., 9(9), 3049–3060, doi:10.5194/acp-9-3049-2009, 2009.

Cheng, Y., Lee, S. C., Ho, K. F., Chow, J. C., Watson, J. G., Louie, P. K. K., Cao, J. J. and Hai, X.: Chemically-speciated on-road PM2.5 motor vehicle emission factors in Hong Kong, Sci. Total

Environ., 408(7), 1621–1627, doi:10.1016/j.scitotenv.2009.11.061, 2010.

Chirico, R., Prevot, A. S. H., DeCarlo, P. F., Heringa, M. F., Richter, R., Weingartner, E. and Baltensperger, U.: Aerosol and trace gas vehicle emission factors measured in a tunnel using an Aerosol Mass Spectrometer and other on-line instrumentation, Atmos. Environ., 45(13), 2182–2192, doi:10.1016/j.atmosenv.2011.01.069, 2011.

Collier, S., Zhou, S., Kuwayama, T., Forestieri, S., Brady, J., Zhang, M., Kleeman, M., Cappa, C., Bertram, T. and Zhang, Q.: Organic PM Emissions from Vehicles: Composition, O/C Ratio, and Dependence on PM Concentration, Aerosol Sci. Technol., 49(2), 86–97, doi:10.1080/02786826.2014.1003364, 2015.

Graus, M., Müller, M. and Hansel, A.: High resolution PTR-TOF: Quantification and Formula Confirmation of VOC in Real Time, J. Am. Soc. Mass Spectrom., 21, 1037–1044, doi:10.1016/j.jasms.2010.02.006, 2010.

Handler, M., Puls, C., Zbiral, J., Marr, I., Puxbaum, H. and Limbeck, A.: Size and composition of particulate emissions from motor vehicles in the Kaiserm??hlen-Tunnel, Vienna, Atmos. Environ., 42(9), 2173–2186, doi:10.1016/j.atmosenv.2007.11.054, 2008.

Hansel, A., Jordan, A., Holzinger, R., Prazeller, P., Vogel, W. and Lindinger, W.: Proton transfer reaction mass spectrometry: on-line trace gas analysis at the ppb level, Int. J. Mass Spectrom. Ion Process., 149-150(95), 609–619, 1995.

He, L. Y., Hu, M., Zhang, Y. H., Huang, X. F. and Yao, T. T.: Fine particle emissions from on-road vehicles in the Zhujiang Tunnel, China, Environ. Sci. Technol., 42(12), 4461–4466, doi:10.1021/es7022658, 2008.

Hoekman, S. K. and Robbins, C.: Review of the effects of biodiesel on NOx emissions, Fuel Process. Technol., 96, 237–249, doi:10.1016/j.fuproc.2011.12.036, 2012.

Holzinger, R.: PTRwid: a new widget-tool for processing PTR-TOF-MS data, Atmos. Meas. Tech. Discuss., 8(2), 1629–1669, doi:10.5194/amtd-8-1629-2015, 2015.

Holzinger, R., Kasper-Giebl, A., Staudinger, M., Schauer, G. and Röckmann, T.: Analysis of the chemical composition of organic aerosol at the Mt. Sonnblick observatory using a novel high mass resolution thermal-desorption proton-transfer-reaction mass-spectrometer (hr-TD-PTR-MS), Atmos. Chem. Phys., 10(6), 13969–14011, doi:10.5194/acp-10-10111-2010, 2010.

Holzinger, R., Goldstein, A. H., Hayes, P. L., Jimenez, J. L. and Timkovsky, J.: Chemical evolution of organic aerosol in Los Angeles during the CalNex 2010 study, Atmos. Chem. Phys., 13(19), 10125–10141, doi:10.5194/acp-13-10125-2013, 2013.

Hung-Lung, C. and Yao-Sheng, H.: Particulate matter emissions from on-road vehicles in a freeway tunnel study, Atmos. Environ., 43(26), 4014–4022, doi:10.1016/j.atmosenv.2009.05.015, 2009.

Infocidade: Infocidade, [online] Available from: http://infocidade.prefeitura.sp.gov.br/ (Accessed 23 May 2015), 2015.

Jordan, A., Haidacher, S., Hanel, G., Hartungen, E., Märk, L., Seehauser, H., Schottkowsky, R., Sulzer, P. and Märk, T. D.: A high resolution and high sensitivity proton-transfer-reaction time-of-flight mass spectrometer (PTR-TOF-MS), Int. J. Mass Spectrom., 286, 122–128, doi:10.1016/j.ijms.2009.07.005, 2009.

Karavalakis, G., Boutsika, V., Stournas, S. and Bakeas, E.: Biodiesel emissions profile in modern diesel vehicles. Part 2: Effect of biodiesel origin on carbonyl, PAH, nitro-PAH and oxy-PAH emissions., Sci. Total Environ., 409(4), 738–47 [online] Available from: http://www.sciencedirect.com/science/article/pii/S0048969710012167 (Accessed 29 February 2016), 2011.

Karavalakis, G., Short, D., Russell, R. L., Jung, H., Johnson, K. C., Asa-Awuku, A. and Durbin, T. D.: Assessing the impacts of ethanol and isobutanol on gaseous and particulate emissions from flexible fuel vehicles, Environ. Sci. Technol., doi:10.1021/es5034316, 2014.

Kirchstetter, T. W., Harley, R. A., Kreisberg, N. M., Stolzenburg, M. R. and Hering, S. V: On-road measurement of fine particle and nitrogen oxide emissions from light- and heavy-duty motor vehicles, Atmos. Environ., 33, 2955 – 2968, 1999.

Lindinger, W., Hansel, A. and Jordan, A.: On-line monitoring of volatile organic compounds at pptv levels by means of proton-transfer-reaction mass spectrometry (PTR-MS) medical applications, food control and environmental research, Int. J. Mass Spectrom. Ion Process., 173(3), 191–241, 1998.

Machado Corrêa, S. and Arbilla, G.: Carbonyl emissions in diesel and biodiesel exhaust, Atmos. Environ., 42(4), 769–775, doi:10.1016/j.atmosenv.2007.09.073, 2008.

Mamakos, A., Martini, G., Marotta, A. and Manfredi, U.: Assessment of different technical options in reducing particle emissions from gasoline direct injection vehicles, J. Aerosol Sci., 63, 115–125, doi:10.1016/j.jaerosci.2013.05.004, 2013.

Martins, L. D., Andrade, M. F., Freitas, E. D., Pretto, A., Gatti, L. V, Albuquerque, E. L., Tomaz, E., Guardani, M. L., Martins, M. H. R. B. and Junior, O. M. A.: Emission factors for gas-powered vehicles traveling through road tunnels in São Paulo, Brazil., Environ. Sci. Technol., 40(21), 6722–6729, 2006.

Matti Maricq, M.: Soot formation in ethanol/gasoline fuel blend diffusion flames, Combust. Flame, doi:10.1016/j.combustflame.2011.07.010, 2012.

Miguel, A. H., Kirchstetter, T. W., Harley, R. A. and Hering, S. V.: On-road emissions of particulate polycyclic aromatic hydrocarbons and black carbon from gasoline and diesel vehicles, Environ. Sci. Technol., 32(4), 450–455, doi:10.1021/es970566w, 1998.

Miranda, R. M. and Andrade, M. F.: Physicochemical characteristics of atmospheric aerosol during winter in the São Paulo Metropolitan area in Brazil, Atmos. Environ., 39(33), 6188–6193, doi:10.1016/j.atmosenv.2005.06.055, 2005.

Miranda, R. M., Andrade, M. F., Worobiec, A. and Grieken, R. Van: Characterisation of aerosol particles in the São Paulo Metropolitan Area, Atmos. Environ., 36, 345–352, 2002.

MME: Ministério de Minas e Energia, [online] Available from: http://www.mme.gov.br/programas/biodiesel/menu/programa/objetivos_diretrizes.html (Accessed 23 March 2015), 2015.

Naik, C. V., Westbrook, C. K., Herbinet, O., Pitz, W. J. and Mehl, M.: Detailed chemical kinetic reaction mechanism for biodiesel components methyl stearate and methyl oleate, Proc. Combust. Inst., 33(1), 383–389, doi:10.1016/j.proci.2010.05.007, 2011.

Pérez-Martínez, P. J., Miranda, R. M., Nogueira, T., Guardani, M. L., Fornaro, A., Ynoue, R. and Andrade, M. F.: Emission factors of air pollutants from vehicles measured inside road tunnels in São Paulo: case study comparison, Int. J. Environ. Sci. Technol., doi:10.1007/s13762-014-0562-7, 2014.

Pierson, W. R., Gertler, A. W., Robinson, N. F., Sagebiel, J. C., Zielinska, B., Bishop, G. A., Stedman, D. H., Zweidinger, R. B. and Ray, W. D.: Real-world automotive emissions - summary of studies in the Fort McHenry and Tuscarora Mountain Tunnels, Atmos. Environ., 30(12), 2233–2256, doi:10.1016/1352-2310(95)00276-6, 1996.

Ramadhan, O. M. and Al-Hyali, E. A.: New Experimental and Theoretical Relation To Determine the Research Octane Number (Ron) of Authentic Aromatic Hydrocarbons Could Be Present in the Gasoline Fraction, Pet. Sci. Technol., 17(February 2015), 623–635, doi:10.1080/10916469908949737, 1999.

Rico, J. A. P. and Sauer, I. L.: A review of Brazilian biodiesel experiences, Renew. Sustain. Energy Rev., 45, 513–529, doi:10.1016/j.rser.2015.01.028, 2015.

Rollins, A. W., Browne, E. C., Pusede, S. E., Wooldridge, P. J., Gentner, D. R., Goldstein, A. H., Liu, S., Day, D. A. and Cohen, R. C.:) affect atmospheric organic aerosol (OA) production. However, these effects have not been directly observed in ambient OA. We report measurements of particulate organic nitrates in Bakersfield, California, the nighttime formation of which increases with , , 267(1989), 2–4, 2011.

Salvo, A. and Geiger, F. M.: Reduction in local ozone leves in urban São Paulo due to a shift from ethanol to gasoline use, Nat. Geosci., 7(6), 450–458, doi:10.1038/NGEO2144, 2014.

Samy, S. and Zielinska, B.: Secondary organic aerosol production from modern diesel engine emissions, Atmos. Chem. Phys., 10(2), 609–625, doi:10.5194/acp-10-609-2010, 2010.

Souza, D. Z., Vasconcellos, P. C., Lee, H., Aurela, M., Saarnio, K., Teinilä, K. and Hillamo, R.: Composition of PM2.5 and PM10 collected at Urban Sites in Brazil, Aerosol Air Qual. Res., 14(1), 168–176, doi:10.4209/aaqr.2013.03.0071, 2014.

Stattman, S. L., Hospes, O. and Mol, A. P. J.: Governing biofuels in Brazil: A comparison of ethanol and biodiesel policies, Energy Policy, 61, 22–30, doi:10.1016/j.enpol.2013.06.005, 2013.

Suarez-Bertoa, R., Zardini, A. A., Keuken, H. and Astorga, C.: Impact of ethanol containing gasoline blends on emissions from a flex-fuel vehicle tested over the Worldwide Harmonized Light duty Test Cycle (WLTC), Fuel, 143, 173–182, doi:10.1016/j.fuel.2014.10.076, 2015a.

Suarez-Bertoa, R., Zardini, A. A., Platt, S. M., Hellebust, S., Pieber, S. M., El Haddad, I., Temime-Roussel, B., Baltensperger, U., Marchand, N., Pr??v??t, A. S. H. and Astorga, C.: Primary emissions and secondary organic aerosol formation from the exhaust of a flex-fuel (ethanol) vehicle, Atmos. Environ., 117, 200–211, doi:10.1016/j.atmosenv.2015.07.006, 2015b.

Szwarcfiter, L., Mendes, F. E. and La Rovere, E. L.: Enhancing the effects of the Brazilian program to reduce atmospheric pollutant emissions from vehicles, Transp. Res. Part D Transp. Environ., 10(2), 153–160, doi:10.1016/j.trd.2004.12.002, 2005.

Timkovsky, J., Dusek, U., Henzing, J. S., Kuipers, T. L., Röckmann, T. and Holzinger, R.: Offline thermal-desorption proton-transfer-reaction mass spectrometry to study composition of organic aerosol, J. Aerosol Sci., 79, 1–14, doi:10.1016/j.jaerosci.2014.08.010, 2015.

Zhang, Y., Wang, X., Li, G., Yang, W., Huang, Z., Zhang, Z., Huang, X., Deng, W., Liu, T., Huang, Z. and Zhang, Z.: Emission factors of fine particles, carbonaceous aerosols and traces gases from road vehicles: Recent tests in an urban tunnel in the Pearl River Delta, China, Atmos. Environ., 122, 876–884, doi:10.1016/j.atmosenv.2015.08.024, 2015.

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* (µg m^{-3})	OA** (µg m^{-3})	Inside		Outside	
				LDV	HDV			CO_2	CO	CO_2	CO
								(ppm)			
TJQ 01	4th May 08:16	6	5	13920	29	17.6	4.7	513.6	5.10	403.2	1.33
TJQ 02	4th May 17:00	3	3	12856	34	--	4.2	526.3	6.15	401.1	1.14
TJQ 03	4th May 20:28	12	11	13584	36	10.2	1.9	456.0	2.66	416.2	1.09
TJQ 04	5th May 08:22	5	5	14759	49	14.7	4.0	513.6	5.47	403.2	1.33
TJQ 05	5th May 17:00	3	3	12252	6	--	4.4	526.3	7.06	401.1	1.14
TJQ 06	5th May 20:10	12	11	13538	18	20.7	4.2	456.0	4.42	416.2	1.09
TJQ 08	6th May 08:13	6	5	13338	19	18.0	4.9	513.6	7.25	403.2	1.33
TJQ 09	6th May 17:00	3	2	12660	6	--	5.8	526.3	7.37	401.1	1.14
TJQ 10	6th May 20:15	12	11	12363	43	12.9	2.6	456.0	3.58	405.1	1.09
TJQ 11	7th May 08:05	12	11	24510	272	12.8	2.4	510.5	3.47	400.4	1.24
TJQ 12	9th May 08:10	12	11	25067	387	10.5	2.2	511.0	5.04	394.5	1.26
TJQ 13	9th May 20:10	12	11	11546	36	8.2	1.8	425.9	2.05	390.5	0.75
TJQ 14	10th May 08:11	12	11	31258	79	12.5	2.7	498.9	5.41	405.4	1.45
TJQ 15	10th May 20:15	12	11	13113	111	8.3	2.1	437.5	2.50	392.5	0.49
TJQ 16	11st May 08:22	12	11	36288	1223	14.7	2.9	507.3	5.45	395.7	0.73
TJQ 17	11st May 20:33	12	11	13274	86	15.2	3.6	488.1	3.32	458.5	1.88
TJQ 18	12nd May 08:37	11	10	32800	283	15.3	3.2	512.2	5.79	393.9	1.29
TJQ 19	12nd May 19:45	13	12	14209	35	8.3	2.1	436.3	2.40	393.2	0.76
TJQ 20	13rd May 08:25	12	11	27162	87	12.3	2.4	510.0	5.35	403.1	1.35

* measured by TOT **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* ($\mu g\ m^{-3}$)	OA** ($\mu g\ m^{-3}$)	Inside		Outside	
				LDV	HDV			CO_2	CO	CO_2	CO
								(ppm)			
TRA 01	7th July 16:30	6	6	10497	4189	32.5	10.3	671.5	3.90	405.7	0.78
TRA 02	8th July 08:45	6	5	8406	4401	57.9	11.2	681.7	3.49	415.5	0.83
TRA 03	8th July 14:20	6	6	14432	5171	54.3	10.5	661.9	3.91	416.8	0.74
TRA 04	11st July 08:53	5	5	7675	3960	71.4	11.4	678.1	4.56	417.1	1.49
TRA 05	11st July 14:26	7	6	10807	4865	57.8	9.6	689.4	3.91	416.8	0.91
TRA 06	12nd July 08:18	6	5	9836	5030	98.1	12.1	746.5	5.35	417.6	2.09
TRA 07	12nd July 14:19	6	6	12860	5441	54.1	11.5	679.1	3.85	416.8	0.96
TRA 08	13rd July 08:10	6	5	10585	5426	60.2	14.8	696.1	4.79	417.6	1.01
TRA 09	13rd July 14:10	7	8	11739	5311	63.9	8.9	678.8	4.62	416.8	1.04
TRA 10	14th July 08:28	6	5	10751	5386	68.2	13.6	754.1	6.68	417.6	2.43
TRA 11	14th July 14:28	6	5	11795	5112	70.0	11.5	683.5	4.31	416.8	1.15
TRA 15	15th July 08:10	6	5	10400	5354	54.2	15.1	694.4	4.83	417.6	1.15
TRA 12	15th July 14:10	5	6	14351	5142	47.8	11.6	689.0	3.62	416.8	1.00

* measured by TOT **measured by TD-PTR-MS

Table 3: OA (TD-PTR-MS), OC (TOT) and $PM_{2.5}$ averages emission factors (mg kg^{-1} of burned fuel) and standard deviation of the filters, for LDV and HDV (Values in brackets correspond to the EF in mg km^{-1})

	PTR-MS			**TOT**		**Gravimetry**[b]
	up to 300°C	**Total**[a]		**at 310°C**	**310 - 870°C**	**$PM_{2.5}$**
		All compounds	**Compounds with O**			
LDV	27.2 ± 7.5	30.3 ± 8.5	21.5 ± 6.5	23.3 ± 8.4	84.3 ± 66.3	300 ± 100
	(1.7 ± 0.5)	(1.9 ± 0.5)	(1.3 ± 0.4)	(1.5 ± 0.5)	(5.2 ± 4.2)	(20 ± 8)
HDV	74.9 ± 12.4	80.8 ± 13.0	52.2 ± 8.4	89.2 ± 10.2	423.7 ± 87.0	700 ± 300
	(18.9 ± 3.1)	(20.4 ± 3.3)	(13.2 ± 2.1)	(22.5 ± 2.6)	(107.0 ± 22.0)	(277 ± 108)

[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	**Empiracal Formula**	**Average ± SD**	**Med (Min, Max)**
149.024	$C_8H_4O_3H^+$	4.89 ± 2.00	4.523 (2.228, 8.142)
150.027	$^{13}CC_7H_4O_3H^+$	0.463 ± 0.189	0.410 (0.210, 0.076)
149.131	$C_{11}H_{16}H^+$	0.250 ± 0.094	0.256 (0.122, 0.405)
299.289	$C_{19}H_{38}O_2H^+$	0.243 ± 0.127	0.189 (0.112, 0.476)
31.017	CH_2OH^+	0.239 ± 0.420	0.104 (0.017, 1.657)
177.055	$C_{10}H_8O_3H^+$	0.237 ± 0.327	0.107 (0.052, 1.262)
399.391	$C_{25}H_{50}O_3H^+$	0.227 ± 0.042	0.242 (0.124, 0.289)
114.091	$C_6H_{11}ONH^+$	0.207 ± 0.149	0.207 (0.036, 0.534)
99.008	$C_4H_2O_3H^+$	0.206 ± 0.118	0.205 (0.043, 0.399)
397.377	$C_{29}H_{48}H^+$	0.203 ± 0.041	0.210 (0.103, 0.256)

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

m/z	**Empiracal Formula**	**Average ± SD**	**Med (Min, Max)**
149.024	$C_8H_4O_3H^+$	3.08 ± 0.54	2.89 (2.58, 4.30)
199.041	$C_{12}H_6O_3H^+$	1.45 ± 0.20	1.45 (1.12, 1.78)
299.289	$C_{19}H_{38}O_2H^+$	1.01 ± 0.22	0.993 (0.749, 1.47)
203.087	$C_9H_{14}O_5H^+$	1.01 ± 0.15	0.974 (0.829, 1.35)
181.080	$C_5H_{12}O_5N_2H^+$	0.771 ± 0.129	0.765 (0.584, 1.03)
207.117	$C_{16}H_{14}H^+$	0.746 ± 0.134	0.692 (0.496, 0.819)
213.060	$C_6H_{12}O_8H^+$	0.630 ± 0.099	0.632 (0.486, 0.819)
297.272	$C_{19}H_{36}O_2H^+$	0.584 ± 0.138	0.572 (0.407, 0.860)
163.040	$C_9H_6O_3H^+$	0.583 ± 0.132	0.560 (0.408, 0.844)
41.038	$C_3H_4H^+$	0.577 ± 0.088	0.576 (0.400, 0.691)

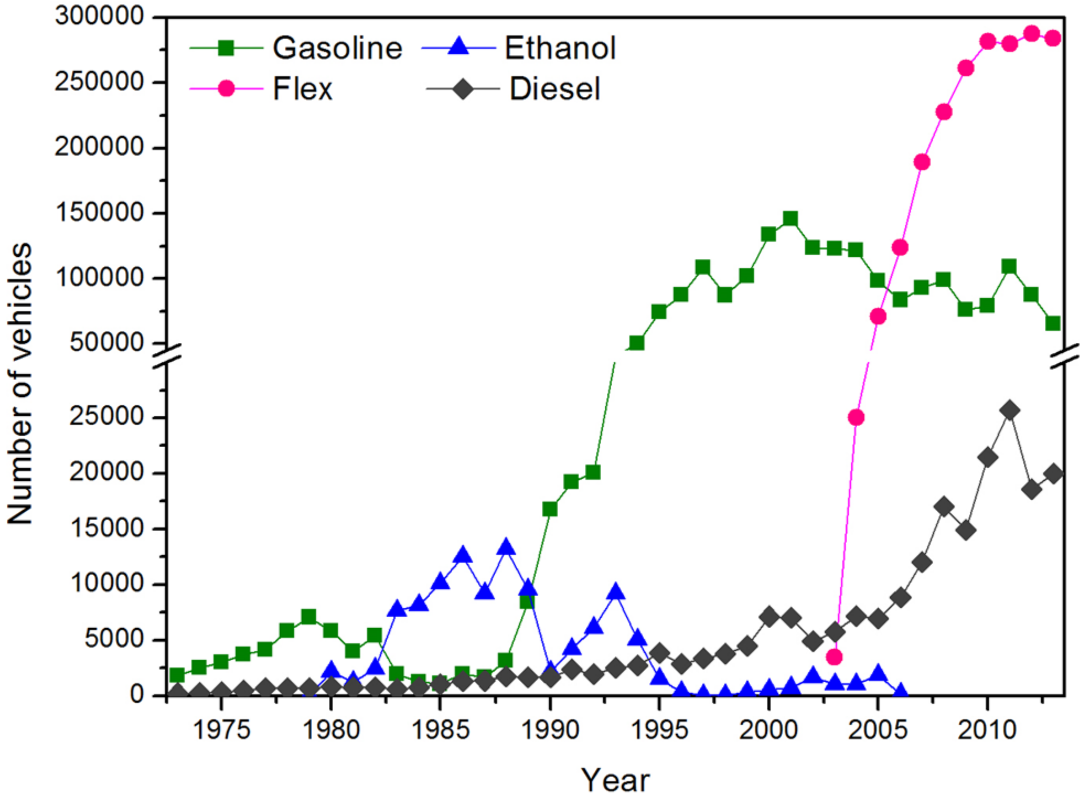

Figure 1: Annual registrations of new vehicles in the city of Sao Paulo.

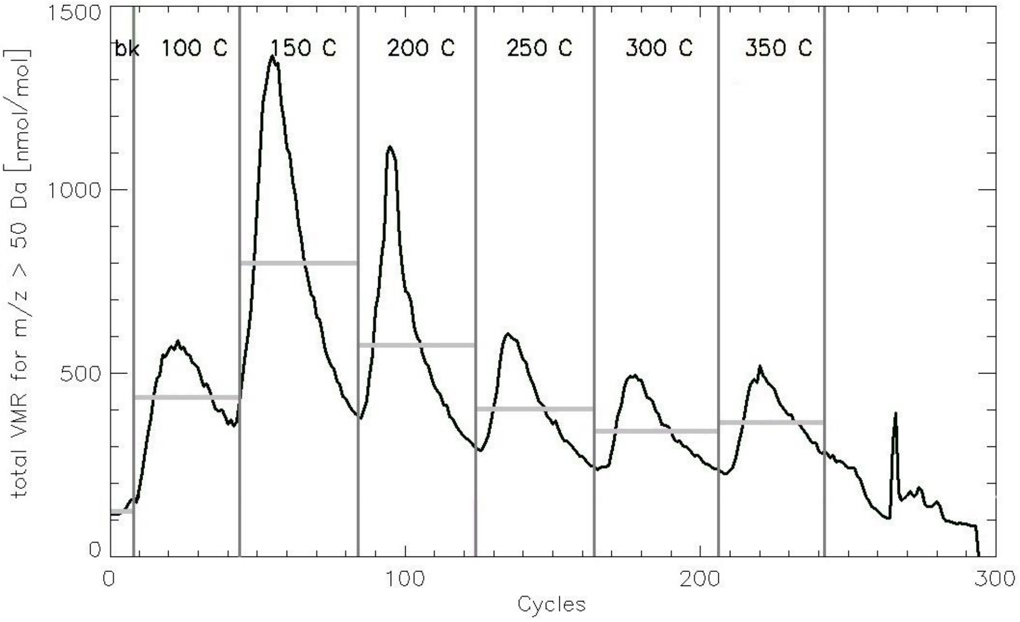

Figure 2: Result of an analysis of filter TRA 10 by TD-PTR-MS. The figure shows the total volume mixing ratios (VMR) of all the ions above 50 Da (in nmol mol^{-1}) with a temporal resolution of 5s. The vertical lines represent the heating steps as indicated on the top of the figure. The horizontal gray 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.

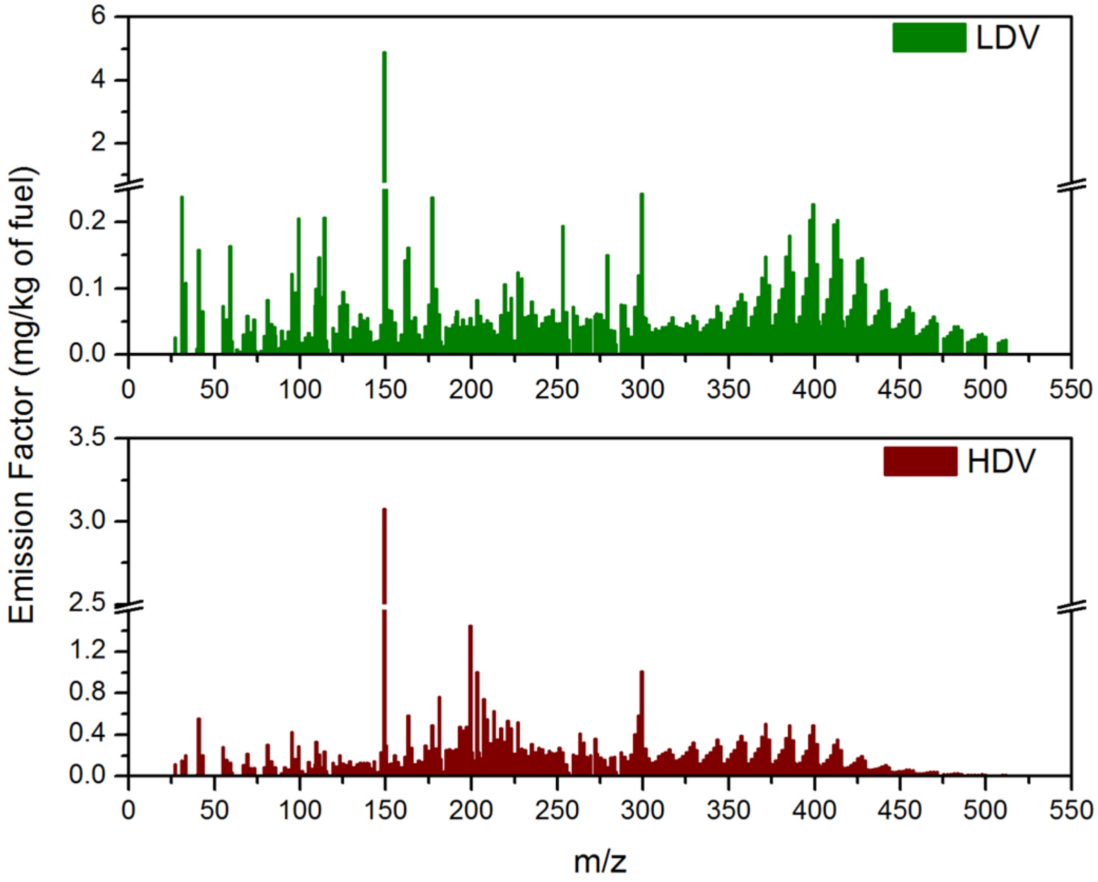

Figure 3: Average emission factors (mg kg^{-1} of fuel burned) mass spectra identified by the TD-PTR-MS for (a) LDV and (b) HDV.

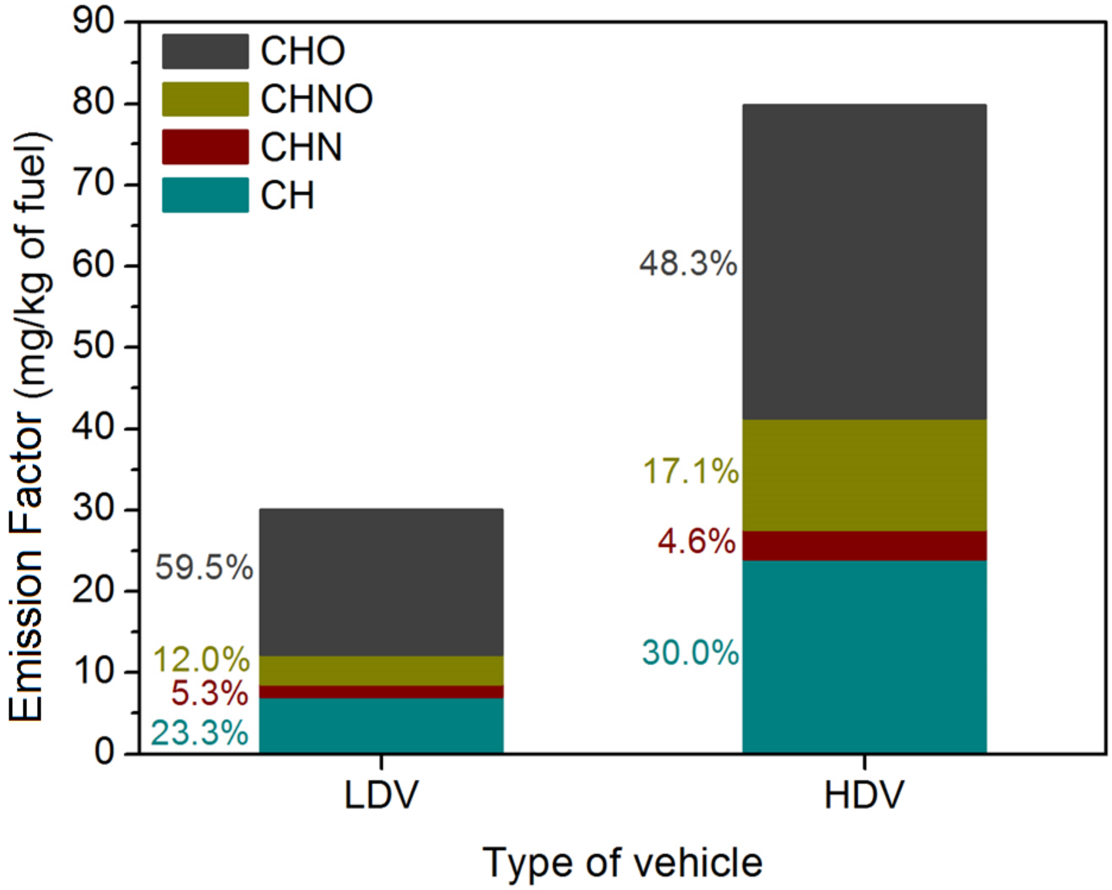

Figure 4: Total average emission factors calculated for LDV and HDV divided in groups containing CH, CHO, CHN, and CHON.

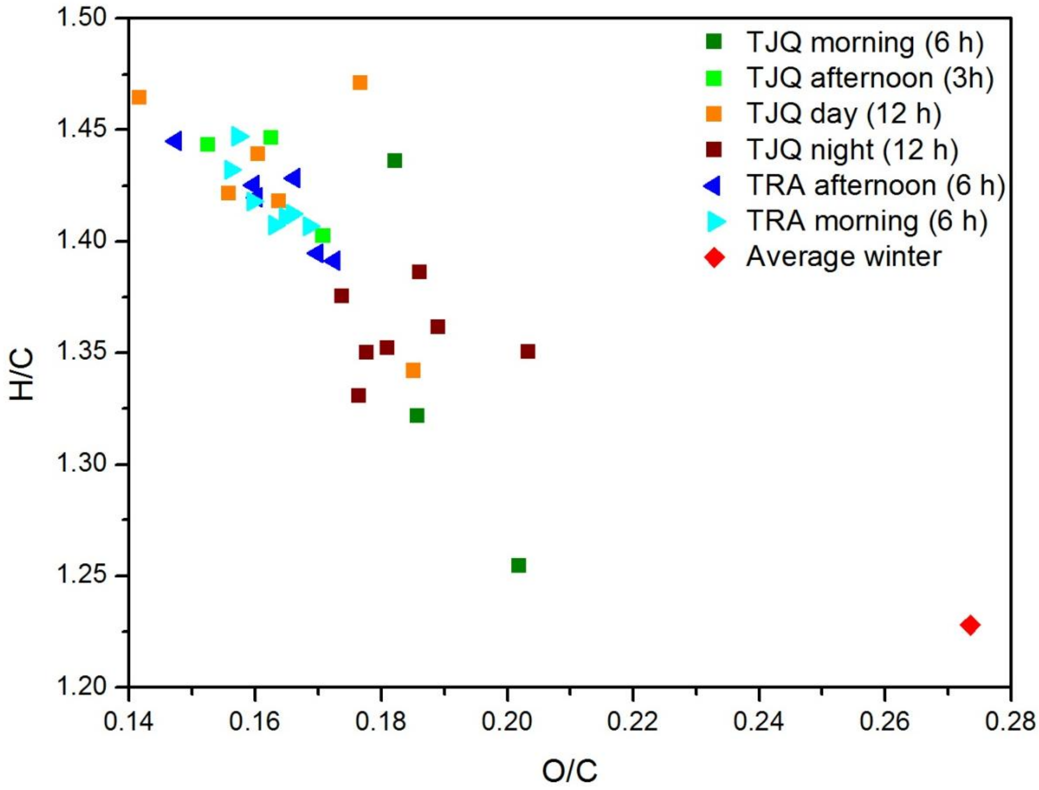

Figure 5: Scatter plot of atomic ratios O/C and H/C (van Krevelen diagram) of TD-PTR-MS data for measurements in the TRA and TJQ tunnels that have been corrected for ambient background. The red marker represents average H/C and O/C values from ambient aerosol samples (collected in Sao Paulo, between August and September 2012) that were also analyzed with TD-PTR-MS (unpublished results).

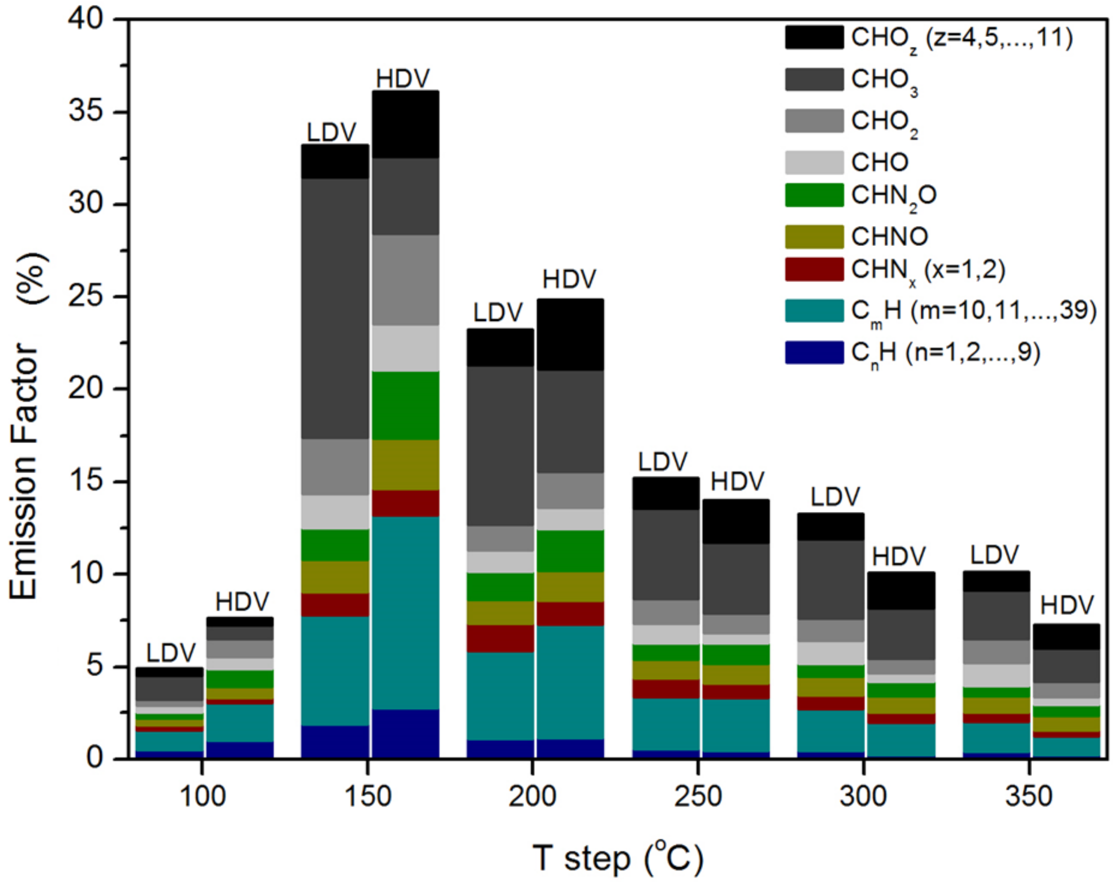

Figure 6: Fraction of total average emission (in %) divided into groups containing CH, CHO, CHON, and CHN, considering different numbers of carbon and oxygen atoms in the compounds, for LDV and HDV at each temperature step.