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Determining VOCs Reactivity for Ozone Forming Potential in the Megacity of São Paulo

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ABSTRACT

High ozone (O₃) concentrations are a major concern about air quality in the São Paulo Metropolitan Area (SPMA). During 2016, the 8-hour state standard of 140 µg m⁻³ was exceeded on 32 days, whereas the 1-hour national standard of 160 µg m⁻³ was exceeded on 76 days. Exposure to such unhealthy O₃ levels and other pollutants can lead to respiratory disease. The focus of this study is to determine the main O₃ precursor in terms of the volatile organic compounds (VOCs) in order to provide a scientific basis for controlling this pollutant. In this work, 66 samples of hydrocarbons, 62 of aldehydes and 42 of ethanol were taken during the period from September 2011 to August 2012 from 7:00 to 9:00 a.m. The OZIPR trajectory model and SAPRC atmospheric chemical mechanism were used to determine the major O₃ precursors. During the studied period, aldehydes represented 35.3% of the VOCs, followed by ethanol (22.6%), aromatic compounds (15.7%), alkanes (13.5%), ketones (6.8%), alkenes (6.0%) and alkadienes (less than 0.1%). Considering the concentration of VOCs and their typical reactivity, the simulation results showed that acetaldehyde contributed 61.2% of the O₃ formation. The total aldehydes contributed 74%, 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 O₃ levels was reducing the VOC emissions, mainly the aldehydes.

Keywords: Ozone-forming potential; Air quality; VOCs; Incremental reactivity.

INTRODUCTION

São Paulo is among the ten most populous cities in the world. It lies at the core of the São Paulo Metropolitan Area (SPMA), which contains 39 municipalities in total. With nearly 21.3 million inhabitants, the SPMA had surpassed the populations of New York, Beijing and Mexico City. It is the most populated urban area in the Americas, and is the fifth most populous in the world according to 2016 UN data. It comprises one tenth of Brazil's population, and is

about 40% higher than that of the Metropolitan Area of Rio de Janeiro, the second largest in the country (with 12 million inhabitants). The marked rise in population in the SPMA, accompanied by a substantial industrial and commercial development during recent decades, has not been accompanied by an improvement in the public transportation system (IBGE, 2015).

In the SPMA, air quality problems are mainly the result of vehicular emissions. The region concentrates 49% of the vehicular fleet of the state in just 3.2% of its area. According to the State Environmental Agency (CETESB), in 2016, emissions from mobile and stationary sources totalled 131 kt of CO, 38 kt of HC, 80 kt of NO_x, 5.1 kt of PM and 6.7 kt of SO_x. The current vehicular fleet of 7.5 million vehicles accounts for 97% of CO emissions, 76% of HC, 68% of NO_x, 17% of SO_x and 40% of PM.

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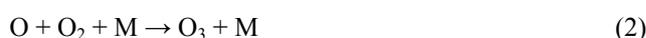
Over the past decade, the fleet has increased more than in the 1990s and it is still increasing with an annual rate of 6%. Until 10 years ago, fuel sales were still rising at an annual rate of 10%. However, fuel consumption is now finally stabilizing (CETESB, 2017). Nevertheless, the population in the region has been suffering chronic health problems caused by air pollution, such as a life expectancy decrease of 3 years (Miraglia and Gouveia, 2014). Exposure to pollutants can lead to respiratory diseases, such as asthma, emphysema, and chronic bronchitis, and a consequent deterioration in the quality of life. Moreover, ozone-forming reactions involving VOCs can also contribute to Secondary Organic Aerosol (SOA) formation. These aerosol particles are extremely small and can penetrate deep into the respiratory system further exacerbating respiratory-related illnesses.

During 2016, a large automatic ozone monitoring network comprised of 48 stations in the SPMA showed that the 8-hour state standard of $140 \mu\text{g m}^{-3}$ was exceeded on 32 days (according to the State Air Quality Report of 2016). During this same period, the state attention level of $200 \mu\text{g m}^{-3}$ was also exceeded on one day. The 1-hour national standard of $160 \mu\text{g m}^{-3}$ was exceeded on 76 days (according to the state air quality report by CETESB). To give an idea of the magnitude of the present pollution in SPMA, we plot in Fig. 1 the monthly average of the O_3 concentrations at selected monitoring stations for the period between 2010 and 2016. The highest concentrations occur during austral spring and summer, on days with high temperatures and insolation rates.

Since the quantitative emissions changes in O_3 precursors are relatively small from year to year, in situ O_3 formation rate must be controlled by local weather. Therefore, the main objective of this article is to identify the main VOCs ozone precursors and the influence of meteorology in triggering episodes of high ozone concentrations. We hope that our findings would provide the scientific basis for the creation of carefully considered legislation actions by environmental agencies, so emissions reduction targets in SPMA can be finally achieved.

Tropospheric Ozone Formation, Main Precursors, and its Underlying Causes

Tropospheric ozone is produced by the photochemical oxidation of carbon monoxide (CO), methane (CH_4), and non-methane volatile organic compounds (NMVOCs) in the presence of nitrogen oxides ($\text{NO}_x = \text{NO} + \text{NO}_2$), as per Eqs. (1)–(2), by the recombination of the oxygen atom with the oxygen molecule. However, the oxygen atom cannot be formed at the troposphere by the photodissociation of the oxygen molecule, because this reaction requires short wavelengths solar radiation ($\lambda < 242 \text{ nm}$) that is unavailable in the troposphere. NO_2 is the only known molecule to photodissociate (releasing an oxygen atom) in the presence of only longer wavelength radiation as follows:



In the presence of NO, O_3 is consumed as shown in Eq. (3).



In an unpolluted atmosphere, such as that presented in Eqs. (1)–(3), there is no net ozone production, as these reactions only recycle O_3 and NO_x . The net O_3 production occurs when other species, such as CO, CH_4 , NMHC or other VOCs are present in the atmosphere. A condensed set of reactions can be visualized as Eqs. (4)–(11), in Eq. (4) RH represents an alkane, and where OH^\bullet , HO_2^\bullet , NO and NO_2 act as catalysts.

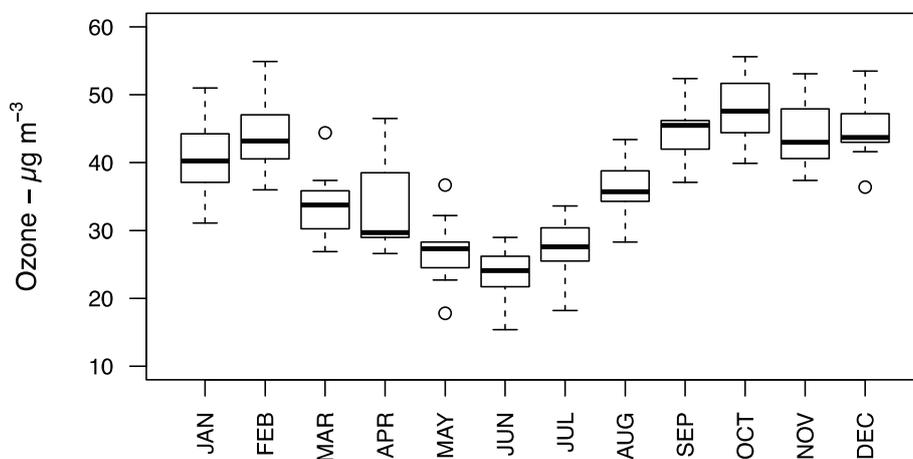


Fig. 1. Monthly average ozone concentrations ($\mu\text{g m}^{-3}$) at nine air quality monitoring stations in the SPMA between 2010 and 2016. Source: adapted from the State Air Quality report (CETESB, 2017).



Net:



Aldehydes (CH_2O) photodissociate to generate other radicals, which can also produce O_3 (Finlayson-Pitts and Pitts, 2000; Jacobson, 2002; Wallace and Hobbs, 2006). O_3 production is favoured during sunny and hot days during spring and summer. O_3 is also a greenhouse gas and a toxic air pollutant, with serious implications for climate, human health, and agricultural productivity (IPCC, 2007).

As already stated, the O_3 problem in the SPMA is mostly a result of vehicular emissions of NO_x and VOCs, which are impacted by the type of fuel used and the age of the vehicles. Since 1975, Brazil has been a leading country in the development of ethanol as fuel. The combustion of ethanol in vehicles is cleaner than gasoline and diesel, in terms of NO_x , CO, SO_x , hydrocarbons and particulate matter (PM) emissions. Presently, gasoline in Brazil is mixed with 25% anhydrous ethanol, replacing tetraethyl lead. The sulphur content in fuels is currently below 50 ppm. Although fuels with higher amounts of ethanol emit less NO_x and CO (Ginnebaugh and Jacobson, 2012), they produce higher amounts of aldehydes, which have a relevant impact on O_3 formation (Nogueira *et al.*, 2014). In a recent study, Salvo and Geiger (2014) showed that an increase in O_3 levels in the SPMA was related to ethanol consumption. Ethanol vehicles emit four times less CO than gasoline vehicles. However, the incomplete combustion of ethanol produces more formaldehyde and acetaldehyde than gasoline powered vehicles, and the state environmental agency (CETESB) has not yet implemented air quality standards or a temporally and spatially representative monitoring of VOCs. In Brazil, studies on aldehydes in the atmosphere started in the 1980s, when ethanol was introduced as vehicular fuel. Aldehydes are more reactive in the atmosphere than alcohols. Due to ethanol's increasing usage, understanding the atmospheric chemistry of oxygenated VOCs is essential in order to develop solutions for the problems caused by the high O_3 concentrations (Grosjean, 1997; Salvo and Geiger, 2014; Alvim *et al.*, 2017; CETESB, 2017).

However, limits imposed by federal programs aimed to control air pollution from vehicles and motorcycles (PROCONVE and PROMOT), and the usual renewal of the fleet have been insufficient to decrease pollution emission loads. Even with vehicular technological advances, the increase in the vehicle fleet, and its use for residential, passenger and cargo transportation in recent years has resulted in an overall increase in emissions (CETESB, 2017). Therefore, the control of air pollution levels in SPMA is a complex task, and should not be based solely on technological measures to reduce vehicle emissions alone. Integrated actions including several sectors of society,

such as the development of a first-rate public transportation system, among others, must be studied, evaluated and implemented.

As reported by de Fatima Andrade *et al.* (2017) in an extensive study over the last 30 years the greatest challenge for SPMA is to control secondary pollutants such as ozone and fine particles. Despite the intensive use of biofuels in SPMA, O_3 concentration still increase, mainly during weekends when there is a decrease in the NO emissions from buses and trucks, the so-called weekend effect (higher ozone concentrations on weekends than on weekdays) might be related to the reduction in NO emissions due to the low circulation of heavy vehicles over the weekends, which increase the VOC/ NO_x ratio, and also NO is the main ozone sink. This phenomenon has been reported in some areas of the United States since the 1970s; in SPMA with fewer vehicles circulating during the weekend, and consequently less emission of pollutants, it has cleaner air and less concentration of NO and NO_2 , there is the ideal setting to the formation of troposphere ozone, despite the lower concentration of NO_2 (de Silva Junior *et al.*, 2009).

According to Pacheco *et al.* (2017), 90% of the light duty vehicles run on ethanol or gasohol. They form a low fraction of the total fleet but account for 90% of total PM emissions from road vehicles. The emission control programs have been successful in reducing the vehicular exhaust emissions, but other sources such as evaporative losses during refuelling, as well as from tires, brakes and road surface increased with the fleet increase.

Other main cities in Brazil are also impacted by $\text{PM}_{2.5}$ from vehicular sources. The study of de Miranda *et al.* (2012) measured $\text{PM}_{2.5}$ in São Paulo, Rio de Janeiro, Belo Horizonte, Curitiba, Porto Alegre and Recife and found average values of 28.0, 17.2, 14.4, 13.4 and 7.3 $\mu\text{g m}^{-3}$, respectively, and for São Paulo and Rio de Janeiro, black carbon explained 30% of $\text{PM}_{2.5}$ mass and vehicular emissions, 40%.

A recent study published by da Silva *et al.* (2017) indicated that O_3 is mainly formed by the most reactive VOCs, and using multivariate statistical analysis showed that for Rio de Janeiro, VOCs speciation was not seasonally dependent. Using Venn diagrams, they found a minimum of 14 VOCs with represent the most of VOCs mixture, and this reduced set described in a reasonable way the O_3 formation with a difference of 8% than using the complete VOCs speciation.

In the present work the speciation for SPMA will be presented and the main VOCs which are O_3 precursors will be addressed for the SPMA, indicating possible route to reduce this pollutant.

METHODS

Sampling Site

Sixty-six samples of hydrocarbons, 62 of aldehydes and 42 of ethanol were measured between September 2011 and August 2012 at a CETESB air quality monitoring station (AQMS) located inside the University of São Paulo campus,

at an altitude of 800 m, in the western region of the city. Measurements were taken on weekdays between 7 to 9 a.m., during the peak traffic hours and a time of low photochemical activity. São Paulo State, São Paulo city and the SPMA are shown in Fig. 2.

There are approximately 40 thousand industries and 7.5 million private vehicles in the SPMA (21% of the Brazilian fleet). The SPMA has an area of 8,051 km², less than one thousandth of the Brazilian land surface area. Nonetheless, São Paulo city holds 11 million people (61% of the total of SPMA) in an area of just 1,051 km². Between 1962 and 2010, the urbanized area increased from 874 km² to 2,209 km². This extensive urbanized area is located on a floodplain basin (the São Paulo Sedimentary Basin) drained by the Tietê River, which runs east–west. Towards its north, the São Paulo Sedimentary Basin meets the Serra da Cantareira mountain range, also oriented east–west and with altitudes that reach up to 1,200 m. To the east and south, this basin faces the Serra do Mar mountain ridge along the Atlantic coast, with altitudes that exceed 800 m (while the average altitude of the SPMA is of 780 m). Although São Paulo state has a coastline that is 600 km long, the SPMA is about 45 km inland from the Atlantic Ocean. These topographic features can interfere with local airflow, and consequently exacerbate pollution episodes.

Sampling and Chemical Analyses

The hydrocarbon sampling methodology used was based on the TO-14A and TO-15 methods from (U.S. EPA, 1999a; U.S. EPA, 1999b). These well-established methods use electropolished stainless steel canisters. Prior to collection, the canisters were cleansed and evacuated to less than 10 mTorr.

For the formaldehyde and acetaldehyde samplings, the TO-11A method from U.S. EPA (1999c) was used with silica cartridges, coated with C18 and impregnated with a 2,4-dinitrophenylhydrazine (DNPH) acid solution. Ethanol was sampled with Florisil cartridges. Samples of aldehydes and ethanol were collected with a KNF pump (N815 KNDC) at a flow rate of 1.0 L min⁻¹ for two hours, simultaneously with the hydrocarbons sampling.

The ethanol chemical analyses were performed by gas chromatography with mass spectrometry (GC-MS) on a Varian CG 450 MS 220 with a CombiPAL injector. The ions monitored were 45–46 m/z, and a Varian VF-5MS column was used (30 m, 0.25 μm, 0.25 mm). The methodology used in this work is detailed in our previous publication (Alvim *et al.*, 2017).

OZIPR Trajectory Model

The OZIPR (Ozone Isopleth Package for Research) trajectory model was used, coupled with the SAPRC

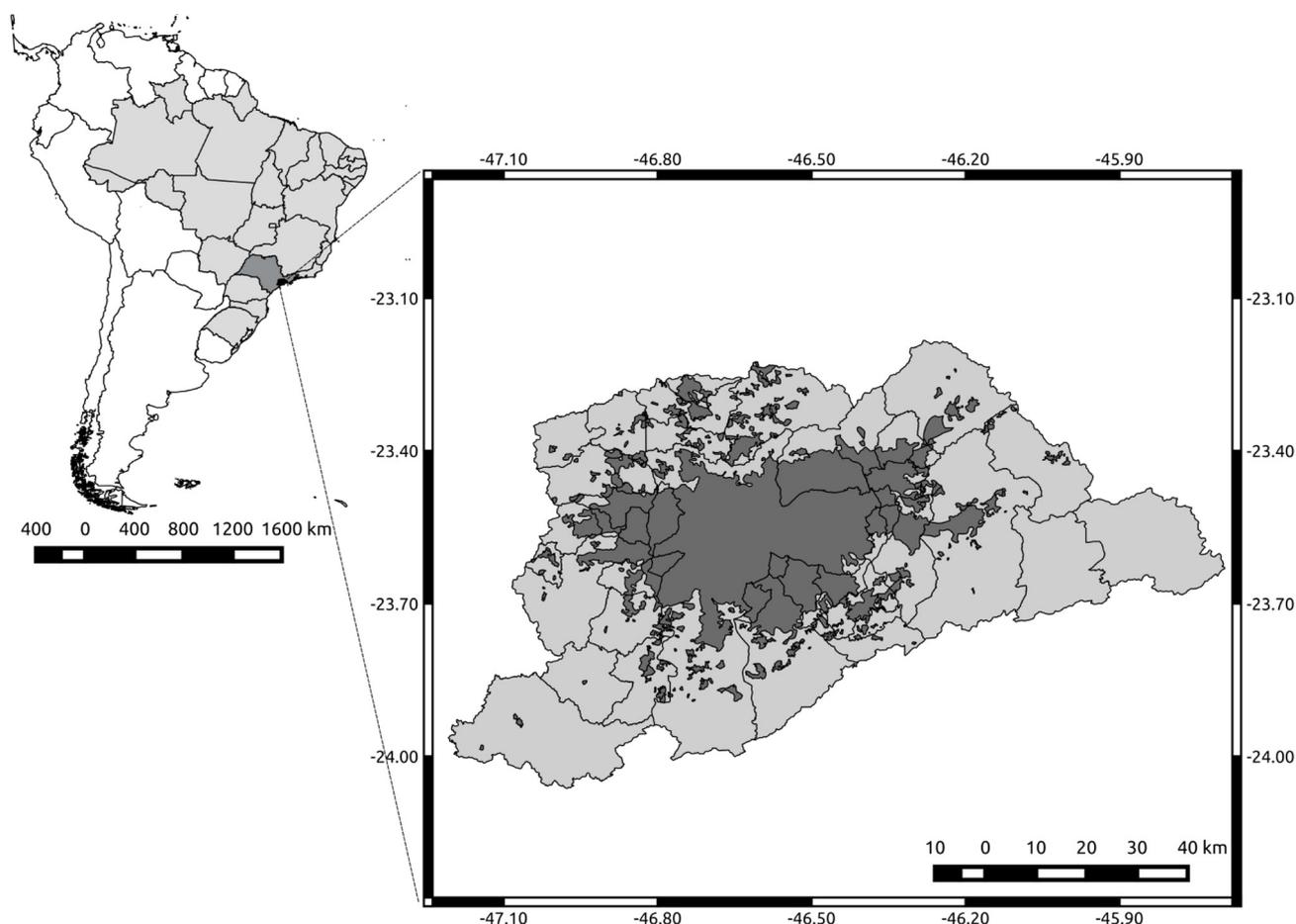


Fig. 2. Location of the SPMA in Brazil and its urban sprawl.

(Statewide Air Pollution Research Center) chemical model. They are public domain models and are widely accepted in the international academic community (Gery and Crouse, 1990; Tonnesen, 2000; Kumar *et al.*, 2008; Orlando *et al.*, 2010; Corrêa *et al.*, 2012).

The OZIPR trajectory model (Gery and Crouse, 1990; Tonnesen, 2000) is a unidimensional model that requires initial concentrations of CO, NO_x and VOCs, their hourly emissions, VOC speciation and hourly meteorological parameters, without a spatial resolution. This model allows multiple simulations for various VOCs and NO_x conditions, and provides an ozone isopleth as a function of these two precursors (Gery and Crouse, 1990; Tonnesen, 2000). Finally, it is a useful tool for estimating VOCs reactivity scales and has been extensively used by the international community to help policymakers desiring to reduce ozone-associated primary emissions to improve air quality (Do *et al.*, 2007; Orlando *et al.*, 2010; Corrêa *et al.*, 2012; Jin *et al.*, 2012; Shin *et al.*, 2012).

The chemical model SAPRC encompasses thermal and photochemical reactions. It has been updated by our group to add a number of reactions, and currently employs 214 reactions and 83 species (Carter, 2000, 2010). Only the more reactive species for ozone formation are included explicitly within the mechanism. A class-grouping methodology has been established based on similarity of structure and reactivity. In this work, five groups of alkanes, two groups of alkenes, two groups of aromatics and several explicit species were used.

The incremental reactivity (IR) scale was used to calculate the main O₃ precursors emitted in the SPMA. This calculation was performed as detailed in Orlando *et al.* (2010), using the mean (Eq. (14)) of positive IR (Eq. (12)) and negative IR (Eq. (13)). The individual IRs were then calculated by increasing and decreasing each VOC species by 0.2% of its total concentration (ppbC) at a time. The simulated ozone changes were also computed as the maximum concentration reached after each addition or decrease of 0.2% of VOC, and subtracted from the ozone base.

$$IR_+ = \frac{[O_3^+] - [O_3^{base}]}{[O_3^{base}]} \quad (12)$$

$$IR_- = \frac{[O_3^-] - [O_3^{base}]}{[O_3^{base}]} \quad (13)$$

where:

[O₃⁺] = O₃ concentration after VOC increment of 0.2%.

[O₃⁻] = O₃ concentration after VOC decrease of 0.2%.

The average IR is calculated as Eq. (14).

$$IR = \frac{IR_+ + IR_-}{2} \quad (14)$$

Average CO, NO_x, and VOCs concentrations in the beginning of the day were used as model input. The values

for NO_x, CO, temperature and relative humidity were obtained from the local AQMS. The boundary layer heights were obtained using a PLC LIDAR (Light Detection and Ranging) sensing system.

RESULTS AND DISCUSSION

Table 1 shows the average concentrations of 54 VOCs from 66 samples, separated by seasons between September 2011 and August 2012. These values were used as input for the OZIPR model to calculate the ozone precursors in SPMA.

Ethanol was among the VOCs with the highest concentration during 2011 and 2012, specially during spring and autumn. According to global emission estimates, plants release three times more ethanol than anthropogenic sources. However, measurements of 13C/12C isotope ratios conducted in the urban air of Miami (Florida, USA) showed that 74.9% of the atmospheric ethanol emissions came from manmade biofuels (Giebel *et al.*, 2011). Considering the environmental conditions in the SPMA, it is logically assumed that the vehicular emissions are greater than biogenic ones, possibly even greater than Miami's due to the increased vehicular emissions. 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). In this study, formaldehyde and acetaldehyde were also present in relatively higher concentrations. Similar results were obtained by Corrêa *et al.* (2010), in a five-year campaign in Rio de Janeiro city. Ethanol vehicles emit more aldehydes than gasoline vehicles. The formaldehyde/acetaldehyde concentration ratio found in this study was 0.75, with no important seasonal fluctuations. Such low ratio is due to the consumption of ethanol as fuel, as its combustion releases more acetaldehyde than formaldehyde. Acetaldehyde is a precursor for peroxyacetyl radical and peroxyacetyl nitrate (PAN). So, an increase in ethanol use leads to increased PAN levels, as has been verified in other studies in Brazil (Tanner *et al.*, 1988; Grosjean *et al.*, 1990; Keim *et al.*, 2008). Currently in the SPMA the majority of vehicles in use are flex-fuel vehicles. The fact that Brazilian gasoline already contains 25% anhydrous alcohol guarantees a very significant portion of its annual consumption.

The aldehydes represented 35.3% of the VOCs measured, followed by ethanol (22.6%), aromatics (15.7%), alkanes (13.5%), acetone (6.8%), alkenes (6.0%) and alkadienes (less than 0.1%).

Main Ozone Precursors

The OZIPR model was run separately for each season. Average CO, NO_x and VOCs concentrations between 7 to 9 a.m., and hourly average data (from 6 a.m. to 6 p.m.) of temperature, pressure and relative humidity were used as model input. Hourly CO, VOC and NO_x emissions were based on information from the CETESB inventory, and took in account the hourly distribution of traffic congestions (Branco and Branco, 2007; CETESB, 2013; CET, 2014). The initial concentrations (7 to 9 a.m.) of CO, NO_x and

Table 1. Average VOC concentrations separated by seasons during 2011/2012.

VOC	Spring	Summer	Autumn	Winter
	ppb			
Ethanol	30.67	44.61	22.42	47.43
Acetaldehyde	35.6	27.58	23.38	23.44
Formaldehyde	26.3	19.84	17.68	17.23
Acetone	7.74	11.76	11.68	12.35
Propane	4.82	4.87	5.69	6.86
Ethene	4.88	4.18	4.76	5.56
Ethane	4.43	1.72	1.63	4.15
Butane	2.55	2.91	3.06	3.24
1-Ethyl-4-methylbenzene	3.15	3.09	2.62	2.56
1,2,4-trimethylbenzene	2.40	2.41	2.44	2.49
Propionaldehyde	1.71	2.54	2.43	2.89
1,3,5-Trimethylbenzene	2.31	2.31	2.40	2.32
1-Ethyl-3-methylbenzene	2.34	2.35	2.30	2.32
1,2,3-Trimethylbenzene	2.29	2.27	2.27	2.34
1-Ethyl-2-methylbenzene	2.29	2.28	2.28	2.30
Propylbenzene	2.28	2.19	2.19	2.26
Butiraldehyde	1.68	2.23	2.05	2.06
Toluene	2.26	1.78	1.51	2.35
Isopentane	1.46	1.65	1.68	2.34
p-Xylene	1.61	1.60	1.60	1.74
1-Butene	1.67	1.45	1.48	1.71
o-Xylene	1.62	1.48	1.50	1.54
m-Xylene	1.46	1.44	1.48	1.57
Propene	1.16	1.55	1.34	1.70
Ethylbenzene	1.45	1.27	1.35	1.50
Isobutane	1.21	1.18	1.02	1.32
Acroleine	0.53	1.06	1.16	1.47
Pentane	0.73	0.97	0.83	1.12
2-Methyl heptane	0.79	1.00	0.79	0.82
Octane	0.85	0.86	0.81	0.84
Decane	0.81	0.81	0.80	0.84
Undecane	0.87	0.73	0.70	0.78
Benzaldehyde	0.56	0.60	0.60	1.29
Trans-2-butene	0.47	0.60	0.69	0.71
Cis-2-butene	0.44	0.52	0.45	0.63
Benzene	0.45	0.46	0.31	0.59
Hexane	0.35	0.52	0.30	0.56
3-hexene	0.34	0.30	0.32	0.49
Heptane	0.32	0.33	0.34	0.41
2-Methylpentane	0.27	0.32	0.25	0.41
Methyl cyclohexane	0.28	0.33	0.30	0.34
2-Methyl hexane	0.27	0.28	0.25	0.34
Cyclohexane	0.36	0.17	0.23	0.36
3-Methyl hexane	0.26	0.27	0.25	0.35
cis-1,3-Dimethylcyclopentane	0.20	0.24	0.18	0.21
2,3-Dimethylpentane	0.21	0.20	0.17	0.23
Pentene	0.08	0.16	0.08	0.21
1,1-Dimethylcyclopropane	0.06	0.09	0.08	0.10
1,2-Dimethylcyclopropane	0.08	0.08	0.07	0.09
Isoprene	0.06	0.08	0.06	0.06
Trans-2-pentene	0.07	0.05	0.06	0.07
3-Methylpentane	0.05	0.06	0.05	0.07
Cis-2-pentene	0.05	0.06	0.05	0.05
Cyclopentane	0.04	0.06	0.05	0.05

VOC for spring, summer, autumn and winter seasons of 2011/2012 are presented in Table 2.

Hourly average data for temperature and relative humidity are presented in Table 3. Mixing height values from 6 a.m. to 6 p.m. were obtained from Lidar observations and adjusted based on Orlando *et al.* (2010). In the adjustment, the characteristics of each season were considered, including their temperature variations, so the maximum value was raised to 2000 m, as shown in Table 4.

The input values used were retrieved from SPMA annual CO emissions (160,610 tons year⁻¹) published at the Air Quality Report of 2012 by CETESB, and spatial distribution of the urbanized area (2,209 km²) according to the Brazilian Institute of Geography and Statistics (IBGE, 2015). The conversion factor was obtained, as per Eq. (15), assuming that the duration of effective vehicle circulation is about 16 daily hours, while CO emissions occur on 304 days per year (Sundays and holidays are ignored, due to decreased vehicle circulation). In order to obtain these values, the annual CO emission estimated by CETESB was taken into account from the Air Quality Report of 2012. According to this report, 160,610 tons of CO are emitted per year in the SPMA.

$$160610 \frac{\text{t}}{\text{year}} \cdot 1000 \frac{\text{kg}}{\text{t}} \cdot \frac{1}{2,209 \text{ km}^2} \cdot \frac{1 \text{ year}}{304 \text{ days}} \cdot \frac{1 \text{ day}}{16 \text{ h}} \quad (15)$$

$$= 15 \text{ kg km}^{-2} \text{ h}^{-1}$$

The same method was used to calculate the hourly NO_x and VOCs emissions. For NO_x hourly emission calculation, we use the data from the PROCONVE reports inventory (of 139 thousand tons year⁻¹; Branco and Branco, 2007), as

the model did not reproduce the measured concentration using the CETESB input data, with simulated values of less than half the observed values. For VOCs we use 35.37 thousand tons/year (CETESB, 2013). The emission input values for CO, NO_x and VOC were in kg km⁻² h⁻¹ units.

The temporal distribution of CO, VOC and NO_x emissions were obtained from the SPMA vehicle congestion mileage provided by the Traffic Engineering Company (CET) during the campaign period. Table 5 shows the km of congestion and distribution of CO, NO_x and VOC. The same emissions were used for the different seasons of the year.

Fig. 3 presents the simulated and observed CO values for each season during 2011/2012. The first adjustment of the model uses CO data, as this pollutant is a less reactive compound. After adjusting the simulated CO profile using the mean observed data, the NO_x and O₃ profiles were also adjusted. In this stage, an adjustment was made in the NO_x and VOCs hourly emissions, in order to reproduce results closer to the measured values, while at the same time keeping the daily average of 13 and 3.0 kg km⁻² h⁻¹, for NO_x and VOCs, respectively. The same distributions were used during the different seasons of the year. Adjustments were also made to the deposition rates and mixing height profile, as explained previously (Table 4). Figs. 4 and 5 show the results for observed and simulated values for NO_x and O₃. Next, we validated our model by comparing simulated values to the experimental observed results. We then estimated O₃ concentration changes (in %) by performing simulations decreasing CO, VOCs and NO_x emissions independently and/or in tandem for each season (Table 6).

Results suggest that the most effective strategy to reduce urban ozone during all seasons would be to decrease VOCs emissions (Table 6). To attain a reduction of 3–7% of O₃, a

Table 2. Initial concentrations of VOC, NO_x and CO for each season of 2011/2012.

Compound	Spring	Summer	Autumn	Winter
VOC – ppmC	0.74	0.74	0.67	0.79
NO _x – ppm	0.04	0.06	0.04	0.07
CO – ppm	0.47	0.36	0.30	0.45

Table 3. Temperature and relative humidity hourly average values during 2011/2012.

Hour	Spring		Summer		Autumn		Winter	
	RH %	T °C	RH %	T °C	RH %	T °C	RH %	T °C
6:00	90	17.2	92	19.6	96	16.9	92	14.4
7:00	87	18.1	90	20.3	92	17.1	92	14.3
8:00	82	19.3	85	21.5	95	18.0	87	15.5
9:00	76	20.7	78	22.7	87	19.1	81	16.8
10:00	70	22.1	72	24.1	81	20.4	75	18.4
11:00	66	23.2	67	25.3	76	21.6	68	19.9
12:00	62	24.1	64	26.1	72	22.5	62	21.3
13:00	76	24.6	62	26.7	68	23.2	58	22.1
14:00	62	24.6	63	26.6	67	23.5	55	22.6
15:00	66	23.7	66	26.0	68	23.5	56	22.6
16:00	70	22.7	72	24.8	72	22.6	59	22.2
17:00	74	21.7	78	23.8	79	21.1	64	21.1
18:00	78	20.6	81	22.8	85	19.7	71	19.5

Table 4. Mixing height hourly average values for 2011/2012.

Hour	Spring	Summer	Autumn	Winter
	M			
6:00	300	425	350	350
7:00	400	550	400	400
8:00	400	600	400	400
9:00	550	700	450	450
10:00	1000	850	900	750
11:00	1350	1450	1500	1350
12:00	1600	1700	1750	1500
13:00	1700	1900	1800	1600
14:00	1750	1950	1850	1650
15:00	1650	1950	1850	1700
16:00	1550	1800	1650	1450
17:00	1150	1600	1350	1150
18:00	750	1400	950	800

Table 5. CO, NO_x and VOCs hourly emissions and traffic congestion (km) during 2011/2012.

Hour	km	CO	NO _x	VOC
6:00	2.0	3	4	1.0
7:00	4.3	5	7	1.5
8:00	10.1	14	11	2.8
9:00	17.6	25	15	4.0
10:00	20.1	23	16	4.5
11:00	15.7	15	14	3.7
12:00	12.4	12	13	2.8
13:00	8.5	12	12	1.8
14:00	7.2	12	12	1.6
15:00	8.0	13	13	1.6
16:00	9.3	15	14	1.9
17:00	12.4	18	15	2.4
18:00	16.1	23	17	3.2

decrease of nearly 30% in VOCs would be required. Similarly, a reduction of 4–7% of O₃ can be achieved, if 30% reductions in CO and VOC can be achieved simultaneously, while the current levels of NO_x are maintained. In contrast, a decrease in NO_x would lead to an increase in O₃ concentrations, a finding that is consistent with results obtained in other study in the SMPA using the WRF/Chem model (Chiquetto *et al.*, 2015).

However, decreasing all VOCs by the selected percentage values shown in Table 6 resulted in no significant

reduction of O₃ levels. A 30% decrease in O₃ was obtained when aldehydes were selectively removed to assess ozone formation. Starting with the spring scenario, reducing acetaldehyde to a negligible concentration in the atmosphere resulted in ozone concentrations that were 16% lower. Doing the same with acetaldehyde and formaldehyde, and decreasing the concentrations of both VOCs by 22%, a 26% decrease was observed in ozone. The decrease of all aldehydes for the other seasons resulted in a reduction of 30% in the ozone concentration during summer, 28% in the winter and 25% in the autumn.

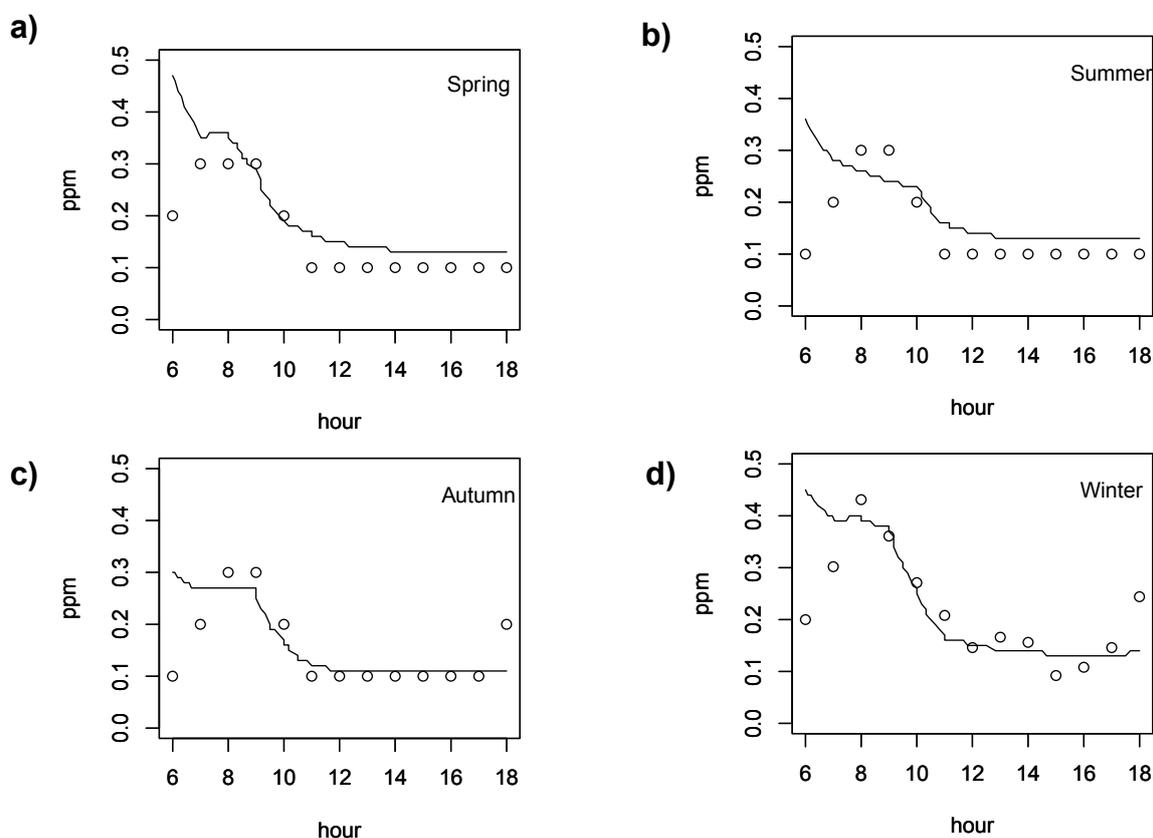


Fig. 3. CO simulated (solid line) and experimental observed values (open circles) for each season of 2011/2012.

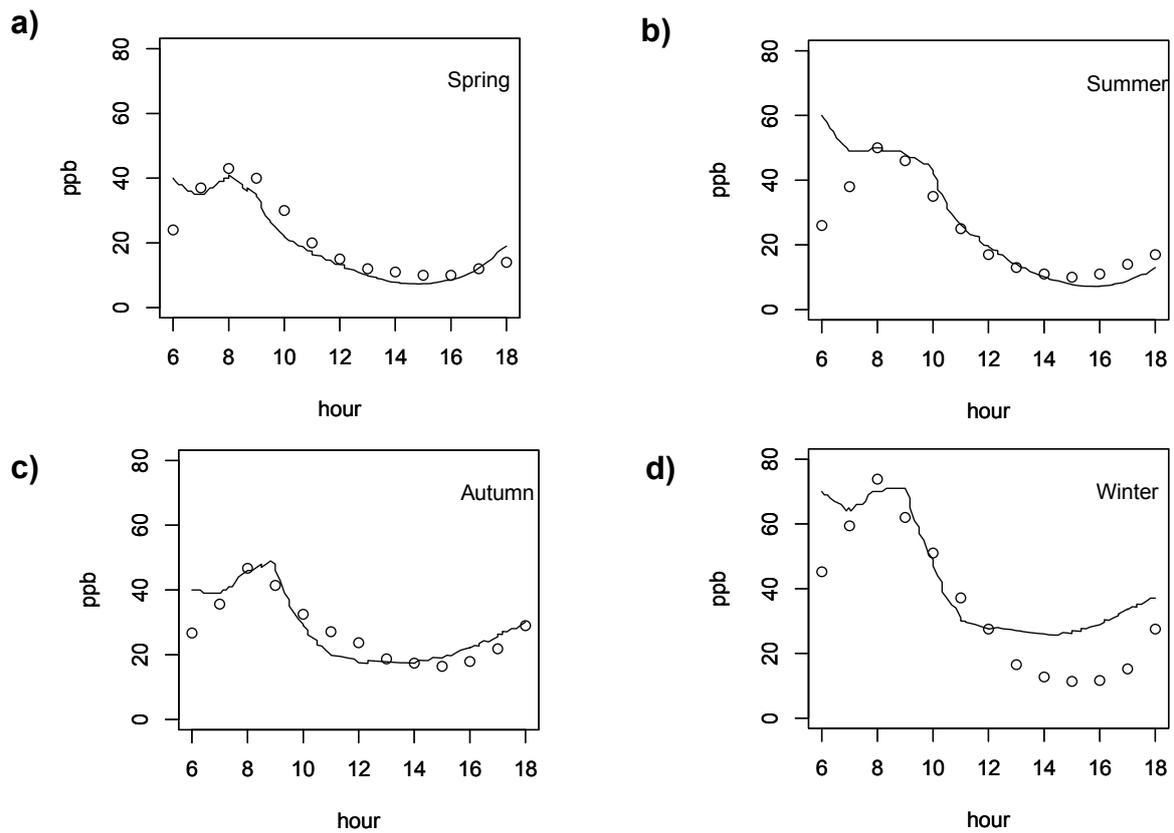


Fig. 4. NO_x simulated (solid line) and experimental observed values (open circles) for (a–d) each season of 2011/2012.

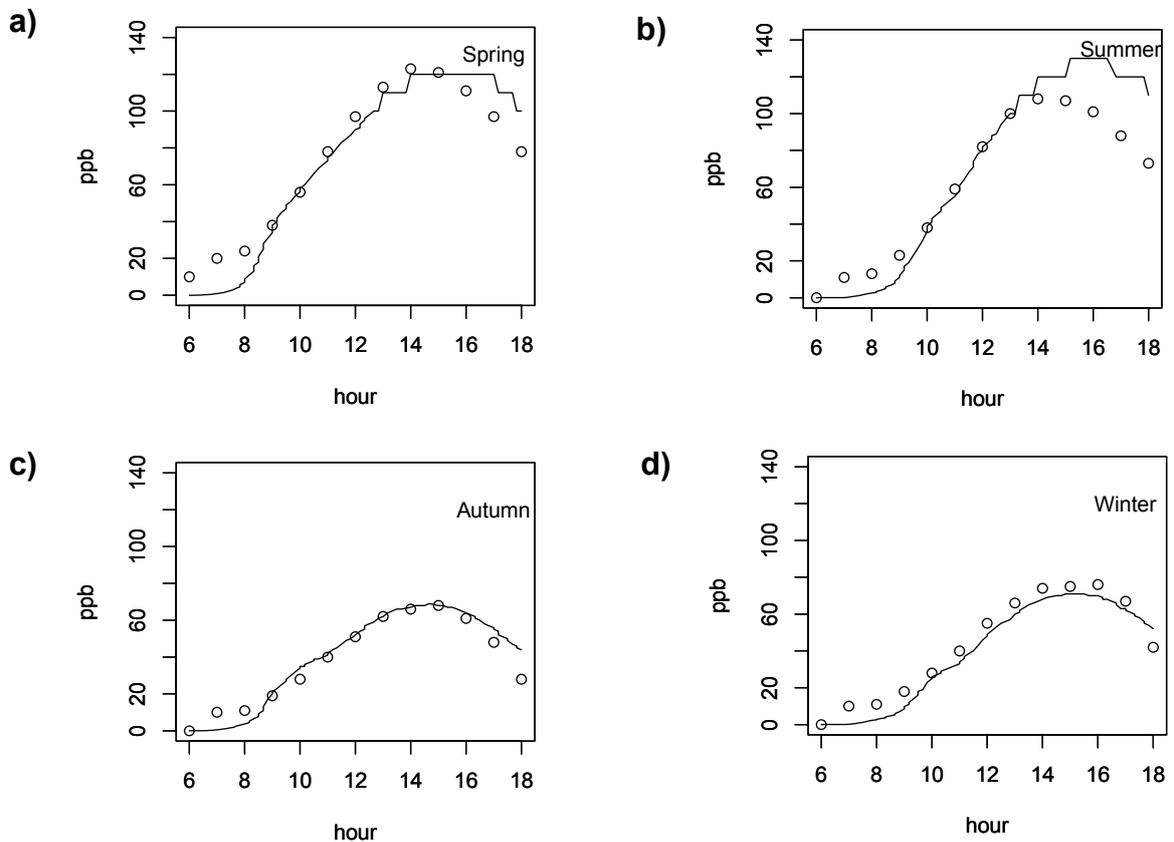


Fig. 5. O₃ simulated (solid line) and experimental observed values (open circles) for (a–d) each season of 2011/2012.

Table 6. Changes in ozone concentration due to hourly emission reductions of CO, VOCs and NO_x for each season of 2011/2012.

Season	Emission Reduction	O ₃ changes (%)					
		CO	VOC	NO _x	CO + VOC	CO + NO _x	VOC + NO _x
Spring	5%	0.2	−1.4	3.2	−0.3	3.0	3.3
Summer		0.2	0.8	2.9	0.4	3.1	3.1
Autumn		−0.01	−0.8	4.7	−1.0	3.9	3.9
Winter		−0.3	−0.8	4.8	−0.7	5.3	4.4
Spring	10%	−2.3	−2.6	3.8	−2.4	3.8	2.0
Summer		−3.9	0.1	3.9	−0.4	3.7	2.8
Autumn		−4.3	−0.1	6.4	−1.0	6.5	5.2
Winter		−3.9	−1.5	6.8	−1.3	6.5	5.0
Spring	20%	−1.2	−5.0	7.5	−5.8	7.0	3.5
Summer		−0.3	−3.2	6.8	−3.5	6.6	4.1
Autumn		−0.9	−4.3	13.8	−4.5	14.3	11.4
Winter		0.1	−3.8	14.8	−3.9	14.7	11.6
Spring	30%	−0.7	−6.5	9.2	−7.3	7.9	6.0
Summer		−0.7	−3.0	7.3	−3.6	6.9	5.1
Autumn		−0.4	−5.3	19.7	−5.2	19.3	17.1
Winter		−0.6	−4.8	21.9	−5.1	21.0	18.3

With the output data from the simulations, it was possible to calculate ozone isopleths (Fig. 6) for each season of the year. The VOCs/NO_x ratio is important in the behaviour of the VOCs-NO_x-O₃ system. Moreover, it has a major effect on how reductions in VOCs and NO_x affect ozone concentrations. Fig. 6 supports the results presented above, showing that in the isopleth region where ozone concentration values are found in these simulations, VOCs and O₃ are positively correlated, and a decrease in VOCs in the SPMA would lead to surface ozone depletion.

The NO_x-limited region is typical of locations downwind of urban and suburban areas, whereas the VOC-limited region is typical of highly polluted urban areas as the SPMA. The VOCs/NO_x ratios found during this study for spring, summer, autumn and winter were 4, 3, 3 and 2, respectively. In places with an abundance of NO_x in relation to VOCs, the VOC/NO_x ratio is low and ozone formation will be dependent on the VOCs concentration. In the literature, ratios of 8 to 15 characterize intermediate locations, where both VOCs and NO_x control are effective in decreasing O₃ levels. Ratios above 15 are considered NO_x-limiting (Finlayson-Pitts and Pitts, 2000; Kumar *et al.*, 2008). Table 7 shows the increase in reactivity of the VOCs found ordered by the ozone formation potential.

Table 7 shows that the VOC compounds are more reactive during summer and spring due to the greater availability of solar shortwave radiation on surface atmospheric levels. During summer, we found 29 compounds with positive IR, while there were 26 in spring, 23 in winter and 21 in autumn. We hypothesise that the higher VOCs concentration in winter compared to autumn could be attributed to the stronger atmospheric stability during the winter season. Considering only the mean of the positive IR increases, the aldehydes group represented 32.7% of the ozone formation, aromatics (25.4%), alkenes (22.5%), alkanes (17.5%) and alkadienes (e.g., isoprene; 1.9%). The IR increase for ethanol was negative, while acetone had a positive IR only

during winter. Fig. 7 shows the average positive IR for all seasons, for the 19 main ozone precursors found examined in this study.

Another calculation to estimate ozone forming potential is multiplying IR by its concentration in the atmosphere (Table 8). Considering the results from Table 8, acetaldehyde was responsible for the formation of 61.2% of the ozone in SPMA in 2011/2012. Aldehydes accounted for 74% of the ozone formation, followed by aromatics with 14.5%, alkenes with 10.2%, alkanes with 1.3% and alkadienes (e.g., isoprene) with 0.03%. Although alkanes represent 13.5% in terms of mass in the atmosphere, they accounted for only 1.3% of the ozone formation, due to their low reactivity. These results are relevant, as they effectively show the main VOCs that influence ozone formation in the SPMA.

VOC compounds such as propane, octane, 2-methyl heptane are associated with ozone depletion. This is due to the fact that these compounds are saturated, and so, less reactive. The understanding of the SAPRC mechanism suggests that this decrease in O₃ levels occurs not because these compounds interfere with the production of this pollutant, but rather because an increase in the concentration of a low-reactive VOC decreases the fraction relative to the more reactive ones.

Silva *et al.* (2016) published a similar work for Rio de Janeiro Metropolitan Area (RJMA) during July and October of 2013, and the results indicated that acetaldehyde, formaldehyde and toluene were the main ozone precursors. Martins *et al.* (2015) published a work in the RJMA using data for 2012 and 2013 that identified a similar pattern in the ozone forming potential for aldehydes. They also assessed that O₃ levels are higher during weekends due to a reduction in NO emissions by diesel heavy vehicles, leading to a decrease on ozone removal by titration. Silva *et al.* (2016) monitored 43 VOCs in the Botanical Garden of Rio de Janeiro. Concentrations ranged from 43.52 to 168.75 μg m^{−3}, with isoprene representing 4–14% of the

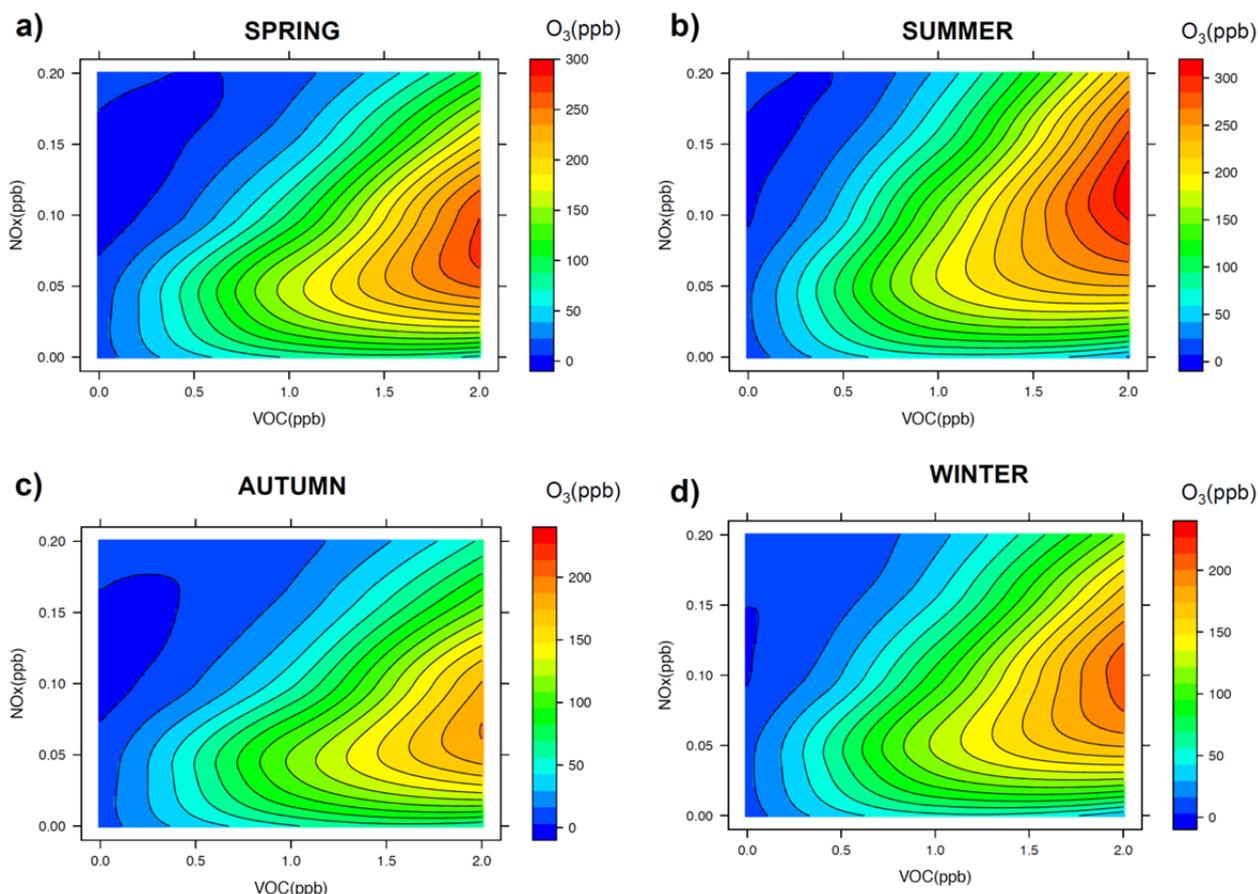


Fig. 6. (a–d) Ozone isopleths (ppb) for different levels of VOC and NO_x during 2011/2012.

total VOC mass. Although alkanes were the most abundant class in terms of mass, alkenes, aromatics and isoprene were the most significant classes, considering kinetic and mechanistic reactivity.

In our previous survey work in the SPMA, Alvim *et al.* (2017), using 2008 data, we showed that the main ozone precursors were formaldehyde (42.8%), acetaldehyde (13.9%), ethene (12.2%), propene (5.1%), 1-methyl cyclopentene (3.0%), p-xylene (2.4%), 1-butene (2.1%), trans-2-pentene (1.9%), 2-methyl 2-butene (1.7%) and trans-2-butene (1.6%). Alkanes represented 46% of the total VOC mass distribution followed by alkenes (27%), aromatics (14%), alkadienes (1%) and aldehydes (12%). Total aldehydes accounted for 57% of the ozone formation in 2008 and 74% in 2011/2012, indicating an increase in the importance of these VOCs in the ozone formation in the SPMA. Aromatics also increased in ozone formation potential, from 10% to 14.5%. However, a decrease in the importance of alkenes was found: in 2008, they were responsible for 32% of ozone formation, compared to 10% in 2011/2012. Comparing the studies of 2006/2008, and 2011/2012, the composition of the atmosphere in the SPMA has undergone important changes. Consumption of ethanol increased by 64%, gasoline 23% and diesel increased by 25%. The emission of VOCs, CO and NO_x depend on the quality of fuels and vehicles (deterioration, etc.) that will directly affect the efficiency of fuel combustion and

other factors. Another negative aspect is the increase of aromatics in the atmosphere, related to the increase of this class in the composition of gasoline. According to the 309/01 ordinance of the National Agency of Petroleum, Natural Gas and Biofuels (ANP), the aromatic content for common and premium C gasoline (gasool) is 45%, and, specifically for benzene, the allowed content is 1% for gasoline C and 1.5% for premium gasoline. The increase in ethanol use from 2006 to 2011/2012 might have also influenced a fivefold increase (409%) in the concentrations of aldehydes, which are the main precursors of ozone, followed by more than a threefold increase (252%) in the aromatics class, probably due to the increase of these compounds in the gasoline composition and in the fuel usage in general. The aromatics class is the second most reactive for the formation of O_3 in the SPMA. Aldehydes and aromatics, besides resulting in high ozone formation potential, are also reactive for the formation of secondary organic aerosols (SOA) (Dechapanya *et al.*, 2003; Suarez-Bertoa *et al.*, 2015). SOA are a major component of fine particle pollution ($\text{PM}_{2.5}$), which has been found to cause lung and heart problems, are associated to genotoxic risks, among other health effects (Kumar *et al.*, 2008; Cai *et al.*, 2015; Newby *et al.*, 2015). Changes in VOCs, because of their complex chemical interactions, also lead to changes in a variety of other pollutants associated with ozone, such as peroxyacetyl nitrate, nitrogen dioxide, and aerosol

particles. Some of these pollutants have known harmful effects on human health and welfare. Hence, it is important to recognize that control strategies implemented for ozone will simultaneously affect other species. These results are

important in determining which processes are most likely associated with ozone production in the SPMA over time and the future trends that would be expected if no changes in policy are enacted.

Table 7. VOC Incremental Reactivity results for each season of 2011/2012.

VOC	Spring	Summer	Autumn	Winter
but-1-ene	0.4218	0.0883	0.4359	0.1135
Butiraldehyde	0.4184	0.1970	0.3539	0.0567
Acetaldehyde	0.4252	0.2208	0.2683	0.1072
Propionaldehyde	-0.0748	0.3906	0.2347	0.2018
Propene	0.2313	0.2615	-0.0484	0.2301
n-heptane	0.5714	0.0374	0.1080	-0.2837
3-methyl hexane	0.5714	0.0374	0.1080	-0.2837
Methylcyclohexane	0.5714	0.0374	0.1080	-0.2837
Benzene	0.3129	0.1800	-0.2273	0.0883
1,2,4-trimethylbenzene	0.3163	-0.0679	0.0484	0.0536
1,2,3-trimethylbenzene	0.3163	-0.0679	0.0484	0.0536
1,3,5-trimethylbenzene	0.3163	-0.0679	0.0484	0.0536
c9 benzene disubstituted	0.3163	-0.0679	0.0484	0.0536
n-propylbenzene	0.1905	-0.1834	0.1714	0.0378
2-methyl hexane	0.3367	0.0374	0.1080	-0.2837
ethene	0.3095	0.1698	-0.2198	-0.0631
Isoprene	0.0816	0.0476	0.0931	-0.0599
Toluene	0.0238	-0.0136	0.1118	0.0315
Ethylbenzene	0.0000	0.0272	-0.0522	0.0788
Cyclohexane	-0.0272	0.0102	0.1006	-0.1198
1,3-dimethylcyclopentane	0.1156	0.0374	-0.0633	-0.1482
cis-2-butene	0.2177	-0.2412	-0.1639	0.0914
trans-2-butene	0.2177	-0.2412	-0.1639	0.0914
p-xylene	-0.2789	0.1427	-0.1118	0.1135
o-xylene	-0.2789	0.1427	-0.1118	0.1135
m-xylene	-0.2789	0.1427	-0.1118	0.1135
isobutene	0.1905	-0.0408	-0.2161	-0.1702
n-butane	0.1905	-0.0408	-0.2161	-0.1702
cyclopropane branched	-0.2891	0.2751	-0.2645	-0.0126
2-methylpentane	0.2857	-0.0034	-0.3614	-0.2144
n-hexane	0.2857	-0.0034	-0.3614	-0.2144
3-methylpentane	-0.0442	0.1562	-0.2459	-0.1797
trans-3-hexene	-0.5544	0.0442	0.0298	0.0631
Cyclopentane	-0.3741	0.2072	-0.2645	-0.0126
2,3-dimethylpentane	-0.3192	0.1732	-0.0633	-0.2837
Isopentane	-0.1735	0.0849	-0.4173	-0.0032
n-pentane	-0.1735	0.0849	-0.4173	-0.0032
Acetone	-0.3129	-0.0849	-0.2012	0.0441
trans-2-pentene	-0.8027	0.2683	0.0335	-0.1009
1-pentene	0.1531	0.1970	-0.9970	0.0032
n-decane	-0.4898	-0.1800	-0.1006	0.0158
Ethane	-0.5510	0.2004	-0.1565	-0.2648
2-methyl heptane	-0.1156	-0.2004	-0.2943	-0.1702
n-octane	-0.1156	-0.2004	-0.2943	-0.1702
Ethanol	-0.5510	-0.0306	-0.0708	-0.1702
Formaldehyde	-0.4218	-0.7711	0.0931	0.2333
Acroleine	-0.5510	0.0476	-0.1565	-0.2806
cis-2-pentene	-0.8027	-0.0815	0.0335	-0.1009
Benzaldehyde	-0.4218	-0.0442	-0.2757	-0.2491
Propane	-0.5510	-0.0306	-0.1565	-0.2648
n-undecane	-1.1054	-0.1393	0.2906	-0.1293

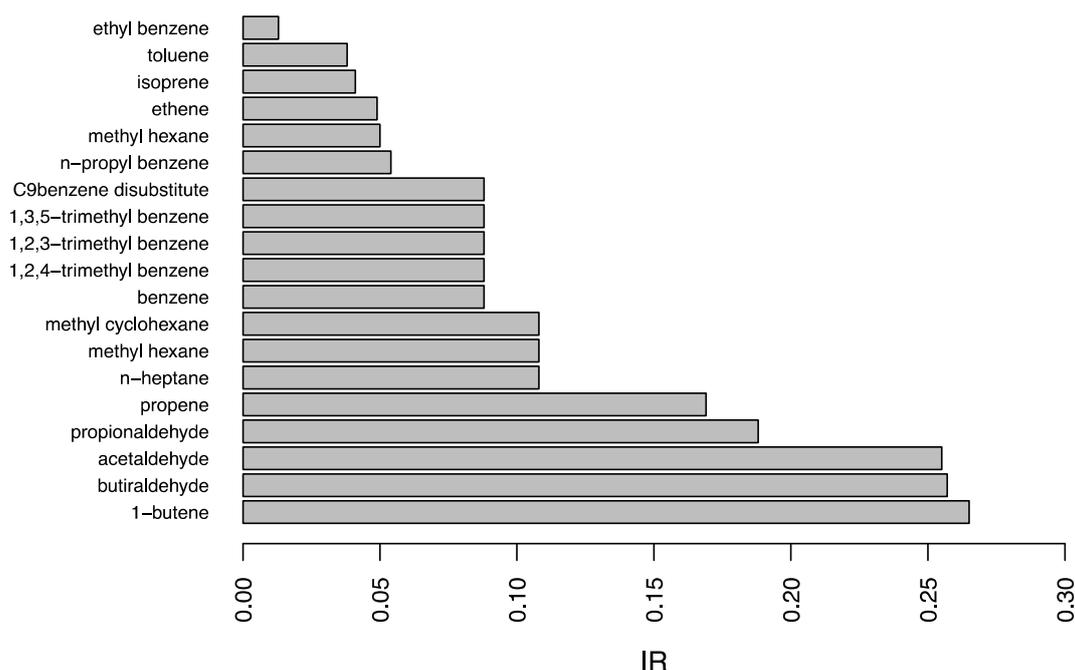


Fig. 7. IR for the main 19 ozone precursors between 2011/2012.

Table 8. The role of the main VOCs on ozone formation in the SPMA during 2011/2012.

VOC	Conc. × IR	% O ₃ formation
Acetaldehyde	5.40	61.2
propionaldehyde	0.61	6.92
butiraldehyde	0.52	5.85
1-butene	0.42	4.74
C9 benzene disubstituted	0.40	4.59
Propene	0.24	2.75
Ethene	0.24	2.70
1,2,4-trimethylbenzene	0.21	2.41
1,3,5-trimethylbenzene	0.20	2.32
1,2,3-trimethylbenzene	0.20	2.27
n-propyl benzene	0.12	1.37
Toluene	0.08	0.86
Benzene	0.04	0.45
n-heptane	0.04	0.43
methyl cyclohexane	0.03	0.38
3-methyl hexane	0.03	0.34
ethyl benzene	0.02	0.21
2-methyl hexane	0.01	0.16
Isoprene	0.003	0.03

CONCLUSIONS

The objective of this work was to analyse the reactivity of VOCs in the atmosphere of the SPMA and determine the major O₃ precursors using the OZIPR trajectory model and the SAPRC chemical mechanism. 66 samples of hydrocarbons, 62 of aldehydes and 42 of ethanol were collected during the period from September 2011 to August 2012, from 7:00 to 9:00 a.m. Samples were analysed and, together with meteorological data, used as model input.

The 10 most abundant VOCs in the SPMA atmosphere

were ethanol, acetaldehyde, formaldehyde, acetone, propane, ethane, ethane, butane, 1-ethyl-4-methyl benzene and 1,2,4-trimethylbenzene. The aldehydes represented 35.3% of the VOCs analysed, followed by ethanol (22.6%), aromatics (15.7%), alkanes (13.5%), acetone (6.8%), alkenes (6.0%) and alkadienes (less than 0.1%). The total aldehydes accounted for 74% of the ozone formation, followed by aromatics (14.5%), alkenes (10.2%), alkanes (1.3%) and alkadienes (e.g., isoprene; 0.03%). Comparing these results with 2008 data, the importance of aldehydes has increased from 57% to 74%, which can be associated with increased ethanol use in the SPMA. Since global ethanol production has almost doubled from 2007 to 2014, the findings in this work are an important indicator of what to expect in terms of the air quality in megacities, should the trend of using plant-based fuels continue to increase globally (Scovronick *et al.*, 2016).

Multidisciplinary studies and regulatory actions must be undertaken in order to reduce unburned ethanol emissions from vehicles as well as acetaldehyde emissions, as reducing all the aldehydes to a negligible concentration in the atmosphere results in a reduction of approximately 30% in ozone concentrations. Controlling the ozone in the SPMA by reducing VOC concentrations can also affect the concentrations of many secondary pollutants formed in VOC-NO_x mixtures, some of which are hazardous to human health, plants or materials. It is thus important to recognize that changes in other secondary pollutants will occur concurrently with ozone control. Some studies could assess fuel injection technologies, cylinder geometry and after-treatment processes, such as the design of a new generation of catalysts to reduce emissions in flex-fuel vehicles. Using a catalyst or another technology that is able to convert aldehydes into CO₂ or other less reactive VOCs would be an effective strategy for decreasing the

ozone formation potential in areas polluted by VOCs in the atmosphere. Developing different transport models, mainly public transit without fuel burning, such as a subway system, would also be effective, due to the hazardous emissions produced by both fossil fuels (with higher emission factors of CO and NO_x) and plant-based fuels (with higher emission factors of VOCs). Nevertheless, more research should be performed using atmospheric and chemical models in order to improve our understanding of VOC-polluted atmospheres in megacities.

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