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

Beatriz Sayuri Oyama^{1,2}, Maria de Fátima Andrade¹, Pierre Herckes³, Ulrike Dusek^{2,4}, Thomas Röckmann², and Rupert Holzinger²

¹Institute of Astronomy, Geophysics and Atmospheric Sciences, University of São Paulo, São Paulo, Brazil

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

³School of Molecular Sciences, Arizona State University, Tempe, USA

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

Correspondence to: Beatriz Sayuri Oyama (beatriz.oyama@iag.usp.br)

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Abstract. This study reports emission of organic particulate matter by light-duty vehicles (LDVs) and heavy-duty vehicles (HDVs) in the city of São Paulo, Brazil, where vehicles run on three different fuel types: gasoline with 25 % ethanol (called gasohol, E25), hydrated ethanol (E100), and diesel (with 5 % biodiesel). The experiments were performed at two tunnels: Jânio Quadros (TJQ), where 99 % of the vehicles are LDVs, and RodoAnel Mário Covas (TRA), where up to 30 % of the fleet are HDVs. 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 (EFs) for organic aerosol (OA) and organic carbon (OC) were calculated for the HDV and the LDV fleet. We found that HDVs emitted more PM_{2.5} than LDVs, with OC EFs of 108 and 523 mg kg⁻¹ burned fuel for LDVs and HDVs, respectively. More than 700 ions were identified by TD-PTR-MS and the EF profiles obtained from HDVs and LDVs 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 (i.e. the OA) originates from oxygenated compounds from LDVs and HDVs, 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 OA emission. The thermal-desorption analysis showed that HDVs emitted compounds with higher volatility, and with mainly oxygenated and longer chain hydrocarbons than LDVs.

1 Introduction

The metropolitan area of São 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 % biodiesel) hydrated ethanol (E100) and gasohol (gasoline with 25 % 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 São 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 São 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 (Proálcool) in Brazil during the 1980s had an important influence on the increase in vehicles running on E100. The

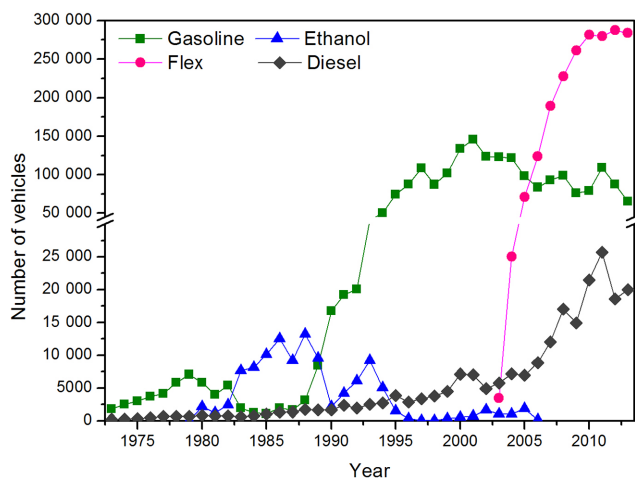


Figure 1. Annual registrations of new vehicles in the city of São Paulo.

production of ethanol increased from 1 million cubic meters (in the 1970s) to more than 10 million (in the mid-1980s) (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 % ethanol to gasoline was legally mandated. Following a governmental change in 1985, the subsidy for alcohol decreased dramatically, thus alcohol price increased, followed by a fall in sales of ethanol-fueled vehicles (Fig. 1).

In the early 1990s the number of vehicles increased substantially due to a political decision to increase the sale of vehicles in order to stimulate the economy. Following international regulations for vehicular emissions, the Program for Controlling Vehicular Emissions (PROCONVE) was implemented in the late 1980s. 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 improved air quality with lower concentrations of carbon monoxide (CO), sulfur dioxide (SO₂), 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 (O₃), 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 of increasing the ethanol blend in gasoline by flex-fuel 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 with a sharp increase in acetaldehyde. Furthermore, they 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 % ethanol in gasoline respectively) in two different studies, Suarez-Bertoa et al. (2015a and b) concluded that a higher amount of ethanol resulted in a reduction of nitrogen oxide (NO+NO₂=NO_x) emissions, however, it increased acetaldehyde and ethanol emissions, which leads to a significant increase in ozone formation potential. 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 amounts of ethanol in fuel.

Regarding the use of diesel, 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 % biodiesel to conventional diesel fuel was authorized, but only since 2008 has this addition become mandatory. Until 2010, the percentage has gradually increased to the current 5 % (MME, 2016). 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 biodiesel have many important differences that affect the formation of secondary organic aerosol (OA) 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 Arbillá, 2008) and also some polyaromatic 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 São 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 have 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 or-

ganic carbon (OC) measurements that approximately 26 % of the $PM_{2.5}$ was composed of organic particulate matter. Recently, Brito et al. (2013) discussed the aerosol composition including OC and PAHs in a tunnel study. They performed a chemical characterization of $PM_{2.5}$ by separating the total mass into OC, elemental carbon (EC), and contributions from other trace elements. They concluded that the OA fraction estimated from OC measurements represented around 40 % of $PM_{2.5}$ emitted by both light-duty vehicles (LDVs) and heavy-duty vehicles (HDVs).

Since the vehicular emission in São Paulo city is the main source for $PM_{2.5}$, it is of importance to distinguish the contributions from LDVs and HDVs. Different methods can be used in order to estimate the emissions from the vehicular fleet. Emission factors (EFs) for gaseous and total $PM_{2.5}$ have been calculated based on tunnel measurements by Pérez-Martínez et al. (2014), showing that LDVs emitted similar levels of CO than HDVs, but much lower amounts of NO_x and $PM_{2.5}$ (EF_{SPM_{2.5}} of 20 and 277 mg km⁻¹ for LDVs and HDVs, 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 São Paulo, which has the unique characteristic of using biofuels on a large scale. We discuss the composition of OA and EFs of condensed organics from LDVs and HDVs, obtained from aerosol filter samples ($PM_{2.5}$) collected in traffic tunnels. For the first time, thermal-desorption proton-transfer-reaction mass spectrometry (TD-PTR-MS) was used to filter samples from São 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 Jânio Quadros tunnel (TJQ), from 4 to 13 May 2011; and a second campaign was performed in the RodoAnel Mário Covas tunnel (TRA), from 6 to 17 July 2011.

TJQ is a two-lane tunnel located in the center of São Paulo and characterized mainly by LDV traffic. The direction of the traffic in this tunnel alternated twice a day at 06:00 and 09:00. TJQ has a length of 1.9 km, a 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 HDVs due to traffic restrictions in the center of São 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 video. The fleet was classified into four different groups: HDVs, LDVs, motorcycles, and taxis. For this study, the motorcycles and taxis were considered as LDVs, 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: LDVs and HDVs. The other two kinds of vehicles were excluded mainly due to the fact that motorcycles hardly circulate on highways with high speed limits 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 particulate sampler, with a sampling rate of 16.6 L min⁻¹) simultaneously collected $PM_{2.5}$ 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) that sampled only the $PM_{2.5}$ fraction. These samples were collected on preheated quartz fiber filters (800 °C, for 12 h), subsequently wrapped in aluminum foil (precleaned 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 (CO₂) were performed inside and outside of the tunnels during the entirety of both campaigns. CO measurements were done with nondispersive infrared photometry equipment (Thermo Electron 48B). CO₂ was measured using a LICOR 6262 instrument inside and a Picarro G1301 instrument outside the tunnels, as described in detail elsewhere (e.g. 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 Tables 1 and 2. The gaseous concentration was obtained on an hourly basis 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 (H₃O⁺) and organic species in the sample lead to mostly non-dissociative proton transfers, with the advantage that most organic com-

Table 1. Filter identification number, sampling start time, sampling duration, volume sampled for organic aerosol (OA) samples, vehicle counts, organic carbon (OC) and OA concentrations, and average CO₂ and CO concentrations during sampling inside and outside of the TJQ tunnel during 2011.

Filter no.	Sampling start	Sampling duration (h)	Volume sampled (m ³)	No. vehicles		OC ¹ (μg m ⁻³)	OA ² (μg m ⁻³)	Inside		Outside	
				LDVs	HDVs			CO ₂	CO	CO ₂	CO
TJQ 01	04 May 08:16	6	5	13 920	29	17.6	4.7	513.6	5.10	403.2	1.33
TJQ 02	04 May 17:00	3	3	12 856	34	–	4.2	526.3	6.15	401.1	1.14
TJQ 03	04 May 20:28	12	11	13 584	36	10.2	1.9	456.0	2.66	416.2	1.09
TJQ 04	05 May 08:22	5	5	14 759	49	14.7	4.0	513.6	5.47	403.2	1.33
TJQ 05	05 May 17:00	3	3	12 252	6	–	4.4	526.3	7.06	401.1	1.14
TJQ 06	05 May 20:10	12	11	13 538	18	20.7	4.2	456.0	4.42	416.2	1.09
TJQ 08	06 May 08:13	6	5	13 338	19	18.0	4.9	513.6	7.25	403.2	1.33
TJQ 09	06 May 17:00	3	2	12 660	6	–	5.8	526.3	7.37	401.1	1.14
TJQ 10	06 May 20:15	12	11	12 363	43	12.9	2.6	456.0	3.58	405.1	1.09
TJQ 11	07 May 08:05	12	11	24 510	272	12.8	2.4	510.5	3.47	400.4	1.24
TJQ 12	09 May 08:10	12	11	25 067	387	10.5	2.2	511.0	5.04	394.5	1.26
TJQ 13	09 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

¹ measured by thermal–optical transmittance (TOT). ² measured by thermal-desorption proton-transfer-reaction mass spectrometry (TD-PTR-MS).

pounds 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 (ToF-MS).

The PTR-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 $U_s = 140$ V, $U_{so} = 92$ V, and $E/N = 130$ Td. The extraction voltage at the end of the drift tube (U_{dx}) was 28 V. We assumed a reaction rate constant of 3×10^{-9} cm³ 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 on 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-MS 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 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 50–350 °C; and the second oven worked at a constant temperature of 180 °C. A piece of 0.20 cm² area from each filter was introduced to the first oven at 50 °C and heated in temperature steps of 50 degrees centigrade from 100 to 350 °C, allowing 3 min for the measurement at each temperature step. The N₂ flow rate (ultrapure nitrogen, 5.7 purity; Air Products and Chemicals, Inc.; Netherlands) was usually adjusted by a thermal mass-flow controller (MKS Instruments GmbH, 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 N₂ 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 N₂ 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) and separated into OC and EC using thermal–optical transmittance (TOT) with a Sunset Laboratory Inc. (Tigard, USA) instrument as described by Brito et al. (2013). The evaluation of OC occurred at temperature steps: 310, 475, 615, and

Table 2. Filter identification number, sampling start time, sampling duration, volume sampled for OA samples, vehicle counts, OC and OA concentrations, and average CO₂ and CO concentrations during sampling inside and outside of the TRA tunnel during 2011.

Filter no.	Sampling start	Sampling duration (h)	Volume sampled (m ³)	No. vehicles		OC ¹ (μg m ⁻³)	OA ² (μg m ⁻³)	Inside		Outside	
				LDVs	HDVs			CO ₂	CO	CO ₂	CO
TRA 01	07 Jul 16:30	6	6	10 497	4189	32.5	10.3	671.5	3.90	405.7	0.78
TRA 02	08 Jul 08:45	6	5	8406	4401	57.9	11.2	681.7	3.49	415.5	0.83
TRA 03	08 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

¹ measured by TOT. ² measured by TD-PTR-MS.

870 °C; with heating times ranging from 60 to 200 s. Here, the discussion focus is on organic particulate matter. Thus, the EC and TC values are not presented.

Pérez-Martínez et al. (2014) presented EFs 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 under controlled conditions using an electronic microbalance with a sensitivity of 1 μg.

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 (CH₂OH⁺) and 33.033 (CH₄OH⁺). Additionally, ions associated with the inorganic ion NO₂⁺ and higher water clusters ((H₂O)₂H₃O⁺) were removed. After this screening, the final mass list contained 712 ions that were attributed to organic molecules.

The data (volume mixing ratios, VMRs; 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*,instrbgd}), identified in Fig. 2 by the first horizontal gray line (close to zero), was subtracted from the measured volume mixing ratio (VMR_{*i*,measured}) for an ion, *i* at each temperature step according to the following equation:

$$\text{VMR}_i = \text{VMR}_{i,\text{measured}} - \text{VMR}_{i,\text{instrbgd}} \quad (1)$$

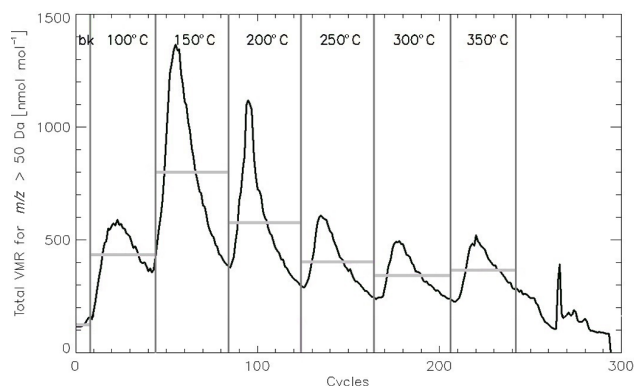


Figure 2. Analysis result of filter TRA 10 by TD-PTR-MS. The figure shows the total volume mixing ratios (VMRs) of all the ions above 50 Da (in nmol mol⁻¹) with a temporal resolution of 5 s. The vertical lines represent the heating steps as indicated at the top of the figure. The horizontal gray lines between these vertical lines are the concentration averages at each temperature step, and the background level (bk; first horizontal gray line, close to zero) is subtracted from these values before further analysis.

where VMR_{*i*} is the volume mixing ratio corrected by the background. This calculation was done for all filter samples and all field blanks (FBs). 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 horizontal gray 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 ($\overline{\text{VMR}}_i$). Note that all $\overline{\text{VMR}}_i$ values have been normalized to a N_2 carrier gas flow of 100 mL min^{-1} .

A Student's 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 the 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 FBs was subtracted from the average VMR of the sampled filters ($\overline{\text{VMR}}_{i,\text{sampled}}$) for each ion, i and each temperature step according to the following equation:

$$\text{VMR}_{i,\text{final}} = \overline{\text{VMR}}_{i,\text{sampled}} - \overline{\text{VMR}}_{i,\text{FB}}_{\text{MED}} \quad (2)$$

The $\text{VMR}_{i,\text{final}}$ 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):

$$C_i = \frac{\text{VMR}_{i,\text{final}} \cdot M_i \cdot V_{\text{nitrogen}}}{V_{\text{samp}} \cdot f} \quad (3)$$

where M_i is the molecular weight of the ion, i (minus 1 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 collected 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 EFs of organic species

The EFs in units of milligrams of pollutant per kilogram 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, according to the following equation:

$$\text{EF}_P = 10^3 \left(\frac{\Delta[\text{P}]}{\Delta[\text{CO}_2] + \Delta[\text{CO}]} \right) \omega_c \quad (4)$$

where EF_P is the EF of pollutant, P (milligrams of pollutant per kilogram of burned fuel); $\Delta[\text{P}]$ is the increase in [P] above the background levels (in ng m^{-3}); $\Delta[\text{CO}_2]$ and $\Delta[\text{CO}]$ 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 grams of carbon per gram of fuel) for a fuel $c - \omega_G = 0.757$ for E25 and $\omega_D = 0.818$ for diesel.

The EFs for LDVs were directly calculated from the filters sampled in the TJQ tunnel due to the fact that LDVs 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 HDVs and LDVs emit comparable amounts of CO per traveled distance (Kirchstetter et al., 1999; Miguel et al., 1998; Pierson et al., 1996). The CO_2 emissions from diesel burning could be estimated according to the following equation:

$$\frac{\Delta[\text{CO}_2]_{\text{D}}}{\Delta[\text{CO}_2]} = \frac{f_{\text{D}} U_{\text{D}} \rho_{\text{D}} \omega_{\text{D}}}{f_{\text{D}} U_{\text{D}} \rho_{\text{D}} \omega_{\text{D}} + ((1 - f_{\text{D}}) U_{\text{G}} \rho_{\text{G}} \omega_{\text{G}})} \quad (5)$$

where $\Delta[\text{CO}_2]_{\text{D}}$ is the component of $\Delta[\text{CO}_2]$ related to the emissions from diesel vehicles (equal to HDVs), f_{D} is the fraction of HDVs, U is the average fuel consumption rate in grams per kilometer (75 g km^{-1} for E25 and 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 HDVs to the concentration of a pollutant, P, can be estimated by the following equation:

$$\Delta[\text{P}]_{\text{HDVs}} = \Delta[\text{P}] - \Delta[\text{CO}](1 - f_{\text{D}}) \left(\frac{\Delta[\text{P}]_{\text{LDVs}}}{\Delta[\text{CO}]_{\text{LDVs}}} \right)_{\text{TJQ}} \quad (6)$$

where $\Delta[\text{P}]_{\text{HDVs}}$ is the contribution of $\Delta[\text{P}]$, related to HDV emissions, $\Delta[\text{CO}](1 - f_{\text{D}})$ is the fraction of $\Delta[\text{CO}]$ attributed to the LDV emissions. The last term in Eq. (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 that operate 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 the inside and the outside (ΔCO) is directly related to vehicular emissions (for São 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 HDVs, while most CO originated from LDVs. 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 milligrams of pollutant per kilogram of burned fuel) for OC, OA, and total $PM_{2.5}$, as obtained from TOT, TD-PTR-MS, and gravimetric analyses (Pérez-Martínez et al. 2014), respectively. All EFs were higher for HDVs than for LDVs.

The EF of OC represented 28 and 60 % of the EF of $PM_{2.5}$ for LDVs and HDVs, 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 ~ 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, 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 of the total organic matter measured by TOT analysis over all thermal fractions (up to 870 °C).

Table 3 also presents the EF of compounds containing oxygen (O) for LDVs and HDVs. We found high contributions from oxygenated compounds of around 70 and 65 % for LDVs and HDVs, 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) and 5.6 (LDV) $mg\ km^{-1}$, and another study in the Zhujiang Tunnel 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 missing due to the 350 °C limit for thermal desorption. Additional effects could be due to the different fuel compositions used in Brazil, since Brazilian gasoline includes 25 % ethanol. It has been shown that an increased percentage of biofuel can lead to the reduction of the particulate matter emissions (Karavalakis et al., 2014; Mamakos et al., 2013). This may explain the larger difference observed for LDVs compared to HDVs.

Regarding the EFs (OC), most of the references found did not distinguish between the contribution of LDVs and HDVs for EF calculations. In a diesel emission characterization study conducted in the Shing Mun Tunnel, China, Cheng et al. (2010) found an EF of 67.9 $mg\ km^{-1}$ for OC. Zhang et al. (2015) found 19.2 $mg\ km^{-1}$, 12 % HDVs and 27 % liq-

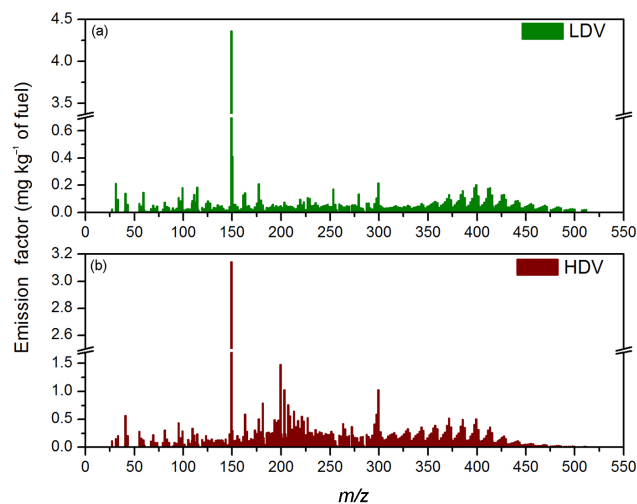


Figure 3. Average EFs ($mg\ kg^{-1}$ of fuel burned) mass spectra identified by the TD-PTR-MS for (a) LDVs and (b) HDVs.

uefied petroleum gas vehicles. Hung-Lung and Yao-Sheng (2009) and Handler et al. (2008) found 4.7 (~ 15 % HDVs) and 2.3 (~ 10 % HDVs) $mg\ km^{-1}$, respectively. These values, although comparable, were lower than EFs (OC) considering only LDVs. In conclusion, we can affirm that the vehicles in São Paulo city emit more OC per kilometer than in several other cities.

Figure 3 shows the average EF (in $mg\ kg^{-1}$ of fuel) profiles for LDVs and HDVs obtained from the TD-PTR-MS. As discussed above, HDVs emitted higher concentrations of organic particulate compounds than the vehicles using E25. Differences between LDVs and HDVs 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 EFs of 0.100 $mg\ kg^{-1}$ of fuel. In contrast, many compounds emitted by HDVs 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.

Tables 4 and 5 show the 10 highest average EF values for both types of vehicles, as well as their m/z , tentative empirical formula, the median, maximum and minimum EF values. The complete list of all compounds is shown in the Supplement (Table S2). Using improved routines described in Holzinger et al. (2010), it was possible to attribute empirical formulae 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 LDVs and HDVs with the value of 4.9 and 3.1 $mg\ kg^{-1}$ 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)

Table 3. OA (TD-PTR-MS), OC (TOT) and PM_{2.5} average emission factors (EFs, mg kg⁻¹ of burned fuel), and standard deviations of the filters for LDVs and HDVs (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				
LDVs	27.2 ± 7.5 (1.7 ± 0.5)	30.3 ± 8.5 (1.9 ± 0.5)	21.5 ± 6.5 (1.3 ± 0.4)	23.3 ± 8.4 (1.5 ± 0.5)	84.3 ± 66.3 (5.2 ± 4.2)	300 ± 100 (20 ± 8)
HDVs	74.9 ± 12.4 (18.9 ± 3.1)	80.8 ± 13.0 (20.4 ± 3.3)	52.2 ± 8.4 (13.2 ± 2.1)	89.2 ± 10.2 (22.5 ± 2.6)	423.7 ± 87.0 (107.0 ± 22.0)	700 ± 300 (277 ± 108)

^a The sum of all EFs per temperature step (from 100 to 350 °C). ^b Values obtained from Pérez-Martínez et al. (2014).

Table 4. The 10 highest EFs (mg kg⁻¹ of fuel) for LDVs.

<i>m/z</i>	Empirical formula	Average ± SD	Median (min, max)
149.024	C ₈ H ₄ O ₃ H ⁺	4.89 ± 2.00	4.523 (2.228, 8.142)
150.027	¹³ CC ₇ H ₄ O ₃ H ⁺	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 ₂ H ⁺	0.243 ± 0.127	0.189 (0.112, 0.476)
31.017	CH ₂ OH ⁺	0.239 ± 0.420	0.104 (0.017, 1.657)
177.055	C ₁₀ H ₈ O ₃ H ⁺	0.237 ± 0.327	0.107 (0.052, 1.262)
399.391	C ₂₅ H ₅₀ O ₃ H ⁺	0.227 ± 0.042	0.242 (0.124, 0.289)
114.091	C ₆ H ₁₁ ONH ⁺	0.207 ± 0.149	0.207 (0.036, 0.534)
99.008	C ₄ H ₂ O ₃ H ⁺	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 10 highest EFs (mg kg⁻¹ of fuel) for HDVs.

<i>m/z</i>	Empirical formula	Average ± SD	Median (min, max)
149.024	C ₈ H ₄ O ₃ H ⁺	3.08 ± 0.54	2.89 (2.58, 4.30)
199.041	C ₁₂ H ₆ O ₃ H ⁺	1.45 ± 0.20	1.45 (1.12, 1.78)
299.289	C ₁₉ H ₃₈ O ₂ H ⁺	1.01 ± 0.22	0.993 (0.749, 1.47)
203.087	C ₉ H ₁₄ O ₅ H ⁺	1.01 ± 0.15	0.974 (0.829, 1.35)
181.080	C ₅ H ₁₂ O ₅ N ₂ H ⁺	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 ₆ H ₁₂ O ₈ H ⁺	0.630 ± 0.099	0.632 (0.486, 0.819)
297.272	C ₁₉ H ₃₆ O ₂ H ⁺	0.584 ± 0.138	0.572 (0.407, 0.860)
163.040	C ₉ H ₆ O ₃ H ⁺	0.583 ± 0.132	0.560 (0.408, 0.844)
41.038	C ₃ H ₄ H ⁺	0.577 ± 0.088	0.576 (0.400, 0.691)

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, FBs, and ambient air background subtractions were performed before calculating the EFs and give no indication of artifacts. Therefore this ion most likely originates from the collected aerosol on the filters. Furthermore, phthalic anhydride (C₈H₄O₃, detected on *m/z* 149.024) has been posi-

tively 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 Supplement), 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 (C₁₁H₁₆H⁺), as presented in Table 4, was tentatively attributed to pentylbenzene. Pentylbenzene is a potential unique tracer for gasoline, as this compound is a known constituent of gasoline, e.g. Ramadhan and Al-Hyali (1999) used pentylbenzene 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 C₁₉H₃₈O₂H⁺, and tentatively attributed to methyl stearate, which is one of the main components found in biodiesel (Naik et al., 2011). The EF for LDVs was approximately a factor of 6 lower (see the Supplement) than for HDVs 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 LDVs and HDVs divided into groups containing: CH, CHO, CHON, and CHN. The hydrocarbon group (CH) presented an important contribution to the total EFs: for the LDVs close to a quarter and for the HDVs the contribution was around a third. Oxygenated hydrocarbons (CHO) showed highest contribution to emissions for both vehicle types, where LDVs (60 %) exhibited a larger fraction than HDVs (48 %). The high fraction of oxygen-containing compounds shows that chemical processing close to the engine / tailpipe region is an important factor influencing primary OA emission. Our findings are in line with Collier et al. (2015) who measured high O / C ratios in primary OA 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 NO₃ rad-

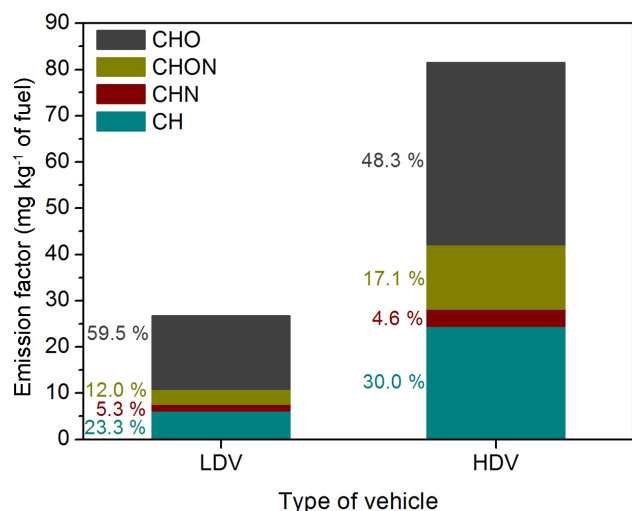


Figure 4. Total average EFs calculated for LDVs and HDVs divided into groups containing CHO, CHON, CHN, and CH.

icals formed by anthropogenic NO_x emissions (e.g. Rollins et al., 2011). The question remains open as to what extent the production of CHON compounds can be attributed to the use of biodiesel, however, it is worthwhile to note that Hoekman and Robbins (2012) associated biodiesel 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, Fig. 5 also presents the average ratios from an ambient campaign performed in São Paulo city (5 km away from TJQ and 15 km from TRA) during the Southern Hemisphere winter, between August and September 2012 (unpublished results). The average ambient O/C was higher than measured in the tunnels, which is associated with photochemical reactions in the presence of sunlight producing more oxygenated aerosol. The high H/C ratios found for the tunnel 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 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 (primary organic aerosol) emissions. The afternoon samples (sampled for 3 h) were collected during the traffic congestion periods (between 17:00 and 20:00, 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 profiles.

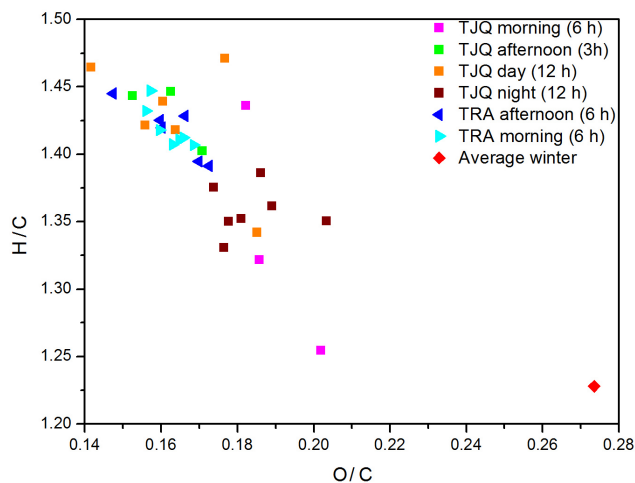


Figure 5. Scatter plot of atomic ratios O/C and H/C (van Krevelen diagram) of TD-PTR-MS data for measurements in the TRA and TJQ tunnels that have been corrected for ambient background. The red marker represents average H/C and O/C values from ambient aerosol samples (collected in São Paulo, between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

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 biodiesel.

Chirico et al. (2011) found H/C ratios ranging between 1.84 and 1.71, for workdays and weekends, 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 compared 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 (aerosol mass spectrometer) operates at high vaporization temperatures (usually constantly at 600 °C), measuring

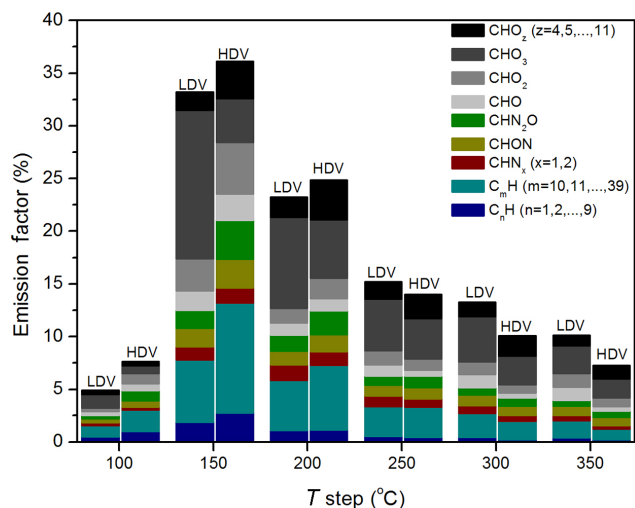


Figure 6. Fraction of total average emission (in %) divided into groups containing CH, CHO, CHON, and CHN, considering different numbers of carbon and oxygen atoms in the compounds for LDVs and HDVs at each temperature step.

smaller particles (PM_{10}) 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 Fig. 6. This analysis indicated that OA produced from HDVs were more volatile than OA from LDVs. As expected, hydrocarbons represented the most volatile group. Their volatility was related to the number of carbons present in molecules: short-chain hydrocarbons (up to nine carbon atoms) were more volatile than the long-chain ones (more than nine carbon atoms). The short-chain hydrocarbon contribution was very low at 250 °C and higher temperatures, while the long-chain hydrocarbon contribution was still significant at 350 °C.

HDVs emitted more volatile nitrogen compounds than LDVs. 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 three oxygen atoms was predominant due to m/z 149.024, mainly at 150 and 200 °C, for LDV emissions. 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 on-line AMS measurements sampled during rush hour on work-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 of this study was the characterization of average emission factors of organic particulate compounds for light- and heavy-duty vehicles. The study was performed in the city of São Paulo, Brazil. Its atmosphere is impacted by the burning of different fuels: gasohol (gasoline with 25 % 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 São Paulo by 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 HDVs emitted more fine particles than LDVs (per kilogram of fuel burned). OC represented a significant fraction of emitted $PM_{2.5}$: factors of 108 and 523 $mg\ kg^{-1}$ burned fuel for LDVs and HDVs, respectively. The amount of oxygen found in the desorbed aerosol samples of up to 350 °C 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 LDVs and HDVs 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 HDVs emitted more volatile compounds, mainly oxygenated hydrocarbons containing up to two oxygen atoms and long-chain hydrocarbons, than LDVs.

5 Data availability

The data are provided in the Supplement.

The Supplement related to this article is available online at doi:10.5194/acp-16-14397-2016-supplement.

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