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Concentrations of Volatile Organic Compounds in the Megacity of São Paulo in 2006 and 2011/2012 – A Comparative Study

Concentrações de Compostos Orgânicos Voláteis na Megacidade de São Paulo em 2006 e 2011/2012 – Um Estudo Comparativo

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Abstract

The focus of this study was to measure the Volatile Organic Compounds (VOCs) concentrations in the megacity – São Paulo Metropolitan Area (SPMA). The measurements analyzed in this study included 78 hydrocarbon (HC) samples collected during 2006, and 66 samples of HC, 62 of aldehydes and 42 of ethanol collected during 2011-2012. The observational results showed that the consumption of ethanol, gasoline and diesel from 2006 to 2012 increased by 64 %, 23 % and 25 %, respectively, with substantial changes in the atmospheric composition. The 10 most abundant VOCs in the atmosphere found during 2011/2012 at CETESB IPEN/USP air quality monitoring station were ethanol, acetaldehyde, formaldehyde, acetone, propane, ethene, ethane, butane, 1-ethyl-4-methyl benzene, and 1,2,4-trimethyl benzene. During the 2006 campaign, alkanes represented 54.8 % of the total HC concentration, alkenes 29.2 %, aromatics 13.6 %, and alkadienes 2.4 %. On the other hand, during the 2011-2012 campaign, aldehydes represented 35.3 % of the VOCs, ethanol 22.6 %, aromatics 15.5 %, alkanes 13.5 %, acetone 6.8 %, alkenes 6.0 %, and alkadienes with less than 0.1 %. An increase in VOCs concentrations in the SPMA atmosphere from 2006 to 2012, such as aldehydes and aromatics (which are important ozone precursors) was measured.

Keywords: *ozone; air pollution; volatile organic compounds*

Resumo

O foco deste estudo foi determinar as concentrações de compostos orgânicos voláteis (COV) na megacidade de São Paulo Metropolitana (SPMA). As medidas analisadas neste estudo incluíram 78 amostras de hidrocarbonetos (HC) coletadas em 2006 e 66 amostras de HC, 62 de aldeídos e 42 de etanol coletadas durante 2011-2012. Os resultados observacionais mostram, que o consumo de etanol, gasolina e diesel, aumentou 64 %, 23 % e 25 % respectivamente, entre 2006 e 2012, com mudança considerável na composição atmosférica. Os 10 COV mais abundantes na atmosfera encontrados durante 2011/2012 na estação da CETESB IPEN/USP de monitoramento da qualidade do ar foram etanol, acetaldeído, formaldeído, acetona, propano, eteno, etano, butano, 1-etil-4-metilbenzeno e 1,2,4-trimetilbenzeno. Durante a campanha de 2006, os alcanos representaram 54,8% da concentração total de HC, alcenos 29,2 %, aromáticos 13,6 % e alcadienos 2,4%. Por outro lado, na campanha 2011-2012, os aldeídos representaram 35,3 % dos COV, etanol 22,6%, aromáticos 15,7%, alcanos 13,5 %, acetona 6,8 %, acetona 6,0 %, 6,0 % alcenos e alcadienos com menos de 0,1 %. Foi medido um aumento nas concentrações de COV na atmosfera da SPMA de 2006 a 2012, como aldeídos e aromáticos (que são importantes precursores de ozônio).

Palavras-chave: *ozônio; poluição do ar; compostos orgânicos voláteis*

1 Introduction

São Paulo is among the ten most populated cities in the world. Its Metropolitan Area (SPMA, hereafter) includes more 38 surrounding cities, with more than 20 million people (11 million in the São Paulo city), making it the most populated urban area in the Americas and the fifth most populous in the world, according to United Nations (UN) 2016 data. São Paulo State, City and Metropolitan Area (which bear the same name) are shown in Figure 1.

In cities, Volatile Organic Compounds (VOCs) contribute significantly to the air quality, apparently resulting in the production of secondary pollutants like ozone and secondary organic aerosols (SOA) (Seinfeld & Pandis, 2016), and can lead to harmful effects on human health (Laurent & Hauschild, 2014). Hence, accurate observations of VOCs are essential in assessing their sources and subsequently predicting the formation of its precursors towards improving air quality policies (Alvim, 2013).

Likewise, the speciation of VOC concentrations that was carried out in this study is substantial for the creation of accurate emission inventories, in the metropolitan region of São Paulo and other metropolises in Brazil, VOC speciation is still done in sporadic campaigns at the level of research, differently from what happens in the USA and European countries where these measurements are carried out routinely at air quality monitoring stations *(Coll et al.,* 2010; Wang *et al.,* 2014; Salameh *et al.,* 2016).

Ozone (O_3) is a pollutant of great concern for air quality in the SPMA. In the latest report by the state environmental company (CETESB) for the year 2018, the state air quality standard for ozone (140 μg m^{-3} for 8 hours) was exceeded on 9, 35, 26, 16 and 14 days during 2014, 2015, 2016 and 2017 respectively. In Rio de Janeiro city (also located in southeast Brazil), high ozone events are also frequent and concentrations are higher on weekends than on weekdays (Martins *et al*., 2015; CETESB, 2019).

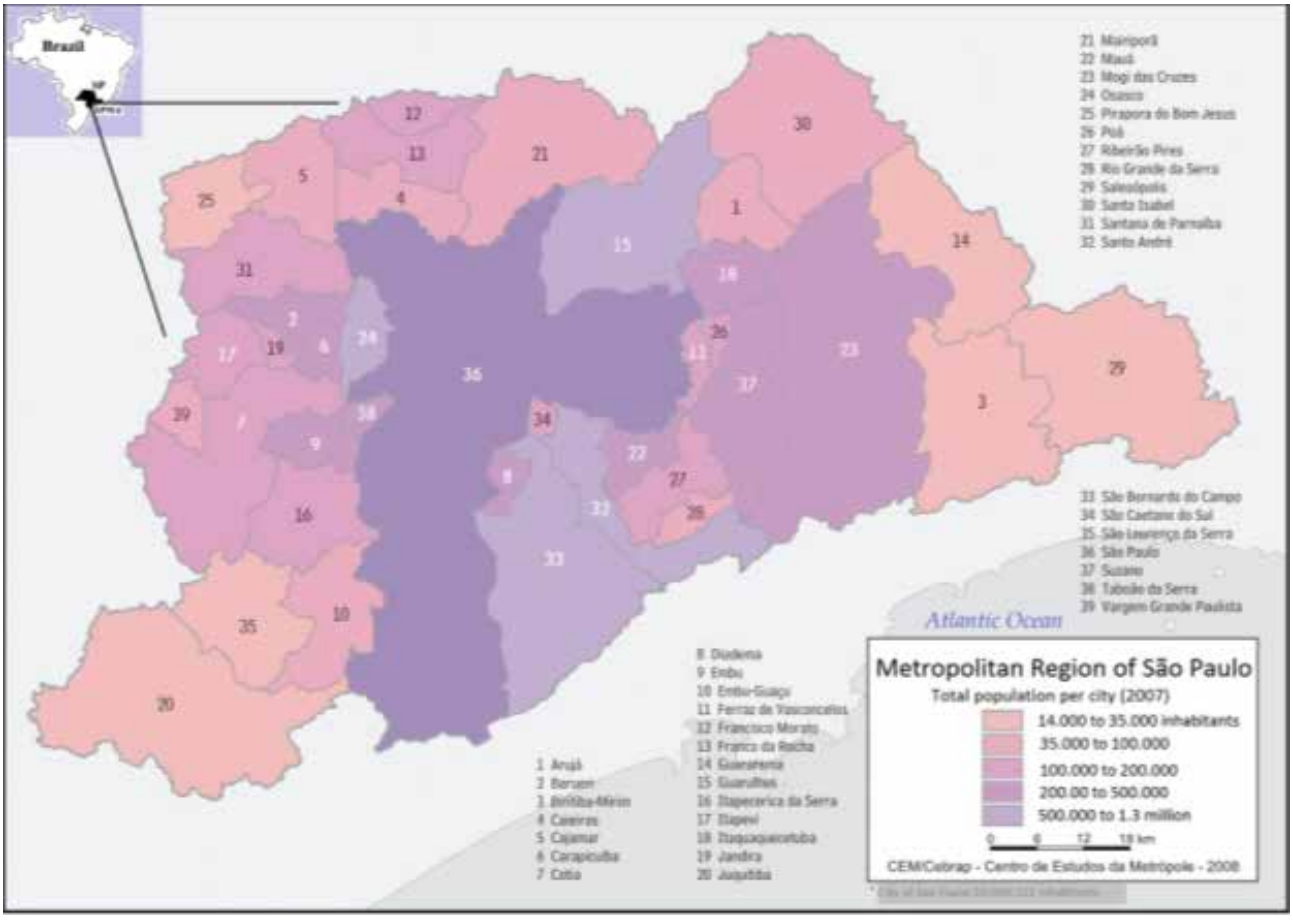

Figure 1 The São Paulo Metropolitan Area (SPMA) is the largest urban agglomeration in South America. It consists of São Paulo city, as urban core and its immediate surroundings.

Significant decreases in emissions by mobile sources have been observed due to control programs such as the Brazilian Control Program of Air Pollution from Motor Vehicles (PROCONVE), started in 1986, and the Control Program of Air Pollution by Motorcycles and Similar Vehicles (PROMOT), since 2000. A challenge in the SPMA, as in many other urban centers, is to control air pollution caused by tropospheric ozone. The Brazilian Control Program of Air Pollution from Motor Vehicles (PROCONVE), the most important public policy implemented in Brazil to control air pollution caused by vehicle emissions and is currently in its 6th phase. Based on the protocols laid by the California Low Emission Vehicle Regulation (California Air Resources Board, 2019), new phases – L7 and L8 (CONAMA, 2018) of PROCONVE is launched that will be able to establish the limit for VOCs by considering their ozone forming potential. There is uncertainty in estimating the ozone forming potential (OFP) based on the typical composition of Brazilian gasoline.

Although this scenario, limited environmental measurements of ethanol have been carried out in recent years and the sources, load and destination of this compound in the atmosphere remain unexplored (Naik *et al.,* 2010; Kirstine & Galbally, 2012). Few short-term ethanol measurements have been made at the SPMA over the past two decades, which have applied a wider range of measurement techniques at different locations sampling methods (traffic, road tunnels, urban and environment). The concentrations of ambient ethanol observed in the SPMA were quite different, reaching between 18 and 460 ppb (Schilling *et al.,* 1999; Colón *et al.,* 2001; Nguyen, 2001; Scaramboni, 2018; Brito *et al.,* 2018). Therefore, in view of the high uncertainties surrounding global and regional emissions estimates, specifically for VOCs, there is an urgent need to measure your concentrations as realized in this study to perform more accurate emissions calculations. In this study, which will be shown below, 42 ethanol samplings were carried out for one year in the city of São Paulo, from September 2011 to August 2012, between 7 am and 9 am on weekdays. Nevertheless, air quality in the region remains unhealthy and is likely to continue being an environmental concern for many years, as reported by a 30-years study conducted by Andrade *et al.* (2017). The main cause of air pollution problems has been the prioritization of private transport in the urbanization process of the SPMA, currently with more than 7.4 million vehicles.

The vehicle fleet in SPMA has increased dramatically since the 1950s, from 20 persons per vehicle in the 1950s to 3 persons per vehicle in 2018 (CETESB, 2019). In the SPMA, 86 % of daily commuter travel is done via cars or buses and only 14 % via subway and trains. In contrast, in other megacities, such as New York and Tokyo, 72 % and 61 % of trips are made by subway, respectively. The subway system in São Paulo is only 101 km long, much shorter than those of other megacities, such as Beijing (442 km), Shanghai (420 km), New York (418 km), Tokyo (292 km), Seoul (286 km), and even to other metropolitan areas with fewer than 10 million inhabitants, such as London (408 km), Madrid (293 km) and Paris (212 km). An efficient public transportation system, integrated with all its modes, constitutes a key strategy to reduce vehicular traffic and pollutant emissions.

The type of fuel, traffic speed, vehicle age and condition, among other factors, directly influence vehicle emissions. Brazil played a pioneering role in the development of ethanol fuel, cleaner than gasoline and diesel, in terms of NOx, CO, SOx, HC, and particulate matter (PM) emissions, and also is a renewable fuel. Today, gasoline in Brazil is mixed with 27% anhydrous ethanol, and the sulfur content in fuels is below 50 ppm. Despite technological improvements in engines and fuel quality, there are still events of poor air quality, especially for ozone (Colón *et al.*, 2001; CETESB, 2019).

This solution, implemented on a large scale in Brazil during the 1970s, in order to reduce dependence on fossil fuels. Nowadays, many countries are adopting mandatory mixtures of biofuels with gasoline and diesel, expanding the prospects for the consolidation of a global market for renewable fuels. By the end of 2014, the number of countries using mandates for biofuel blending reached 64. Ethanol is the most widely used biofuel in the world. The study reported by Dunmore *et al.* (2016) indicates that ethanol is the main VOC in London, with a mean mixing ratio of 5 ppb, reaching maximum values of 30 ppb. The adoption of ethanol as fuel goes from the concern with the reduction of greenhouse gases emissions to the energy security of countries. The effects of ethanol use are detailed in a study performed by Brito *et al.* (2015). Global ethanol fuel consumption has notably increased in the last decade, with the economies of the United States of America (USA), European Union (EU) and Brazil contributing substantially to its production and consumption (de Gouw *et al.*, 2012). In the USA and Brazil, policies that determine biofuel mix for fossil fuels are leading to a current 10 % yearly increase in ethanol use. Over 1/3 of the world's economies, including the Americas, EU member states, and several Asian nations, have pledged to make ethanol a prime component in their transportation fuels over the next decade (Anderson, 2009; BAA, 2015).

Surveys campaigns using spatial and temporal observations of traffic levels, meteorological data, pollutant concentrations and a consumer demand model have shown that tropospheric ozone concentrations decreased 20 % when the number of flex-fuel vehicles using gasoline increased from 14 to 76 %. In contrast, nitrogen monoxide

(NO) and carbon monoxide (CO) concentrations increased (Salvo & Geiger, 2014). Even though gasoline consumption appears to decrease the ozone levels in the SPMA when compared with ethanol use, strategies to reduce ozone levels require knowledge of the local physical and chemical transformations, and mainly the VOCs speciation.

In the SPMA, mobile and stationary sources emit approximately 129 kt of CO, 38 kt of VOCs, 72 kt of NOx, 5 kt of PM and 7 kt of SOx, annually, to the atmosphere. Mobile sources are responsible for 97 % of CO, 75 % of VOCs, 64 % of NOx, 17 % of SOx and 40 % of PM (CETESB, 2019).

The focus of this study was to determine Volatile Organic Compounds (VOCs) concentrations in the São Paulo Megacity and compare the changes in the concentrations in the year 2006 with the year 2011/ 2012. VOCs were measured during the 2006 and 2011-2012 campaigns, in which criteria pollutants and meteorological parameters were also measured. These previous studies were detailed in Alvim *et al.* (2014, 2017, 2018) e Orlando *et al.* (2010), as well as a comparison with other recent studies for the city of São Paulo (Dominutti *et al.,* 2020; Andrade *et al.,* 2017; Dominutti *et al.,* 2016; Nogueira *et al.,* 2014; Pérez-Martínez *et al.,* 2014; Salvo & Geiger, 2014).

2 Methodology and Data

2.1 Sampling Site

Seventy-eight hydrocarbons (HC) samples were collected at the CETESB IPEN/USP automatic monitoring station (AMS), 800 m above sea level, located in the western part of the SPMA. The samples were collected from January to December 2006. Sixty-six HC samples, 62 of aldehydes and 42 of ethanol were collected from September 2011 to August 2012. All samples for both sampling campaigns were collected on weekdays between 7:00 and 9:00 am, when the traffic was heavy and the solar radiation was low. Samplings of aldehydes, HC and ethanol were carried out on the same inlet air of the CETESB AMS. CO, O_3 and NOx were measured using automated analyzers from Thermo Environmental Instruments Inc., models 48C, 49C, 42C, respectively (CETESB, 2013, 2019).

All sample preparation and treatment and chemical analyses were performed at IPEN-LQA (Nuclear and Energetic Research Institute – Atmospheric Chemistry Laboratory). Hydrocarbons were analyzed at performed at IPEN-LQA (Nuclear and Energetic Research Institute – Atmospheric Chemistry Laboratory). Carbonyls and ethanol were analyzed at Faculty of Technology of Rio de Janeiro State University.

2.2 VOCs

2.2.1 HC Determination

The HC sampling and chemical analysis were based on methodologies TO-14A and TO-15 (U.S. EPA, 1999a, 1999b). Samples were collected using 6 L stainless steel electropolished canisters, previously cleaned using Xontech system (Model 960), e.g. heating (120 °C), high vacuum (< 10 mTorr), Helium 5.0 as a cleaning gas and water vapor. Each sample was collected at 50 mL min^{-1} for 2 h. Blank canisters were also analyzed before and after each campaign.

A Varian 3800 gas chromatograph (GC), with simultaneous detection by mass spectrometry (MS) (Saturn 2000) and flame ionization detection (FID), was used for the chemical analyses. MS was used for the HC identification, and FID was used for quantification. This GC-MS-FID system was used for determining HCs greater than 4-carbon atoms. 200 mL samples were analyzed directly in the gas phase, using the Sample Pre Concentration (SPT) technique at −180 °C in a 1/8″ tube filled with a silanized glass bead. A DB-1 capillary column (60 m, 1.0 μm and 0.32 mm) was used, and a temperature program started at −50 °C and increased up to 200 °C at 6 °C min^{-1}. At the end of the chromatographic column, the gas sample was split in half using a low-dead volume Valco T-connector. One aliquot was carried into the MS, while the other half was quantified in the FID. An evacuated fused silica tube of 0.1 mm (ID) and 50 cm was used for MS and 0.32 mm (ID) and 25 cm for FID. The dimensions of these tubes were adjusted to compensate for the high vacuum conditions required by the MS and atmospheric pressure in the FID.

For the identification and quantification of the light HCs (2 and 3 carbon atoms), another Varian 3800 GC-FID system was used, with a fused silica PLOT column of Al_2O_3/Na_2SO_4 (50 m, 0.53 mm and 10 μm). The SPT was also used, except for a slightly different temperature range (−50 to 180 °C at 10°C min^{-1}). External calibration was performed using a 10 ppbv standard gas mixture with 30 ozone precursors from the National Physical Laboratory (NPL). This standard gas contains alkanes, alkenes, alkynes, alkadienes and aromatic compounds balanced in nitrogen. Analytical curves were constructed by injecting the different standard volumes measured by a mass flow controller (Sierra Instrument 902C). Samples and standards were analyzed in triplicates, following standard protocols (INMETRO, 2003; U.S. EPA, 1999c).

2.2.2 Carbonyl Determination

Carbonyl determinations followed the TO-11A methodology.(U.S. EPA, 1999c). Samples were collected

using a KNF N815 KNDC air pump and a 150 mg SiO_2-C_{18} cartridge impregnated with an acid solution of 2,4-dinitrophenylhydrazine (2,4-DNPH) at 1.0 L min^{-1} for 2 h at 1.5 m. During sampling carbonyls react with hydrazine forming hydrazine derivatives.

The hydrazones were extracted with 5 mL of acetonitrile (HPLC grade) and analyzed by HPLC using a Perkin Elmer series 200 equipment with a C18 column (40 cm x 4.6 mm x 5.0 µm), mobile phase water and acetonitrile (1:1) at 2 mL min^{-1} for 20 min at 30 °C and detection at 365 nm.

The quantification was performed using a standard mixture (Supelco CARB Carbonyl-DNPH Mix 1), which contained: formaldehyde, acetaldehyde, acrolein, acetone, propionaldehyde, butyraldehyde and benzaldehyde. Calibration was carried out in a range from 0.05 to 2.5 mg L^{-1} with a determination coefficient (R^2) better than 0.99. This methodology is explained in detail in recent publications of the group (Corrêa *et al.*, 2010; Silva *et al.*, 2016; Alvim *et al.*, 2017).

2.2.3 Ethanol Determination

Ethanol samples were collected using a KNF N815 KNDC air pump with a 400 mg Florisil cartridge at 1.0 L min^{-1} for 2 h, simultaneous with the sampling of carbonyls and HCs. Cartridge beds were placed with 5 mL of milliQ water in 10 mL Headspace vials and in an ultrasound bath for 10 min.

Chemical analyses were performed via gas chromatography (Varian GC 450 MS 220) with a CombiPAL autosampler. A Varian VF-5MS column (30 m x 0.25 mm x 0.25 µm) was used starting at 40 ºC for 3 min, heated at 10 ºC min^{-1} up to 120 ºC, with Helium 5.0 as carrier gas at 1.0 mL min^{-1}. The injector was operated at 120ºC in split mode at 1:20. The MS detector was operated with a transfer line at 150 ºC, manifold at 50 ºC and ion trap at 150 ºC.

The headspace used syringe at 80 °C, shaker at 70 °C, 2 min incubation, 500 rpm, stirrer on for 2 s and off for 4 s, syringe filling rate of 100 µL s^{-1} and injection speed of 500 µL s^{-1} and syringe cleaning time of 90 s with Nitrogen 5.0.

Analytical curves used absolute ethanol from Merck between 0.14 to 2.80 mg L^{-1}, dissolved in milliQ water.

3 Results

3.1 Results for the 2006 and 2011/2012 campaigns

Table 1 shows the mean concentrations of 74 VOCs (n = 78) separated by season from the 2006 campaign. The average standard deviations between the triplicates used in the chemical analyses are within the TO-14A and TO-15 requirements.

Compound	Summer	Autumn	Winter	Spring
Ethane	4.89±0.13	5.2±0.14	10.75±0.29	4.17±0.11
Propane	3.56±0.05	3.92±0.05	9.14±0.12	3.40±0.04
Butane	3.72±0.01	3.41±0.01	6.37±0.03	2.93±0.01
Ethane	3.09±0.16	2.92±0.15	6.37±0.34	2.78±0.15
Isobutene	4.88±0.03	4.67±0.03	2.99±0.02	1.48±0.01
2-methyl butane	3.48±0.05	3.1±0.05	5.58±0.08	1.29±0.02
1-butene	2.7±0.06	2.28±0.05	5.25±0.13	3.43±0.08
Propene	2.94±0.02	2.26±0.01	5.88±0.04	1.46±0.01
Toluene	2.62±0.11	2.35±0.1	4.84±0.2	2.27±0.09
Hexane	2.78±0.08	4.72±0.14	1.37±0.04	1.96±0.06
Pentane	2.29±0.05	1.65±0.03	2.57±0.05	1.52±0.03
1.3-butadiene	-	-	1.02±0.02	2.17±0.05
2-methyl pentane	1.48±0.04	1.17±0.03	1.95±0.05	1.03±0.03
3-methylpentane	1.36±0.04	1.29±0.04	1.36±0.04	1.22±0.03
methyl cyclopentane	0.62±0.02	1.57±0.05	0.89±0.03	1.55±0.05
p-xylene	0.68±0.06	0.82±0.07	1.84±0.17	0.98±0.09

Table 1 Average concentration (ppbv) of 74 VOCs for each season, for the samples collected at CETESB IPEN/USP AMS during 2006 and analyzed in triplicate.

Compound	Summer	Autumn	Winter	Spring
2-methyl-2-butene	0.83±0.02	0.82±0.02	1.18±0.03	0.86±0.02
ethylbenzene	0.61±0.02	0.64±0.02	1.4±0.04	1.01±0.03
1.1-dimethyl cyclopropane	0.76±0.02	0.78±0.02	1.33±0.03	0.72±0.02
trans-2-butene	0.79±0.02	0.73±0.02	1.52±0.04	0.55±0.01
Benzene	0.68±0.02	0.63±0.02	1.2±0.03	0.9±0.03
1-ethyl-4-methyl benzene	-	-	0.86±0.03	0.71±0.03
cis-2-butene	0.72±0.02	0.61±0.02	1.33±0.03	0.48±0.01
trans-2-pentene	0.59±0.02	0.69±0.02	1.12±0.03	0.66±0.02
1-pentene	1.13±0.03	0.66±0.02	0.76±0.02	0.43±0.01
Isoprene	0.84±0.02	0.54±0.01	0.64±0.02	0.64±0.02
cyclohexane	0.48±0.02	0.64±0.02	0.88±0.03	0.57±0.02
Heptane	0.62±0.02	0.47±0.02	0.90±0.03	0.48±0.02
1,3,5-trimethyl benzene	-	-	0.57±0.02	0.58±0.02
o-xylene	0.33±0.01	0.36±0.01	0.83±0.02	0.52±0.01
1-methyl cyclopentene	0.42±0.01	0.39±0.01	0.71±0.02	0.42±0.01
methyl cyclohexane	0.41±0.02	0.39±0.02	0.71±0.03	0.36±0.01
1-hexene	0.51±0.01	0.42±0.01	0.5±0.01	0.42±0.01
cis-2-pentene	0.38±0.01	0.34±0.01	0.69±0.02	0.45±0.01
2,3-dimethyl butane	0.48±0.01	0.43±0.01	0.49±0.01	0.42±0.01
Cyclopentene	0.38±0.01	0.45±0.01	0.6±0.01	0.34±0.01
2-methyl-1-pentene	0.42±0.01	0.4±0.01	0.43±0.01	0.52±0.01
m-xylene	0.28±0.01	0.34±0.02	0.69±0.03	0.42±0.02
2-hexene	0.42±0.01	0.39±0.01	0.5±0.01	0.4±0.01
3-methyl hexane	0.3±0.01	0.33±0.01	0.63±0.02	0.36±0.01
1,2,3-trimethyl benzene	0.47±0.03	0.20±0.01	0.44±0.03	0.48±0.03
Naphthalene	-	-	0.28±0.01	0.47±0.02
Cyclopentane	0.34±0.01	0.31±0.01	0.54±0.01	0.36±0.01
2-methyl hexane	0.35±0.01	0.15±0.01	0.53±0.01	0.29±0.01
1-ethyl-3-methyl benzene	0.19±0.01	0.17±0.01	0.42±0.01	0.37±0.01
1-ethyl-2-methyl benzene	-	-	0.30±0.01	0.27±0.01
Octane	0.26±0.01	0.23±0.01	0.39±0.01	0.21±0.01
Nonane	0.21±0.01	0.19±0.01	0.37±0.01	0.34±0.01
Decane	0.14±0.01	0.13±0.01	0.32±0.01	0.43±0.01
Undecane	0.11±0.01	0.09±0.01	0.23±0.01	0.50±0.01
Propyl benzene	-	-	0.23±0.01	0.22±0.01
Isopropyl benzene	0.26±0.02	0.34±0.02	0.11±0.01	0.09±0.01
Styrene	0.08±0.01	0.14±0.01	0.38±0.01	0.10±0.01
cis-1,2-dimethyl cyclopentane	0.14±0.01	0.10±0.01	0.24±0.01	0.16±0.01
1,3-dimethyl cyclopentane	0.16±0.01	0.14±0.01	0.21±0.01	0.09±0.01
trans-1,2-dimethyl cyclopentane	0.15±0.01	0.14±0.01	0.18±0.01	0.07±0.01
Ethyl cyclopentane	0.09±0.01	0.10±0.01	0.20±0.01	0.10±0.01
2,3-dimethyl pentane	0.10±0.01	0.10±0.01	0.18±0.01	0.09±0.01

Table 1 Cont.

Compound	Summer	Autumn	Winter	Spring
Ethyl cyclohexane	0.07±0.01	0.08±0.01	0.19±0.01	0.13±0.01
Dodecane	0.04±0.01	0.03±0.01	0.09±0.01	0.33±0.02
2-methyl heptane	0.05±0.01	0.05±0.01	0.24±0.01	0.11±0.01
trans-1,3-dimethyl cyclohexane	0.08±0.01	0.09±0.01	0.20±0.01	0.07±0.01
Limonene	0.09±0.01	0.06±0.01	0.19±0.01	0.11±0.01
1,1,3-trimethylcyclohexane	0.09±0.01	0.07±0.01	0.15±0.01	0.12±0.01
Indane	0.05±0.01	0.07±0.01	0.18±0.01	0.10±0.01
3-methyl heptane	0.05±0.01	0.05±0.01	0.17±0.01	0.06±0.01
2,4-dimethylpentane	0.06±0.01	0.06±0.01	0.08±0.01	0.08±0.01
2,2,4-trimethylpentane	0.05±0.01	0.05±0.01	0.10±0.01	0.06±0.01
1,2-dimethylcyclohexane	0.06±0.01	0.06±0.01	0.09±0.01	0.05±0.01
1,2,4-trimethylpentane	0.05±0.01	0.05±0.01	0.09±0.01	0.05±0.01
cis-1,3-dimethylcyclohexane	0.09±0.01	0.05±0.01	0.05±0.01	0.05±0.01
1,1,3-trimethylcyclopentane	0.07±0.01	0.06±0.01	0.05±0.01	0.05±0.01
1,3,5-trimethylcyclohexane	0.06±0.01	0.04±0.01	0.04±0.01	0.04±0.01
Total HC	**58.2**	**56.9**	**96.3**	**52.9**

Table 1 Cont.

Table 2 shows the mean concentrations of 54 VOCs (n = 66) in each season during September 2011 to August 2012. The average deviations between the triplicates used in the chemical analyses are within the TO-11A, TO-14A and TO-15 requirements.

Table 3 presents a comparison between the concentrations of the fifteen most abundant VOCs found in the Jânio Quadros Tunnel on March 23, 24 and 25, 2004 between 8:00 a.m. and 6:00 p.m. and the VOCs measured at CETESB IPEN/USP AMS, during 2006.

Table 3 shows the VOCs with high concentrations in both campaigns, e.g. during 2006 at IPEN/USP AMS and in the samples collected inside/outside the Jânio Quadros Tunnel in 2004, are typically derived from vehicular emissions. They were: m+p-xylenes, pentane, toluene, butane, benzene, 1-butene, isobutane and pentane. These compounds are representative not only of automobile exhaust but also gasoline volatilization (Na & Kim, 2001; Corrêa *et al.*, 2012). Results for criteria pollutants at the same place can be found in a campaign conducted by Pérez-Martínez *et al.* (2014).

Isoprene concentrations were 26 % higher on average during the summer season in 2006. In the campaign carried out in May 2011 in the Jânio Quadros Tunnel, no isoprene was found (Table 4). The higher isoprene concentrations during the summer were probably related to higher biogenic emissions during the summer. During this season, the biogenic VOC emissions are generally strongest and photochemical reactions are most active. Recent inventories highlight the importance of biogenic sources of VOCs emissions in urbanized regions, especially in the pan-tropical region where biological activity is more intense (Jacob, 1999; Hewitt, 1999; Wang *et al.*, 2007).

Compound	Spring	Summer	Autumn	Winter
Ethanol	30.67±0.15	44.61±0.22	22.42±0.11	47.43±0.23
Acetaldehyde	35.6±0.20	27.58±0.13	23.38±0.11	23.44±0.11
Formaldehyde	26.3±0.15	19.84±0.09	17.68±0.08	17.23±0.08
Acetone	7.74±0.03	11.76±0.05	11.68±0.05	12.35±0.06
Propane	4.82±0.06	4.87±0.06	5.69±0.07	6.86±0.08
Ethane	4.88±0.13	4.18±0.11	4.76±0.12	5.56±0.15
Ethane	4.43±0.23	1.72±0.09	1.63±0.08	4.15±0.21
Butane	2.55±0.01	2.91±0.01	3.06±0.01	3.24±0.01
1-ethyl-4-methylbenzene	3.15±0.11	3.09±0.11	2.62±0.09	2.56±0.09
1,2,4-trimethylbenzene	2.40±0.14	2.41±0.14	2.44±0.15	2.49±0.15
Propionaldehyde	1.71±0.01	2.54±0.01	2.43±0.01	2.89±0.01
1,3,5-trimethylbenzene	2.31±0.09	2.31±0.09	2.40±0.09	2.32±0.09
1-ethyl-3-methylbenzene	2.34±0.09	2.35±0.09	2.30±0.09	2.32±0.09
1,2,3-trimethylbenzene	2.29±0.14	2.27±0.14	2.27±0.14	2.34±0.14
1-ethyl-2-methylbenzene	2.29±0.01	2.28±0.01	2.28±0.01	2.30±0.01
Propyl benzene	2.28±0.08	2.19±0.08	2.19±0.08	2.26±0.08
Butyraldehyde	1.68±0.01	2.23±0.01	2.05±0.01	2.06±0.01
Toluene	2.26±0.09	1.78±0.07	1.51±0.06	2.35±0.09
Isopentane	1.46±0.02	1.65±0.02	1.68±0.02	2.34±0.03
p-xylene	1.61±0.14	1.60±0.14	1.60±0.14	1.74±0.15
1-butene	1.67±0.04	1.45±0.03	1.48±0.03	1.71±0.04
o-xylene	1.62±0.04	1.48±0.03	1.50±0.03	1.54±0.03
m-xylene	1.46±0.06	1.44±0.06	1.48±0.06	1.57±0.07
Propene	1.16±0.01	1.55±0.01	1.34±0.01	1.70±0.01
Ethylbenzene	1.45±0.03	1.27±0.03	1.35±0.03	1.50±0.04
Isobutane	1.21±0.01	1.18±0.01	1.02±0.01	1.32±0.01
Acrolein	0.53±0.01	1.06±0.01	1.16±0.01	1.47±0.01
Pentane	0.73±0.01	0.97±0.02	0.83±0.01	1.12±0.02
2-methyl heptane	0.79±0.03	1.00±0.04	0.79±0.03	0.82±0.03
Octane	0.85±0.05	0.86±0.05	0.81±0.04	0.84±0.04
Decane	0.81±0.04	0.81±0.04	0.80±0.04	0.84±0.04
Undecane	0.87±0.10	0.73±0.08	0.70±0.08	0.78±0.09
Benzaldehyde	0.56±0.01	0.60±0.01	0.60±0.01	1.29±0.01
trans-2-butene	0.47±0.01	0.60±0.01	0.69±0.01	0.71±0.01
cis-2-butene	0.44±0.01	0.52±0.01	0.45±0.01	0.63±0.01
Benzene	0.45±0.01	0.46±0.01	0.31±0.01	0.59±0.01
Hexane	0.35±0.01	0.52±0.01	0.30±0.01	0.56±0.01
3-hexene	0.34±0.01	0.30±0.01	0.32±0.01	0.49±0.01

Table 2 Average concentration (ppbv) of 54 VOCs for each season, for samples collected from September 2011 to August 2012 at CETESB IPEN/USP AMS and analyzed in triplicate.

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Compound	Spring	Summer	Autumn	Winter
Heptane	0.32±0.01	0.33±0.01	0.34±0.01	0.41±0.01
2-methylpentane	0.27±0.01	0.32±0.01	0.25±0.01	0.41±0.01
Methylcyclohexane	0.28±0.01	0.33±0.01	0.30±0.01	0.34±0.01
2-methyl hexane	0.27±0.01	0.28±0.01	0.25±0.01	0.34±0.01
Cyclohexane	0.36±0.01	0.17±0.01	0.23±0.01	0.36±0.01
3-methyl hexane	0.26±0.01	0.27±0.01	0.25±0.01	0.35±0.01
cis-1,3-dimethylcyclopentane	0.20±0.01	0.24±0.01	0.18±0.01	0.21±0.01
2,3-dimethylpentane	0.21±0.01	0.20±0.01	0.17±0.01	0.23±0.01
Pentene	0.08±0.01	0.16±0.01	0.08±0.01	0.21±0.01
1,1-dimethylcyclopropane	0.06±0.01	0.09±0.01	0.08±0.01	0.10±0.01
1,2-dimethylcyclopropane	0.08±0.01	0.08±0.01	0.07±0.01	0.09±0.01
Isoprene	0.06±0.01	0.08±0.01	0.06±0.01	0.06±0.01
trans-2-pentene	0.07±0.01	0.05±0.01	0.06±0.01	0.07±0.01
3-methylpentane	0.05±0.01	0.06±0.01	0.05±0.01	0.07±0.01
cis-2-pentene	0.05±0.01	0.06±0.01	0.05±0.01	0.05±0.01
Cyclopentane	0.04±0.01	0.06±0.01	0.05±0.01	0.05±0.01
Total VOCs	**161**	**164**	**134**	**171**

Table 2 Cont.

VOCs	Inside[a]	Outside[a]	IPEN/USP[b]
m+p-xylenes	27.8±1.88	7.80±0.53	1.50±0.10
Pentane	22.3±0.47	5.00±0.11	2.00±0.04
Toluene	19.6±0.80	8.60±0.35	3.00±0.12
Butane	18.7±0.09	4.70±0.02	4.10±0.02
Benzene	16.4±0.48	2.80±0.08	0.90±0.03
1-butene	16.0±0.38	4.70±0.11	3.40±0.08
2-methylpentane	11.8±0.31	2.10±0.05	1.40±0.04
Hexane	10.4±0.30	2.30±0.07	2.70±0.08
o-xylene	9.39±0.23	2.60±0.06	0.50±0.01
Ethylbenzene	9.39±0.25	3.20±0.09	0.90±0.02
Heptane	6.71±0.25	1.80±0.07	0.60±0.02
1-ethyl-4-methylbenzene	5.32±0.20	2.10±0.08	0.40±0.02
Isobutane	5.03±0.03	1.00±0.01	3.50±0.02
Octane	3.78±0.22	0.90±0.05	0.30±0.02
1-pentene	3.65±0.09	0.30±0.01	0.70±0.02
Total HC	**186**	**49.9**	**25.9**

Table 3 Average concentration for the fifteen most abundant VOCs measured inside Jânio Quadros Tunnel (March 2004) and at CETESB IPEN/USP AMS, during 2006.

Compounds	Inside[a]	IPEN/USP[b]
Ethene	46.7±1.26	4.84±0.13
Ethane	17.9±0.95	2.98±0.16
Isopentane	14.7±0.22	1.78±0.03
Pentane	8.25±0.17	0.91±0.02
Propene	7.66±0.05	1.43±0.01
Butane	7.48±0.03	2.94±0.01
Toluene	7.34±0.30	1.97±0.08
1-butene	6.44±0.15	1.57±0.03
Benzene	5.04±0.15	0.45±0.01
Propane	4.41±0.06	5.56±0.07
1,2,4-trimethylbenzene	4.15±0.26	2.43±0.15
2-methylpentane	3.65±0.09	0.31±0.01
p-xylene	3.64±0.33	1.63±0.15
1-ethyl-4-methylbenzene	3.54±0.13	2.85±0.11
m-xylene	2.78±0.12	1.48±0.07
o-xylene	2.77±0.07	1.53±0.04
1,2,3-trimethylbenzene	2.75±0.17	2.29±0.14
1-ethyl-3-methylbenzene	2.74±0.11	2.32±0.09
Hexane	2.60±0.08	0.43±0.01
Propyl benzene	2.59±0.10	2.23±0.08
1,3,5-trimethylbenzene	2.59±0.10	2.33±0.09
1,1-dimethylclopropane	2.58±0.05	0.08±0.01
1-ethyl-2-methylbenzene	2.53±0.11	2.28±0.10
Ethylbenzene	2.40±0.06	1.39±0.04
Indane	2.40±0.07	0.77±0.02
Isopropyl benzene	2.38±0.07	-
3-hexene	2.29±0.06	0.36±0.01
Isobutane	2.21±0.01	1.18±0.01
trans-2-pentene	2.20±0.06	0.06±0.01
Octane	1.87±0.11	0.83±0.05
Heptane	1.72±0.06	0.35±0.01
trans-2-butene	1.70±0.04	0.61±0.01
3-methylpentane	1.63±0.05	0.05±0.01
2-methyl hexane	1.58±0.05	0.28±0.01
Methyl cyclohexane	1.54±0.06	0.31±0.01
3-methyl hexane	1.41±0.05	0.28±0.01
cis-2-butene	1.36±0.03	0.51±0.01
2-methyl heptane	1.28±0.06	0.85±0.04
Decane	1.03±0.05	0.81±0.04

Table 4 Average concentrations in ppbv of the 47 most abundant HCs from samples collected at CETESB IPEN/USP AMS during the 2011/2012 campaign and inside the Jânio Quadros Tunnel during May 2011.

Compounds	Inside[a]	IPEN/USP[b]
cis-1,3-dimethylcyclopentane	0.53±0.02	0.21±0.01
Limonene	0.52±0.03	-
Cyclopentane	0.27±0.01	0.05±0.01
cis-2-pentene	0.19±0.01	0.05±0.01
Pentene	0.11±0.01	0.13±0.01
1-methylcyclopentene	0.10±0.03	-
2,3-dimethylbutane	0.05±0.01	-
Total HC	**196**	**56**

Table 4 Cont.

The measurements presented in Table 3 (outside and inside the tunnel), demonstrate conditions characterized by heavy vehicular emissions, with high concentrations of compounds such as m+p-xylenes, toluene, butane, 1-butene, hexane, ethyl benzene, o-xylene, 1-ethyl-4-methyl benzene and styrene. In 2006, the main source of these compounds in the SPMA atmosphere was the incomplete burning of fuels from vehicle exhaust. In May 2011, another campaign was carried out inside Jânio Quadros Tunnel and the main HCs measured, presented in Table 4, were ethene, ethane, isopentane, pentane, propene, butane, toluene, 1-butene, benzene and propane. These compounds were among the 20 HCs with the highest concentration at the CETESB IPEN/USP AMS during 2011/2012, except for benzene, maintaining the same characteristics of the comparisons between the tunnel campaigns in 2004 with the CETESB IPEN/USP AMS in 2006. Similar results were found by Dominutti *et al.* (2016, 2020) for SPMA, with the most abundant NMHC propane, ethylene, ethane, acetylene, 2,2,4-trymethylpentane, i-propyl benzene, n-butane, toluene, i-pentane and propylene.

Ethanol, acetaldehyde, formaldehyde and acetone showed the highest concentrations among the analyzed VOCs in 2011/2012 (in 2006 these compounds were not determined). According to global emission estimates, plants emit three times more ethanol than anthropogenic sources. But in a study in Miami, the $^{13}C/^{12}C$ isotopic ratio showed that 74.9 % of the ethanol emissions to the atmosphere come from mobile sources (Giebel *et al.*, 2011). Considering the current emission conditions in the SPMA, vehicular emissions are very likely to be greater than biogenic sources. Ethanol, introduced as a fuel or fuel additive in many countries, plays a crucial role in tropospheric chemistry, where its oxidation is a substantial source of aldehydes in the atmosphere (Martins *et al.,* 2008; Anderson, 2009; de Andrade *et al.,* 1998; Corrêa e*t al.*, 2010). Ethanol has low reactivity for ozone formation, however aldehydes are produced in its burning which have high reactivity for O_3 formation, impacting the chemistry of the atmosphere, contributing to the formation of radicals and photochemical processing in the atmosphere (Goldan *et al.,* 2004; de Gouw *et al.,* 2012). Ethanol in the atmosphere is converted into acetaldehyde, a highly reactive compound for ozone formation, which is also toxic to human health (Sarkar *et al*., 2017). Ethanol was the highest concentration VOCs found in the 2011/2012 campaign, followed by acetaldehyde in this study. With the ethanol program (Proalcool) started in 1975, Brazil has become the only country in the globe where ethanol is widely used resulting in increase in its production together with the development of E100 vehicles. Since 2003, there has been an increase in ethanol production and consumption due to the introduction of off-fuel vehicles (Stolf & Oliveira, 2020), which led Brazilian ethanol production to reach 27 billion liters in 2008 and since then, remained practically constant. According to the Energy Yearbook by Municipality in the State of São Paulo - 2019 base year 2018 of the largest consumers of hydrated ethanol in the state of São Paulo were the cities of São Paulo Capital with 2.2 billion liters, followed by Campinas 325 million, Ribeirão Preto 265 mi, Guarulhos 223 mi and Sorocaba 213 mi (SE, 2019). In 2018, there was a significant increase in the consumption of vehicular ethanol in the state of São Paulo and a 5.3 % reduction in the use of petroleum products. This substitution reflected in the decrease in the emission of carbon monoxide into the atmosphere, probably a decrease in NOx, but an increase in O_3 due to the greater amount of acetaldehyde and formaldehyde in the atmosphere due to the burning of ethanol. However, the increase in O_3 is not only related to the increase in the consumption of ethanol as a vehicle fuel and a decrease in the consumption of gasoline, but there is also an influence of a decrease in NOx, an increase in VOCs and an increase in temperature and a decrease in precipitation in the RMSP. The decrease in the atmospheric concentration of NOx increases O_3 and the decrease in VOCs, mainly of the aldehyde class, decreases the concentration of O_3 in the

RMSP (Orlando *et al.,* 2010; Alvim *et al.,* 2018; Chiquetto *et al.,* 2018; Chiquetto *et al.,* 2020). Flex vehicles can burn 100 % hydrated ethanol (7.5 % of the maximum water mass content) and a mixture called gasohol (73 % gasoline + 27 % anhydrous ethanol).

Figure 2 shows the monthly averages values of ethanol, acetaldehyde, formaldehyde, acetone, acrolein and total HC. Figure 2 shows that the concentrations of acetone, formaldehyde, acrolein and acetaldehyde are highly correlated to each other, and present trends similar to those of HC. The behavior of ethanol is similar in certain months only. The concentrations of ambient ethanol observed in other researches carried out in SPMA were quite different, reaching between 18 and 460 ppb, in this study an annual average of 36 ppb was found (Schilling *et al.,* 1999; Colón *et al.,* 2001; Nguyen *et al.,* 2001; Brito *et al.,* 2018; Scaramboni, 2018). In cities where ethanol is used as fuel additive, for example in Los Angeles and London, increased levels on an average of 5 ppb and 9 ± 5 ppb respectively were observed (de Gouw *et al.,* 2012; Dunmore *et al.,* 2016). Previous studies reported an increase in aldehydes, together with some alkenes in emissions. Alvim *et al.* (2018) report aldehydes representing 74 % in the formation of O_3 at SPMA, followed by aromatics (14.5 %), alkenes (10.2 %), alkanes (1.3 %) and alkadienes (e.g., isoprene; 0.03 %). Simulation results for the SPMA showed that the most effective alternative for limiting the O_3 levels was reducing the VOC emissions, mainly the aldehydes (Niven, 2005; Suarez-Bertoa *et al.,* 2015; Alvim *et al.,* 2018).

Formaldehyde and acetaldehyde showed the highest concentrations among VOCs after ethanol. Vehicles using ethanol emit more aldehydes than gasoline-powered vehicles. The formaldehyde/acetaldehyde ratio found in this study was 0.75, with no significant variation during the year. In other studies for São Paulo, such as Vasconcellos *et al.* (2005), values ranged from 0.2 to 0.9. found concentration values of 0.8 in 2006 by Alvim *et al.* (2017) and 0.9 in 2008 by Nogueira *et al.* (2014), ratios ranged between 0.65 and 3.1. This lower value for the formaldehyde/acetaldehyde ratio suggests that ethanol consumption increased from 2006 to 2012, consistent with the fact that, in the SPMA, most new vehicles sold are flex-fuel vehicles. An increase in the level of aldehydes when compared to other locations in the globe is attributed to fleet composition and regional practices in Brazil (Grosjean *et al.,* 1990; Grosjean, 1997; Martins *et al.,* 2007; Nogueira *et al.,* 2014). Concentrations of aldehydes in the environment is regulated by an increase in consumption of ethanol is demonstrated in a recent study of the seasonal variation in the concentrations of formaldehyde and acetaldehyde based on a 5-year measurements in SPMA which showed an increase of about 60 % and 40 % respectively in both the compounds that is from 1.35 to 2.80 ppb/ppm ERs for formaldehyde and 2.08 to 2.93 ppb/ppm ERs for acetaldehyde in 2015 (Nogueira *et al.,* 2017). The increase in the emission ratios (ER) could be associated to the change in the fuel consumption observed, characterized by an increase in the ethanol and bio-diesel sales and a decrease in the gasohol sales in 2015 (Dominutti *et al.*, 2020). According to Branco & Branco (2007), drivers

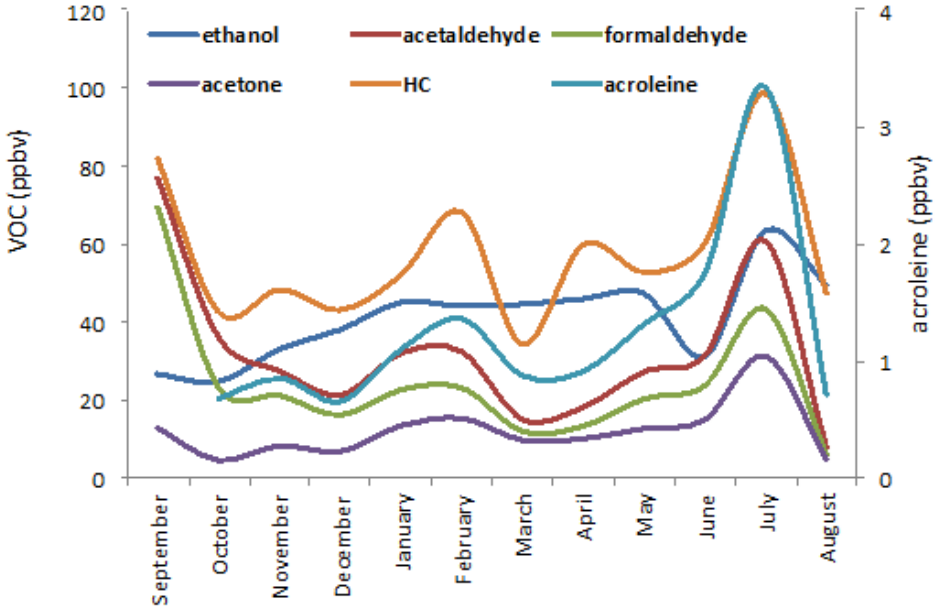

Figure 2 Ethanol, acetaldehyde, formaldehyde, acetone, acrolein and HC at CETESB IPEN/USP AMS during 2011/2012.

of flex-fuel vehicles preferentially use ethanol during the harvest season (e.g., August until December). During the off-season (e.g., January until July), ethanol use is 30 % lower as the price increases and more drivers choose to use gasoline. But even with the preferential use of gasoline during the off-season, it is important to point out that this fuel in Brazil still contains 27 % anhydrous ethanol.

Table 1 also shows that the concentration of most compounds was higher in winter than in the summer of 2006, except for hexane, isobutane, methyl cyclopentane, 1-pentene, isoprene, decane, and isopropyl benzene. Table 2 shows that during 2011-12, the average concentrations of ethanol, acetone, acrolein and HCs were also higher in winter. For spring, carbonyls concentrations were higher (except for acrolein) and there were no significant variations during the other seasons.

The subtropical climate of the SPMA is predominantly influenced, during winter, by low altitude inversion layers at 200, 400 and 600 meters, the breaking of the late-night layer and the fast arrival of cold fronts from the south of the continent. A decrease in precipitation and temperatures is characterized this season, also by and greater atmospheric stability, thus providing extremely unfavorable conditions for pollutant dispersion (CETESB, 2007; CETESB, 2013).

Comparing the results from different seasons for the year 2006, there was significant variability in HCs concentrations during winter, particularly an average increase of 72.3 % for styrene, 70.3 % for 2-methyl heptane, 67.8 % for 3-methyl heptane, 62.2 % for propene and 60.3 % for propane.

Calculating the average values of the other seasons and comparing them with the 2011/2012 winter values, shows that only acetaldehyde, formaldehyde, 1-ethyl-4-methyl benzene, 1,3,5-trimethyl benzene, 1-ethyl-3-methyl benzene, 2-methyl heptane, octane, isoprene and cis-2-pentene showed higher values.

Figure 3 and Figure 4 show the average monthly VOCs concentrations, total HCs, and precipitation values, respectively, for 2006 and 2011-2012.

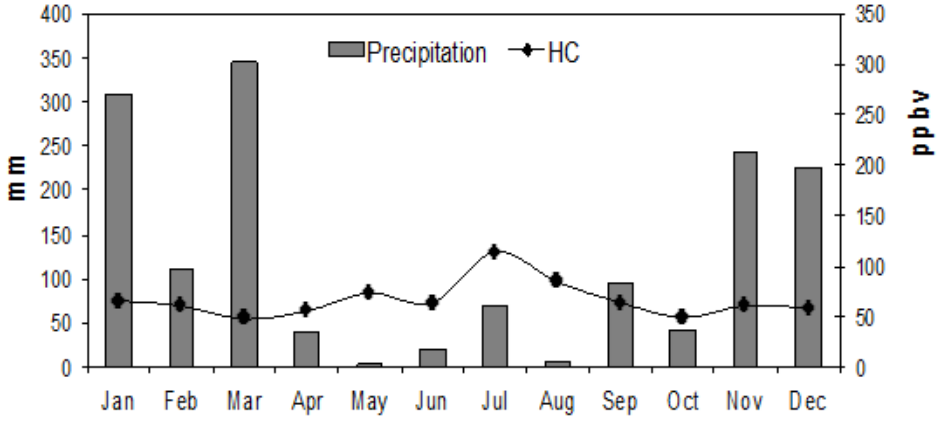

Figure 3 Total HCs (ppbv) and precipitation (mm) at CETESB IPEN/USP AMS during 2006.

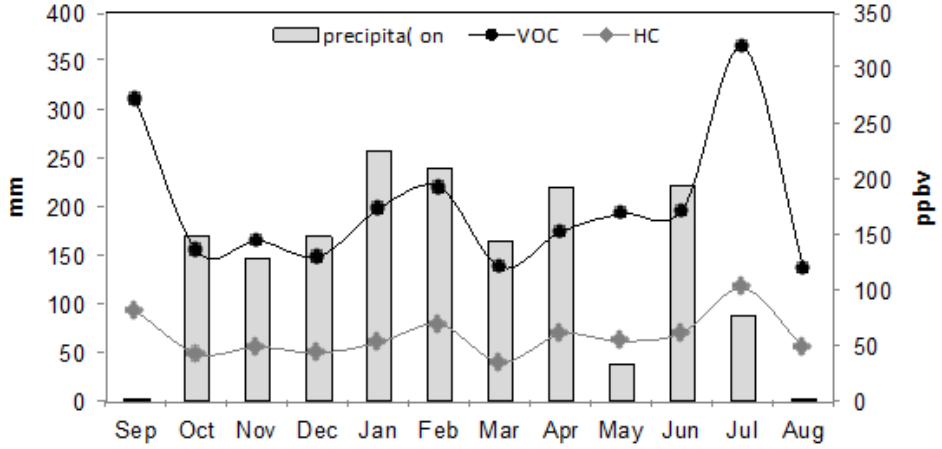

Figure 4 Total VOCs, HCs (ppbv) and precipitation (mm) at CETESB IPEN/USP AMS during Sep 2011- Aug 2012.

The total VOCs concentrations underwent significant changes during the 2006 campaign, with lower values in March and higher in July, an increase of 141 % throughout the year. The highest VOCs concentration were due to meteorological conditions, as this month presented the highest percentage of calm winds, the highest number of thermal inversions below 200 m, and 19 days with unfavorable dispersion conditions, as presented in Table 5.

During the months of May, July and August 2006, the higher concentrations of total VOCs are likely due to the lower average precipitation rates, more thermal inversions, calmer winds, and higher number of days with unfavorable conditions for pollutant dispersion, as shown in Table 5 and Figure 3. March 2006 was the month with the lowest total HCs. This fact was attributed to the high number of rainy days (21 days). For the 2011-2012 campaign, the lowest HCs values occurred in September. For the total VOCs, the lowest value was in August, which also showed the second lowest value for total HCs. The highest VOCs concentration, in both campaigns, occurred in July.

Benzene, ethyl benzene, n-hexane, toluene, xylenes, 1,3-butadiene, formaldehyde are on the Urban Air Toxics list of the U.S. Clean Air Act. In Brazil, air quality standards have not been defined yet for organic pollutants such as these. However, the average benzene values found in this study were 2.7 and 1.9 μg m^{-3} for the 2006 and 2011-2012 campaigns, respectively, and did not exceed the maximum regulated limit of 10 μg m^{-3} for several countries (IARC, 2016), in any of the studied months. Hester (1998) demonstrated that six people in a population of one million can develop leukemia when exposed to a benzene concentration of 1 μg m^{-3} over a lifetime (WHO, 2010). Benzene is carcinogenic and toluene, ethylbenzene and xylenes are mutagenic, and probably carcinogenic. Toluene was the 9th and 12th HC with the highest concentration in 2006 and 2011/2012, respectively, and benzene was the 28th and 36th in 2006 and 2011/2012, respectively.

Figure 5 and Figure 6 present the average values of benzene, toluene, ethyl benzene and xylenes (BTEX), for the 2006 and 2011/2012 campaigns. Benzene showed values similar to ethyl benzene and xylenes in 2006, but lower values in 2011-2012. Toluene was found at higher concentrations than xylenes during the whole of 2006 and 2011/2012. Higher concentrations of this pollutant were observed in the months of September and October of 2011, and February, April, June, July and August of 2012, which is due to the lower reactivity of toluene compared to xylenes, and because toluene is present in higher concentrations in fossil fuel composition (Carter, 2000; Alves & Tomé, 2007; Okada *et al*., 2012). On the Maximum Incremental Reactivity (MIR) scale, the following order for the reactivity of these HCs in the ozone formation is (from least to most reactive): toluene, p-xylene, o-xylene and m-xylene. The estimated lifetime of these compounds in the atmosphere is 2.4 days for toluene and less than 24 hours for xylenes (Carter, 2010).

In the campaign carried out inside the Jânio Quadros tunnel in 2004, toluene was the third most abundant compound among HCs with more than four carbons, and in 2011, it was the fourth most abundant. For the HCs with more than two carbons it was the seventh most abundant compound.

During 2006 at the CETESB IPEN/USP AMS, the mass distributions of HCs by the class of compounds showed that alkanes represented 54.8 %, alkenes 29.2 %, aromatics 13.6 % and dienes 2.4 %.

Month	Thermal Inversions			Calm winds	WS	UD
	0-200 m	201-400 m	401-600 m	(%)	(m s^{-1})	
January	-	2	5	14.0	1.7	0
February	-	5	1	11.9	1.7	0
March	4	4	7	9.5	1.7	0
April	1	9	2	11.2	1.8	0
May	3	4	3	14.2	1.6	2
June	7	5	7	17.3	1.7	11
July	18	9	-	26.4	1.5	19
August	10	9	3	16.6	1.8	13
September	5	5	5	9.8	2.0	4
October	-	4	8	7.2	1.8	0
November	1	5	1	8.4	2.0	0
December	1	1	4	4.5	2.0	0

Table 5 Frequency of thermal inversions (TI), average percentage of calm winds, average wind speed, and monthly distribution of favorable and unfavorable days (UD) for the dispersion of pollutants for SPMA during 2006.

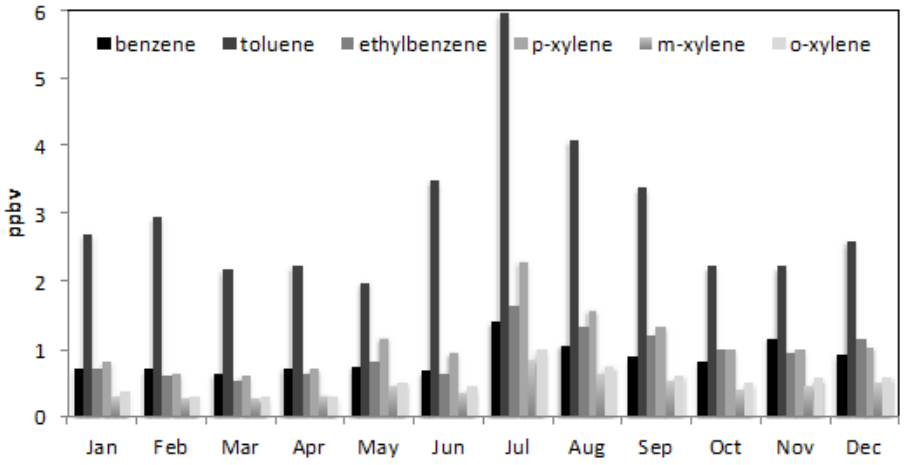

Figure 5 Average values for BTEX at CETESB IPEN/USP AMS during 2006.

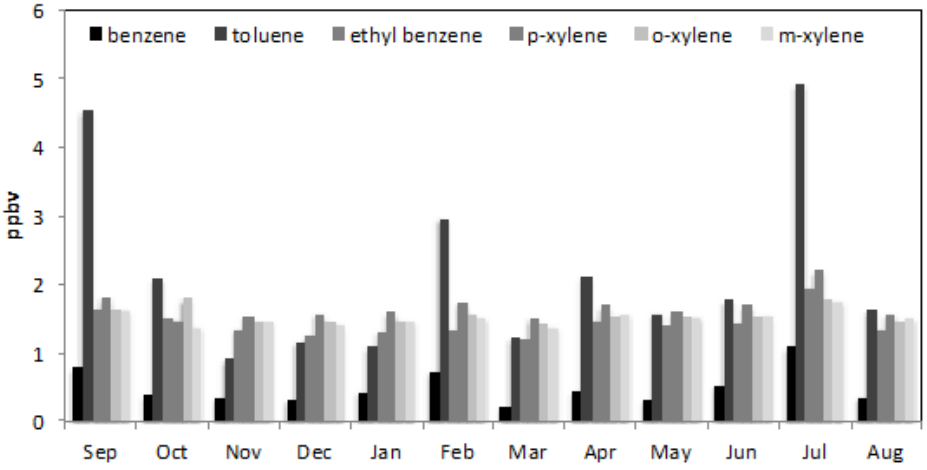

Figure 6 Average values for BTEX at CETESB IPEN/USP AMS during Sep 2011- Aug 2012.

During 2011/2012 carbonyls represented 42.1 % of the VOCs analyzed, followed by ethanol (22.6 %), aromatics (15.7 %), alkanes (13.5 %), alkenes (6.0 %) and alkadienes (less than 0.1 %). During 2011/2012, an increase of aromatics was observed, the second most reactive group for ozone formation.

Table 6 shows: (1) the CO and NOx concentrations during 2006 at CETESB Pinheiros AMS and 2011/2012 measured at the CETESB IPEN/USP AMS. (2) The HCs measured at the CETESB IPEN/USP Station in 2006 and 2011/2012, the carbonyls measured at the Cerqueira César AMS in 2006 and IPEN/USP AMS in 2011/2012. (3) The emissions of CO, NOx and VOCs, the fuel consumption in the SPMA and the size its urbanized area in km^2 (SE, 2008; CETESB, 2013; IBGE, 2015).

This study indicated that, between 2006 and 2012, the atmospheric composition in the SPMA changed considerably; for example, an increase in aromatics was measured, due to its increase in gasoline (1.0 % and 1.5 % of benzene for gasoline type C and premium, respectively), which is a negative aspect. Ethanol consumption increased by 64 %, gasoline by 23 % and diesel by 25 %. During the same period, the increased use of ethanol led to a 409 % increase in aldehydes, which are the main ozone precursors (Orlando *et al.*, 2010, Alvim *et al*., 2018). VOCs, CO and NO_x concentrations in the atmosphere are heavily influenced by combustion efficiency, which is determined by the fuel quality and engine technology.

Concentration	2006	2011/2012
CO (ppm)	1.17[a]	0.40[b]
NO_x (ppb)	0.12[a]	0.05[b]
alkanes (ppb)	36.8[b]	21.6[b]
alkenes (ppb)	19.7[b]	9.59[b]
alkadienes (ppb)	2.4[b]	0.07[b]
aromatics (ppb)	10.0[b]	25.2[b]
acetaldehyde (ppb)	6.5[c]	32.3[b]
formaldehyde (ppb)	6.0[c]	24.5[b]
other aldehydes (ppb)	-	6.7[b]
ketones (ppb)	-	12.1[b]
ethanol (ppb)	414[d]	41.2
total VOCs (ppmC)	1.38	0.74
Emissions		
CO (t $year^{-1}$)	1.503.000[g]	160.610[e]
NOx (t $year^{-1}$)	137.529[g]	139.216[f]
VOCs (t $year^{-1}$)	373.294[g]	35.370[e]
Fuel Consumption		
gasoline (L)	2.849.767.333[h]	3.517.460.111[i]
ethanol (L)	1.152.939.645[h]	1.893.911.067[i]
diesel (L)	1.949.145.150[h]	2.430.476.53[j]
Number of vehicles		
Gasoline	6.000.000[g]	2.861.781[e]
flex fuel	445.300[g]	2.423.887[e]
Diesel	430.000[g]	348.405[e]
Motorcycles	870.000[g]	778.426[e]
Urbanized Area (km^2)[j]	1747	2209

a: CETESB Pinheiros AMS; b: CETESB IPEN/USP AMS; c: CETESB Cerqueira César AMS; d: (Colón *et al.,* 2001); e: (CETESB, 2013); f: (Branco & Branco, 2007); g: (CETESB, 2018); h: (SE, 2008); i: (SE, 2012); j: (IBGE, 2017). *Gasoline, diesel and motorcycles number is lower in 2011 than 2006 due to a change in the quantification methodology.

Table 6 CO, NOx, VOCs concentration at CETESB Pinheiros, Cerqueira César and IPEN/USP AMS, CO, NOx and VOCs emissions, fuel consumption, number of vehicles and urbanized area of the SPMA.

Another important aspect is the predominance of flex-fuel vehicles, which are not optimized for either gasoline or ethanol usage. This implies in a loss of combustion efficiency in both cases. Despite the controversies regarding CO emission factors, nowadays, its annual emission is around 10 % of what was found in 2006. We observed that CO concentration in the atmosphere is only a third of 2006 levels, according to Table 6. However, the 2006 concentrations refer to the Pinheiros AMS and its decrease may be higher, as the AMS site is close to a very busy road. NOx decreased by 58 %, although diesel consumption increased by 25 %, showing a significant improvement in engine technology and perhaps fuel itself.

4 Conclusions

The aim of this observational study was to determine Volatile Organic Compounds (VOCs) concentrations in the São Paulo metropolitan area (SPMA). For that, we used 78 and 66 samples of hydrocarbon during 2006 and 2011-2012 respectively. In addition, we used 62 samples of aldehydes and 42 of ethanol during 2011-2012. The main results can be summarized as follows:

During 2006 at the CETESB IPEN/USP AMS, the mass distributions of HCs by class of compounds, showed that alkanes represented 54.8 %, alkenes 29.2 %, aromatics 13.6 % and dienes 2.4 %.

The 10 most abundant VOCs in the atmosphere found during 2011/2012 at the CETESB IPEN/USP AMS were ethanol, acetaldehyde, formaldehyde, acetone, propane, ethene, ethane, butane, 1-ethyl-4-methyl benzene, and 1,2,4-trimethyl benzene. During 2011/2012 investigations, carbonyls represented 42.1 % of the VOCs analyzed, followed by ethanol (22.6 %), aromatics (15.7 %), alkanes (13.5 %), alkenes (6.0 %) and alkadienes (less than 0.1 %). During 2011/2012, an increase in aromatics, the second most reactive group for ozone formation, was observed compared to 2006.

An increase in VOCs concentrations in the SPMA atmosphere from 2006 to 2012, such as aldehydes and aromatics (which are important ozone precursors) was measured. This shows that the consumption of ethanol, gasoline and diesel increased by 64 %, 23 % and 25 %, respectively, from 2006 to 2012, with substantial changes in the atmospheric composition. During the 2006 campaign, alkanes represented 54.8 % of the total HC mass, alkenes 29.2 %, aromatics 13.6 %, and alkadienes 2.4 %. On the other hand, during the 2011-2012 campaign, aldehydes represented 35.3 % of the VOCs, ethanol 22.6 %, aromatics 15.5 %, alkanes 13.5 %, acetone 6.8 %, alkenes 6.0 %.

On a final note, greater attention should be given to the carbonyl and aromatic emissions, which are the main ozone precursors, together with the alkenes (Alvim *et al.*, 2017, 2018). The alkenes are more difficult to control in the fuel composition, as well as in the emission and formation of carbonyls by intensive use of ethanol. But aromatics can be more easily reduced in the fuel composition. Thus, our results showed that a change in the atmospheric composition causes a change in the role of each chemical species in the mechanism. This implies that developing policies that can help decreasing ozone concentrations is a complex task, requiring frequent and multi-faceted monitoring, as was accomplished here.

Therefore, it is not an overstatement that a technological leap on urban mobility is a must, for example, substituting internal combustion engines for electrical motors, both for automobiles and mass transportation. Such paradigmatic change is already on the horizon, as countries like Germany have already outlawed the use of internal combustion engines on their roads in the near future. Also, this is a trend that is likely to be followed in all of Europe and other countries, which are already advanced in the design and production of zero-emission vehicles. With its abundant resources, Brazil shows enormous potential to become completely free from fossil fuels, by means of wind, water and solar (WWS) energies, as the study was done by Stanford University for the USA (Jacobson *et al.*, 2015; Nobre *et al.*, 2019). Emission inventories are fundamental inputs to air quality models and it is essential to continuously improve the representation of different species by collecting their comprehensive activity, analysis and better specification of emission sources. Speciation of VOCs is a key step in making emission inventories and plays a pivotal role in estimating air pollution and in the formation of secondary pollutants. The findings from this study are important for decision makers and public policy makers in Brazil who thrive to control the emissions of VOCs, given their high reactivity. Efforts to reduce tropospheric ozone by controlling its precursors (NOx and VOCs) is the future phase L7 of PROCONVE, with the reduction of NMOG and ozone forming potential calculation (2018).

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