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One decade of VOCs measurements in São Paulo megacity: composition, variability, and emission evaluation in a biofuel usage context

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Abstract

In South America, the observations of atmospheric pollutants are deficient, and few cities have implemented air quality monitoring programs. In addition, Volatile Organic Compounds (VOCs) observations are still missing, and little is known about their contributions to the atmospheric composition and impacts in a large ethanol usage context like Brazil. Here, we present a wide range of VOCs that have been measured for ten years in São Paulo Megacity (SPM) in different campaigns at traffic, urban and background sites. When compared with other cities worldwide, the average VOCs ambient concentrations in SPM were higher by factors of 2 to 10. However, the ambient VOCs distribution among these cities is homogeneous even for ethanol, aldehydes and alkenes species. Emission ratios (ER) were established related to carbon monoxide and acetylene, which did not depict strong seasonal and interannual variability in SPM. When compared with previous studies, ERs showed an enrichment from road-tunnel to background, suggesting the presence of other sources than traffic. A good agreement in ER was found with Los Angeles and Paris; but limited consistencies with Middle East and Asia cities. Our ethanol measurements show that contrasted ER can be obtained depending on the emission process involved, with a strong impact of evaporation on ethanol concentrations. The multiyear acetaldehyde analysis displayed that ER could be a valuable metric to assess the long-term changes in emissions sources. Finally, VOCs emissions were calculated from ER

and compared with those estimated by the global emission inventory (Edgar). The total VOC emissions estimated by the global inventory agree very well with those from our observations up to 75%. Nevertheless, the VOCs speciation is misrepresented in the inventory, mainly for oxygenated and heavier alkanes compounds. These inconsistencies will also have an impact on the quantification of secondary atmospheric pollutants formation associated to road transport emissions.

Keywords: VOCs, ethanol, emission ratios, megacities, emission inventory, South America

1. Introduction

Volatile Organic Compounds (VOCs) are crucial pollutants present in urban environments, which affect air quality by producing secondary pollutants such as ozone and secondary organic aerosols (SOA) (Seinfeld and Pandis, 2006) and causing harmful effects on human health (Laurent and Hauschild, 2014). Accurate VOCs field observations can provide relevant information for a better assessment of their sources and prediction of ozone and SOA formation towards the improvement of air quality policies. Likewise, VOCs speciation at emission is substantial for building up accurate emission inventories (Coll et al., 2010; Wang et al., 2014; Salameh et al., 2016), which strongly depends on the knowledge of their primary emissions. Nevertheless, speciation and quantification of VOCs emissions and their spatial distribution are still misestimated (Huang et al., 2017). In places like Africa and South America, where the anthropogenic pressure is high, there is still an urgent need of information for developing emission inventories (Dominutti et al., 2019; Huang et al., 2017). The lack of speciated VOCs observations along with the uncertainties of emission sources in urban regions have an impact in the quality of global and regional emission inventories, which frequently use observations to estimate anthropogenic emissions (Dominutti et al., 2019; Salameh et al., 2016b). Several studies in northern mid-latitude cities have estimated the urban enhancement emission ratios (ER) from VOCs ambient observations relative to an inert tracer of combustion, such as carbon monoxide (CO) and acetylene (C₂H₂) (Baker et al., 2008; Warneke et al., 2007; von Schneidmesser et al., 2010; Borbon et al., 2013; Boynard et al., 2014; Wang et al., 2014). These calculated ER were successfully used as constraints to evaluate regional and global emission inventories. Large discrepancies were found in previous studies between the ER derived from inventory and the ones derived from observations. For instance, discrepancies were observed in Paris and Los Angeles up to a factor of 4 (Borbon et al., 2013). Similarly, a quite large difference of 2 orders of magnitude was also revealed by comparing VOCs emissions derived from the ER to the ones from global downscaled inventories in Cote d'Ivoire (South Western Africa, (Dominutti et al, 2019). The oxygenated VOCs fraction (OVOCs) frequently presents the more substantial discrepancies in the emission comparison, not only because of the

misunderstanding of their sources (Karl et al., 2018) but also of the lack of ambient observations of these compounds. Saturated and unsaturated alcohols are OVOCs commonly emitted into the atmosphere by biogenic sources (Grosjean, 1997). However, in urban atmospheres their emissions are mainly ruled by anthropogenic sources (Brito et al., 2018; Colón et al., 2001; de Gouw et al., 2012; Giubbina et al., 2017, de Gouw et al., 2018). OVOCs have been pointed out as primary emissions of biofuels usage (Niven, 2005; Pouloupoulos et al., 2001a; Suarez-Bertoa et al., 2015b), which can be released either from combustion or evaporative processes (Gentner et al., 2009). Ethanol, introduced as a fuel or fuel additive in many countries, plays a crucial role in the tropospheric chemistry where its oxidation is a substantial source of aldehydes in the atmosphere (Anderson, 2009; Corrêa et al., 2010; Martins et al., 2008; Miguel and de Andrade, 1990; Nogueira et al., 2014; Pinto and Solci, 2007). Because of their high reactivity, the emissions of OVOCs impact the atmospheric chemistry, contributing to the radical's formation and photochemical processing in the atmosphere (de Gouw et al., 2018; Goldan et al., 2004).

Brazil is the only country worldwide where a large-scale alcohol program has been underway for more than 40 years. The Brazilian Ethanol Program (Proalcool) started in 1975 and enabled the increase of ethanol production together with the development of E100 vehicles. Since 2003, an increase in ethanol production and consumption has been observed due to the introduction of flex-fuel vehicles (Cortez et al., 2016), which led to Brazilian ethanol production reaching 27 billion litres in 2008 and, since then, has remained practically constant (UNICA, 2019). Flex-fuel vehicles can burn both 100% hydrous ethanol (7.5% of maximum water mass content) and a mixture called gasohol (73% gasoline + 27% anhydrous ethanol) (Cortez et al., 2016). The Metropolitan area of São Paulo (MASP, Figure 1) with more than 22 million inhabitants and more than 7 million vehicles is among the ten most populous regions worldwide and one of the main urban centres in South America. São Paulo Megacity (hereafter SPM, Figure 1), corresponds to half of the MASP population (~11 million inhabitants) and 4 million vehicles. In São Paulo, 50% of the fleet is composed of flex-fuel and ethanol vehicles and the annual ethanol consumption can overpass gasoline consumption depending on the price's fluctuation (Nogueira et al., 2017; Salvo and Geiger, 2014). A challenge in SPM, as in many other urban centres, is to control air pollution caused by tropospheric ozone. The Brazilian vehicle emissions control program (PROCONVE), the most important public policy implemented in Brazil to control air pollution caused by vehicle emissions, was created in the 1980s and it is currently on his 6th phase. Following the guidelines applied in California, US (California Environmental Protection Agency, 2015) and The California Low-Emission Vehicle Regulations (California Air Resources Board, 2019), the Brazilian government released the new PROCONVE phases (L7 and L8, (Diário Oficial da União,

2018). These new phases will start establishing limits for non-methane organic gases (NMOG) taking into account their ozone formation potential (OFP). However, up to now, there is a lack of official data for the OFP estimation based on the typical Brazilian gasoline composition and little is known about how the VOCs emissions could be affected considering the large biofuel content. Despite that scenario, limited ethanol ambient measurements were performed over the last years and the sources, burden and fate of this compound in the atmosphere remain unexplored (Naik et al., 2010). Few short-term ethanol measurements were performed in SPM during the last two decades, which applied a wide range of measurement techniques at different sampling sites (traffic, road tunnels, urban background and background). Ambient ethanol concentrations observed at SPM were quite dissimilar, reaching between 18 to 460 ppb (Pereira et al., 1999; Schilling et al., 1999; Colón et al., 2001; Nguyen et al., 2001; Alvim, 2013; Brito et al., 2018; Scaramboni, 2018). Hence, in view of the high uncertainties surrounding the global and regional emission estimations, specifically for VOCs, there is an urgent need for the assessment of their emissions. Particularly in specific ethanol contexts and in less covered areas such as South America, where that kind of evaluation has not been yet addressed.

This work aims to evaluate ethanol, aldehydes and non-methane hydrocarbons (NMHCs) ER by using field measurements collected during several campaigns in SPM, Brazil. In particular, this work relies on a four-year monitoring programme of more than 50 NMHCs at an urban background site. Urban enhancement emission ratios (ER) were established here by applying the linear regression fit (LRF) method. Afterwards, in order to investigate ER trends in the last decade our results were compared to previous near-source measurements at SPM, such as urban road-tunnel and traffic sites. In addition, an evaluation of the spatial variability was performed by comparing ER in SPM with those collected in contrasted urban environments worldwide, in order to assess commonalities and discrepancies in VOCs composition. Finally, speciated VOCs emissions were estimated and compared with a global inventory in order to investigate the distribution of VOCs species for the road transportation sector and their implications on atmospheric chemistry.

2. Materials and Methods

2.1 Ethanol measurements

Ethanol measurements were performed by a commercial gas monitor (INNOVA1412i Luma Science), based on a photoacoustic infrared detection technique (more details can be found in the SM). A similar system has been used in previous studies to analyse the ethanol, CO and CO₂ concentrations from direct tailpipe vehicular emissions in Europe (Suarez-Bertoa et al., 2017). However, to the best of our knowledge, this is the first time that a photoacoustic ethanol instrument has been used to measure

ambient concentrations. This method enables the measurement of gases which absorb infrared light. In our study, the sampling strategy for ethanol integrates different intensive online field campaigns. One of them was developed inside a semi-confined residential parking garage to assess the contribution of evaporative emissions. This campaign was developed for 2 weeks and the ethanol measurements were performed every 10 minutes. The residential garage has a capacity of approximately 400 light-duty vehicles burning ethanol and gasohol, representative of the fleet running on SPM. More than 90% of vehicles go out in the morning and return in the evening. The sampling point inside the garage, chosen to minimize external influences, was located ~100 meters from the unique entrance of the garage. Additionally, near-traffic measurements were achieved for six weeks in 2013, by measuring ethanol, CO and CO₂ concentrations next to the main University of São Paulo entrance enclosed by high traffic avenues. Furthermore, urban background measurements were also performed at the same point of NMHCs online measurements. These data were collected for several months in 2013 and 2014. However, due to instrument detection limits, the number of missing values was significant, restricting the diurnal-basis analysis at the background site.

2.2 VOCs measurements in São Paulo megacity

The non-methane hydrocarbons (NMHCs) dataset used in this study was obtained by long term real-time measurements deployed at an urban background site and by offline sampling at various urban-traffic sites. Long-term NMHCs measurements were performed between 2012 and 2015 inside the University of São Paulo Campus (USP), by using a gas chromatography flame ionization detection (GC-FID) instrument. More details about the instrument and the percentage of data available for each year are shown in the supplementary material (Table S1). The chemical families analysed targeted several species of alkanes, alkenes, aromatics and acetylene. To complete this unprecedented dataset, the data reported in previous studies performed in SPM at traffic (UTr), urban road tunnel (UT) and urban background (UB) sites (Colón et al., 2001; Martins & Andrade, 2008; Alvim et al., 2011; Brito et al., 2015; Alvim, 2013; Alvim et al., 2016; Dominutti et al., 2016; Nogueira et al., 2017, 2015) were re-analysed. The sampling times and data availability from each compound are shown in Figure 2, and the details about the instrumentation and time resolution are disclosed in Table 1. Aldehydes measurements were performed by deploying the 2,4-DNPH technique during intense field campaigns at UB (Nogueira et al., 2014), UTr (Alvim et al., 2016; Nogueira et al., 2017) and inside UT (Nogueira et al., 2015). Aldehydes concentrations were also measured in long-term campaigns developed by the São Paulo State Environmental Agency (CETESB) (Nogueira et al., 2017). More details about the instrumentation and time resolution can be found in Table 1.

Ancillary data of CO and nitrogen oxides (NO, NO₂ and NO_x) concentrations were obtained from CETESB and were also considered in the data analysis of this study (CETESB, 2018b).

2.3. Determination of VOCs enhancement emission ratios

The VOC enhancement emission ratio refers to the ratio of a selected VOC to a vehicular tracer compound in fresh emissions without undergoing photochemical processing. The first step in the derivation of ER is the selection of a reference compound. Commonly, combustion tracers compounds, CO and C₂H₂ (Borbon et al., 2013; Salameh et al., 2016b; von Schneidmesser et al., 2010; Warneke et al., 2007), both have low reactivity in the atmosphere ($k_{OH} = 0.90 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for C₂H₂ and $k_{OH} = 1.4 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for CO) (Atkinson and Arey, 2003). A good linear correlation ($R^2=0.78-0.82$) between CO and acetylene was obtained with similar slope and high correlation coefficients. Overall, better correlation coefficients were obtained in winter than in summer for both vehicular combustion tracers (CO and C₂H₂). Therefore, considering global comparisons, ER were established relative to both compounds (CO and C₂H₂) for all the VOCs under study to provide a complete analysis. A commonly applied method to determine these ratios is the LRF by estimating the slope of the scatter plot between a selected VOC and C₂H₂ or CO as a tracer (Borbon et al., 2013; Warneke et al., 2007) (Figure S1). The ER performed for the night-time data presented a very well mixed scatterplot, when compared with the daytime data, for most NMHCs (Figure S1). Consequently, we applied the LRF method to all the data obtained without any filtering to determine enhancement of NMHCs ER. As for aldehydes measured at the UB site, only the measurements obtained between 6-8 a.m. were considered to determine ER in order to avoid their secondary formation contribution during the daytime. However, the aldehydes ER established at the traffic site were collected by 24-hour-passive sampling and, consequently, the effect of secondary sources needs to be considered. In general, a reduced number of samples were obtained at urban traffic and road-tunnel sites, limiting the application of the LRF method. Since road-tunnel concentrations are mainly impacted by direct vehicular emissions, ERs were established from concentration ratios, after subtracting the VOC background concentrations obtained from measurements outside the tunnel.

2.4 Comparison with a global emission inventory

The emissions of fifty-three VOCs were estimated in annual basis for SPM (Figure 2). Our estimations were calculated by using the São Paulo State inventory which was developed by CETESB based on emission factors (EF) obtained for different vehicle categories, considering the fuel, age and vehicular technology used (CETESB, 2018c). Hence, the annual emissions of CO, NO_x, PM, SO₂ and total

NMHC were estimated for São Paulo State. We used here a top-down approach to estimate the total CO emissions of the vehicular fleet in SPM, based on the number of vehicles circulating in the SPM. Subsequently, our detailed ER (VOC/CO) database was scaled by the total annual CO emissions estimated by the local environmental agency to assess speciated VOCs emissions from road transportation sector at SPM. Afterwards, species were grouped into VOCs families following the GEIA groups provided by the global VOC inventory, EDGAR v4.3.2 (<http://edgar.jrc.ec.europa.eu/>). Based on the species observed, sixteen VOCs emission families are here investigated from VOC1 to VOC21, including ethanol (VOC1), ethane (VOC2), propane (VOC3), alkenes (VOC7-8 and 12), butanes (VOC4), pentanes (VOC5), heavier alkanes (VOC6), acetylene (VOC9), isoprene (VOC10), benzene (VOC13), toluene (VOC14), C₈- and C₉- aromatics (VOC 15-16), formaldehyde (VOC21) and other aldehydes (VOC22). The VOCs emissions provided by the inventory were obtained by integrating the eight grids covering SPM, at a spatial resolution of 0.1° x 0.1° (EDGAR database, Huang et al., 2017). Finally, our VOCs emission estimation is compared with the annual total VOCs emissions provided by the global inventory for the road transportation sector.

3. Results and discussion

3.1 VOCs concentration levels in SPM from 4-years measurements

Figure 3 displays the average and standard deviation for a selected number of VOCs mixing ratios obtained during the 4-year measurements at SPM including also ethanol and aldehydes (formaldehyde and acetaldehyde), at the UB site. Higher mixing ratios of all VOCs were observed in SPM during the period under study, when compared with those reported in other urban atmospheres, such as London, Los Angeles, Beijing and Paris. The VOCs values observed in SPM were higher by a factor of 2 to 9 for aromatics, 1.8 to 5 for alkanes and 1.5 to 10 for alkenes. In spite of the high levels of ethanol also observed in Los Angeles and London (average of 5 ppb and 9±5 ppb, respectively, de Gouw et al., 2012; Dunmore et al., 2016), where ethanol is used as a fuel additive; acetaldehyde, formaldehyde and ethanol were greater in SPM by factors of 4 to 7. The increase of these compounds together with some alkenes in the emissions has been pointed out in previous studies as a result of ethanol combustion processes (Niven, 2005; Suarez-Bertoa et al., 2015a). Nevertheless, and despite the large biofuel use in SPM, there is not a clear enrichment for those compounds in São Paulo when compared to other locations. Even though the higher levels observed, the distribution profile does not depict any difference in the VOCs distribution. First, our results suggest that the number of circulating vehicles compensate the effect of cleaner biofuel and vehicular technologies used in SPM when looking at the high concentrations observed. Second (1) vehicular emissions in general have a strong influence in the

VOCs levels in SPM; (2) surprisingly, the large ethanol usage does not affect on average the distribution of OVOC.

3.2 Seasonal and inter-annual variations in VOCs emission ratios in SPM.

In this section we assess the VOC to C₂H₂ and VOC to CO ER obtained from the measurements performed between 2013 and 2015 at the UB site. ERs were established individually for each VOC species and then grouped into VOC families, such as aromatics, alkanes, alkenes, CO and oxygenates. The ER were also evaluated on seasonal basis (summer and winter, Figure S2) and inter-annual basis (summer and winter of each year, Figure S3). Globally, all the VOCs species showed a good correlation with C₂H₂ and CO in summer and winter (Table 2). The calculated correlation coefficients (R²) with C₂H₂ ranged from 0.4 for weaker correlated species such as butenes to 0.9 for most of the species such as pentanes, butanes, aromatics and alkenes. Regarding aromatics, most of them showed a reasonably good correlation with coefficients ranging from 0.5-0.76. When related to CO, strong correlation values were also obtained for all alkanes, alkenes and aromatics with exception of o-xylene and 1,2,4-trimethylbenzene (R²=0.48 and 0.3, respectively). Since ethanol concentrations concomitantly with CO were only measured during short-term campaigns, the correlations were performed related to this tracer. The correlation coefficients were dissimilar about the sampling sites, ranging from 0.23 to 0.99 in UB and UTr site, respectively. Aldehydes ER derived from UTr observations presented a good correlation to CO for acetaldehyde (0.75-0.90) and moderate correlation for formaldehyde (0.40-0.70), but lower coefficients were obtained at the UB site (0.43).

Figure 4 shows the seasonal averaged ERs of each VOC versus C₂H₂ and versus CO for the whole period. In general, no significant differences were found within summer and winter for the UB site, in more than 90% of the evaluated species. These results contrast with the findings in other places. For instance, Wang et al. (2014) reported lower ERs in winter than in summer by a factor of 2 for most VOCs species measured in Beijing. Similar results were also found in French urban areas where a strong effect of seasonality was found for C₄-C₅ alkanes and C₇-C₉ aromatics (Boynard et al., 2014). This difference usually affects specific VOCs species, such as pentane and isopentane due to seasonal adjustment in the fuel formulation among winter and summer to reduce the effect of summertime vapour pressure (Boynard et al., 2014; Gentner et al., 2009). In contrast, a study in Lebanon, showed a similar profile without a strong seasonal variation in the urban ERs obtained (Salameh et al., 2016a). These findings show a common non-seasonal behaviour between SPM and Lebanon, contrasting the results obtained in northern mid-latitude cities in Europe, United States and Asia (Borbon et al., 2013; Boynard et al., 2014; Wang et al., 2014; Warneke et al., 2007). One reason could be an unchanged

contribution of evaporative emissions in SPM between winter and summer and also to the absence of domestic heating due to the high temperatures in winter (13-23 °C). The non-seasonality observed in the averaged values for the whole period, was also observed between the years 2013, 2014 and 2015, agreeing within a factor of 2. These results show that ERs are not strongly affected by seasonality, suggesting that emission patterns and source composition are almost constant all through the year in SPM.

3.3 VOCs ERs variability in SPM: from urban background to traffic emissions

A few previous studies were developed in SPM, reporting a limited number of VOCs species by short-term measurements at UTr, UB and UT sites. To analyse the VOCs spatial distribution in SPM, the average ERs obtained at the UB site were selected as reference and then compared with those obtained in previous studies. Figure 5 shows the comparison between the ERs estimated in the UB site with those derived from UTr, UT and UB measurements. As shown in the previous section, there is no significant seasonal and interannual variability in the calculated ERs. Therefore, the comparison is based on ERs averages integrating all seasons and years at the UB site. A very good consistency between UTr and UB sites is observed, with slightly higher ERs for heavy alkanes (nonane and decane) at the UTr site (Figure 5a). This would suggest that the urban VOCs composition is mostly affected by vehicular emissions. On the other hand, most compounds showed lower ERs inside the urban road-tunnel than at the UB site. The differences observed between these sites could be associated with the higher CO levels from direct combustion emissions inside road tunnel where the fleet mainly comprises light-duty vehicles. These also could be influenced by the combustion emission of buses and diesel vehicles, circulating near the UTr and UB sites, affecting the CO, NO_x and VOCs emission profiles. These findings also suggest that, besides sources by transport-related ones there is the presence of other sources at the UB and UTr sites. Indeed, there were more discrepancies for alkanes (propane, i-butane and n-butane, in particular) which presented higher ERs at the UB than inside the road tunnel. The high ambient concentrations of these compounds at the UB site were already referred to the presence of sources associated with the use of both liquefied petroleum and natural gases (LPG and NG) in SPM (Dominutti et al., 2016). Similar results were found in the ERs comparison in Los Angeles, where a considerable difference of light alkanes related to gas use and production was detected (de Gouw et al., 2012). Likewise, discrepancies were also observed for oxygenated compounds, alkene species (1-pentene, cis-pentene and cis-butene) and aromatics (ethylbenzene and m+p-xylene), all presenting higher ERs at the UB site. Additionally, a VOCs dataset obtained during an urban road-tunnel campaign performed in 2004 was also evaluated (not

shown here) to elucidate possible ERs variations due to the changes in the Brazilian fleet between 2004 and 2011. Main differences are associated with aromatics, which were larger within factors of 1.5 to 6.6 in 2004 compared with those obtained in the road-tunnel in 2011. A decrease on the aromatic ERs is also observed when compared to those obtained in 2011 at UB site with our VOCs dataset. Main discrepancies were detected for C8 to C10 aromatics, which could be related to the emission by other sources such as solvents and chemical products. This 7-year-change in aromatic contributions could be also associated to changes in SPM fleet, the increase of ethanol consumption and the improvements in vehicular technologies.

3.4 Sources of ethanol in SPM

Here we analysed the results obtained by online ethanol measurements in different short-term campaigns in SPM. Figure 6 shows the concentrations profile of ethanol and CO measured at an UTr site (Figure 6a); the scatterplot between both compounds obtained at the UTr site (Figure 6b) and inside a semi-confined residential garage (Figure 6c). A good agreement is observed in the time series of ethanol and CO obtained at the UTr site, suggesting the emission from a similar traffic source (Figure 6a). The average concentrations of ethanol and CO were 66.2 ± 39.5 ppb and 0.88 ± 0.55 ppm, respectively. These concentrations were higher than those observed at the urban background site, where average concentrations were 35.0 ± 14.0 ppb and 1.35 ± 0.40 ppm for ethanol and CO, respectively. In addition, the average concentrations observed during our campaigns were higher than those measured in other studies in MASP (Brito et al., 2018; Scaramboni, 2018). This fact could be related to the distance to the emission sources and other external factors such as ethanol consumption and usage, atmospheric and meteorological conditions, and differences on the measurement techniques used. Ethanol concentrations were even higher inside the semi-confined residential garage than at the UTr site, where online observations were performed for two weeks (average concentrations of 600.0 ppb and 3.23 ppm, for ethanol and CO, respectively). The correlations between both compounds at the UTr site and the residential garage site are shown in Figures 6b and 6c, respectively. The scattered correlation at the traffic site suggests the additional contribution either of non-combustion sources or other processes affecting the concentrations observed. In contrast, a good correlation is depicted ($R^2=0.89$) when analysing the daytime observations inside the residential garage (light-blue dots, Figure 6c). Interestingly, the highest ethanol concentrations inside the garage were reported at night-time rather than during peak traffic times (early in the mornings and evenings, not shown here). The correlation of these night-time observations is reported in Figure 6c (dark-blue dots). The emission ratio obtained (0.16 ppm/ppm) could be related to evaporation losses since ethanol concentrations are higher than those observed for CO, and the correlation coefficient lower than the one from exhaust

emissions ($R^2=0.45$). On the opposite, when considering the daytime observations inside the garage (light-blue dots, Figure 6c), a lower ER is reported (0.12 ppm/ppm) with higher CO concentrations suggesting the contribution from exhaust emissions. However, it is not possible to separate both evaporation loss and exhaust emission contributions for all the observations obtained. Therefore, we consider the ER obtained as a mixture of evaporation and exhaust emissions.

Ethanol ERs were also established from the observations obtained at other sampling sites and compared with the ER at UTr and at the residential garage, previously discussed (Figure 6b). The ERs obtained at UTr and UB sites were 0.046 and 0.036, respectively. Considering the studies performed in MASP fifteen years ago, a decrease in ER (0.282 ppm/ppm) and ethanol concentrations (468 ppb, Colón et al., 2001) in traffic sites is depicted, by factors of 6.5 and 5, respectively. A similar but less pronounced decrease pattern was observed in the UB site. Previous ethanol measurements in the UB site displayed average concentrations of 47.4 ppb in 2011 and ethanol/CO molar ratios of 0.060 ppm/ppm (Alvim, 2013). However, weak correlations were obtained between ethanol and CO in our UB observations, which could suggest the contribution from other sources rather than only traffic emissions.

3.5 Biofuel consumption and its implications in aldehydes emission ratios

Several studies have investigated the aldehydes concentrations in Brazil and then compared those levels with other places worldwide. Most of these studies suggested that major differences are related to fleet composition and regional practices in Brazil, increasing the levels of aldehydes in the atmosphere (Correa et al., 2012; Grosjean et al., 2002; Martins et al., 2007; Nogueira et al., 2014). A recent study discussed the seasonal variations in the ambient concentrations of formaldehyde and acetaldehyde over 5-year measurements in SPM (Nogueira et al., 2017). In that study, no evidence in the aldehydes trends was found, indicating that an increase in ethanol consumption could affect the aldehydes concentrations in the atmosphere. We evaluate here those observations by applying the LRF to obtain acetaldehyde and formaldehyde ERs related to CO. Figure 7a shows the formaldehyde and acetaldehyde ERs obtained for each year. An increase in the formaldehyde (1.35 to 2.80 ppb/ppm) and acetaldehyde (2.08 to 2.93 ppb/ppm) ERs was noticed in 2015. This shift was up to 60% and 40 %, respectively higher when compared with the ER obtained in previous years. The increase in the ER could be associated to the change in the fuel consumption observed, characterized by an increase in the ethanol and biodiesel sales and a decrease in the gasohol sales in 2015 (Figure 7b). Ethylene (ethene, C_2H_4), a compound identified in ethanol combustion emissions (Niven, 2005; Suarez-Bertoa et al., 2015a), also underwent a change in the ERs in the winter 2015. Ethylene to CO ER increased by 80 %

and 56% in 2015, when compared with those in the winters 2014 and 2013, respectively. These results suggest that the analysis of ERs provide more sensitive information to assess the impact that a change in fuel consumption can imply in the primary combustion emissions and thus, in the atmospheric chemistry. Regarding atmospheric concentrations, higher formaldehyde and acetaldehyde levels were usually observed in winter in SPM (Nogueira et al., 2017). However, the ERs display a dissimilar pattern when analysed on seasonal basis. Since aldehydes were passively sampled during these campaigns, the separation of secondary formation sources could not be achieved. Figure 7c shows the scatterplot of acetaldehyde and formaldehyde versus CO, colour-coded by the season under analysis (winter and summer). A higher acetaldehyde to CO ER is depicted in winter (2.11 ppb/ppm) when compared to that in the summer (1.70 ppb/ppm). Conversely, a lower ER is observed for formaldehyde in winter when compared with that in the summer 1.38 ppb/ppm and 1.68 ppb/ppm, respectively. The opposite trend between both compounds and the lower correlation coefficients between formaldehyde and CO could suggest the presence of secondary formation rather than traffic-related ones.

3.6 Comparison of São Paulo megacity ER with other cities worldwide

In order to assess the spatial heterogeneity of our results, the average ERs obtained here were compared with those reported in previous studies in cities of North America (Bon et al., 2011; de Gouw et al., 2018, 2012), Europe (Borbon et al., 2013; McMeeking et al., 2012; von Schneidmesser et al., 2010), Asia and Middle East (Salameh et al., 2016; Simpson et al., 2014; Wang et al., 2014).

For each comparison, seasonal means were applied considering the same season in the studied city. For those ERs relative to C_2H_2 , discrepancies with aromatics were found, which were higher in Paris, Beirut (summer and winter) and Mecca, by factors of 3, 2.5 and 1.2, respectively (Figure S4). In SPM, alkenes ERs showed higher values when compared with those in London (by a factor of 2.4), Beirut (by a factor of 1.3) and slightly higher than those in Mecca and Beijing. Regarding alkanes, ERs in SPM presented higher values than those in Beijing (within a factor of 2.3) and Beirut (within a factor of 1.7). However, the CO versus C_2H_2 ratio was lower in SPM when compared with that in the cities investigated. The VOCs versus CO ERs were also reported in some megacities previously discussed or estimated when CO data was provided. Additionally, ERs for oxygenated compounds (acetaldehyde, formaldehyde and ethanol) were included in the comparison when available. Figure 8 shows the global $\Delta VOC/\Delta CO$ ERs comparison between SPM and other cities worldwide. In general, a high consistency with northern mid-latitude cities (Los Angeles and Paris) was found, especially for aromatics (benzene, C_8 -aromatics) and alkanes (butanes, pentanes and n-octane). ERs reported in Beijing and Mexico presented a moderate consistency when compared with those obtained in São Paulo for C_9 -aromatics,

benzene, n- nonane and n-pentane. However, a few differences were found especially for alkenes, being higher in SPM by factors of 3 to 12. Mexico also presented higher ERs of light alkanes (by factors of 2 to 6), especially for those NG/LPG-related compounds, whose high ambient concentrations were already pointed out in a previous study (Bon et al., 2011). Regarding the ERs comparison with Middle East cities, Beirut and Mecca, dispersed correlations were obtained. São Paulo presented higher aromatic ERs when compared to Beirut, by factors of 2 to 6. In general, the largest differences were usually observed in SPM for alkanes and alkenes ERs, especially for propane, butanes, ethylene, propylene and butenes. The larger ERs of these species in SPM could be related to the large biofuel usage in the megacity affecting the distribution and intensity of the VOCs emissions. Regarding oxygenated compounds, higher ERs within factors of 1.2 to 5.8 were observed in SPM. As already discussed in section 3.4, the dissimilar profile also observed for ERs could be associated with a difference in fuel consumption and acetaldehyde emissions by ethanol burning process. Interestingly, similar ethanol ERs were found between São Paulo and Los Angeles and in general a comparable emission profile between the megacities is observed (Figure 8). This good agreement suggests that ethanol emissions are mainly related to road transportation in São Paulo and despite the extended use of biofuels, the distribution of the VOCs emissions is analogous to the ones observed in other places where ethanol has been used as a fuel additive. Nevertheless, other sources of ethanol such as solvent and volatile chemical usage cannot be ignored, and they need to be further investigated.

3.7 VOCs emissions in SPM: a comparison with a global emission inventory

In South America, the observations of atmospheric pollutants are deficient, and few cities have implemented air quality monitoring programs. Likewise, the availability of VOCs data in terms of speciation, temporal and spatial resolution, remains limited. As a result, regional emission inventories are scarcely developed or missing in most of the Latin American countries. Most of them, only estimated CO, NO_x and particulate matter emissions from the road transportation sector. Here we estimate the speciated VOCs emissions from the ERs established in SPM and then we compare to those provided by the global emission inventory, EDGAR V4.3.2. Since the vehicular emissions were pointed out as the main sources of air pollution in SPM, we evaluate the VOCs contribution for the road transport sector. The regional emission inventories developed by CETESB, provide information about CO emissions detailed by type of fuel and vehicular categories. This data was used to estimate total CO emissions in São Paulo and later applied to estimate the VOC emissions by using the ERs ($\Delta\text{VOC}/\Delta\text{CO}$) established in our study. Nevertheless, since CO emissions could have high uncertainties, our estimation should be considered as a lower limit, implying an underestimation of

VOC emissions. Figure 9 shows the comparison between the VOCs emissions estimated by the global inventory and the ones calculated from our ERs on year basis. The total annual VOCs emissions related to the road transport sector in EDGAR inventory were estimated to be 22 Gg year⁻¹ in SPM, which represents almost 30 percent lower than the annual emissions obtained via our ERs results (32Gg year⁻¹). This difference is expected to be a lower limit regarding the fact that our study only considers 53 VOCs species for the road transport sector. In terms of VOCs speciation, main differences were obtained in the estimation of oxygenated emission, such as aldehydes (VOC21 and VOC22) and ethanol (VOC1). Our ERs estimation presented higher values by factors 6 and 7 respectively, when compared with EDGAR contributions. These results suggest that the extensive use of biofuels in Brazil has greater contribution on the road transport emissions than that estimated by the global inventory. Inconsistencies were also observed for the heavy alkanes (VOC6) which presented greater emissions in the global inventory by factors of 2.3. Similarly, higher contributions were observed for most of the aromatic species, which together with heavy alkanes dominate the global inventory profile. On one hand, this disparity could be associated to the restricted number of heavy alkanes measured in our study and the absence of VOCs of intermediate volatility, which are significantly emitted by vehicles burning diesel. On the other hand, this difference suggests that conventional gasoline and diesel emission profiles have been prevailing the road transportation VOCs profile estimated by the global inventory. Although the differences in VOCs distribution among the inventory and our estimation are not significant, they can have a substantial impact in terms of atmospheric reactivity. Even though some VOC families present low OH reactivity, they can have an important contribution in the formation of secondary organic aerosols, as is the case of heavy alkanes and aromatic compounds. Thus, it is necessary to well represent the contribution of each VOC family to better evaluate their effects on the urban atmosphere. Figure 9b shows our VOCs emissions contribution weighted by k_{OH} and compared with those reported by the global inventory. Thus, averaged k_{OH} rate constants were obtained for each VOCs family and then multiplied by an assumed emission of 100 tonnes. Despite that discrepancies in the mass profile of VOC6 were fairly large (Figure 9c), heavy alkanes have relative low reaction constants which do not produce a great difference in terms of OH reactivity. However, for other VOC families a small difference in mass can lead to a high increase in reactivity. For instance, despite the minor differences observed in the alkenes mass emissions (VOC12), these discrepancies are remarkable when weighted by the k_{OH} constants, dominating all the VOCs reactivity profiles (Edgar and ERs estimation). It is important to note that we have only evaluated here the VOCs reactivity in OH-basis, nonetheless other alkenes reaction pathways should be considered, such as ozone and nitrate reactions which dominate the night-time

removal processes of these species (de Gouw et al., 2017). On the other hand, the high ethanol levels observed by our estimation do not seem to have a substantial direct impact on the k_{OH} contribution. Nevertheless, ethanol oxidation is an important source of aldehydes in the atmosphere, thus its high concentrations could lead to an indirect increase of atmospheric reactivity. Indeed, despite the moderate contribution of aldehydes species (VOC21 and VOC22) on the total emission mass (6.3%), they represent a meaningful input on the k_{OH} profile. Furthermore, our estimation only contemplates the emissions from two aldehydes species (formaldehyde and acetaldehyde) which should be considered as a lower limit. It should be emphasized that despite the good agreement between observed emissions and inventory total estimations, the VOCs speciation is still not well represented in global inventory. VOCs emission inventories are fundamental inputs of air quality models, playing a meaningful role in the estimation of air pollution and secondary pollutants formation. Consequently, to ameliorate the prospective VOCs emission estimations, more efforts are needed in the development of representative local and regional ERs, the collection of comprehensive activity data and the better speciation of emission sources. These findings are important for decision makers and public policy makers in Brazil who now intend to implement the control of hydrocarbon emissions considering the reactivity of these species.

4. Conclusions

In this work, we analysed an extensive dataset of VOCs obtained by several field campaigns in São Paulo megacity (SPM) over the last decade. Our long-term measurements of ethanol, aldehydes and NMHCs were complemented with previous short-term field campaigns performed in different sampling sites in SPM. Our study provides a comprehensive observational database for the assessment of local and regional VOCs levels in SPM, the evaluation of emission inventories considering the observations performed in the last decade and the implications of the large use of biofuels in one of the most important megacities of the world.

The VOCs urban enhancement emission ratios (ERs) related to CO and acetylene were successfully derived from ambient measurements in summer and winter for three years of measurements, by applying the linear regression fit method. Our results depict the high concentrations of ethanol and ethanol emission-related VOCs in the urban atmosphere. The ERs of ethanol relative to CO derived from the observations showed the different sources and processes being responsible for the emission of this compound into the atmosphere. Our results bring to light that evaporative emissions are a substantial source of ethanol that needs to be contemplated. Analysing the relation between fuel consumption and aldehydes ER, our results suggest a change in the emission profiles of acetaldehyde

and formaldehyde when the ethanol sales over passed the gasoline ones. These compounds are one of the main limitations associated to “clean” biofuel combustion emissions and their high concentrations in Brazilian atmospheres were commonly associated with the large consumption of ethanol. However, our findings suggest that other sources than vehicular emissions could be responsible for the presence of oxygenated compounds in the atmosphere, such as secondary formation processing. In general, the ERs derived from the observations did not show significant seasonality regardless of the species, unlike the seasonality usually observed in other cities. We compared the composition of VOCs emissions with those from other traffic studies and generally a good agreement was found with a few notable exceptions. When compared with tunnel emissions, higher ERs were observed in the urban background site for 40% of the species evaluated. Those results suggest not only the strong contribution of vehicular sources but also the influence of other sources in the urban background. When compared with other cities worldwide, a good consensus met the ERs obtained for Los Angeles. These findings highlight that none changes are observed in the VOCs distribution by the extensive use of biofuels in SPM.

Finally, the establishment of ERs allowed the estimation of VOCs emissions by the road transportation sector. The comparison with the global emission inventory has shown an underestimation of oxygenated compounds (aldehydes and ethanol) by a factor of 6. Those discrepancies have consequences on the atmospheric reactivity and on the estimation of the effects that vehicular emissions can have on the regional air quality. At a local and regional level, long term measurements integrating different sampling sites and regional-specific tracers, are of great interest in order to provide more reliable information to improve the VOCs magnitude and speciation of emission estimations.

Authors contributions

PD, TN and AF designed the project and field campaigns; PD and TN operated, calibrated and performed QC/QA of instrument measurements; all authors contributed to the interpretation of data; PD and AB led the manuscript preparation, with TN and AF contributing and critically reviewing the paper.

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References

- Alvim, D.S., 2013. Estudo dos Principais Precursores de Ozônio na Região Metropolitana de São Paulo. University of Sao Paulo.
- Alvim, D.S., Gatti, L.V., Corrêa, S.M., Chiquetto, J.B., Souza Rossatti, C., Pretto, A., Santos, M.H., Yamazaki, A., Orlando, J.P., Santos, G.M., 2016. Main ozone-forming VOCs in the city of Sao Paulo: observations, modelling and impacts. *Air Qual. Atmos. Heal.* <https://doi.org/10.1007/s11869-016-0429-9>
- Alvim, D.S., Gatti, L.V., Santos, M.H. dos, Yamazaki, A., 2011. Estudos dos compostos orgânicos voláteis precursores de ozônio na cidade de São Paulo. *Eng. Sanit. e Ambient.* 16, 189–196. <https://doi.org/10.1590/S1413-41522011000200013>
- Anderson, L.G., 2009. Ethanol fuel use in Brazil: air quality impacts. *Energy Environ. Sci.* 2, 1015. <https://doi.org/10.1039/b906057j>
- Atkinson, R., Arey, J., 2003. Atmospheric Degradation of Volatile Organic Compounds. *Chem. Rev.* 103, 4605–4638. <https://doi.org/10.1021/cr0206420>
- Baker, A.K., Beyersdorf, A.J., Doezema, L. a., Katzenstein, A., Meinardi, S., Simpson, I.J., Blake, D.R., Sherwood, F.R., 2008. Measurements of nonmethane hydrocarbons in 28 United States cities. *Atmos. Environ.* 42, 170–182. <https://doi.org/10.1016/j.atmosenv.2007.09.007>
- Bon, D.M., Ulbrich, I.M., de Gouw, J. A., Warneke, C., Kuster, W.C., Alexander, M.L., Baker, A., Beyersdorf, A. J., Blake, D., Fall, R., Jimenez, J.L., Herndon, S.C., Huey, L.G., Knighton, W.B., Ortega, J., Springston, S., Vargas, O., 2011. Measurements of volatile organic compounds at a suburban ground site (T1) in Mexico City during the MILAGRO 2006 campaign: measurement comparison, emission ratios, and source attribution. *Atmos. Chem. Phys.* 11, 2399–2421. <https://doi.org/10.5194/acp-11-2399-2011>
- Borbon, A., Gilman, J.B., Kuster, W.C., Grand, N., Chevaillier, S., Colomb, A., Dolgorouky, C., Gros, V., Lopez, M., Sarda-Esteve, R., Holloway, J., Stutz, J., Petetin, H., McKeen, S., Beekmann, M., Warneke, C., Parrish, D.D., de Gouw, J.A., 2013. Emission ratios of anthropogenic volatile organic compounds in northern mid-latitude megacities: Observations versus emission inventories in Los Angeles and Paris. *J. Geophys. Res. Atmos.* 118, 2041–2057. <https://doi.org/10.1002/jgrd.50059>
- Boynard, A., Borbon, A., Leonardis, T., Barletta, B., Meinardi, S., Blake, D.R., Locoge, N., 2014. Spatial and seasonal variability of measured anthropogenic non-methane hydrocarbons in urban atmospheres: Implication on emission ratios. *Atmos. Environ.* 82, 258–267. <https://doi.org/10.1016/j.atmosenv.2013.09.039>
- Brito, J., Carbone, S., Monteiro Dos Santos, D.A., Dominutti, P., De Oliveira Alves, N., Rizzo, L., Artaxo, P., 2018. Disentangling vehicular emission impact on urban air pollution using ethanol as a tracer. *Sci. Rep.* 8, 1–10. <https://doi.org/10.1038/s41598-018-29138-7>

- Brito, J., Rizzo, L. V., Herckes, P., Vasconcellos, P.C., Caumo, S.E.S., Fornaro, A., Ynoue, R.Y., Artaxo, P., Andrade, M.F., 2013. Physical–chemical characterisation of the particulate matter inside two road tunnels in the São Paulo Metropolitan Area. *Atmos. Chem. Phys.* 13, 12199–12213. <https://doi.org/10.5194/acp-13-12199-2013>
- Brito, J., Wurm, F., Yáñez-Serrano, A.M., de Assunção, J.V., Godoy, J.M., Artaxo, P., 2015. Vehicular Emission Ratios of VOCs in a Megacity Impacted by Extensive Ethanol Use: Results of Ambient Measurements in São Paulo, Brazil. *Environ. Sci. Technol.* 49, 11381–11387. <https://doi.org/10.1021/acs.est.5b03281>
- CETESB, 2018a. Qualidade do ar no estado de São Paulo 2017 - Recurso electrónico. Sao Paulo.
- CETESB, 2018b. Companhia Ambiental do Estado de São Paulo [WWW Document]. URL <https://cetesb.sp.gov.br/ar/qualar/> (accessed 6.25.18).
- CETESB, 2018c. Relatório de emissões veiculares no estado de Sao Paulo 2017. Sao Paulo.
- Coll, I., Rousseau, C., Barletta, B., Meinardi, S., Blake, D.R., 2010. Evaluation of an urban NMHC emission inventory by measurements and impact on CTM results. *Atmos. Environ.* 44, 3843–3855. <https://doi.org/10.1016/j.atmosenv.2010.05.042>
- Colón, M., Pleil, J.D., Hartlage, T.A., Lucia Guardani, M., Helena Martins, M., 2001. Survey of volatile organic compounds associated with automotive emissions in the urban airshed of São Paulo, Brazil. *Atmos. Environ.* 35, 4017–4031. [https://doi.org/10.1016/S1352-2310\(01\)00178-9](https://doi.org/10.1016/S1352-2310(01)00178-9)
- Correa, S.M., Arbilla, G., Marques, M.R.C., Oliveira, K.M.P.G., 2012. The impact of BTEX emissions from gas stations into the atmosphere. *Atmos. Pollut. Res.* 3, 163–169. <https://doi.org/10.5094/APR.2012.016>
- Corrêa, S.M., Arbilla, G., Martins, E.M., Quitério, S.L., de Souza Guimarães, C., Gatti, L.V., 2010. Five years of formaldehyde and acetaldehyde monitoring in the Rio de Janeiro downtown area – Brazil. *Atmos. Environ.* 44, 2302–2308. <https://doi.org/10.1016/j.atmosenv.2010.03.043>
- de Gouw, J.A., Gilman, J.B., Borbon, A., Warneke, C., Kuster, W.C., Goldan, P.D., Holloway, J.S., Peischl, J., Ryerson, T.B., Parrish, D.D., Gentner, D.R., Goldstein, A.H., Harley, R.A., 2012. Increasing atmospheric burden of ethanol in the United States. *Geophys. Res. Lett.* 39. <https://doi.org/10.1029/2012GL052109>
- de Gouw, J.A., Gilman, J.B., Kim, S.-W., Lerner, B.M., Isaacman-VanWertz, G., McDonald, B.C., Warneke, C., Kuster, W.C., Lefer, B.L., Griffith, S.M., Dusanter, S., Stevens, P.S., Stutz, J., 2017. Chemistry of Volatile Organic Compounds in the Los Angeles basin: Nighttime Removal of Alkenes and Determination of Emission Ratios. *J. Geophys. Res. Atmos.* 122, 11,843–11,861. <https://doi.org/10.1002/2017JD027459>
- de Gouw, J.A., Gilman, J.B., Kim, S.W., Alvarez, S.L., Dusanter, S., Graus, M., Griffith, S.M., Isaacman-VanWertz, G., Kuster, W.C., Lefer, B.L., Lerner, B.M., McDonald, B.C., Rappenglück, B., Roberts, J.M., Stevens, P.S., Stutz, J., Thalman, R., Veres, P.R., Volkamer, R., Warneke, C., Washenfelder, R.A., Young, C.J., 2018. Chemistry of Volatile Organic Compounds in the Los Angeles Basin: Formation of Oxygenated Compounds and Determination of Emission Ratios. *J. Geophys. Res. Atmos.* 123, 2298–2319. <https://doi.org/10.1002/2017JD027976>
- de Gouw, J.A., Middlebrook, A.M., Warneke, C., Goldan, P.D., Kuster, W.C., Roberts, J.M., Fehsenfeld, F.C., Worsnop,

- D.R., Canagaratna, M.R., Pszenny, A.A.P., Keene, W.C., Marchewka, M., Bertman, S.B., Bates, T.S., 2005. Budget of organic carbon in a polluted atmosphere: Results from the New England Air Quality Study in 2002. *J. Geophys. Res.* 110. <https://doi.org/10.1029/2004JD005623>
- Dominutti, P., Keita, S., Bahino, J., Colomb, A., Lioussé, C., Yoboué, V., Galy-Lacaux, C., Bouvier, L., Sauvage, S., Borbon, A., 2019. Anthropogenic VOC in Abidjan, southern West Africa: from source quantification to atmospheric impacts. *Atmos. Chem. Phys. Discuss.* 1–39. <https://doi.org/10.5194/acp-2018-1263>
- Dominutti, P.A., Nogueira, T., Borbon, A., Andrade, M. de F., Fornaro, A., 2016. One-year of NMHCs hourly observations in São Paulo megacity: meteorological and traffic emissions effects in a large ethanol burning context. *Atmos. Environ.* 142, 371–382. <https://doi.org/10.1016/j.atmosenv.2016.08.008>
- Dunmore, R.E., Whalley, L.K., Sherwen, T., Evans, M.J., Heard, D.E., Hopkins, J.R., Lee, J.D., Lewis, A.C., Lidster, R.T., Rickard, A.R., Hamilton, J.F., 2016. Atmospheric ethanol in London and the potential impacts of future fuel formulations. *Faraday Discuss.* 189, 105–120. <https://doi.org/10.1039/C5FD00190K>
- Gentner, D.R., Harley, R.A., Miller, A.M., Goldstein, A.H., 2009. Diurnal and Seasonal Variability of Gasoline-Related Volatile Organic Compound Emissions in Riverside, California. *Environ. Sci. Technol.* 43, 4247–4252. <https://doi.org/10.1021/es9006228>
- Giubbina, F.F., Scaramboni, C., De Martinis, B.S., Godoy-Silva, D., Mello, I.N.P.D., Nogueira, R.F.P., Campos, M.L.A.M., 2019. Temporal variation of ethanol in rainwater from the sugar cane belt of São Paulo State (Brazil). *Atmos. Environ.* 216, 116926. <https://doi.org/10.1016/j.atmosenv.2019.116926>
- Giubbina, F.F., Scaramboni, C., De Martinis, B.S., Godoy-Silva, D., Nogueira, R.F.P., Campos, M.L.A.M., 2017. A simple method for simultaneous determination of acetaldehyde, acetone, methanol, and ethanol in the atmosphere and natural waters. *Anal. Methods* 9, 2915–2922. <https://doi.org/10.1039/C7AY00306D>
- Grosjean, D., 1997. Atmospheric chemistry of alcohols. *J. Braz. Chem. Soc.* 8, 433–442. <https://doi.org/10.1590/S0103-50531997000500002>
- Grosjean, D., Grosjean, E., Moreira, L.F.R., 2002. Speciated ambient carbonyls in Rio de Janeiro, Brazil. *Environ. Sci. Technol.* 36, 1389–95.
- Huang, G., Brook, R., Crippa, M., Janssens-Maenhout, G., Schieberle, C., Dore, C., Guizzardi, D., Muntean, M., Schaaf, E., Friedrich, R., 2017. Speciation of anthropogenic emissions of non-methane volatile organic compounds: A global gridded data set for 1970-2012. *Atmos. Chem. Phys.* 17, 7683–7701. <https://doi.org/10.5194/acp-17-7683-2017>
- Kirstine, W. V., Galbally, I.E., 2012. The global atmospheric budget of ethanol revisited. *Atmos. Chem. Phys.* 12, 545–555. <https://doi.org/10.5194/acp-12-545-2012>
- Martins, E.M., Arbilla, G., Bauerfeldt, G.F., de Paula, M., 2007. Atmospheric levels of aldehydes and BTEX and their relationship with vehicular fleet changes in Rio de Janeiro urban area. *Chemosphere* 67, 2096–103. <https://doi.org/10.1016/j.chemosphere.2006.09.088>

- Martins, L.D., Andrade, M.F., 2008. Ozone Formation Potentials of Volatile Organic Compounds and Ozone Sensitivity to Their Emission in the Megacity of São Paulo, Brazil. *Water. Air. Soil Pollut.* 195, 201–213. <https://doi.org/10.1007/s11270-008-9740-x>
- Martins, L.D., Andrade, M.F., Freitas, E.D., Pretto, A., Gatti, L. V., Albuquerque, E.L., Tomaz, E., Guardani, M.L., Martins, M.H.R.B., Junior, O.M.A., 2006. Emission Factors for Gas-Powered Vehicles Traveling Through Road Tunnels in Sao Paulo, Brazil. *Environ. Sci. Technol.* 40, 6722–6729.
- Martins, L.D., Andrade, M.F., Ynoue, R.Y., Albuquerque, È.L. de, Tomaz, E., Vasconcellos, P.C., 2008. Ambiental volatile organic compounds in the megacity of São Paulo. *Quim. Nov.* 31, 2009–2013. <https://doi.org/http://dx.doi.org/10.1590/S0100-40422008000800018>
- McMeeking, G.R., Bart, M., Chazette, P., Haywood, J.M., Hopkins, J.R., McQuaid, J.B., Morgan, W.T., Raut, J.-C., Ryder, C.L., Savage, N., Turnbull, K., Coe, H., 2012. Airborne measurements of trace gases and aerosols over the London metropolitan region. *Atmos. Chem. Phys.* 12, 5163–5187. <https://doi.org/10.5194/acp-12-5163-2012>
- Miguel, A.H., de Andrade, J.B., 1990. Catalyst and noncatalyst exhaust aldehydes emission from brazilian ethanol-fueled vehicles. *J. Braz. Chem. Soc.* 1.
- Naik, V., Fiore, A.M., Horowitz, L.W., Singh, H.B., Wiedinmyer, C., Guenther, A., De Gouw, J.A., Millet, D.B., Goldan, P.D., Kuster, W.C., Goldstein, A., 2010. Observational constraints on the global atmospheric budget of ethanol. *Atmos. Chem. Phys.* 10, 5361–5370. <https://doi.org/10.5194/acp-10-5361-2010>
- Nguyen, H.T.H., Takenaka, N., Bandow, H., Maeda, Y., De Oliva, S.T., Botelho, M.M.F., Tavares, T.M., 2001. Atmospheric alcohols and aldehydes concentrations measured in Osaka, Japan and in Sao Paulo, Brazil. *Atmos. Environ.* 35, 3075–3083. [https://doi.org/10.1016/S1352-2310\(01\)00136-4](https://doi.org/10.1016/S1352-2310(01)00136-4)
- Niven, R.K., 2005. Ethanol in gasoline: environmental impacts and sustainability review article. *Renew. Sustain. Energy Rev.* 9, 535–555. <https://doi.org/10.1016/j.rser.2004.06.003>
- Nogueira, T., Dominutti, P.A., Carvalho, L.R.F., Fornaro, A., Andrade, M.F., 2014. Formaldehyde and acetaldehyde measurements in urban atmosphere impacted by the use of ethanol biofuel: Metropolitan Area of Sao Paulo (MASP), 2012 – 2013. *Fuel* 134, 505–513. <https://doi.org/10.1016/j.fuel.2014.05.091>
- Nogueira, T., Dominutti, P.A., Fornaro, A., Andrade, M. de F., 2017. Seasonal Trends of Formaldehyde and Acetaldehyde in the Megacity of São Paulo. *Atmosphere (Basel)*. 8, 144. <https://doi.org/10.3390/atmos8080144>
- Nogueira, T., Souza, K.F. de, Fornaro, A., Andrade, M. de F., Carvalho, L.R.F. de, 2015. On-road emissions of carbonyls from vehicles powered by biofuel blends in traffic tunnels in the Metropolitan Area of Sao Paulo, Brazil. *Atmos. Environ.* 108, 88–97. <https://doi.org/10.1016/j.atmosenv.2015.02.064>
- Parrish, D.D., 2006. Critical evaluation of US on-road vehicle emission inventories. *Atmos. Environ.* 40, 2288–2300. <https://doi.org/10.1016/j.atmosenv.2005.11.033>
- Pereira, P.A. de P., Santos, E.T.S., Ferreira, T.D.F., Andrade, J.B., 1999. Determination of methanol and ethanol by gas chromatography following air sampling onto florisil cartridges and their concentrations at urban sites in the three

largest cities in Brazil. *Talanta* 49, 245–252. [https://doi.org/10.1016/S0039-9140\(98\)00376-2](https://doi.org/10.1016/S0039-9140(98)00376-2)

- Pinto, J.P., Solci, M.C., 2007. Comparison of Rural and Urban Atmospheric Aldehydes in Londrina, Brazil. *J. Braz. Chem. Soc.* 18, 928–936.
- Poulopoulos, S.G., Samaras, D.P., Philippopoulos, C.J., 2001a. Regulated and unregulated emissions from an internal combustion engine operating on ethanol containing fuels. *Atmos. Environ.* 35, 4399–4406.
- Poulopoulos, S.G., Samaras, D.P., Philippopoulos, C.J., 2001b. Regulated and unregulated emissions from an internal combustion engine operating on ethanol-containing fuels. *Atmos. Environ.* 35, 4399–4406. [https://doi.org/10.1016/s1352-2310\(01\)00248-5](https://doi.org/10.1016/s1352-2310(01)00248-5)
- Salameh, T., Borbon, A., Afif, C., Sauvage, S., Leonardis, T., Gaimoz, C., Locoge, N., 2016a. Composition of gaseous organic carbon during ECOCEM in Beirut, Lebanon: new observational constraints for VOC anthropogenic emission evaluation in the Middle East. *Atmos. Chem. Phys. Discuss.* 1–32. <https://doi.org/10.5194/acp-2016-543>
- Salameh, T., Sauvage, S., Afif, C., Borbon, A., Locoge, N., 2016b. Source apportionment vs. emission inventories of non-methane hydrocarbons (NMHC) in an urban area of the Middle East: local and global perspectives. *Atmos. Chem. Phys.* 16, 3595–3607. <https://doi.org/10.5194/acp-16-3595-2016>
- Salvo, A., Geiger, F.M., 2014. Reduction in local ozone levels in urban São Paulo due to a shift from ethanol to gasoline use. *Nat. Geosci.* 7, 450–458. <https://doi.org/10.1038/ngeo2144>
- Scaramboni, C., 2018. Aspectos do papel do peróxido de hidrogênio como oxidante na atmosfera no contexto das atuais políticas públicas de emissões veiculares. Master's Dissertation. Universidade de Sao Paulo.
- Scaramboni, C., Crispim, C.P., Toledo, J.C., Campos, M.L.A.M., 2018. Investigating hydrogen peroxide in rainwater of a typical midsized city in tropical Brazil using a novel application of a fluorometric method. *Atmos. Environ.* 176, 201–208. <https://doi.org/10.1016/j.atmosenv.2017.12.030>
- Schilling, M., Voigt, G., Tavares, T., Klockow, D., 1999. An enzymatic-fluorimetric method for monitoring of ethanol in ambient air. *Fresenius. J. Anal. Chem.* 364, 100–105. <https://doi.org/10.1007/s002160051307>
- Seinfeld, J.H., Pandis, S.N., 2006. *Atmospheric Chemistry and Physics. From Air Pollution to Climate Change*, Second ed. ed. John Wiley & Sons.
- Simpson, I.J., Aburizaiza, O.S., Siddique, A., Barletta, B., Blake, N.J., Gartner, A., Khwaja, H., Meinardi, S., Zeb, J., Blake, D.R., 2014. Air Quality in Mecca and Surrounding Holy Places in Saudi Arabia During Hajj: Initial Survey. *Environ. Sci. Technol.* 48, 8529–8537. <https://doi.org/10.1021/es5017476>
- Singh, H.B., Salas, L.J., Chatfield, R.B., Czech, E., Fried, A., Walega, J., Evans, M.J., Field, B.D., Jacob, D.J., Blake, D., Heikes, B., Talbot, R., Sachse, G., Crawford, J.H., Avery, M.A., Sandholm, S., Fuelberg, H., 2004. Analysis of the atmospheric distribution, sources, and sinks of oxygenated volatile organic chemicals based on measurements over the Pacific during TRACE-P. *J. Geophys. Res. D Atmos.* 109. <https://doi.org/10.1029/2003JD003883>
- Suarez-Bertoa, R., Clairotte, M., Arlitt, B., Nakatani, S., Hill, L., Winkler, K., Kaarsberg, C., Knauf, T., Zijlmans, R., Boertien, H., Astorga, C., 2017. Intercomparison of ethanol, formaldehyde and acetaldehyde measurements from a

flex-fuel vehicle exhaust during the WLTC. *Fuel* 203, 330–340. <https://doi.org/10.1016/j.fuel.2017.04.131>

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

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

von Schneidemesser, E., Monks, P.S., Plass-Duelmer, C., 2010. Global comparison of VOC and CO observations in urban areas. *Atmos. Environ.* 44, 5053–5064. <https://doi.org/10.1016/j.atmosenv.2010.09.010>

Wang, M., Shao, M., Chen, W., Yuan, B., Lu, S., Zhang, Q., Zeng, L., Wang, Q., 2014. A temporally and spatially resolved validation of emission inventories by measurements of ambient volatile organic compounds in Beijing, China. *Atmos. Chem. Phys.* 14, 5871–5891. <https://doi.org/10.5194/acp-14-5871-2014>

Warneke, C., McKeen, S. A., de Gouw, J. A., Goldan, P.D., Kuster, W.C., Holloway, J.S., Williams, E.J., Lerner, B.M., Parrish, D.D., Trainer, M., Fehsenfeld, F.C., Kato, S., Atlas, E.L., Baker, A., Blake, D.R., 2007. Determination of urban volatile organic compound emission ratios and comparison with an emissions database. *J. Geophys. Res.* 112, D10S47. <https://doi.org/10.1029/2006JD007930>

Table 1. Instrumentation details and data used in this study

Sampling	Instrument	Operating principle /Technique	Species measured	Time resolution	Site	Reference
Online	Perkin Elmer Clarus 500 + Turbo Matrix 650 ATD	GC-FID	NMHCs (55 species)	1 hour	urban background	Dominutti et al., 2016
Online	INNOVA 1421	Photoacoustic infrared detection	Ethanol/ CO/CO ₂	10 min	Traffic / evaporative emissions / urban background	this study
Online	PTR-MS	Proton Transfer Reaction Mass Spectrometry; H ₃ O ⁺ reagent ions	Ethanol + VOCs	1 min	Traffic	Brito et al., 2018
Offline Sorbent tubes	Shimadzu LC-10AD	HPLC -UV + 2,4 – DNPH derivatization	Aldehydes	2 hours	urban background	Nogueira et al., 2014
Offline Sorbent tubes	Shimadzu LC-10AD	HPLC -UV + 2,4 – DNPH derivatization	Aldehydes	2 hours	Road tunnel	Nogueira et al., 2015
Offline Sorbent tubes	Shimadzu LC-10AD	HPLC -UV + 2,4 – DNPH derivatization	Aldehydes	24 hours	Traffic	Nogueira et al., 2017
Offline Canisters	Varian 3800 + Saturn 2000	GC-MS	NMHCs (69 species)	2 hours	Traffic	Alvim, 2013; Alvim et al., 2016, 2011
Offline Canisters	Varian 3800 + Saturn 2000	GC-MS	NMHCs (69 species)	2 hours	urban background	Alvim, 2013; Alvim et al., 2016, 2011
Offline Canisters	Varian 3800 + Varian Saturn 2000 ion trap	GC-MS	NMHCs (69 species)	2 hours	Road tunnel	Alvim, 2013; Martins et al., 2006
Offline tubes and canisters	Perkin Elmer ATD 400 + Varian Star 3400 CX + Varian Saturn 2000 ion trap CA)	GC-MS	Ethanol + NMHCs	1-2 hours	Road tunnel	Colón et al., 2001
Online	Thermo 48i	Infrared Photometry	CO	hourly	traffic/ urban background	(CETESB, 2018)
Online	Thermo 42i	Chemiluminescence	NO _x	1 hour	traffic/ urban background	(CETESB, 2018)

Table 2. Average and standard deviation of VOC emission ratios obtained in Sao Paulo megacity related to acetylene (VOC/C₂H₂) and related to CO (VOC/CO) in summer and winter for 3 years of data.

Compound	Summer	Winter	Summer	Winter
	Mean ± SD	Mean ± SD	Mean ± SD	Mean ± SD
	$\Delta\text{VOC}/\Delta\text{C}_2\text{H}_2$	$\Delta\text{VOC}/\Delta\text{C}_2\text{H}_2$	$\Delta\text{VOC}/\Delta\text{CO}$	$\Delta\text{VOC}/\Delta\text{CO}$
ethane	0.85±0.14	0.77±0.14	6.02±0.14	5.20±2.67
propane	2.11±0.62	1.70±0.32	7.93±0.62	10.0±3.15
n-butane	1.42±0.20	0.91±0.08	6.27±0.20	5.63±1.31
iso-butane	0.68±0.13	0.48±0.09	4.25±0.13	3.38±1.70
n-pentane	0.69±0.16	0.50±0.03	4.10±0.16	3.37±1.19
isopentane	0.89±0.13	0.66±0.01	3.91±0.13	3.89±0.66
cyclopentane	0.08±0.02	0.05±0.01	0.45±0.02	0.40±0.12
2-methylpentane	0.24±0.09	0.12±0.07	1.38±0.09	1.16±1.02
n-hexane	0.08±0.00	0.12±0.04	0.26±0.03	1.13±0.72
methylcyclopentane	0.16±0.10	0.16±0.00	0.86±0.10	2.11±0.07
cyclohexane	0.12±0.02	0.11±0.01	0.94±0.02	0.85±0.25
2-methylhexane	0.09±0.01	0.06±0.01	0.53±0.01	0.66±0.32
2,3-dimethylpentane	0.06±0.00	0.03±0.00	0.40±0.01	0.18±0.02
3-methylhexane	0.08±0.07	0.06±0.03	0.48±0.07	0.63±0.43
2,2,4-trimethylpentane	0.06±0.04	0.07±0.01	0.32±0.04	0.34±0.02
n-heptane	0.12±0.08	0.09±0.06	0.64±0.08	0.88±0.81
methylcyclohexane	0.08±0.07	0.06±0.04	0.47±0.07	0.65±0.63
2-methylheptane	0.02±0.02	0.02±0.00	0.09±0.02	0.21±0.08
3-methylheptane	0.04±0.01	0.03±0.00	0.20±0.01	0.29±0.08
n-octane	0.05±0.03	0.04±0.03	0.30±0.03	0.31±0.20
nonane	0.03±0.02	0.02±0.00	0.14±0.02	0.08±0.06
n-decane	0.02±0.01	0.03±0.00	0.15±0.01	0.17±0.00
n-undecane	0.07±0.04	0.05±0.00	0.29±0.04	0.38±0.06
ethylene	1.42±0.08	1.43±0.25	7.40±0.08	8.94±2.47
propylene	0.53±0.12	0.49±0.13	4.54±0.12	3.22±0.80
1-butene	0.14±0.01	0.11±0.03	0.63±0.01	0.81±0.23
trans-2-butene	0.13±0.04	0.17±0.05	0.85±0.04	1.26±0.40
cis-2-butene	0.14±0.05	0.19±0.03	0.69±0.05	1.31±0.30
trans-2-pentene	0.08±0.07	0.08±0.04	0.65±0.07	0.72±0.53
1-pentene	0.10±0.08	0.09±0.04	0.63±0.08	1.29±1.05
c-2-Pentene	0.04±0.03	0.03±0.01	0.54±0.03	0.33±0.27
trans-2-hexene	0.12±0.05	0.04±0.01	0.42±0.05	0.26±0.04
cis-2-hexene	0.69±0.02	0.43±0.00	7.26±0.10	4.95±0.00
benzene	0.17±0.04	0.13±0.07	0.86±0.04	1.17±1.05
toluene	0.89±0.19	0.80±0.10	5.08±0.19	4.59±2.21
ethylbenzene	0.14±0.01	0.12±0.03	0.83±0.01	0.80±0.40
m+p-xylene	0.32±0.04	0.25±0.06	1.80±0.04	1.62±0.38
o-xylene	0.10±0.01	0.06±0.01	0.53±0.01	0.47±0.22
m-ethyltoluene	0.04±0.03	0.02±0.00	0.25±0.03	0.14±0.08

1,2,4-trimethylbenzene	0.06±0.04	0.04±0.02	0.35±0.04	0.36±0.28
styrene	0.05±0.02	0.05±0.01	0.22±0.02	0.42±0.13
n-propylbenzene	0.01±0.00	0.01±0.00	0.06±0.00	0.11±0.00
p-Ethyltoluene	0.02±0.01	0.03±0.00	0.10±0.01	0.18±0.00
1,3,5-trimethylbenzene	0.02±0.01	0.03±0.01	0.09±0.01	0.24±0.00
o-Ethyltoluene	0.02±0.01	0.02±0.01	0.10±0.01	0.17±0.02
1,2,3-trimethylbenzene	0.03±0.00	0.02±0.01	0.19±0.00	0.21±0.17
p-Diethylbenzene	0.02±0.00	0.03±0.01	0.1±0.00	0.26±0.01
Sum of C8-aromatics	0.58±0.19	0.48±0.16	3.55±0.19	3.19±1.37
Sum of C9-aromatics	0.38±0.17	0.20±0.03	1.55±0.17	1.36±0.32
acetylene				5.54±1.28

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Figure 1. Location and extent of São Paulo Megacity (SPM) and São Paulo Metropolitan area (MASP) in Sao Paulo State and Brazil.

Figure 2. Data availability and sampling times of the various VOCs measurements analysed in this study. Continuous lines represent online measurements, dashed lines represent the off-line continuous measurements and markers represent the data obtained by short term campaigns. More instrumentation details can be found in Table 1.

Figure 3. Mean and standard deviation for the VOCs concentrations observed by long-term measurements in Sao Paulo and compared with those levels in other cities worldwide. Green squares represent the average NMHC concentrations obtained for 4-years of online measurements and the error bars display their standard deviation. Ethanol and aldehydes average values (green squares) are those obtained at the urban background by the campaigns developed in 2013-2014 and 2012-2014, respectively. VOC data from other cities was obtained from previous studies in Los Angeles, Paris, London and Beijing.

Figure 4. Seasonal average VOC relative to CO (above) and acetylene (below) emission ratios, obtained for 2013-2015 measurements. Solid line represents the 1:1 relationship between seasons and dashed lines represent the difference by a factor of 2.

Figure 5. Average emission ratios of VOC/CO derived from urban background (UB) observations and compared with those obtained at (a) an urban traffic (UTr) site and b) an urban road-tunnel (UT) in SPM. Color-coded markers represent VOC families, solid line represents the 1:1 relationship between sampling sites compared and dashed lines represent the difference by a factor of 2

Figure 6. Ethanol measurements and emission ratios obtained in different campaigns in MASP. a) time series of ethanol and CO concentrations observed at urban traffic site (UTr), b) scatterplot of ethanol versus CO measurements performed at UTr site, purple line represents the ER obtained at the UTr site, dark blue line the ER obtained for evaporative emissions at a residential garage and light blue line represents the ER obtained from total emission sources at a residential garage and c) scatterplot of ethanol and CO observations at a residential garage integrating daytime data in light blue (exhaust + evaporative emissions) and night-time data (evaporative emissions) in dark blue.

Figure 7. Aldehydes ERs (a) and fuel sold (b) in SPM between 2012 and 2016. Figure a) represents the ERs of acetaldehyde and formaldehyde versus CO obtained by the LRF on annual basis, b) represents the total fuel sold in m³ of diesel, gasohol (25-27% anhydrous ethanol + 75-73% gasoline), total ethanol (hydrous and anhydrous) and biodiesel consumptions for SPM, and c) shows the correlation between acetaldehyde and formaldehyde versus CO for all the years under analysis, colour-coded by winter and summer measurements.

Figure 8. Comparison of VOC to CO (ppb/ppm) emission ratios derived at São Paulo urban background site (UB) with those reported at Los Angeles (de Gouw et al., 2017), Paris (Borbon et al., 2013); Beijing (Wang et al., 2014), Mecca (Simpson et al., 2014); Beirut (Salameh et al., 2016a) and Mexico (Bon et al., 2011). Markers are colour-coded by VOC chemical group; solid line represents the 1:1 relationship between sampling sites compared and dashed lines represent the difference by a factor of 2.

Figure 9. Comparison of VOC road transport emission profiles for Sao Paulo Megacity (SPM) estimated from the measurements of this study (ER SPM) and the EDGAR v4.3.2 global inventory (Edgar SPM) (Huang et al., 2017). The profile analysis of EDGAR integrates the road transportation based on the sector activity for 2012. (a) Absolute emissions, in Gg yr⁻¹, (b) relative mass weighted by KOH, (c) relative mass contribution calculated for each VOC family.

Declaration of competing interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

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Graphical abstract

Highlights

Homogeneous VOCs distribution to other cities despite higher concentrations by factors of 2 to 10.

No significant seasonality in emission ratios regardless of the species

Ethanol measurements show a strong impact of fuel evaporation processes

Multiyear acetaldehyde ER displayed the impact of a higher biofuel consumption in SPM

Consistency with Edgar inventory up to 75%, however inconsistencies in the speciation profile

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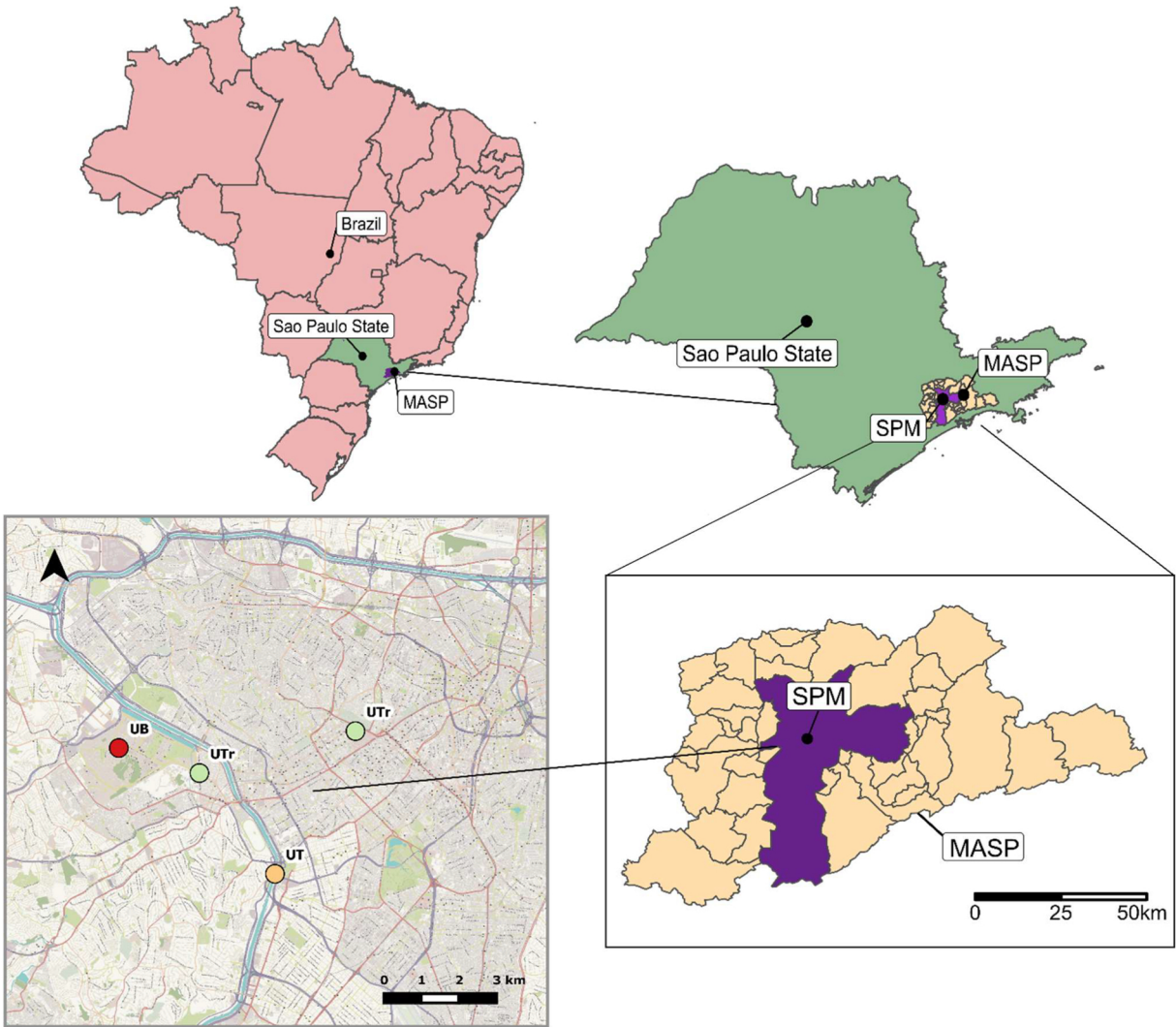


Figure 1

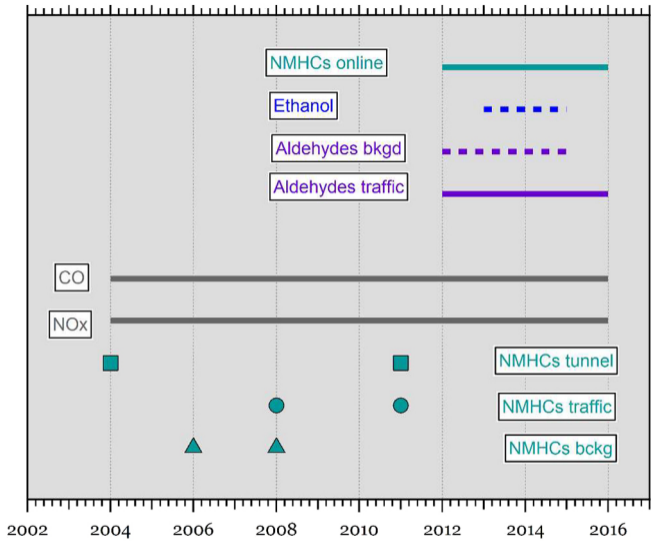


Figure 2

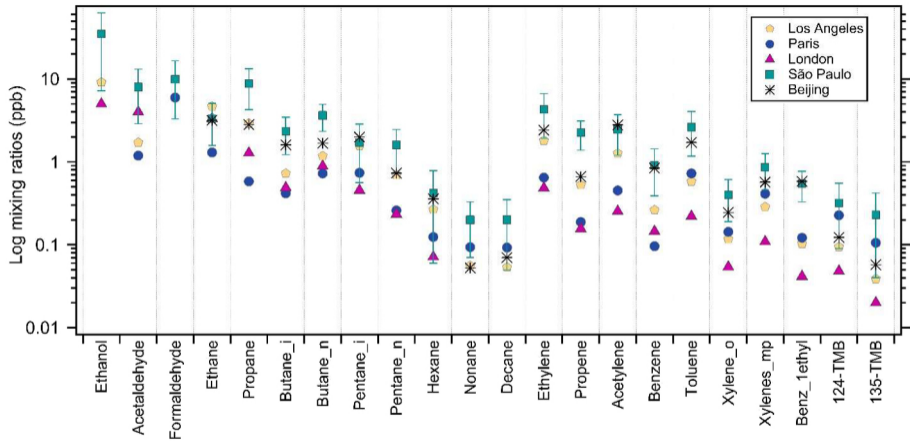


Figure 3

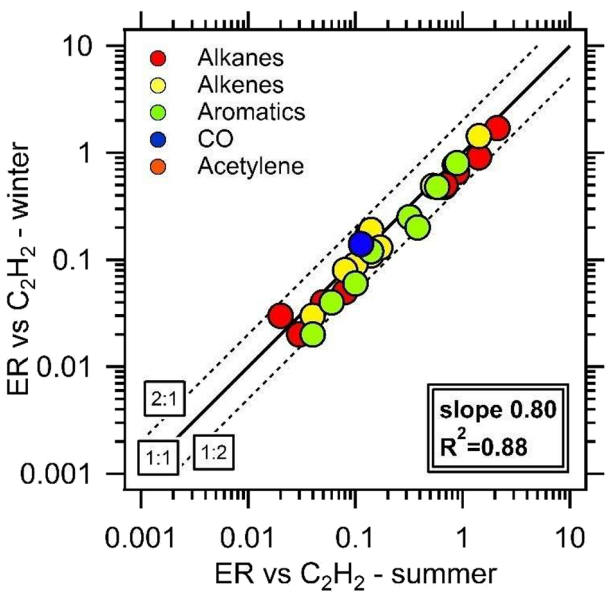
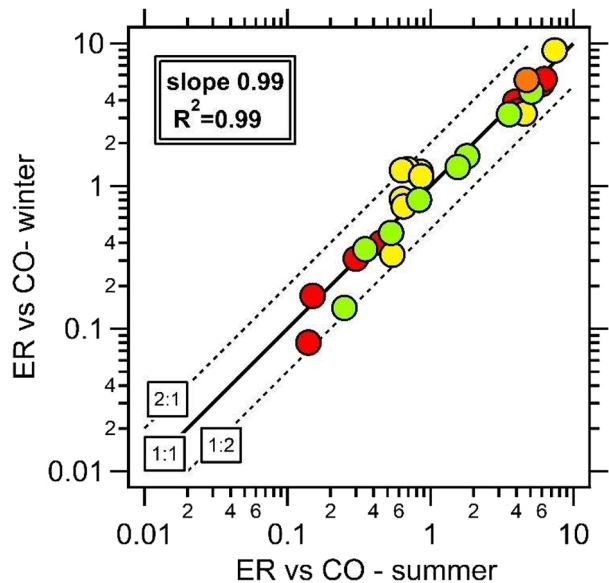


Figure 4

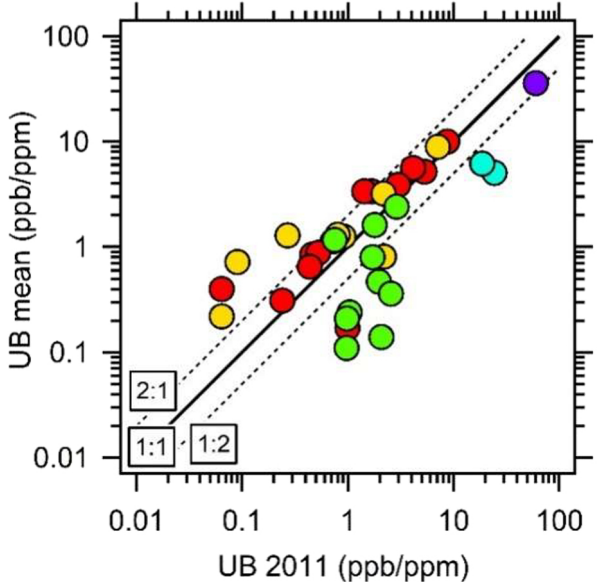
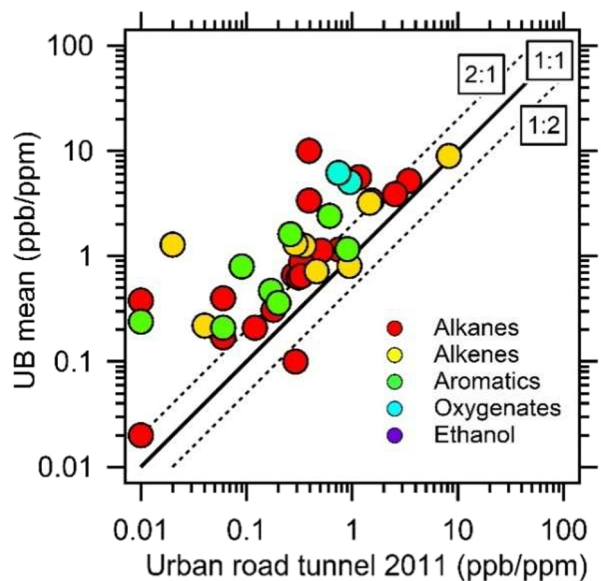
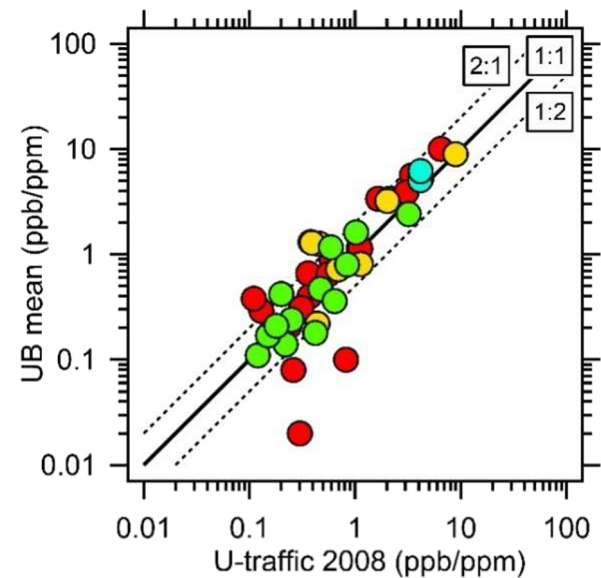


Figure 5

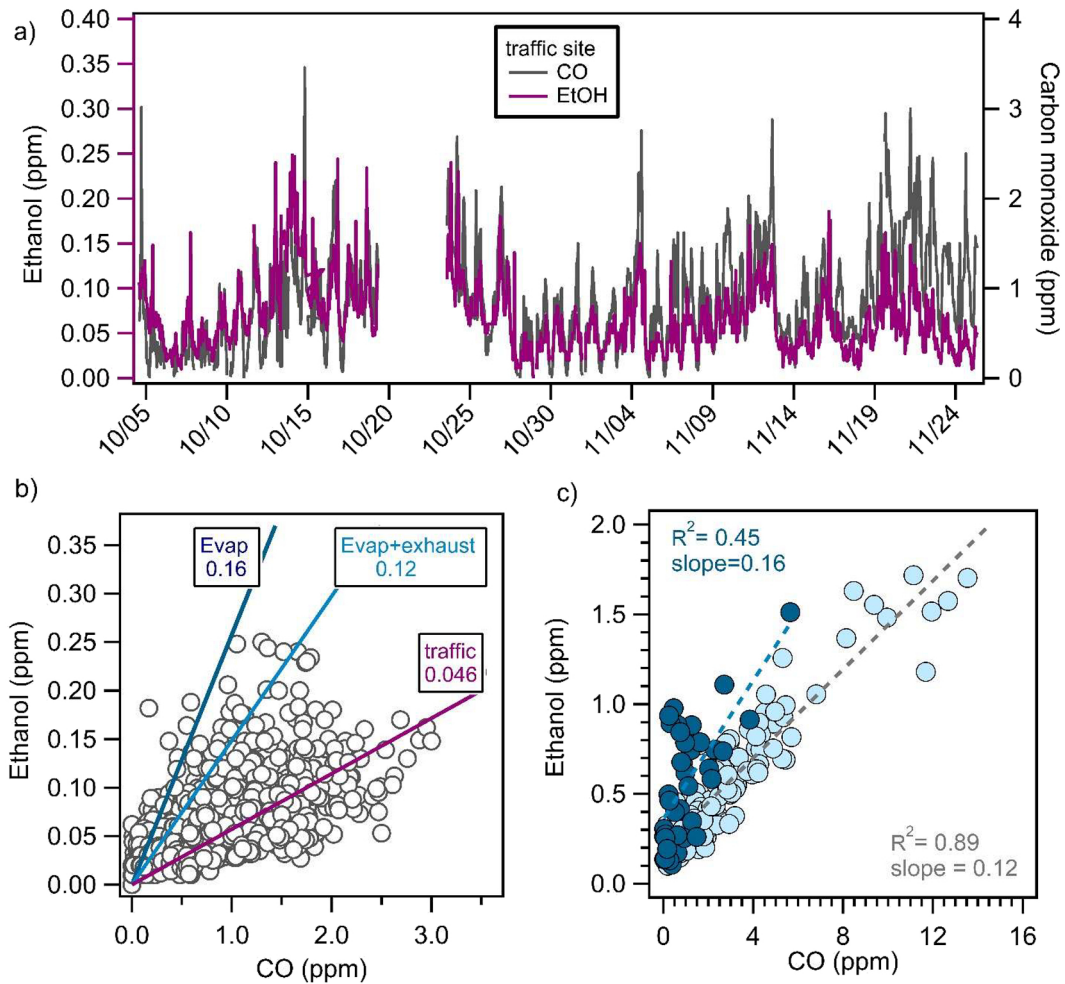


Figure 6

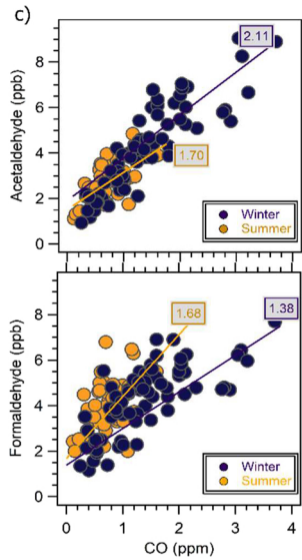
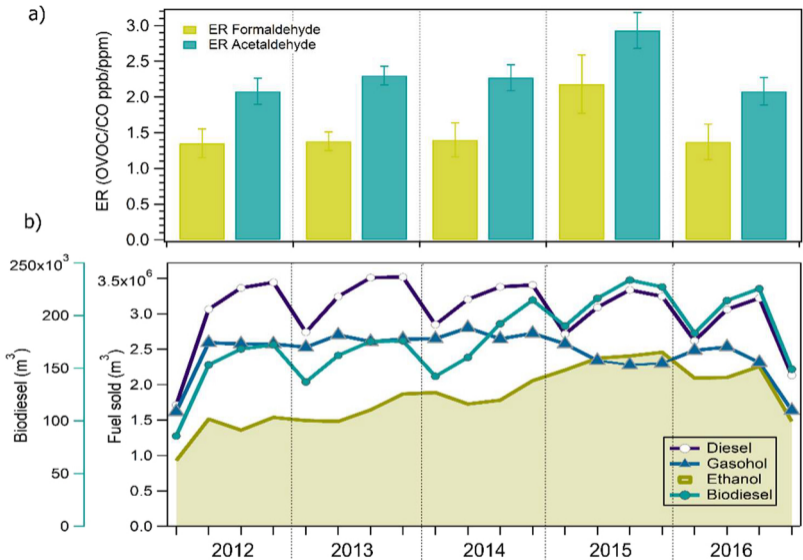


Figure 7

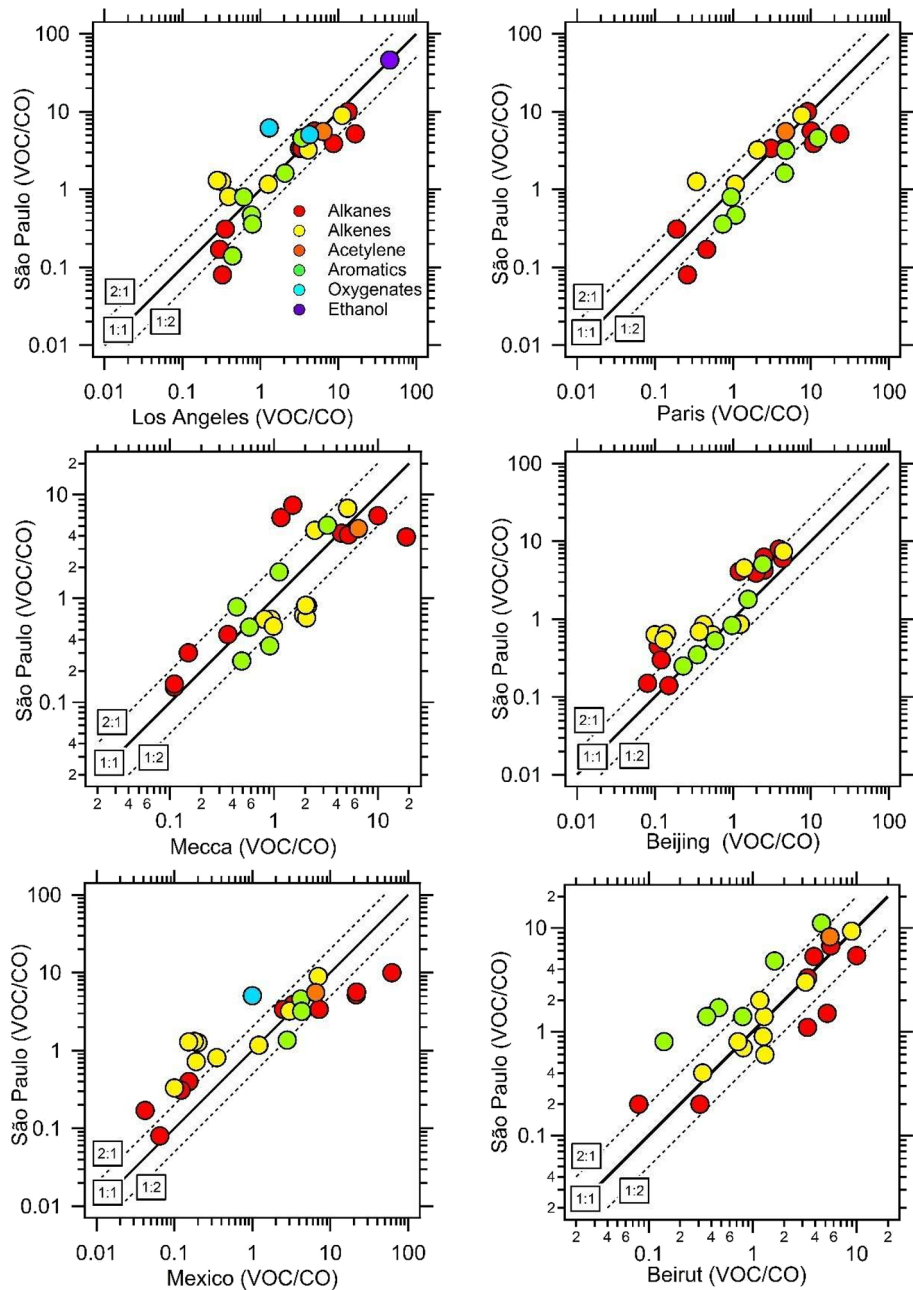


Figure 8

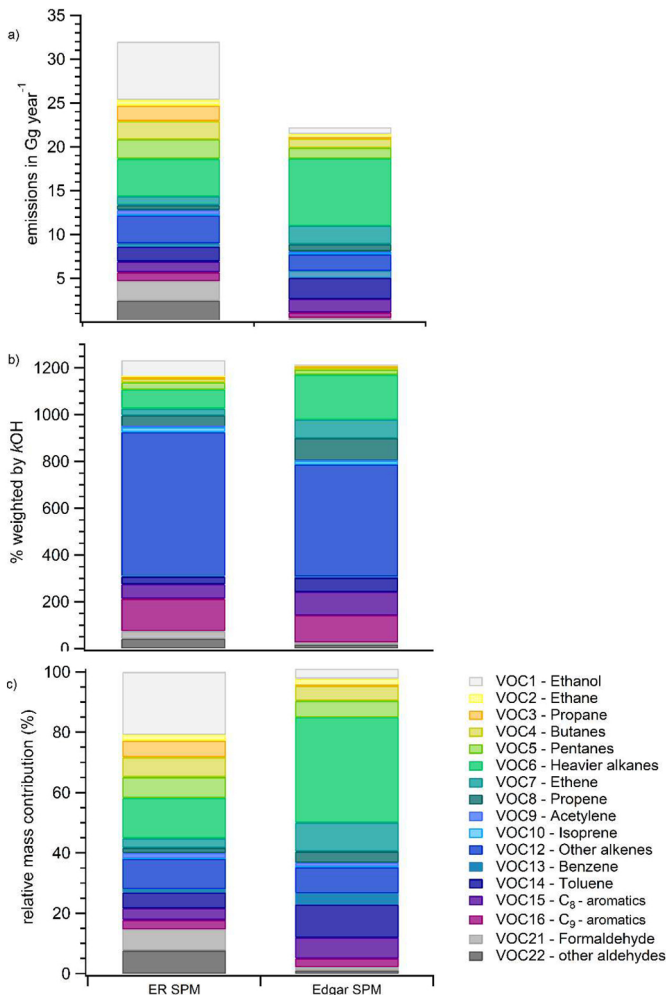


Figure 9