



Physical-chemical
characterization of
the particulate matter
in tunnels

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Physical-chemical characterization of the particulate matter inside two road tunnels in the São Paulo Metropolitan Area

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Abstract

The notable increase in biofuel usage by the road transportation sector in Brazil during recent years has significantly altered the vehicular fuel composition. Consequently, many uncertainties are currently found in particulate matter vehicular emission profiles. In an effort to better characterize the emitted particulate matter, measurements of aerosol physical and chemical properties were undertaken inside two tunnels located in the São Paulo Metropolitan Area (SPMA). The tunnels show very distinct fleet profiles: in the Jânio Quadros (JQ) tunnel, the vast majority of the circulating fleet are Light Duty Vehicles (LDVs), fuelled on average with the same amount of ethanol as gasoline. In the Rodoanel (RA) tunnel, the particulate emission is dominated by Heavy Duty Vehicles (HDVs) fuelled with diesel (5 % biodiesel). In the JQ tunnel, $PM_{2.5}$ concentration was on average $52 \mu\text{g m}^{-3}$, with the largest contribution of Organic Mass (OM, 42 %), followed by Elemental Carbon (EC, 17 %) and Crustal elements (13 %). Sulphate accounted for 7 % of $PM_{2.5}$ and the sum of other trace elements was 10 %.

In the RA tunnel, $PM_{2.5}$ was on average $233 \mu\text{g m}^{-3}$, mostly composed of EC (52 %) and OM (39 %). Sulphate, crustal and the trace elements showed a minor contribution with 5 %, 1 % and 1 %, respectively. The average OC : EC ratio in the JQ tunnel was 1.59 ± 0.09 , indicating an important contribution of EC despite the high ethanol fraction in the fuel composition. In the RA tunnel, the OC : EC ratio was 0.49 ± 0.12 , consistent with previous measurements of diesel fuelled HDVs. Besides bulk carbonaceous aerosol measurement, Polycyclic Aromatic Hydrocarbons (PAHs) were quantified. The sum of the PAHs concentration was $56 \pm 5 \text{ ng m}^{-3}$ and $45 \pm 9 \text{ ng m}^{-3}$ in the RA and JQ tunnel, respectively. In the JQ tunnel, Benzo(a)pyrene (BaP) ranged from 0.9 to 6.7 ng m^{-3} (0.02–0.1 ‰ of $PM_{2.5}$) in the JQ tunnel whereas in the RA tunnel BaP ranged from 0.9 to 4.9 ng m^{-3} (0.004–0.02 ‰ of $PM_{2.5}$), indicating an important relative contribution of LDVs emission to atmospheric BaP.

Real-time measurements performed in both tunnels provided aerosol size distributions and optical properties. The average particle count yielded $73\,000 \text{ cm}^{-3}$ in the JQ

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tunnel and $366\,000\text{ cm}^{-3}$ in the RA tunnel, with an average diameter of 48 nm in the former and 39 nm in the latter. Aerosol single scattering albedo, calculated from scattering and absorption observations in the JQ tunnel, showed a minimum value of 0.4 at the peak of the morning rush hour, reached 0.6 around noon and stabilized at 0.5 in the afternoon and evening. Such single scattering albedo range is close to other tunnel studies results, despite significant biofuel usage. Given the exceedingly high Black Carbon loadings in the RA tunnel, real time light absorption measurements were possible only in the JQ tunnel. Nevertheless, using EC measured from the filters a single scattering albedo of 0.32 for the RA tunnel has been estimated. The results presented here characterize particulate matter emitted from nearly 1 million vehicles fuelled with a considerable amount of biofuel, providing an unique experimental site worldwide.

1 Introduction

Megacities, large urban conglomerates with a population of 10 million or more inhabitants, are increasingly receiving attention as strong pollution hotspots with significant global impact (Gurjar et al., 2008; Beirle et al., 2011; Butler et al., 2012). The emissions from such large centres in both the developed and developing parts of the world are strongly impacted by the transportation sector. The São Paulo Metropolitan Area (SPMA), located in the Southeast of Brazil, is a megacity with a population of 19 million people and 7.4 million vehicles, many of which fuelled by a considerably amount of ethanol. Such fleet is considered a unique case of large scale biofuel usage worldwide. Despite the large impact on human health and atmospheric chemistry/dynamics, many uncertainties are found in terms of gas and particulate matter emissions from vehicles and their atmospheric reactivity, e.g. secondary organic aerosol formation (de Abrantes et al., 2009; Ferreira da Silva et al., 2010; Kirstine and Galbally, 2012).

Ethanol was first introduced as a commercial alternative to fossil fuels in Brazil in the early 1980s and its use has strongly increased since the 2000s. This is essentially due to a new generation of flexible fuel vehicles (FFV), introduced in 2003, capable of using

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any rate of anhydrous ethanol from 20 % (mixed with gasoline, hereafter named gasohol) to pure hydrous ethanol. In 2011 the consumption of ethanol in São Paulo State was 8 300 millions m³ whereas gasoline was 7 500 millions m³, according to the Brazilian National Agency of Petroleum, Natural Gas and Biofuels (Fig. 1). Currently, roughly 85 % of all new Light Duty Vehicles (LDV) are FFV, which, combined with the current economic expansion, results in a fast changing light duty vehicle fleet. Whereas Heavy Duty Vehicles (HDVs) are renewed much slower (the vehicles are on average more than 10 yr old), the diesel composition has considerably changed in the past years. Combined with significant reduction in sulphur content towards 10 ppm, the minimum biodiesel content was set to 2 % in 2008 and 5 % in 2010.

Tunnel measurements are a powerful tool for characterizing vehicular emissions under real driving conditions (Martins et al., 2006; Handler et al., 2008; Ho et al., 2009; Cheng et al., 2010). Unlike tailpipe emission measurements conducted on a chassis dynamometer (Mulawa et al., 1997; Kleeman et al., 2000), tunnel studies allow the characterization of exhaust emissions, along with the mechanical wear of tires and brakes (Rogge et al., 1993a; Garg et al., 2000), and the ejection of particles from the pavement (Kupiainen et al., 2005) by resuspension processes (Nicholson et al., 1989; Sternbeck et al., 2002). Knowledge of emission source profiles of such fast-changing fleet and/or fuel composition is a crucial step for accurate interpretation of receptor modelling analysis.

Besides the identification of organic compounds and trace elements from vehicular sources, quantification of the emitted carbonaceous aerosol is fundamental for the analysis and interpretation of urban ambient measurements (Pio et al., 2011; El Hadad et al., 2011; Daher et al., 2013). Carbonaceous aerosol is commonly divided into an organic carbon (OC) and an elemental carbon (EC) fraction. While the only source of EC is direct emission from burning of carbonaceous matter, OC may be emitted in the particulate phase or formed through gas-to-particle conversion processes in the atmosphere (Jones and Harrison, 2005; Saylor et al., 2006). EC is a good tracer for emissions from fossil fuel combustion, namely urban emissions from road transport.

Other EC sources such as biomass burning emit at much lower rates and are relevant only in wild fires events or wintertime in rural or urban areas (Gelencsér et al., 2007). Primary OC may result from biomass burning, biological particles, plant debris or from fossil fuel.

Here we present the physical and chemical characterization of the particulate matter inside two tunnels in the SPMA with very distinct circulating fleets. In one tunnel LDVs and motorcycles account for 99.3% of the circulating fleet, whereas in the other a significant fraction (~ 30%) of overall traffic is composed of HDVs. The analysis includes aerosol size distribution, optical properties, elemental composition, quantification of Polycyclic Aromatic Hydrocarbons (PAHs) and Organic and Elemental Carbon (OC-EC) concentrations.

2 Experimental

2.1 Site description

Sample collection was carried out in two tunnels located within the SPMA: the Jânio Quadros (JQ) tunnel and the Tunnel 3 of the Rodoanel Mário Covas (RA). The campaign at the JQ tunnel took place from 2 May to 13 May 2011 whereas the RA tunnel was studied from 6 July to 17 July 2011. This work focuses on weekdays (Monday–Friday) measurements only. The JQ tunnel is located in the southwest portion of the São Paulo city. It is a 1900 m long, two-lane tunnel with traffic flowing in only one direction. The traffic of HDVs through this tunnel is restricted. Diesel-fuelled vehicles within the JQ tunnel are scarce, limited to Urban Cargo Vehicles (UCV), vehicles up to 6.3 m long. The vast majority of the fleet circulating through the JQ tunnel is composed of light duty gasohol- and ethanol powered vehicles and gasohol powered motorcycles. The tunnel has a slight downhill slope with speed limit of 70 km h^{-1} , although average speed may strongly decrease due to traffic congestions. The Rodoanel Mário Covas is a beltway with a radius of approximately 23 km from the geographical centre of the city

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downtown area. The RA tunnel is roughly 1700 m long, four-lane with traffic flowing in only one direction. The tunnel has an important traffic of HDV, especially heavy trucks transporting large payloads to and from the Santos harbour. Its speed limit is 90 km h^{-1} and 70 km h^{-1} for LDV and HDV, respectively. This tunnel features a slight uphill slope.

5 During the studied period, median values of LDV traffic from 08:00 to 20:00 (local time) were $1806 \text{ vehicles h}^{-1}$ and $1152 \text{ vehicles h}^{-1}$ in the JQ and RA tunnels, respectively. Diesel-fuelled vehicles, on the other hand, were $4 \text{ vehicles h}^{-1}$ in the JQ tunnel (consisting only of UCVs) and $330 \text{ vehicles h}^{-1}$ (UCV and large trucks) in the RA tunnels.

2.2 Instrumentation and analytical methods

10 The instrumentation was deployed roughly at the midpoint of both tunnels, located on a trailer from the São Paulo State Environmental Regulation Agency (Table 1). Unless stated otherwise, the data reported here corresponds to the fine fraction of the particulate matter, i.e., aerodynamic diameter below $2.5 \mu\text{m}$. The real-time instrumentation sampled air through a $\text{PM}_{2.5}$ cyclone impactor and a silica diffusion drier keeping
15 $\text{RH} < 50\%$. The inlet line consisted of a 2 m long copper tube with 0.8 cm inner diameter.

Three samplers were deployed to collect particulate matter on filters: a MiniVol sampler (Airmetrics, 5 lpm), a low-volume sampler (16.6 lpm) and a high-volume sampler (1130 lpm). The MiniVol filter (Pall Life Science, 47 mm quartz membrane filter) was
20 used for the quantification of organic and elemental carbon (OC-EC analyses). The low-volume sampler filter (0.4 μm pore size polycarbonate) provided gravimetric and elemental composition whereas the high-volume air sampler filter (quartz fibre) allowed the quantification of PAHs. The MiniVol and low-volume sampler were equipped with $2.5 \mu\text{m}$ impactors. The high-volume sampler was equipped with 10 μm impactors.

25 OC and EC analysis was performed using thermal-optical transmittance (TOT) (Sunset Laboratory Inc.) (Birch and Cary, 1996). The filters were analysed according to a slightly modified Sunset Labs'TOT method with variable time steps lasting between 60 and 200 s during OC evolution at temperature plateaus of 310, 475, 615, and $870 \text{ }^\circ\text{C}$.

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The temperature profile during EC evolution included 45 s plateaus at 550, 625, 700, 775, and 850 °C with a final hold at 870 °C for 120 s. Mass concentrations were obtained gravimetrically using an electronic microbalance with a readability of 1 µg (Mettler-Toledo, model MX5) in a controlled-atmosphere room. Filters were equilibrated for 24 h prior weighing. Electrostatic charges were controlled with radioactive ^{210}Po sources (Castanho and Artaxo, 2001). Trace element concentrations were determined with a X-ray fluorescence spectrometer (PANalytical, model Epsilon 5). Elements from Na to Zn have shown excellent detection limits, e.g., 15.9 ng cm $^{-2}$, 8.6 ng cm $^{-2}$, 2.0 ng cm $^{-2}$ and 10.8 ng cm $^{-2}$ for Al, P, Zn and Pb respectively with 300 s integration time for the light elements and 600 s for the heavy elements (manuscript under preparation). Details of the technique can be found in Spolnik et al. (2005). PAHs were extracted from the high-volume sampler using a Soxhlet apparatus filled with methylene chloride. Quantitative and qualitative analyses were carried out by gas chromatography-mass spectrometry (Varian, model 3800). Thirteen compounds of the 16 major PAH listed by the US-EPA as priority pollutants were analysed. The observed PAHs, according to their elution order, were: Phenanthrene (Phe), Anthracene (Ant), Fluoranthene (Fla), Pyrene (Pyr), Benzo[a]anthracene (BaA), Chrysene (Chr), Benzo[b]fluoranthene (BbF), Benzo[k]fluoranthene (BkF), Benzo[e]pyrene (BeP), Benzo[a]pyrene (BaP), Indeno[cd]pyrene (InP), Dibenzo[ah]anthracene (DBA) and Benzo[ghi]perylene (BPe).

Real-time aerosol light scattering was measured using a Nephelometer (TSI Inc., Model 3563) and light absorption by a Multi Angle Absorption Photometer (MAAP, Thermo Scientific, Model 5012). The instruments were coupled in series with a flow rate of 10 lpm using the MAAP's internal pump downstream of the Nephelometer. The Nephelometer measures light scattering coefficients (σ_s) at 450, 550, 700 nm wavelengths (Anderson and Ogren, 1998). With the scattering coefficients on three wavelengths the Ångström exponents can be determined. Scattering coefficients were corrected for angular truncation error according to Anderson and Ogren (1998). Instrument calibration was done using particle-free air and carbon dioxide. The Nephelometer sampling period was set to 5 min.

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The MAAP instrument measures simultaneously the optical attenuation and reflection of particles deposited on a glass fibrous filter from several detection angles to retrieve the aerosol light absorption (Petzold et al., 2005). The instrument has a sampling period of up to 1 min and measures light absorption (σ_{abs}) at 637 nm. Using the Ångström exponents, light scattering was interpolated to the MAAP wavelength yielding the single-scattering albedo (ω_0) of the aerosol. The ω_0 is a measure of the aerosol particle scattering strength relative to extinction as such:

$$\omega_0 = \frac{\sigma_s}{\sigma_s + \sigma_{\text{abs}}} \quad (1)$$

For purely scattering aerosol particles (e.g., ammonium sulphate) ω_0 approaches 1.0. In situ observations of dry aerosol ω_0 typically show values in the range 0.80–0.98 for urban aerosols (Anderson, 2003), 0.65–0.80 in SPMA (Backman et al., 2012), 0.72–0.88 for fresh biomass burning smoke (Magi, 2003), 0.75–0.95 at an undisturbed forest site in Amazonia (Rizzo et al., 2013) and 0.88–0.99 for coarse mode dominated mineral dust (Anderson, 2003).

The MAAP reports black carbon (BC) concentrations, which were converted from absorption coefficients assuming a constant mass-specific absorption cross-section (MAC) of $6.6 \text{ m}^2 \text{ g}^{-1}$, provided by the manufacturer. The relationship between σ_{abs} and BC mass concentration is

$$\text{BC} = \frac{\sigma_{\text{abs}}}{\text{MAC}} \quad (2)$$

Further discussion on the instrument corrections and site-specific MAC values is given on Sect. 3.4.1.

Aerosol size distribution at the range of 10–430 nm has been measured using a SMPS (Scanning Mobility Particle Sizer, TSI) composed of an electrostatic classifier (TSI, model 3080) along with a CPC (Condensational Particle Counter, TSI, model 3772).

2.2.1 Correction procedure for real-time BC measurements

The MAAP, designed to measure real-time BC mass concentration, was deployed in the JQ and RA tunnels. However, due to considerably high BC loadings, the instrument did not function properly. Whereas the JQ tunnel data could be corrected (independent EC measurement 10–15 $\mu\text{g m}^{-3}$), the instrument within the RA tunnel saturated and unfortunately did not provide reliable data (independent EC measurement $\sim 120 \mu\text{g m}^{-3}$). The JQ tunnel data has been corrected due to an artefact found in the instrument firmware that affects the instrument accuracy in environments characterized by fast changes in the light attenuation, i.e., a high rate of BC deposition on the filter (Hyvärinen et al., 2013). Such parameter, the accumulation rate, is defined as

$$\Delta\text{BC} = \text{BC} \cdot Q \quad (3)$$

where Q is the flow rate of the instrument. The artefact affects system accuracy for $\Delta\text{BC} \geq 0.04 \mu\text{g min}^{-1}$, roughly $\text{BC} \geq 3 \mu\text{g m}^{-3}$ for usual flow of $1 \text{ m}^3 \text{ h}$.

Such artefact caused a weaker light attenuation after a spot change than anticipated. Applying the correction procedure described by Hyvärinen et al. (2013) corrected the artefact for most of the data. However, measurements made shortly after the filter spot change (light attenuation above 80 % of reference) had to be removed due to unrealistic values. The uncorrected and corrected data are shown on Fig. 2.

3 Results and discussion

During the study period, over 930 000 vehicles circulated in both tunnels. In the JQ tunnel, cameras registered the traffic allowing LDVs, UCVs and motorcycles to be counted a posteriori. Given that the vehicle velocity was not measured in the JQ tunnel, traffic congestions events were flagged based on the driving pattern. In the RA tunnel, categorized traffic volume (LDV, HDV) and speed were measured using ground sensors. The LDV were defined to be those with a wheel pair distance smaller than 5.5 m and

vice versa for the HDV (generally this translates to the situation where LDV are lighter than 3.5 t). Figures 3 and 4 show the traffic weekday diurnal variation on the JQ and RA tunnel, respectively. In the following, particulate matter chemical composition, size distribution and optical properties are presented.

3.1 The particulate matter composition

3.1.1 OC, EC and trace elements

The $PM_{2.5}$ mass concentration, OC, EC and elemental composition are shown in Table 2. The average $PM_{2.5}$ concentration in the RA and JQ tunnel is $233 \mu\text{g m}^{-3}$ and $52 \mu\text{g m}^{-3}$, respectively. Given the comparable number of LDV circulating in both tunnels, the high $PM_{2.5}$ concentration found in the RA tunnel (over four times higher as in the JQ tunnel) indicates the large contribution of HDVs to the directly emitted fine particulate matter.

The average OC : EC ratio for samples collected in the JQ tunnel was 1.59 ± 0.09 . Previous tunnel measurements focusing on gasoline fuelled LDVs reported an OC : EC ratio in the fine particulate matter of 2.4 (Landis et al., 2007), a ratio 50 % higher than observed in the JQ tunnel. Furthermore, the OC : EC ratio obtained in the JQ tunnel falls close to the lower bound of literature values for LDVs (OC : EC ratio > 1), including a broad range of fuels (gasoline and diesel with different degrees of sulphur content) and aerosol size cuts ($2.5 \mu\text{m}$ and $10 \mu\text{m}$) (Cadle et al., 1999; Gillies and Gertler, 2000; Allen et al., 2001; Grieshop et al., 2006; Landis et al., 2007; Handler et al., 2008; Ning et al., 2008). Such considerably low OC : EC ratio in the JQ tunnel indicates an important contribution of EC in the Brazilian LDV fleet despite the high biofuel usage. The OC : EC ratio obtained from the RA tunnel was 0.49 ± 0.12 , a value compatible with several tunnel studies of diesel-fuelled HDVs reporting OC : EC ratio close to 0.5 (Cadle et al., 1999; Allen et al., 2001; Grieshop et al., 2006; Landis et al., 2007; Handler et al., 2008; He et al., 2008; Zhang et al., 2009).

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The most abundant trace elements in the JQ tunnel were Fe, S, Si, Cu and Ca. The abundance of such trace elements, with the exception of Cu, are in good agreement with gasohol and ethanol fuelled vehicles measurements in dynamometers (Ferreira da Silva et al., 2010) and in previous tunnel studies (Sánchez-Ccoyllo et al., 2009).

The high abundance of Cu, linked to brake lining, is mainly attributed to a stop-go driving pattern in the JQ tunnel due to traffic congestions. Given the fact that many brake linings use Sb_2S_3 up to at least 5–7 % by weight (Garg et al., 2000). Sternbeck et al. (2002) proposed a diagnostic ratio of Cu : Sb 4.6 ± 2.3 (both $2.5 \mu\text{m}$ and $10 \mu\text{m}$ size cut) to identify such source on ambient air. Here, the ratio for the JQ tunnel is considerably higher (8.2). It has been previously suggested that ethanol processing on copper tanks would enhance gasohol fuelled vehicles Cu emission factors (Castanho and Artaxo, 2001; Sánchez-Ccoyllo et al., 2009), thus indicating higher Cu : Sb ratios than expected only due to brake lining. Whether such difference is due to ethanol usage (and could be used as a marker) or due to different brake lining composition cannot be determined from this study and demands further investigation.

The most abundant elements found in the RA tunnel were S, Fe and Si, respectively. Such result is in good agreement with other studies focusing on HDV diesel emission in tunnels (Landis et al., 2007) and near a freeway (Ntziachristos et al., 2007). Ca, associated with lube oil additives in diesel engines (Matti Maricq, 2007), has been one of the most abundant element in HDV diesel emission in the US (Landis et al., 2007; Ntziachristos et al., 2007). However, such element is not among the most abundant in the RA tunnel. K, however, is the fourth most abundant element in the RA tunnel. Previous receptor modelling studies in the SPMA have found significant amounts of K in profiles linked to LDV and HDV emissions, especially with the latter (Castanho and Artaxo, 2001; Andrade et al., 2012). Given that K is found in vegetation, high levels of this element from vehicular emissions could be due to biofuel usage (Andrade et al., 2012).

In an effort to better constrain the trace elements from vehicular sources, the Enrichment Factor (EF) relative to the upper continental crust (UCC) has been calculated

for a marker for biodiesel fuelled HDVs. In the RA tunnel, the elements Na, Mg, Al, Si, K, Ca, Ti and Ni were assigned to mostly crustal origin whereas elements with both vehicular and crustal sources were P, Cl, V, Cr, Mn and Fe.

3.1.2 Polycyclic Aromatic Hydrocarbons

Previous literature showed that particulate PAH presence is mainly due to unburned PAHs in the fuel and that 95 % fuel PAH input was decomposed during the combustion process (Westerholm and Li, 1994). Yet, a major part (more than 50 %) of the emitted PAH was formed from vehicle engine. Thus, reducing fuel PAH contents, the emissions of PAH to the environment is expected to be reduced.

Table 3 summarizes the PAH concentrations in the JQ and RA tunnel in the size ranges up to 10 μm . The sum of PAH concentrations for the RA tunnel was $56 \pm 5 \text{ ng m}^{-3}$ and for the JQ tunnel was $45 \pm 9 \text{ ng m}^{-3}$. For JQ, a light vehicles tunnel, PHE (16 %), BaA (13 %) and BbF and DBA (11 %) were the most abundant detected PAHs. For RA samples, there were differences between the dominant compounds, yet in the average BaA (12 %) and DBA and BPe (11 %) were the most abundant. Dobbins et al. (2006) showed that 0.2 and 1.0 wt % of the two to four ring PAH survive the combustion process and compose a significant concentration of the mutagenic compounds in the particulate emissions. Given that a substantial fraction of such PAHs are to be found in the gas-phase, large uncertainties are usually associated with filter-based measurement of such compounds. Nevertheless, in the JQ tunnel, 3 and 4 rings particle-phase PAH summed from 24 to 66 % of those identified, while in RA they summed from 37 to 77 %.

Literature shows that ratios between some PAHs can indicate the most important contributions of different vehicles (light and heavy duty cars). Rogge et al. (1993b) attributed the ratio of $\text{InP}/(\text{InP} + \text{BPe})$ in the range 0.35–0.70 to diesel emissions and BaA/Chr ratios over 0.7 indicated gasoline burning contributions. The results obtained here show a $\text{InP}/(\text{InP} + \text{BPe})$ ratio in the RA tunnel of 0.03–0.24 and in the JQ tunnel values of 0.4–0.6. The BaA/Chr ratio in the RA tunnel ranged from 0.8–3.3 and

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1.0–12.4 in the JQ tunnel. A previous study was performed in 2001 in the JQ tunnel (Vasconcellos et al., 2003) and in the Maria Maluf (MM) tunnel, with similar profile as the RA tunnel. Such study reported InP/(InP + BPe) ratios of 0.55 (JQ tunnel) and 0.36 (MM tunnel), linked to LDVs and HDVs, respectively. The BaA/Chr ratio ranged from 0.48 (JQ tunnel) to 0.79 (MM tunnel).

BaP, the most studied PAH due to the carcinogenic potential was found ranging from 0.9 to 6.7 ng m⁻³ (0.02–0.1 ‰ of PM_{2.5}) whereas in the RA tunnel BaP ranged from 0.9 to 4.9 ng m⁻³ (0.004–0.02 ‰ of PM_{2.5}), indicating an important relative contribution of LDVs emission to atmospheric BaP. Such results agree with literature values of BaP mass fraction of PM_{2.5} of 0.1 ‰ for catalyst equipped gasoline powered LDVs and 0.003 ‰ for diesel powered HDVs (Rogge et al., 1993b).

3.1.3 Chemical mass balance

Using the information depicted in Table 2 a mass closure study has been performed. The mass contribution of the trace elements has been calculated according to their common oxides (Kleeman et al., 2000). The sulphate sampled in the tunnels was not considered to be neutralized with ammonia in the form [NH₄]₂SO₄ due to expected excess of sulphur relative to ammonia in vehicular emissions. As such, its mass was estimated from S using a factor of 3. The mass contribution from Crustal elements was calculated according to the source apportionment based on the results of the EF analysis, discussed in Sect. 3.1.1. The Crustal mass was calculated combining the mass of the elements uniquely apportioned to crustal sources and the half of the mass (as approximation) of elements apportioned to both vehicular and crustal sources. The rest of the mass relative to trace elements, excepting sulphate and Crustal, were combined under the label Trace Elements.

The Organic Mass (OM) can be estimated from OC measurements through a multiplying factor dependent on the aerosol source and its level of atmospheric processing. Literature values of the OC:OM ratio in tunnel/freeway measurements impacted by gasoline and/or diesel fuelled vehicles emissions ranges from 1.2 (Allen et al., 2001;

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Kristensson et al., 2004; Grieshop et al., 2006; Huang et al., 2006; Landis et al., 2007) to 1.4 (Geller et al., 2005; Lipsky and Robinson, 2006; He et al., 2008). Considering the large fraction of ethanol usage (and to a less extent, biodiesel), a ratio of 1.6 was chosen for the JQ tunnel and 1.5 for the RA tunnel to reflect the more oxygenated fuel. To our knowledge no direct measurement of OC:OM ratio has been made on such emissions. The difference between PM_{2.5} mass determined gravimetrically and the sum of identified compounds was labelled as “unidentified compounds”.

The results from the chemical mass balance are shown on Fig. 6. The most abundant components in the JQ tunnel are OM (42%), followed by EC (17%) and Crustal (13%). In the RA tunnel, on the other hand, the impact of EC emissions from HDV results in a large abundance of such component (52%), followed by OM (39%). Sulphate ranged from 7% in the JQ tunnel to 5% in the RA tunnel, indicating that a significant fraction of sulphur is either emitted directly from the tailpipe or quickly oxidized to the particle phase. Nonetheless its contribution to PM_{2.5} mass balance is considerably smaller than found in ambient samples in the SPMA (~20%) (Ynoue and Andrade, 2004; Castanho and Artaxo, 2001; Andrade et al., 2012). Trace Elements associated with vehicular sources account for 10% and 1% in the JQ and RA tunnels, respectively. In similar proportion, the unidentified mass in the JQ tunnel accounted for 10% of the PM_{2.5} in the JQ tunnel and 1% in the RA tunnels. The difference in unapportioned mass is probably due to nitrate and ions, not analysed here, or water retained in the filter.

The OC:OM ratio is usually a large source of uncertainty in ambient chemical mass balance analysis. Through the difference between the sum of the identified compounds and the filter mass, the upper limit of the OM:OC ratio in each tunnel can be estimated (Bae et al., 2006). The OM:OC ratios obtained using this method are upper limits instead of an estimative given that nitrate and ions were not included in the chemical mass balance. In the RA tunnel, heavily impacted by diesel emissions, the OM:OC upper limit is 1.6, whereas in the JQ tunnel an OM:OC ratio upper limit of 2.0 was obtained.

3.2 Thermogram profiles

The term thermogram indicates the flame ionization detector (FID) response recorded vs. time during the thermal-optical EC-OC analysis. The signal obtained during each temperature step, i.e., the amount of evolved carbon, reflects the contribution of a given volatility class to the OC or EC loading. The volatility class provides insights on the chemical composition and/or oxidation level of the organic compounds (Donahue et al., 2006; Wang et al., 2010; Cavalli et al., 2010).

The thermograms presented here are the average of 6 filters from the JQ tunnel and 13 filters from the RA tunnel. The signal of each filter has been scaled according to a CH₄ calibration signal performed after each run. Due to different residence time during the temperature steps between filters, the start point of each temperature step has been synced and averages performed accordingly. The average thermograms for the RA and JQ tunnels are presented on Fig. 7. The top plot presents the full thermograms, including the OC and EC analysis stage (He and He/O₂), clearly indicating the large difference of the OC to EC ratio between the circulating fleets. The bottom plot shows a detailed view of the OC analysis. A substantial difference is found between the JQ and RA tunnels during the first two temperature steps (310 and 475 °C), indicating a high contribution of high-volatility and intermediate-volatility compounds from diesel fuelled vehicles compared to ethanol and gasohol fuelled vehicles. Furthermore, one could expect a contribution of VOCs sorbed onto the aerosols, specially in soot (Goss and Eisenreich, 1997). During the third and fourth temperature steps (615 and 870 °C) no significant difference has been found. The higher signal during low temperature steps suggests a larger SOA forming potential from HDVs as LDV in the SPMA fleet. This possibility would be endorsed by Gentner et al. (2012), who, through the characterization of the chemical composition, mass distribution, and organic aerosol formation potential of emissions from gasoline and diesel vehicles in the US concluded that the latter is seven times more efficient at forming aerosol than the former.

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3.3 Particle size distribution

Particle size distribution was measured in the JQ tunnel from 2 May to 6 May 2011, roughly half of the time of the campaign on this tunnel. In the RA tunnel, the SMPS sampled in total for about 16 h, on the 7, 12 and 13 July 2011, mostly during daytime.

5 The average particle count yielded $73\,000\text{ cm}^{-3}$ in the JQ Tunnel and $366\,000\text{ cm}^{-3}$ in the RA tunnel, with an average diameter of 48.4 nm in the former and 38.7 nm in the latter.

The submicron aerosol size distribution data has been fitted in three gaussians modes, assessing the contribution of Nucleation, Aitken and Accumulation modes. The average size number distribution is shown on Figs. 8 and 9. As such, gaussian mode fitting show very little contribution on the Accumulation mode in the RA, whereas its peak height in the JQ tunnel was roughly 60% of the Aitken mode. Nonetheless, the vast majority of the Ultra Fine Particles (UFP) were found in the Nucleation mode for both tunnels. Previous tunnel studies show 80–90% of submicrometer particles with diameters less than 40 nm (Abu-Allaban et al., 2002; Geller et al., 2005). Such results, similar as obtained here, indicates small impact on the use of biofuel on the aerosol size distribution.

3.4 Optical properties

3.4.1 Mass absorption coefficient

20 The mass-specific absorption cross-section (MAC) is an essential parameter used on filter-based BC measurements that rely solely on optical methods. As described earlier, the MAC allows the conversion of light attenuation into BC concentration. The MAAP instrument uses a constant value of $6.6\text{ m}^2\text{ g}^{-1}$, recommended by the manufacturer. However, this value has been subject of a strong debate (Pan et al., 2011; Pandolfi et al., 2011; Healy et al., 2012; Crippa et al., 2013). Here, the aerosol light absorption

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measured using the MAAP in the JQ tunnel was compared with EC determined from the collected filters by means of a Sunset analyser.

The results, indicated in Fig. 10, show a good correlation between corrected σ_{abs} and EC. Through a linear fit it is obtained a MAC of $6.1 \text{ m}^2 \text{ g}^{-1}$, a value within 10% of the reported by the MAAP manufacturer. Such good agreement is probably due to exclusive vehicular source in the tunnel, where little impact of other absorbing compounds at 637 nm is expected (Sandradewi et al., 2008; Gustafsson et al., 2009; Adler et al., 2010; Moosmüller and Chakrabarty, 2011). The point at $\sim 18 \mu\text{g m}^{-3}$ suggests an underestimation of the σ_{abs} measured by the MAAP, possibly due to a saturation of the system not corrected properly by the procedure described in Sect. 2.2.1.

3.4.2 Aerosol light absorption and scattering

In the recent literature, several studies have focused on mass concentration, chemical speciation and BC content of aerosols released by vehicular emissions. Nevertheless, only a few aim to characterize aerosol optical properties like scattering coefficients and albedo (e.g., Japar et al., 1981, 1984). Since aerosol optical properties can usually be measured with high time resolution, it can provide insights on aerosol dynamical processes. Moreover, the single scattering albedo is an intrinsic aerosol property, and a key parameter to determine the effect of vehicular particulate emissions on the radiative balance and climate. To our knowledge, this study provides the first report of single scattering albedo for particles released by vehicular emissions from a blend of gasoline and ethanol fuels. Aerosol single scattering albedo in the JQ tunnel ranged between 0.3 and 0.8. Tunnel measurements by Japar et al. (1981) indicate an average albedo of 0.43 for particulated released from gasoline powered vehicles and of 0.28 from diesel powered vehicles. Strawa et al. (2010), on the other hand, measured an average albedo of 0.31 for light duty gasoline fuelled vehicles in tunnels in the US. The chemical composition of the different fuel combustion sources have impacts on the chemical properties of the emitted aerosols, as well as on dynamical processes that subsequently change aerosol physical properties such as the single scattering

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albedo. More studies are necessary to investigate this issue. The median diurnal cycle of aerosol optical properties inside the tunnels are shown on Fig. 11. In the RA tunnel, aerosol light scattering diurnal variation follows very closely HDV traffic as a result of high particle number emission factor. As previously mentioned, absorption measurements at the RA tunnel could not be validated due to the exceedingly high black carbon concentrations. Nevertheless, using the EC determined from filters and a MAC of $6.1 \text{ m}^2 \text{ g}^{-1}$, determined in the JQ tunnel, an average light absorption during filter sampling (08:00–20:00) of 730 Mm^{-1} has been calculated. As such, an average single scattering albedo of 0.32 can be estimated for the RA tunnel. In the JQ tunnel, the aerosol light absorption increases in the first morning hours by a factor of 4, following the traffic intensity (Fig. 3). Median scattering coefficients do not show a significant variation between 04:00 and 08:00 LT, in the range $50\text{--}70 \text{ Mm}^{-1}$. Consequently, in the first morning hours the single scattering albedo decreases by 40 %, reaching a minimum at 08:00 LT. After that, aerosol scattering coefficients begin to increase, while absorption coefficients remain rather constant. As consequence, single scattering albedo values increase from 08:00 to 12:00 LT, reaching its average value of 0.6. Since the vehicular emission signature is not expected to change significantly along the day inside the JQ tunnel, the delay between scattering and absorption diurnal variation might be related to aerosol dynamical processes. A hypothesis is that LDVs circulation in the first morning hours emit highly absorbing primary particles that act as surfaces for the subsequent condensation of organic and inorganic vapours. In this way, gas-to-particle conversion of scattering species such as sulphate and organic compounds would lead to an increase on scattering coefficients along the day. This hypothesis is reinforced by the diurnal pattern of aerosol size distributions (not shown), which indicates a mean geometric diameter increase from 32 nm at 07:00 to 42 nm at 13:00 LT. In the afternoon, the scattering coefficients keep rather constant, as well as the absorption coefficients and albedo. The fact that absorption coefficients do not follow the afternoon traffic increase could be related to a decrease in vehicle average velocity.

4 Conclusions

The particulate matter in tunnels dominated whether by LDVs or HDVs emission was characterized for its chemical and physical properties. The measurements were carried out in May 2011 in the JQ tunnel, mainly impacted from LDV emissions, and in July 2011 in the RA tunnel, dominated by HDV emissions. In that given year, the fuel consumption by the road transportation sector in the São Paulo State was 8300 millions m³ of ethanol, 7500 millions m³ of gasoline, 11 300 millions m³ of diesel and an estimated 600 millions m³ of biodiesel (mainly from soy bean). The minimum amount of ethanol in gasoline available in petrol stations is 20 % whereas the minimum amount of biodiesel in diesel is 5 %.

The most abundant elements found in the RA tunnel were S, Fe and Si, respectively. An EF analysis relative to the UCC composition using Al as reference has been performed. Results from such analysis indicate that all elements are consistently below the EF calculated from Landis et al. (2007), excepting K, element previously linked to biofuel usage in ambient measurements (Andrade et al., 2012). This suggests indeed a higher emission from such element from Brazilian HDVs as in the US. Nevertheless, the EF of K is quite low (6), indicating, according to the analysis described here, a major crustal origin with small vehicular contribution. In the RA tunnel, the elements Na, Mg, Al, Si, K, Ca, Ti and Ni were assigned to mostly crustal origin whereas elements with both vehicular and crustal sources were P, Cl, V, Cr, Mn and Fe. In the JQ tunnel, the most abundant trace elements were Fe, S, Si, Cu and Ca. With the exception of Cu, such result is in good agreement with gasohol and ethanol fuelled vehicles measurements in dynamometers (Ferreira da Silva et al., 2010) and in previous tunnel studies (Sánchez-Ccoyllo et al., 2009). The high abundance of Cu, linked to brake lining, is attributed to a stop-go driving pattern in the JQ tunnel due to traffic congestions. A ratio of Cu : Sb of 8.2 has been obtained, considerably higher than apportioned to brake linings elsewhere (4.6 ± 2.3 , Sternbeck et al., 2002). Results from the EF analysis in the JQ and RA tunnel shows similar trends as observed in previous studies. The elements

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apportioned to crustal source in the JQ tunnel are Na, Mg, Al, Si, K and Ca whereas elements with both vehicular and crustal sources were P, Cl, Ti, Mn, Fe and Ni. The EF analysis in the JQ tunnel does not suggest a higher emission rate of K from gasohol and ethanol fuelled vehicles in comparison to gasoline powered vehicles. Whether the higher EF from K in the RA tunnel is a result of biofuel usage can not be determined here and demands further analysis.

The $PM_{2.5}$ concentration in the RA tunnel was over four times higher as in the JQ tunnel ($233 \mu\text{g m}^{-3}$ and $52 \mu\text{g m}^{-3}$ respectively). The most abundant specie in the JQ tunnel was OM, accounting for 42 % of $PM_{2.5}$, followed by EC (17 %) and crustal elements (13 %). Sulphate accounted for 7 % and the sum of the other trace elements 10 %. The difference between $PM_{2.5}$ mass determined gravimetrically and the sum of identified compounds represented 10 % of the mass. In the RA tunnel, most of the $PM_{2.5}$ was composed of EC (52 %) and OM (39 %). sulphate, crustal and trace elements showed a minor contribution with 5 %, 2 % and 1 %, respectively. The unapportioned mass accounted for 1.0 % of $PM_{2.5}$. Accounting for the mass of the identified compounds, an upper limit to the OC : OM ratio has been calculated. In the RA tunnel, heavily impacted by diesel emissions, the OM : OC upper limit is 1.6, whereas in the JQ tunnel an OM : OC ratio upper limit of 2.0 was obtained.

The average OC : EC ratio for samples collected in the JQ tunnel was 1.59 ± 0.09 , indicating an important contribution of EC despite the high ethanol fraction in the fuel composition. Previous tunnel measurements focusing on gasoline fuelled LDVs reported an OC : EC ratio in the fine particulate matter of 2.4 (Landis et al., 2007), a ratio 50 % higher than observed in the JQ tunnel. Furthermore, the OC : EC ratio obtained in the JQ tunnel falls close to the lower bound of literature values for LDVs (OC : EC ratio > 1), including a broad range of fuels (gasoline and diesel with different degrees of sulphur content) and aerosol size cuts ($2.5 \mu\text{m}$ and $10 \mu\text{m}$). The OC : EC ratio observed in samples in the RA tunnel is very close to diesel-fuelled HDV results observed in many previous studies reporting values close to 0.5, indicating small impact of the biodiesel in the combustion efficiency and in the carbonaceous material partitioning.

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The sum of PAHs concentration was $56 \pm 5 \text{ ng m}^{-3}$ in the RA tunnel and $45 \pm 9 \text{ ng m}^{-3}$ in the JQ tunnel. BaP, the most studied PAH due to the carcinogenic potential was found ranging from 0.9 to 6.7 ng m^{-3} (0.02–0.1 ‰ of $\text{PM}_{2.5}$) in the JQ tunnel whereas in the RA tunnel BaP ranged from 0.9 to 4.9 ng m^{-3} (0.004–0.02 ‰ of $\text{PM}_{2.5}$), indicating an important relative contribution of LDVs emission to atmospheric BaP.

An analysis on the thermograms resulting from the thermal-optical analysis indicates that the OC from the RA yields a much stronger contribution from the early temperature steps (310°C and 475°C) than in the JQ tunnel, indicating a larger contribution from high-volatility compounds from diesel exhaust in regard to ethanol and gasohol fuelled vehicles. Such result would suggest a larger aerosol forming efficiency potential from HDVs as from LDVs in the SPMA. This possibility would agree with the detailed study from Gentner et al. (2012), who concluded that diesel emissions is seven times more efficient at forming aerosol than gasoline emissions.

The average particle count yielded $73\,000 \text{ cm}^{-3}$ in the JQ Tunnel and $366\,000 \text{ cm}^{-3}$ in the RA tunnel, with an average diameter of 48.4 nm in the former and 38.7 nm in the latter. As such, the vast majority of submicron aerosol particles are found in the nucleation mode in both tunnels, providing a large surface area for condensation and with important health effects. Besides aerosol size distribution, instrumentation for optical properties measurements was deployed on both tunnels. However, due to exceedingly high light absorbing material in the RA tunnel ($\text{EC} \sim 120 \mu\text{g m}^{-3}$), real-time light absorption determination was not possible in this tunnel. In the JQ tunnel ($\text{EC} \sim 9 \mu\text{g m}^{-3}$), a correction procedure for the MAAP instrument based on recent literature (Hyvärinen et al., 2013) has been successfully applied. In the JQ tunnel, the aerosol light absorption ranges from 20 Mm^{-1} up to 80 Mm^{-1} whereas light scattering ranges from 50 Mm^{-1} up to 100 Mm^{-1} . As such, single scattering albedo shows a minimum value of 0.4 at the peak of the morning rush hour, around noon reaches 0.6 and stabilizes in the afternoon and evening in 0.5. By comparing light absorption from the MAAP instrument and EC loading, the aerosol mass-specific absorption cross-section in the JQ tunnel was determined $6.1 \text{ m}^2 \text{ g}^{-1}$. In the RA tunnel, aerosol light scattering diurnal variation

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follows very closely HDV traffic as a result of high particle number emission factor. Median values range from 150 Mm^{-1} up to 400 Mm^{-1} . As stated previously real-time light absorption measurement was not possible in the RA tunnel, however, using the EC determined from filters and a MAC of $6.1 \text{ m}^2 \text{ g}^{-1}$, determined in the JQ tunnel, an average light absorption during filter sampling (08:00–20:00) of 730 Mm^{-1} was calculated. As such, an average single scattering albedo of 0.32 can be estimated for the RA tunnel.

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Table 1. List of instrumentation used on this study.

Instrument	Parameter measured	Time resolution
TSI Scanning Mobility Particle Sizer, Model 3080	Aerosol size distribution 10–430 nm	5 min
3- λ TSI Nephelometer, Model 3563	Aerosol light scattering	5 min
Thermo MAAP, Model 5012	Aerosol light absorption, BC	1 min
GC-FID Varian, model 3800 ^a	Particle phase PAHs	12 h
XR-F PANalytical, model Epsilon 5 ^b	Elemental composition	12 h
OC-EC Sunset analyser ^c	Organic and Elemental carbon	12 h

^a PM collected on high volume sampler on quartz fibre filters.

^b PM collected on low volume sampler on 47 mm polycarbonate membrane filter.

^c PM collected on a Mini-vol sampler on 47 mm quartz fibre filters.

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Table 3. Particle-phase PAH concentration ranges in the JQ and RA tunnels.

PAH (ng m ⁻³)	JQ (n = 5)	RA (n = 11)
Acenaphtylene	0.29–11.81	0.53–3.99
Fluorene	0.41–16.98	0.97–1.67
Phenanthrene	2.16–17.3	5.41–8.21
Anthracene	0.68–9.98	0.67–1.64
Fluoranthene	0.13–1.56	0.24–1.25
Pyrene	0.93–11.52	0.32–3.97
Benzo(a)anthracene	1.95–8.14	4.90–6.35
Chrysene	0.82–4.39	0.28–5.05
Benzo(b)fluoranthene	0.89–13.93	2.15–9.98
Benzo(k)fluoranthene	0.78–8.86	2.07–3.43
Benzo(e)pyrene	0.87–3.60	2.34–3.97
Benzo(a)pyrene	0.90–6.73	2.28–2.87
Indenopyrene	0.77–13.43	1.93–5.50
Dibenzo(a)anthracene	1.54–6.93	3.85–7.97
Benzo(ghi)perylene	0.30–16.26	0.97–3.57

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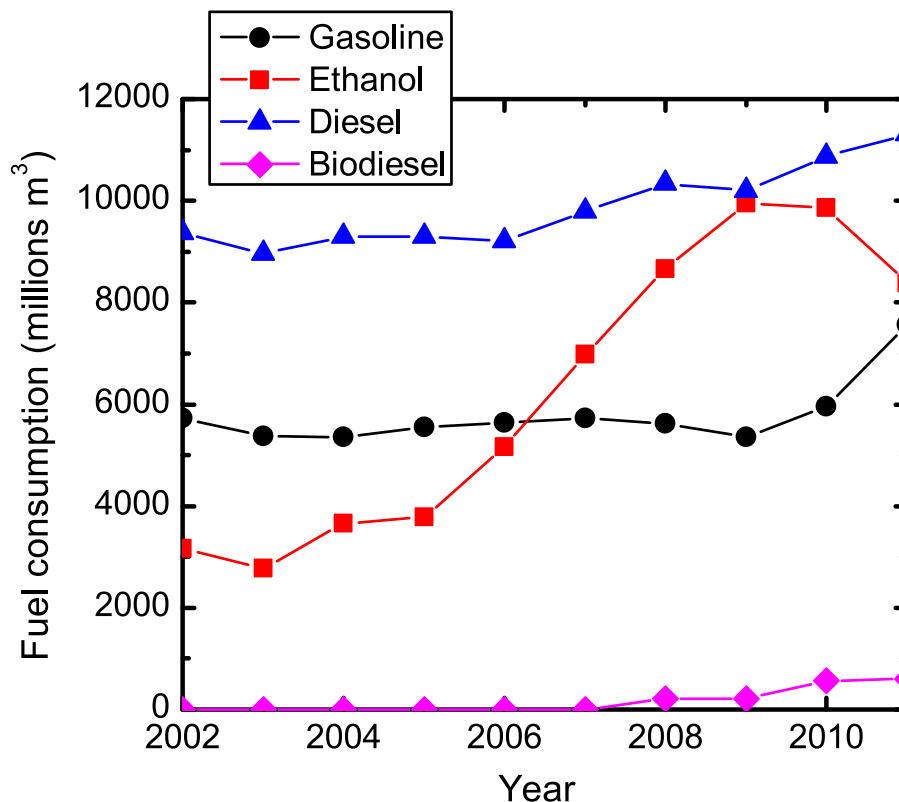


Fig. 1. Fuel consumption in the São Paulo State. Data from the Brazilian National Agency of Petroleum, Natural Gas and Biofuels. The indicated ethanol is the sum of anhydrous (part of gasohol) and hydrous (E100). The biodiesel consumption was calculated considering its minimum content in diesel: 2% in 2008–2009 and 5% 2010–2011.

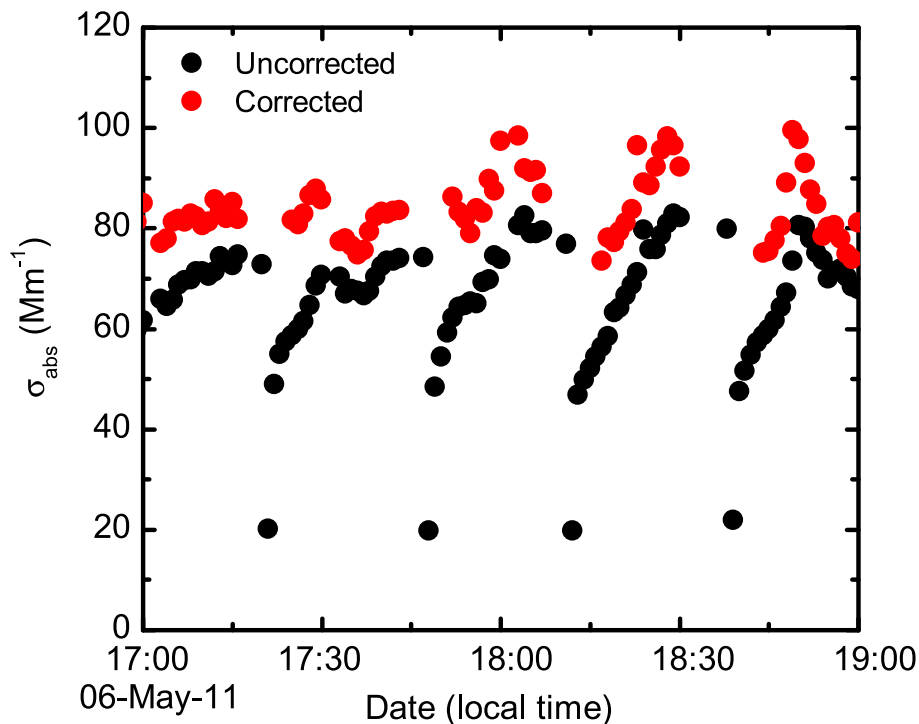


Fig. 2. Detailed view of the uncorrected and correct MAAP data from the JQ tunnel. Correction procedure performed according to Hyvärinen et al. (2013). Furthermore, measurements performed with light attenuation above 80 % of reference (i.e., shortly after filter spot change) were removed.

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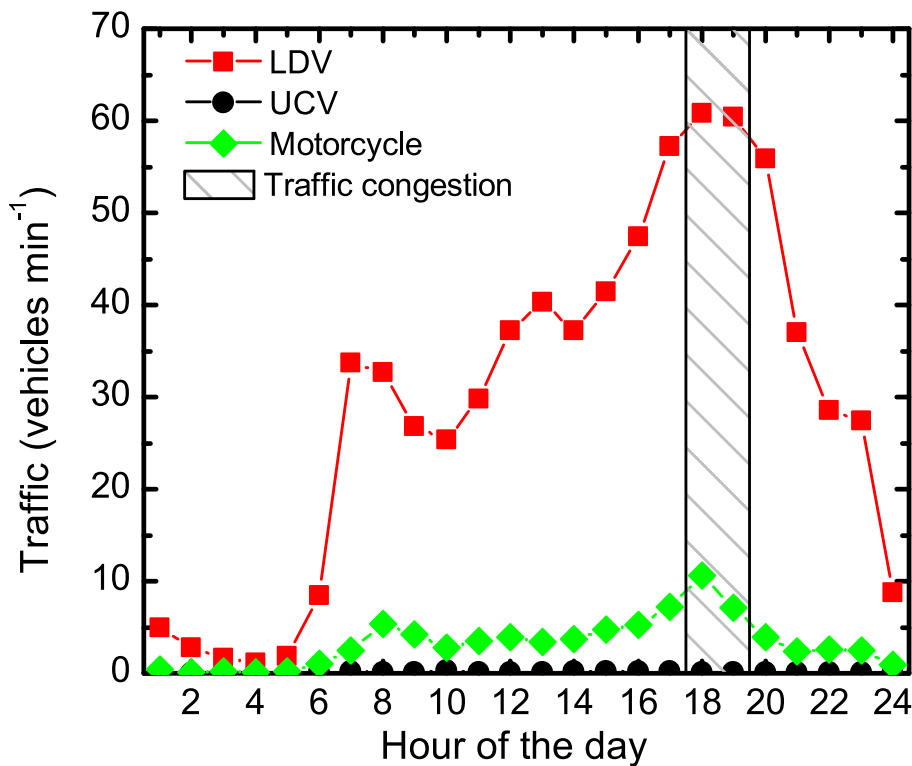


Fig. 3. Median values for vehicular traffic on the JQ tunnel. Hour of the day in local time. The hashed area indicates that at least 50 % of the days traffic congestions were observed on that hour of the day. Urban Cargo Vehicles (UCVs), limited to a length of 6.3 m, are the only diesel-fuelled vehicles allow to use the JQ tunnel. Whereas most of the LDVs are flexible fuel vehicles, motorcycle are limited to Gasohol.

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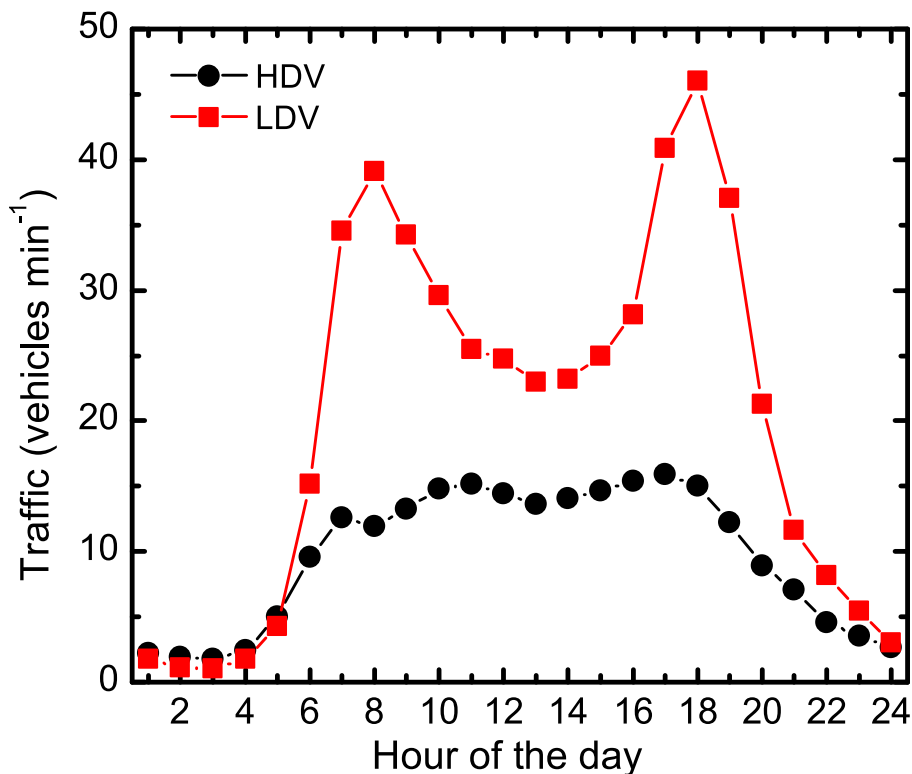


Fig. 4. Median values for vehicular traffic on the RA tunnel. Hour of the day in local time. No traffic congestions were observed in the RA tunnel during the studied period. The majority of HDVs in this tunnel are large trucks. LDV are mostly flexible fuel vehicles. Motorcycles were not apportioned in this tunnel, however, due to its location (outside city limits), very few are expected to be found.

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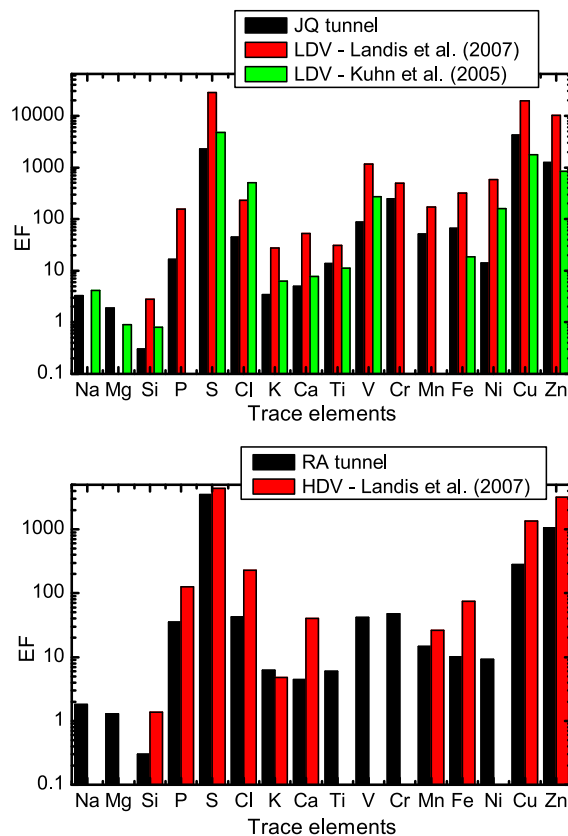


Fig. 5. Enrichment Factor analysis relative to the UCC composition using Al as reference material. Top: results of the JQ tunnel and previous works on gasoline fuelled LDVs near a freeway (Kuhn et al., 2005) and in tunnel (Landis et al., 2007). Bottom: EF results from the RA tunnel and results for diesel fuelled HDVs in tunnels (Landis et al., 2007).

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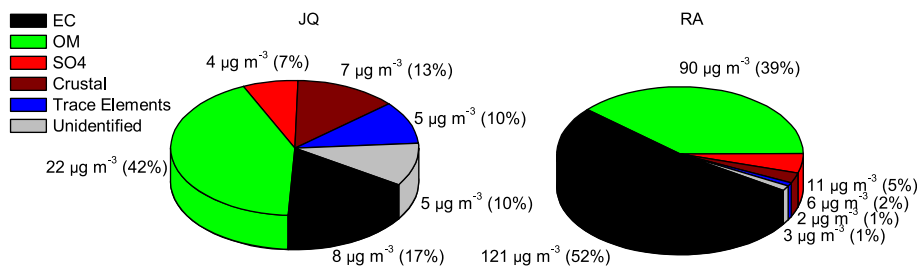


Fig. 6. Chemical mass balance on the JQ (left) and on the RA (right) tunnels. The Crustal mass was calculated combining the mass of the elements uniquely apportioned to crustal sources and the half of the mass (as approximation) of elements apportioned to both vehicular and crustal sources (Sect. 3.1.1). Sulphate mass was estimated from S using a factor of 3 (corresponding to the atomic mass of S relative to SO_4^{2-} mass). The other elements, excluding S and crustal, are grouped under the label Trace Elements. The Organic Mass (OM) is estimated from OC measurements using a ratio of 1.6 in the JQ tunnel and 1.5 in the RA tunnel. The difference between $\text{PM}_{2.5}$ mass determined gravimetrically and the sum of identified compounds was labelled as Unidentified compounds.

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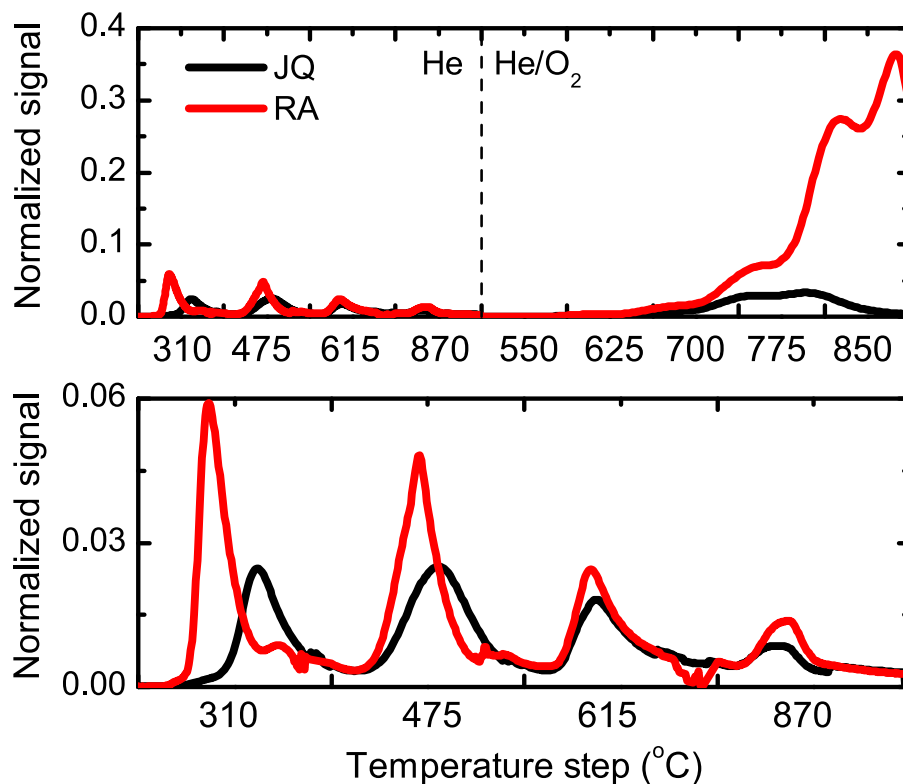


Fig. 7. Average thermogram of the carbonaceous aerosols sampled on both tunnels. Top: complete thermogram indicates the OC (He) and EC (He/O₂) stages. Bottom: detailed view of the OC quantification step.

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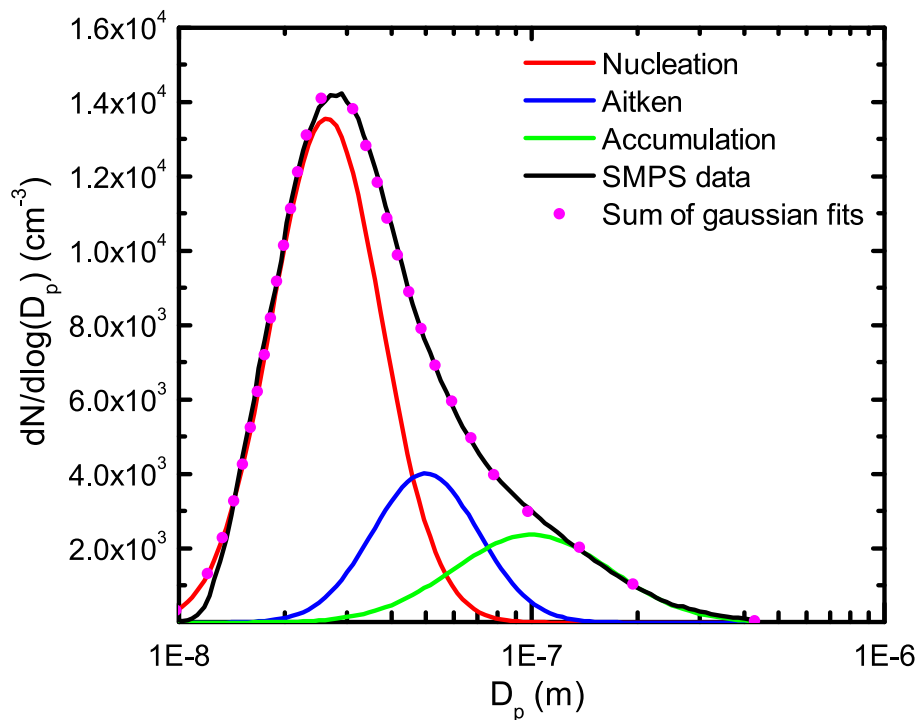


Fig. 8. Average aerosol size distribution in the JQ Tunnel. Particle size distribution was measured from 2 May to 6 May 2011. The average particle number concentration was $73\,000\text{ cm}^{-3}$ with an average diameter of 48.4 nm.

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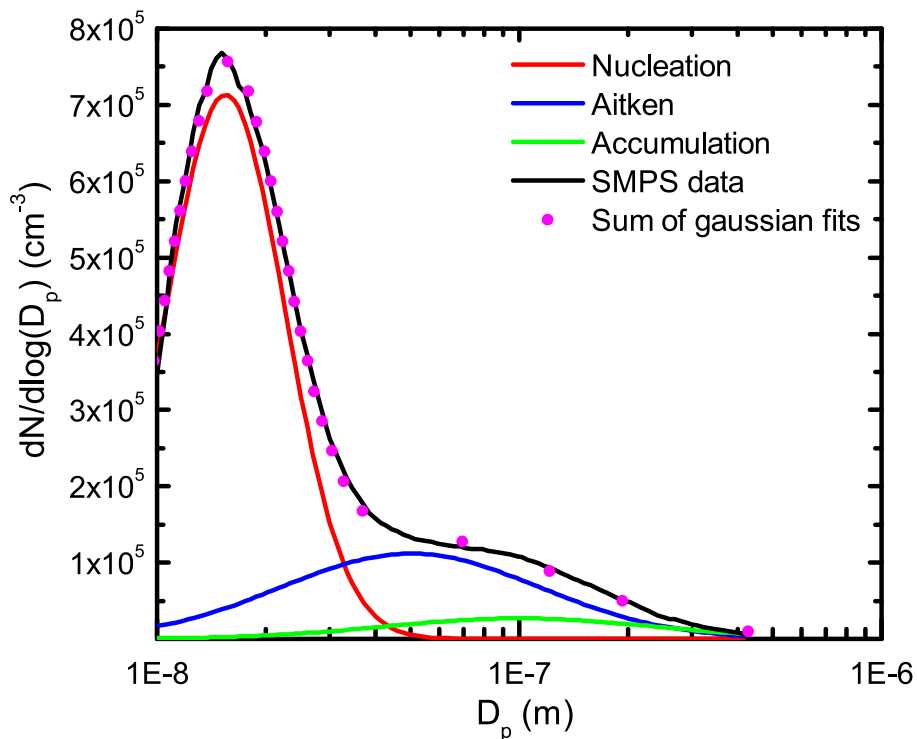


Fig. 9. Average aerosol size distribution in the RA Tunnel. The SMPS sampled in total for about 16 h, on the 7, 12 and 13 July 2011, mostly during daytime. The average particle number concentration was $366\,000\text{ cm}^{-3}$ with an average diameter of 38.7 nm.

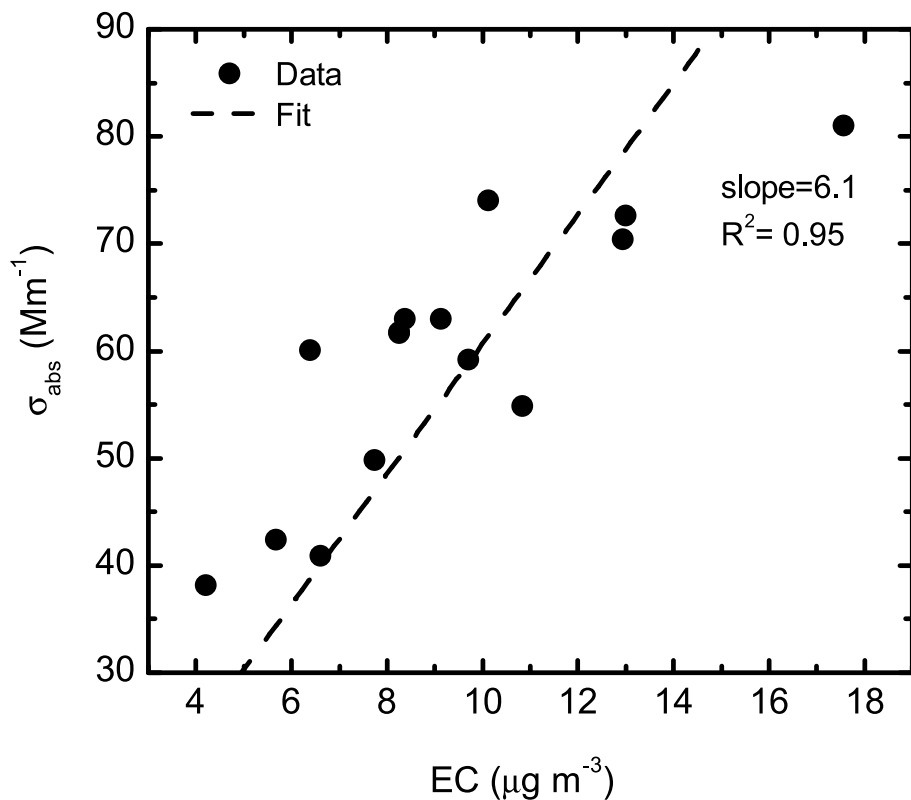


Fig. 10. Correlation between the light absorption measured by the MAAP and EC determined using the collected filters by means of a SUNSET analyser.

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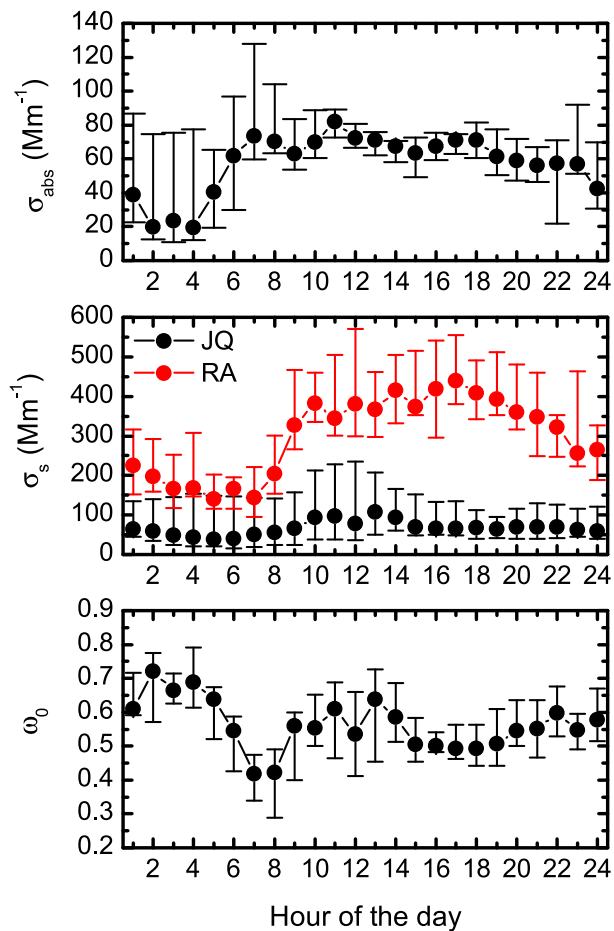


Fig. 11. Median values for (top) light absorption, (middle) light scattering and (bottom) single scattering albedo. The range bars represent the 10 and 90 percentile.