Ozone precursors for the São Paulo Metropolitan Area

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ABSTRACT

Ozone represents the main atmospheric pollutant in the São Paulo Metropolitan Area (SPMA). In this region, its concentration exceeds the national air quality standards for several days out of the year. Ozone is a secondary pollutant and is a product of VOCs, NO_x, and sunlight. Thus, it is very difficult to elaborate efficient strategies for its reduction. Computational simulations may provide an interesting alternative to evaluate the many factors that affect ozone formation. In this study, the trajectory model OZIPR was used together with the SAPRC chemical mechanism to determine the incremental reactivity scale for VOCs in the SPMA. VOC input data were obtained from two campaigns that were performed in the studied area in 2006. Values for CO, NO_x, and meteorological parameters were obtained by automatic monitors. Five base-cases were created to verify the variation in maximum ozone concentration and thus determine the ozone formation potential of each VOC. NO_x and VOC emissions were independently and simultaneously reduced by 5, 10, 20, and 30% to verify variations in ozone formation. With the simulator output data, ozone isopleths charts were generated for the city of São Paulo. Analysis of the obtained results shows that the most frequent compounds found among the ten main ozone precursors in São Paulo, using the reactivity scales created from the five base-cases, were: formaldehyde, acetaldehyde, propene, isoprene, cis-2-butene, and trans-2-butene, with formaldehyde being always the main ozone precursor compound. The simulations also show that an efficient strategy to decrease ozone concentrations in the SPMA would be to reduce total VOC emissions. The same strategy is not possible for NO_x, as the reduction of these pollutants would increase ozone concentrations.

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1. Introduction

Human activities have been changing the chemical composition of the Earth's atmosphere by emitting various pollutants, especially in urban and industrial areas. Many of the compounds released into the atmosphere affect both the environment and human health. The emission of nitrogen oxides (NO_x) and sulphur dioxide (SO_2) causes acid deposition, chlorofluorocarbons (CFCs) destroy the ozone layer, carbon dioxide (CO_2) contributes to global warming, and hydrocarbons include known carcinogenic compounds. Another pollutant commonly found in urban atmospheres is ozone (O_3), which can be damaging to human health and is also a greenhouse gas. Although ozone affects healthy people, it is more harmful to children, elders, and people with cardiorespiratory conditions. Ozone also destroys agricultural crops, due to its ability to attack plant chloroplasts, which are responsible for plant respiration. Ozone reacts with ethylene gas emitted by plants, generating free radicals that cause damage to plant tissues and consequently decreasing photosynthesis. In ozone-rich regions throughout the world, losses in agricultural crops have been

recorded. In urban atmospheres, such as the São Paulo Metropolitan Area (SPMA), vehicular pollution is responsible for 97% of the pollutants (CETESB, 2007). For a long time, people believed that mobile sources produced less pollution than stationary ones. This belief was proven wrong in the mid-1980s, when inventories indicated that vehicles were the major source of atmospheric pollutants in large cities (Corrêa, 2003).

The Brazilian program called PROCONVE (Program for Controlling Air Pollution from Motor Vehicles) has, since 1988, managed to reduce light vehicle emissions, although the vehicle fleet has grown considerably since the 1980s. As can be observed in Fig. 1, the SPMA fleet has doubled in a period of 14 years.

According to CETESB (Environmental Agency of São Paulo), technological improvements made in vehicles, associated with the combustion process and use of catalysts, in addition to improvements in fuel quality, have managed to offset the large increase in the vehicular fleet, regarding the emission of air pollutants.

It is important to remember that, despite the substantial reduction in emissions, days in which ozone levels in the SPMA exceed national standards for air quality are still common (CETESB, 2008). From 1999 to 2007, while the number of days when carbon monoxide (CO) exceeded the standard in the SPMA decreased from 18 to 0, the number of days that O_3 exceeded the limits (1 h: 160 µg m^{-3},

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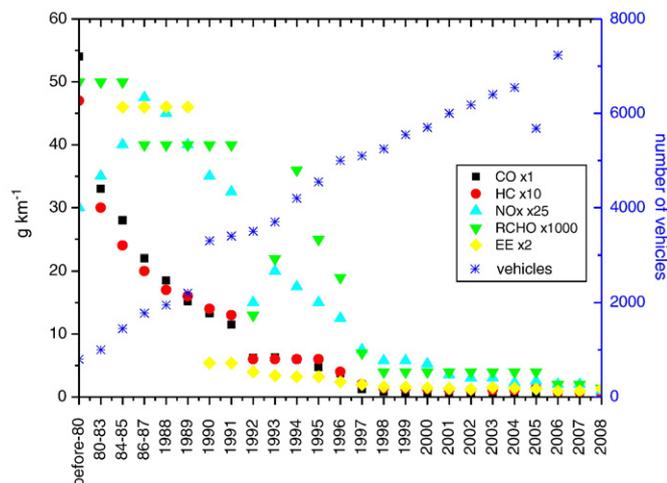
Fig. 1. Vehicular fleet and main pollutants emission (g km^{-1}) evolution for SPMA, as CO, NO$_x$, RCHO (aldehydes), and evaporative emission (EE).

attention level: 200 μg m^{-3}) decreased from 109 to 72. In other words, despite a reduction in most of the pollutants, the reduction in O$_3$ was not significant.

Given the difficulty of reducing ozone levels in the SPMA, as well as in other large cities, it is necessary to perform a detailed study concerning the main ozone precursors. This study could support the development of guidelines in an attempt to minimise this problem.

The SPMA is located at 23°S and 46°W in southeastern Brazil. It has an area of 8051 km^2 with a population of over 19 million, who are erratically distributed throughout an urbanised area of 1747 km^2. The urban site is located in the sedimentary basin of São Paulo, which is the main valley of the Tietê River, in the east–west direction. This area has an average altitude of 720 m and is an extensive flood plain. The basin is surrounded by the Serra da Cantareira in the north, as well as in the east–west direction, with altitudes reaching up to 1200 m. On the southeastern side, the basin is bordered by the Serra do Mar, which has altitudes generally exceeding 800 m. This region is approximately 45 km away from the Atlantic Ocean. The SPMA occupies approximately 0.1% of the Brazilian territory and is the third largest urban conglomerate in the world, accounting for 1/6th of Brazil's economy (CETESB, 2008).

The region has about 2000 industries with high pollution potential and a fleet of approximately 8.4 million registered vehicles (7.0 million Otto-cycle vehicles, 460 thousand diesel vehicles, and 1020 million motorcycles), which corresponds to 1/5th of the national fleet. According to estimates made in 2007, these pollution sources are responsible for the following pollutant emissions, in 1000 tons per year: 1480 CO, 365 hydrocarbons (HC), 339 NO$_x$, 29.5 total particulate matter (PM), and 8.2 sulphur oxides (SO$_x$). As a whole, vehicles are responsible for 97% of CO and HC, 96% of NO$_x$, 40% of PM, and 32% of SO$_x$ emissions (CETESB, 2008).

It should also be noted that Brazil is the only country in the world that has a fleet that uses ethanol on a large scale. This generates a special atmospheric chemical composition, compared to other large cities in the world. In the current SPMA fleet, hydrated-ethanol vehicles represent 11.4% and gasohol (a mixture of 25% ethanol and 75% gasoline) vehicles represent 61%. Considering the anhydrous and hydrated forms, ethanol represents 55.1% of the total fuel consumed on a volume base. Vehicles, such as the "flex-fuel" (bi-fuel) units launched a few years ago, in the market correspond to 10.1%, motorcycles represent 12.1%, and diesel cars represent 5.4% of the fleet. It should also be emphasised that the fleet in the SPMA is quite old. Approximately 49.5% of it is older than 1997 (CETESB, 2008).

The goal of this study was to identify the main ozone precursors in the SPMA, to propose possible strategies to reduce their levels, and

also to verify yearly variances in ozone precursors by season. To perform these studies, pollutant criteria and meteorological data were collected, with the aid of automated monitors, VOCs were sampled and speciated following TO-14 and TO-15 (USEPA, 1999a,b) methodologies, and emission inventories were treated. The input data were processed using an OZIPR trajectory model (Ozone Isoplot Plotting Package) coupled with the SAPRC (Statewide Air Pollution Research Center) chemical mechanism.

2. Methodology

2.1. Modelling studies

Simulation studies were performed using the OZIPR trajectory model coupled to the SAPRC chemical mechanism. The OZIPR trajectory model (Gery and Crouse, 1990) was developed under a contract with the U.S. Environmental Protection Agency (EPA), as a supporting tool for forecasting scenarios of urban pollution. Its main features are:

- It is a relatively simple one-dimensional model, known as a "Box" or trajectory model, which requires data that include initial concentrations, emissions, and meteorological parameters, and has temporal resolution without spatial descriptions of these parameters;
- It allows the use of various chemical mechanisms, including those with a high degree of complexity and detail, within the SAPRC model;
- It has internal mechanisms, such as the EKMA (Empirical Kinetic Modeling Approach), that allow the calculation of pollutant reduction levels in order to meet air quality standards;
- It enables the performance of multiple simulations for different conditions of VOCs and NO$_x$, providing an ozone isopleth plot for different secondary pollutants as a function of these two precursors, making it a useful tool in predicting the development of scenarios and strategies for environmental control.

The OZIPR enables the simulation of complex physical and chemical processes that occur in the urban troposphere, using a trajectory model. The model can be described as an air column that covers the studied area up to the mixture layer of the atmosphere, like a box with a movable lid, which is a function of the mixing layer height during the day. The whole box is considered perfectly homogeneous and moves along the trajectory of the wind, but without horizontal expansion. Emissions from the base of the column are computed and dry and wet deposition can be implemented, together with thermal and photochemical reactions.

In general, the inputs for the simulation are data from the studied area, including: speciation of the VOCs; initial concentrations of NO, NO$_2$, total VOCs, and CO; hourly meteorological data of temperature, pressure, humidity, and mixing layer height; primary emissions, location, and date (to calculate the solar flux); dry and wet deposition coefficients; and the chemical mechanism. The output data are the desired hourly average concentrations of chemical species and the isopleth for secondary pollutants, establishing values for VOCs and NO$_x$.

The SAPRC mechanism was initially developed by Carter in 1990 and was subsequently updated by Carter (1990, 1994, 1995, 1996, 2000), Carter and Atkinson (1996), Carter and Lurmann (1991), and Carter et al. (1997). The structure (text form) and extensive documentation of this mechanism facilitates its use and modification.

The SAPRC is a mechanism that includes thermal and photochemical reactions. In general, it works with approximately 140 reactions and 80 species. Species of low importance and with little information concerning reaction rate and stoichiometry are not treated explicitly within this mechanism. This can also be utilised to reduce computational time.

As it is infeasible to represent the chemical mechanism with all explicit species, a methodology that groups them into classes was established. However, some species having well-established reaction rates and/or great importance to atmospheric chemistry are treated explicitly. The grouping criteria include similarities in structure and reactivity (Carter, 1990). Basically, five groups of alkanes, two groups of alkenes, four groups of carbonyls, and two groups of aromatics are used. Compounds with explicit chemistry are placed in an explicit group. The SAPRAC 2003 version was used in this work and was modified by our group to represent some new reactions, such as ethanol pathways (Corrêa and Arbilla, 2006).

2.2. Emissions data

The emissions values for CO, NO_x, and VOCs were inserted into the model using the unit kg km^{-2} h^{-1}. To obtain these values, an estimate was performed using the annual emission of CO published by CETESB in 2006. This report states that the SPMA has an urbanised area of 1747 km^2. To make hourly emission calculations, a year of 313 days (without Sundays) was considered. For each day, 18 h of effective vehicle circulation were taken into account.

$$1,503,000\,\frac{ton\ CO}{year} \times 1000\,\frac{kg}{ton} \times \frac{1}{1747\ km^2} \times \frac{1\ year}{313\ days} \times \frac{1\ day}{18\ h} = 153\ kg\ CO\ km^{-2}\ h^{-1}$$

Once determined, values for the hourly average CO, NO_x, and VOC emissions were calculated using the environmental ratio, after the emission data for NO_x and VOCs released by CETESB did not seem to be realistic, as demonstrated by Vivanco and Andrade (2006). The NO_x/CO and VOC/CO ratios were determined from the environmental concentrations of these pollutants. To do this, the average of experimental data between 6:00 and 9:00 am throughout 2006 was recorded. An assumption was made that, during that period of time, photochemical processes did not interfere significantly with the concentrations of these pollutants. Data were collected using automated monitors for CO. NO_x, and VOCs were measured using a gas chromatography-mass spectrometer equipped with a flame ionisation detector (GC-MS-FID), which will be detailed later. During the daily time period listed above, ambient levels came mainly from mobile sources, as a fingerprint of the emissions. To determine the VOC/NO_x ratio, the methane concentration was not considered. Monitoring sites used to estimate these ratios were identical to those used for VOC speciation. These will be described later.

For the NO_x/CO ratio 0.09, the average emission value was 14 kg NO_x km^{-2} h^{-1}.

For the VOC/CO ratio 0.25, the average emission value was 38 kg VOC km^{-2} h^{-1}.

The result for the NO_x/CO ratio proposed by CETESB was 0.24, which is very different from 0.09. On the other hand, the VOC/CO ratio proposed here is the same.

2.3. Ambient concentrations

The model input data were the initial concentrations of CO, NO_x, and VOCs, as well as the individual concentrations of each VOC in the mixture. Hourly data of CO, NO_x, and O_3 concentrations were also needed to compare these data with the values obtained by simulation.

The measured concentrations of CO, NO_x, and O_3 were obtained from the CETESB Telemetry Network, which uses automated real-time monitors. VOC analyses were carried out by chromatographic analysis at the LQA (Laboratory of Atmospheric Chemistry — IPEN) and CETESB.

To perform the simulations, pollutants were analysed at two different locations. A sampling campaign for VOCs was carried during August and September of 2006 at the School of Public Health (PSF) of USP (São Paulo University), where there is a CETESB station with CO and NO_x monitors. Its coordinates are 23°33′10″S, 46°40′25″W, its

length is 2300 m, elevation is 831 m, and it is in a downtown area. CETESB also analysed formaldehyde and acetaldehyde, while VOCs were monitored routinely by LQA. Other samplings were performed during 2006. Samples were collected twice a week between 7:00 and 9:00 a.m. at the highest point of IPEN (Institute for Energy and Nuclear Research), which corresponds to the highest point in the University City (23°33′58″S, 46°44′15″W, elevation 775 m, east of the city).

Thermo Environmental Instruments (TEI, Inc.) equipment was used, including the Gas Filter Correlation CO Model TEI 48C, Trace Level chemiluminescence NO–NO_2–NO_x model TEI 42CTL, and UV Photometric O_3 Model TEI 49C.

The VOC sampling methodology was based on TO-14 and TO-15 methodologies from the U.S. EPA (U.S.EPA, 1999a,b). It consisted of sampling with 6-L stainless steel canisters, followed by cryogenic pre-concentration of the sample and subsequent analysis by GC-MS (qualification) and FID (quantification), working in parallel mode. This technique allows the measure of very small concentrations of VOCs, from C2 to C10.

For the analysis of formaldehyde and acetaldehyde, the TO-11A methodology (U.S.EPA, 1997) was used. It consists of sampling with silica cartridges coated with C18 and impregnated with 2,4-dinitrophenylhydrazine (DNPH). During sampling, carbonyls are converted into their hydrazone from.

The cartridges were used at a flow rate of 1.0 L min^{-1} for a period of two hours. The formed hydrazone was eluted from cartridges with acetonitrile and analysed by high-performance liquid chromatography (HPLC) using a C18 column and UV detection at 360 nm.

In this work, five base-cases were proposed to determine the incremental reactivity scale for ozone. In the first base-case, VOC data were used from a campaign that was conducted jointly by LQA/IPEN and CETESB in FSP-USP during the winter of 2006. In this campaign, CETESB measured formaldehyde and acetaldehyde concentrations, while VOCs were measured by LQA. In the other four base-cases, VOC data were used that was analysed by LQA during 2006, with sampling being performed in University City. These base-cases represented the average of VOC measurements in the four seasons: summer, autumn, winter, and spring. As formaldehyde and acetaldehyde data were not available for this campaign, the values of these pollutants from the campaign held at FSP-USP with CETESB in August and September of 2006 were used.

In all base-cases, ethanol and methanol data that were obtained by Colón et al. (2001), in a joint study of the CETESB and U.S. EPA concerning VOCs associated with vehicle emissions in the urban atmosphere of São Paulo, were used.

In the first base-case, the median concentrations of VOCs for eight days in 2006 (August 10th, 15th, 16th, and 17th; September 14th, 15th, 27th, and 28th) were used. All of these days were without rain and had low cloud cover. The model was loaded with median initial concentration data (between 6:00 and 9:00 am), hourly emissions of CO, NO_x, and VOCs, and hourly data of temperature, air humidity, mixing layer height, and VOC speciation. These values are shown in Tables 1 and 2.

VOC concentration data were grouped according to the methodology proposed in the SAPRC chemical mechanism documentation. Table 3 presents the results of the groups.

2.4. Model adjustments

After loading the simulator, initial adjustments were performed to reproduce the actual CO concentrations measured by the automatic

Table 1
Initial concentrations of VOCs, NO_x, and CO for the first base case.

Compound or group	Initial concentration
VOC	1.24 ppmC
NO_x	0.12 ppm
CO	1.15 ppm

Table 2
Values for temperature, relative humidity, mixing height for the base case.

Hour	Temp. (°C)	RH (%)	Mixing height (m)
6:00	15	76.3	300
7:00	15	77.2	500
8:00	15	77.7	530
9:00	17	74.3	650
10:00	19	64.5	750
11:00	21	56.1	900
12:00	23	50.2	1000
13:00	24	45.4	1080
14:00	25	42.6	1150
15:00	25	41.6	1350
16:00	24	42.6	1300
17:00	23	45.5	700
18:00	22	50.0	300

monitor. This initial procedure was actually an adjustment of the base-case. CO was chosen due to its low reactivity; as it is essentially a primary pollutant, it characterises the emissions.

It is important to emphasise that the emission data obtained were hourly average values and that emissions vary greatly throughout the day. This is mainly due to the changing number of vehicles on the streets, as well as to the weather. Therefore, it is necessary to adjust these values.

Depending on the discrepancy between the simulated and experimentally measured values, some adjustments are necessary in the hourly CO emissions to fit these values and always maintain fixed average emissions over the course of the day.

After achieving the best adjustment by changing only CO hourly emissions, a small adjustment in the mixing layer height values was necessary, as average values of a few days of August 2006 were loaded into the model. Fig. 2 presents the results of the simulated values compared with the average values measured for the period, after the aforementioned adjustments.

After adjusting the CO model output, NO_x value adjustments were performed. The NO_x/CO ratio and VOCs/CO ratio did not remain fixed throughout the day, owing to fleet stratification, which varies throughout the day. In this stage, an adjustment in the hourly emissions was performed to reproduce the real situation, always keeping the daily average constant. A small adjustment in the deposition rates of this pollutant was also performed. Fig. 2 shows the results of the simulated values compared with the average values measured for the period, after the aforementioned adjustments.

Once the adjustments were made to CO and NO_x, the base-case was then very close to the final stage. The next step was to adjust the hourly VOC emissions. As the model does not provide data concerning hourly VOC concentrations, this adjustment should be made using the

Table 3
VOCs groups for the 8 sampling days in August and September, 2006.

Groups	Description	ppmC	Fraction	Average C number
ALK 1	1st group of alkanes	0.019	0.0149	2.000
ALK 2	2nd group of alkanes	0.017	0.0137	3.000
ALK 3	3nd group of alkanes	0.026	0.0207	4.042
ALK 4	4nd group of alkanes	0.090	0.0722	5.469
ALK 5	5nd group of alkanes	0.053	0.0430	7.834
OLE 1	1st group of alkenes	0.027	0.0217	4.009
OLE 2	2nd group of alkenes	0.039	0.0312	4.886
ARO 1	1st group of aromatics	0.045	0.0363	7.210
ARO 2	2nd group of aromatics	0.051	0.0414	8.564
TERP	Terpenes	0.001	0.0005	10.000
HCHO	Formaldehyde	0.006	0.0046	1.000
CCHO	Acetaldehyde	0.012	0.0097	2.000
ETHENE	Ethene	0.015	0.0122	2.000
MEOH	Methanol	0.011	0.0085	1.000
ETOH	Ethanol	0.828	0.6664	2.000
ISOPRENE	Isoprene	0.004	0.0029	5.000
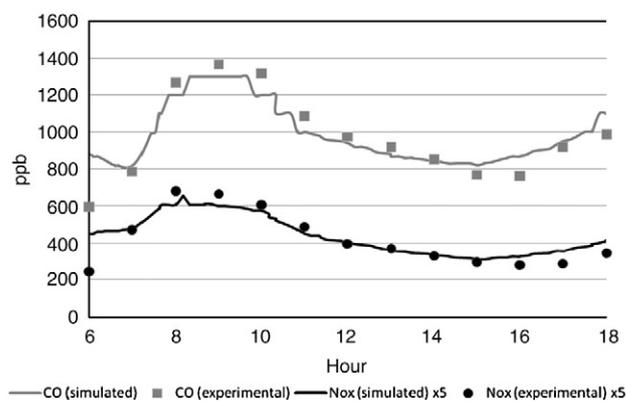
Fig. 2. Comparison between CO and NO_x simulated and experimental values for the base case (School of Public Health of the São Paulo University).

ozone profile. A small adjustment in the ozone deposition rate was also carried out, following the ranges proposed by Finlayson-Pitts and Pitts (2000) (0.1 to 0.8 cm s^{-1}). The ozone profile was adjusted and is presented in Fig. 3 for the four monitoring stations.

Table 4 shows the hourly emission values for CO, NO_x, and VOCs, after all of the adjustments were performed in the model. These are the final values used in the simulations performed in this study. Differences between the initial and adjusted values were smaller than 15%.

After all of these adjustments, the model becomes a powerful tool for the evaluation of several scenarios. For example, it is possible to evaluate ozone changes as a function of concentration changes in a specific VOC or in the total emissions of VOCs and NO_x. It is also possible to evaluate the effects of weather conditions, the effectiveness of vehicle rotation, the influence of a new fuel in the market, and so forth.

2.5. Incremental reactivity scale

To evaluate the incremental reactivity scale of VOCs, an addition/reduction of 0.2% of the total VOCs for each VOC of interest was performed to calculate ozone changes (Tonnesen, 2000).

The average concentration of total VOCs found in the campaign held in spring of 2006 at FSP/USP was 1243 ppbC. Therefore, each VOC found in the atmosphere of the SPMA had its concentration increased by 2.49 ppbC, while the remaining VOCs were kept unchanged. After this procedure, the fractions of the groups were recalculated and loaded into the model. Subsequently, the positive incremental reactivity (IR+) was determined.

$$IR+ = \frac{[O_3]^{inc} - [O_3]^{base}}{+\,0.002 \times [VOCs]^{base}}$$

Then, the concentration of each VOC was decreased by 2.49 ppbC. The change in ozone indicates the negative incremental reactivity (IR−).

$$IR- = \frac{[O_3]^{inc} - [O_3]^{base}}{-\,0.002 \times [VOCs]^{base}}$$

Although the equations presented for IR+ and IR− are the same, the results for each IR are different, because atmospheric chemistry is highly non-linear. The addition/removal of an individual VOC can lead to different values for ozone and other secondary pollutants.

Finally, the average between the values of IR+ and IR− provided values of incremental reactivity (IR) for each VOC found at the SPMA.
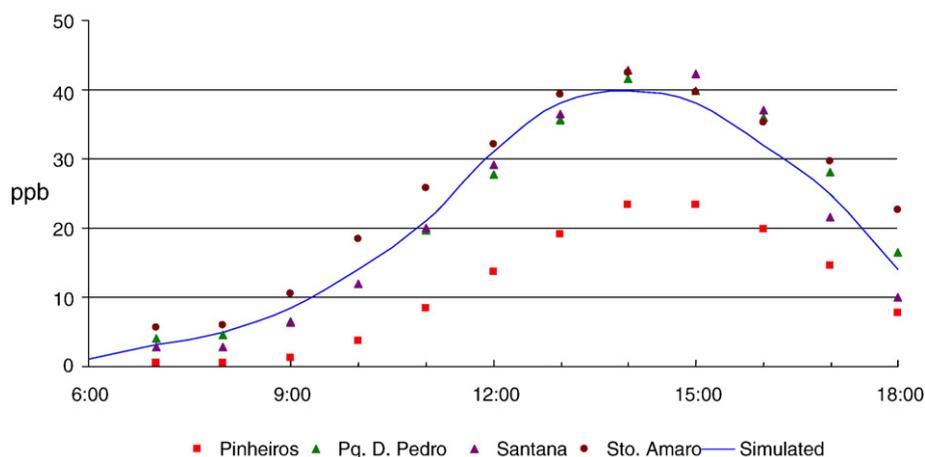
Fig. 3. Comparison between O_3 simulated and experimental values for the base case (August to September 2006 for 4 monitoring stations).

It is important to point out that each individual change for each VOC results in a change of the speciation of VOCs. Therefore, for each new simulation it is necessary to correct the values for the fraction of the VOC group.

With the VOC data obtained during 2006 in the University City samplings, four base-cases were built, one for each season. This was performed to check if the seasonal difference in VOC speciation reflects a significant change in the incremental reactivity scale for VOCs. It was also intended to verify if strategies for the reduction of total VOC and/or NO_x emissions become an interesting alternative to reduce ozone levels in the SPMA in any season.

For all base-cases, incremental reactivity scales were constructed, as described above. Simulations were also performed to verify if reductions in the total emissions of VOCs and/or NO_x would be effective for reducing ozone. In these simulations, the hourly emissions of VOCs and NO_x were independently and simultaneously reduced by 5, 10, 20, and 30%. Using the output data, ozone isopleths plots were constructed to better understand the formation of this pollutant in the SPMA, particularly if ozone formation is VOC- or NO_x-controlled.

3. Results and discussion

As previously described, several simulations were performed to evaluate the influence of a decrease/increase in NO_x and VOC. The results of these simulations demonstrate that a decrease in the emission rate of NO_x would not be an effective strategy for reducing levels of O_3; however, this reduction would result in increased

Table 4
Hourly emissions for CO, NO_x e VOCs.

Hour	Emissions (kg km^{-2})		
	CO	NO$_x$	VOCs
06:00	122	21	31
07:00	380	41	105
08:00	322	25	90
09:00	102	8	24
10:00	102	8	24
11:00	102	8	24
12:00	62	4	14
13:00	82	6	19
14:00	112	8	26
15:00	127	11	30
16:00	132	12	31
17:00	132	12	31
18:00	212	20	48

concentrations of O_3. A 5% reduction in NO_x emissions would represent a 6 to 7% increase in O_3 levels, depending on the season.

Also, the simultaneous reduction of both precursors was not an effective alternative. This is because, although the O_3 variation in these conditions was negligible, it also occurred in the direction of increasing O_3. If the emissions of these pollutants were reduced by 30%, there would be an increase in O_3 production of approximately 2% in simulations for the School of Public Health area, and an increase ranging from 3–9% for simulations in the University City area.

On the other hand, a reduction in the total VOC emissions of approximately 5% led to a very interesting alternative, that is, a reduction of about 6 to 8% in the O_3 concentration. To achieve a reduction between 30 and 42% in O_3 levels, depending on the time of year, a 30% reduction in VOC emissions would be required.

In atmospheres with VOC/NO_x ratios smaller than 5.5, NO_x reacts preferentially with hydroxyl radicals, removing them from the system and delaying O_3 formation. Accordingly, a decreasing NO_x concentration increases the formation of O_3. Therefore, less NO_x would be present in the atmosphere. OH$^•$ would react with VOCs to form peroxide radicals, which in turn would allow the neat formation of O_3 through the regeneration of NO_2 molecules in the atmosphere. This would not be consistent to explain the results for the SPMA in this work, where the reduction of NO_x emissions resulted in elevated levels of O_3, as the VOC/NO_x ratio found in this region was approximately 11. However, it is important to highlight that the high VOC/NOx ratio occurs mainly due to the high concentration of ethanol, which represents around 70% of the total VOCs and is not an important compound in O_3 formation. Calculating the VOC/NO_x ratio without ethanol yields a value of 3.5. Thus, the simulations of this work are in accordance with information found in the literature.

The changes in O_3 as a function of NO_x and VOCs emissions, in the four seasons, are shown in Fig. 4.

By analysing Fig. 4, it is possible to observe that the reduction in VOC emissions is more efficient at reducing O_3 in the winter and less efficient in the spring and summer seasons. These data suggest that, in the spring and summer, O_3 formation is strongly controlled by the incidence of solar radiation. Moreover, in these seasons the air is cleaner and has lower aerosol concentrations as compared to the winter, when temperature inversions concentrate these pollutants, which in turn filter and reflect sunlight. For those reasons, the reduction of VOCs in the spring and summer does not have a high effect in reducing O_3. On the other hand, in the winter, when the incidence of solar radiation is lower and the presence of aerosols in the atmosphere is increased, the reduction of VOC emissions is quite significant in reducing O_3.

Similarly, observing the NO_x reduction effect, there is a greater increase in the production of O_3 in the summer and spring and a less

Fig. 4. O₃ % change in function of NOₓ and VOCs reductions for the 4 seasons of the year.

formation of O₃, the low level of radiation that reaches the Earth in this season limits the increase of this pollutant. On the other hand, in the summer and spring, when radiation is much more abundant, the increase in O₃ production is much more significant.

The analysis of isopleths generated for the four seasons in the University City area can be observed in Fig. 5. These data reinforce the aforementioned results. In this figure, a black circle indicates the actual average O₃ concentration for each season. An increase in VOCs resulted in an increase of O₃; a reduction of VOCs led to a decrease of O₃. In relation to NOₓ, the situation is reversed. For this case, an increase of NOₓ reduces O₃, and a reduction of it increases O₃ levels. These results are consistent with those reported by Andrade et al. (2006) and Vivanco and Andrade (2008). These authors used the Eurelian air quality model CIT (California Institute of Technology) to simulate situations in which the reduction of VOCs resulted in a reduction of O₃ concentrations. It can be observed that the tendency for O₃ formation is independent of the season and also of VOC speciation.

Analysis of the VOC/NOₓ ratio in the SPMA shows a very high ratio between these two pollutants, with a value at approximately 11. This fact is rather interesting, as it differs from other major urban centres in Brazil. According to Corrêa (2003), the VOC/NOₓ ratio for Rio de Janeiro is around 8. However, the ratio found in the SPMA is similar to those found in most U.S. cities, which always have values above 8.

This high VOC/NOₓ ratio found in the SPMA suggests an atmosphere where the formation of O₃ is controlled by VOCs. In

significant increase in the winter. Again, the data suggest that in the winter, O₃ production is severely limited by the lower incidence of solar radiation. Although the removal of NOₓ in the system favours the
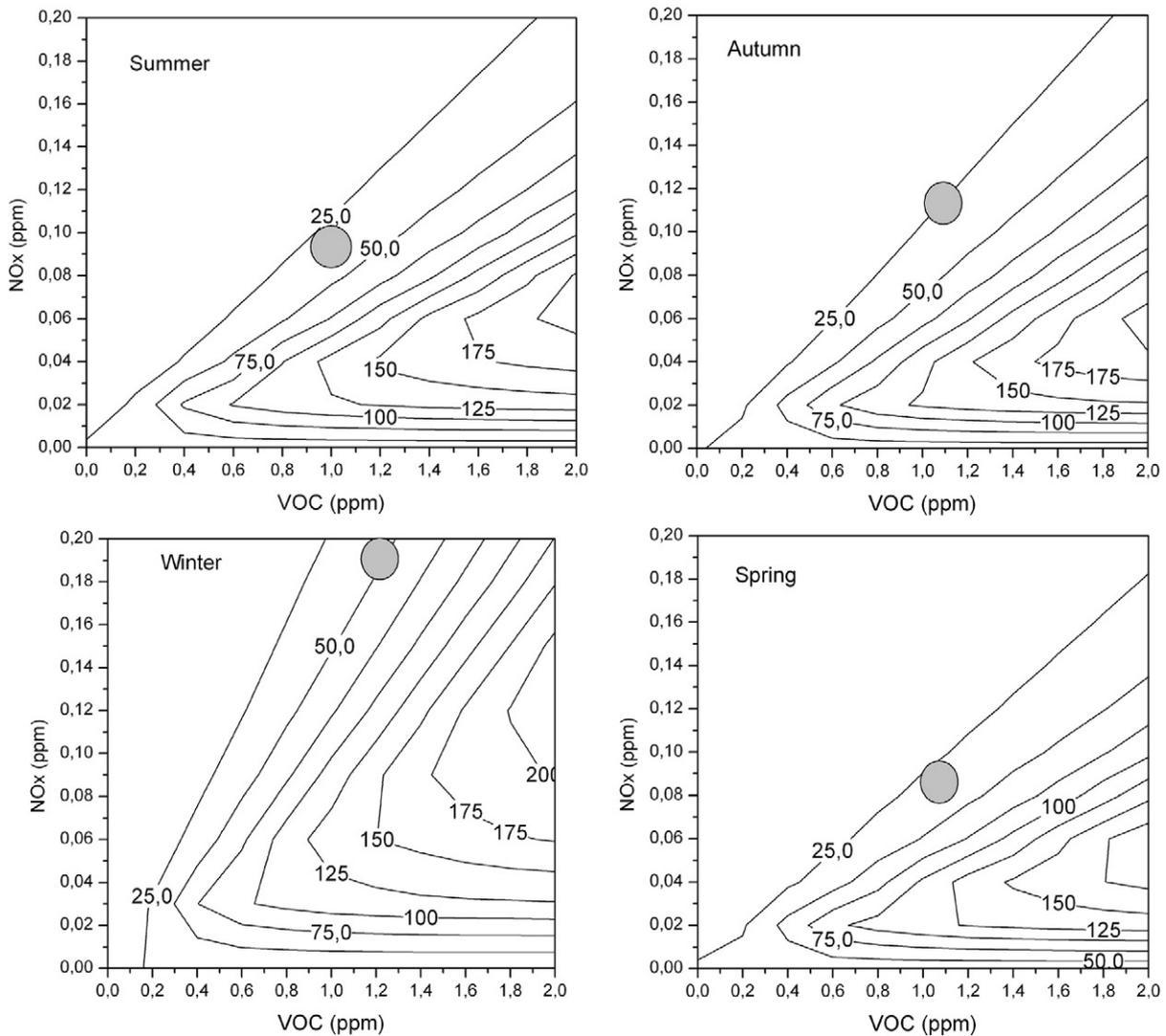
Fig. 5. O₃ isopleths (ppb) for several VOCs and NOₓ concentrations. The circled region is the average O₃ concentration for each season of the SPMA at the University City area.

environments such as that illustrated in Fig. 6, changes in VOC concentrations do not result in significant changes in O_3 concentration. However, changes in NO_x concentrations result in equivalent changes in O_3 concentration.

However, analysis of isopleths produced for the SPMA and the emission reduction simulations shows that, despite the high VOC/NO_x ratio, the SPMA atmosphere is in a situation where changes in VOC concentrations barely result in a change in O_3 concentration. On the other hand, changes in NO_x concentrations result in changes of O_3 concentrations in the opposite direction.

A possible explanation for the difference between the VOC/NO_x ratios found in São Paulo and Rio de Janeiro and for the difference in ozone formation trend observed, when comparing the isopleth produced for the SPMA with those found in the literature, is the huge ethanol concentration found in the SPMA.

According to data from Corrêa (2003), the average ethanol concentration found in Rio de Janeiro is 19.9 ppbv. This is very different from the average concentration of 414.0 ppbv found in São Paulo by Colón et al. (2001) and used in this work. Most likely, this difference and the fact that ethanol represents approximately 70% of the total Non-methane VOCs in the SPMA cause the difference between VOC/NOx ratios for the two cities. It is also important to point out that the methodology used by Colon involves sampling in canisters and the methodology used by Corrêa utilises Florisil cartridges for sampling. However, Corrêa (2003) showed good correlation between ethanol analyses carried out with canisters and cartridges samplings, making it difficult to provide an explanation for the high values found by Colon in the SPMA using canisters. Furthermore, the sampling of polar VOCs in canisters does not yield good results, as these compounds can be adsorbed inside the canisters walls together with water from the atmosphere.

The difference between the O_3 isopleth produced in this work and those found in the literature may also be attributed to the high ethanol concentration in the SPMA. As Brazil is the sole country worldwide to use ethanol as a fuel on the large scale, this explains the high concentrations of this pollutant in the SPMA compared to other urban centres. For example, Los Angeles has an average value of 17.7 ppbv (Lonneman, 1998) and Osaka has an average value 20.0 ppbv (Nguyen et al., 1999). This high ethanol concentration

results in a high VOC/NO_x ratio, but does not represent the ozone formation situations found in literature, as ethanol is a minor compound in the formation of ozone.

3.1. Incremental reactivity scales

To determine the most important VOCs for O_3 formation, as well as if there are seasonal differences for these compounds, the VOCs of each base-case base were arranged according to their reactivity, as in the previously described methodology. The results are presented in Fig. 6 for the 20 main precursors.

The six main O_3 precursors are: formaldehyde, acetaldehyde, propene, isoprene, and _cis-_ and _trans_-2-butene. Aldehydes are very important, followed by alkenes, aromatics, and, finally, alkanes. The latter group, which represents the major group in terms of concentration (45%), begins to emerge on the scale at position 23.

Upon analysing the results for the 74 VOCs found in GC-MS analysis, there was a high occurrence of alkanes with negative values. In other words, an increase in the concentration of these compounds would reduce O_3 concentrations in the city of São Paulo. This occurs because these compounds are saturated and therefore less reactive. According to the SAPRC mechanism, this reduction in O_3 levels was assumed to occur not because alkanes interfere with the production of this pollutant, but owing to the fact that an increase in alkane concentrations decreases the fraction of more reactive VOCs. The same is true regarding ethanol, a very abundant compound in the SPMA atmosphere, which has less importance for O_3 formation in the mechanism.

The minimal importance of ethanol can also be explained by the SAPRC mechanism, which only has one of the four major reactions of this pollutant. Ethanol has four reaction pathways in the atmosphere, including via: hydroxyl radical, hydroperoxide radical, nitrite, and photochemical reaction. Of these, only the reaction rate with hydroxyl radicals is known. Therefore, this is the only reaction of ethanol within the mechanism. Upon comparing the reaction rate of formaldehyde, the main O_3 precursor for all base-cases in this work, with the one of ethanol, it is apparent that the ethanol reaction rate is only a third lower than for formaldehyde. Consequently, if the mechanism was implemented with other ethanol reactions, the importance of this
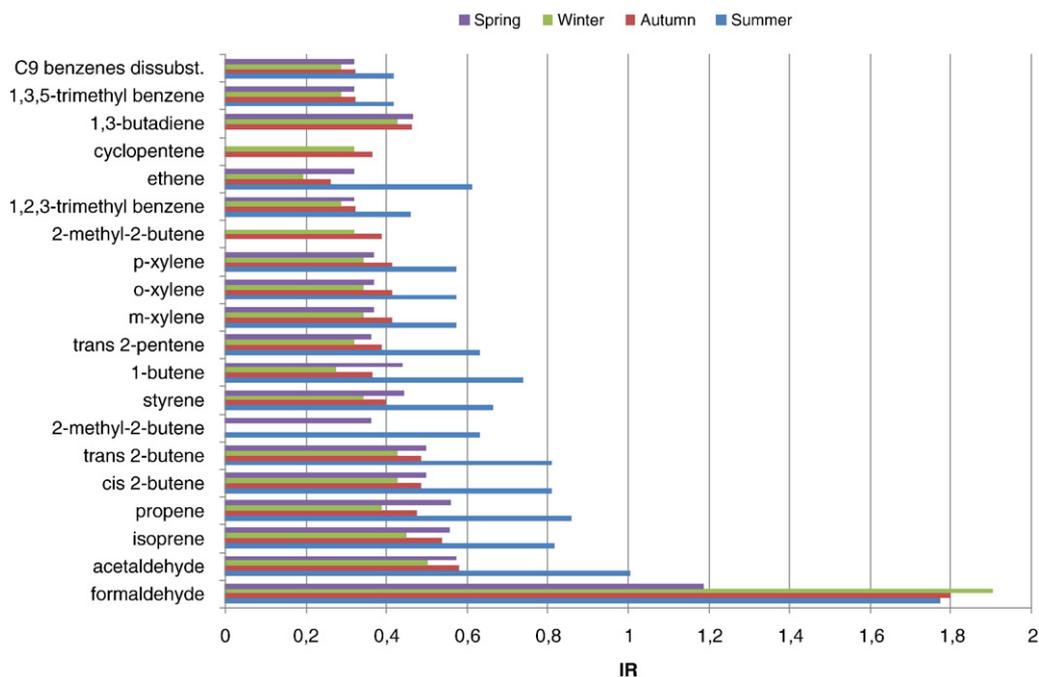
Fig. 6. 20 main O_3 precursors for the 4 seasons of the year.

compound in O_3 formation would tend to increase. However, it would not reach the extent of formaldehyde, because a carbonyl group in a molecule is much more reactive compared to a hydroxyl group.

For the main O_3 precursors for the SPMA, the seasonal scales have a sequence, which is ordered as: aldehydes, alkenes, aromatics, other less-reactive alkenes and aromatics, and finally alkanes.

When considering only the top ten O_3 precursors for the SPMA, the compounds formaldehyde, acetaldehyde, propene, isoprene, *cis*- and *trans*-2-butene were found in the four seasons. The compounds *ortho*-, *meta*-, and *para*-xylene also appeared quite often; however, for the summer base-case, they were not among the top ten. This shows that there is little variation between the reactivity scales for the different seasons. The compounds exchange their positions, but there is not a significant difference between the positions of the same compound in different seasons.

It is important to note that isoprene, a compound always found among the five main O_3 precursors, is emitted into the atmosphere by anthropogenic and natural sources. A simulation study for the city of São Paulo, in which the values used for the emission of isoprene and monoterpenes were obtained by Zimmerman et al. (1988) in the Amazon forest, showed that biogenic emissions may contribute to an approximately 15% increase in O_3 concentration (Martins et al., 2006). These results reinforce the importance of carrying out more detailed studies concerning the natural and anthropogenic contributions of isoprene emissions.

Comparing the incremental reactivity values obtained for the SPMA with the ones proposed by Carter (1994), differences can be found in some main compounds of the scale, particularly for aldehydes. Formaldehyde and acetaldehyde, the main O_3 precursors in this work, have no positions of prominence on the scale proposed by Carter. Formaldehyde appears only after major alkenes. Acetaldehyde appears only after some aromatic compounds. This difference can be related to the levels of these compounds in the SPMA, compared with other cities in the world. Again, this is due to the use of ethanol as a fuel and as an additive in gasoline, which is not common in other countries.

Among the major alkenes, the difference is less significant; however, it still exists. The compounds propene and isoprene, for example, were among the top 20 for Carter's scale, while they were always among the top five precursors in the scales reported in the present work. The same trend can be found when analysing xylenes.

4. Conclusions

The analysis of incremental reactivity scales produced in this work for the four seasons in the SPMA shows that formaldehyde and acetaldehyde are the main O_3 precursors in the area, being on top of all scales.

Although compounds in the groups varied from one season to another, in general, the reactivity scales showed the following sequence: [aldehydes]>[alkenes]>[aromatics]>[less reactive alkenes and aromatics]>[alkanes]. The high O_3 formation potential presented by aldehydes and alkenes can be explained in terms of the instability of these compounds, owing to their unsaturated bonds. Aromatics also have a high potential for O_3 formation, according to the instability of the benzene ring. Alkanes have little importance in O_3 formation, as they are highly stable.

The compounds most often found among the top ten O_3 precursors in the SPMA for the four seasons of the year are: formaldehyde, acetaldehyde, propene, isoprene, and *cis*- and *trans*-2-butene. Reductions in the emissions of these compounds would be an effective strategy to reduce O_3 levels. On the other hand, reductions in alkane and ethanol emissions would have very little or even no importance for O_3 depletion.

This information can be used, for example, to guide the formulation of new fuels, as the gasoline used in Brazil presents around 45% by volume of aromatics and 30% of olefins. These data also serve as a parameter for the development of future laws that may arise in an attempt to effectively reduce VOCs that are more important in O_3 formation. Also, this work shows the need for more frequent studies into the concentration of oxygenated compounds in the SPMA.

This work also demonstrates the importance of determining the VOC reactivity scale for a region of interest, rather than simply searching the literature for scales developed for other cities. Factors such as weather parameters, VOC speciation, pollutant emission rates, and VOC/NOx ratios can vary greatly from one location to another, consequently producing scales with significant differences in reactivity.

Results from the simulations having a reduction in NO_x and/or VOCs emissions, together with analysis of the ozone isopleth produced for the SPMA, show that another alternative to reduce O_3 levels in this region would be to reduce total VOC emissions. Simulations performed here indicate that a 30% reduction in VOCs emissions would result in a total reduction of O_3 concentrations that would vary between 30 and 42%, depending on the season. It can be concluded that this strategy is efficient regardless of the season considered. Furthermore, lower NO_x emissions would increase O_3 concentrations.

Isopleth observations confirm the above findings. They show that, in regions with significant O_3 concentrations in the SPMA, an increase in VOCs would result in an increase in O_3, while a reduction in VOCs would reduce O_3 concentrations. The behaviour of NO_x is exactly the opposite; that is, by increasing the concentration of these pollutants, the O_3 concentration would decrease. On the other hand, a reduction NO_x concentration would increase the O_3 concentration.

It can be also concluded that the SPMA has a high VOC/NO_x ratio of approximately 11. However, this high ratio is due to a high concentration of a compound that has little reactivity toward O_3 production, namely ethanol. Ethanol is not commonly found in high levels in the atmospheres of other cities worldwide. It produces an isopleth chart that is quite unusual. The presence of this atypical compound in the SPMA reinforces the importance of specific studies within a region of interest, providing data to develop strategies for the control of O_3 concentrations.

Acknowledgments

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