STUDY OF MAJOR PRECURSORS OZONE IN THE METROPOLITAN AREA OF SÃO PAULO

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1. Introduction

Air pollution, in urban areas, has increased due to the increasing number of motor vehicles in circulation and increasing industrial activity. The urban air quality has caused serious problems to the living conditions of the people, plants and animals that live in and around large cities.

The metropolitan area of São Paulo (MASP), with about 20 million inhabitants, is the second largest urban agglomeration. In the MASP air quality problems occur mainly due to pollutants from vehicles, this is the reason for emphasizing the importance of controlling the vehicular emissions (IBGE 2011, CETESB 2012).

The MASP has the presence of approximately 40 thousand companies and 7.5 million private vehicles (21% of the national total).

In the MASP there are over 30.5 million trips per day, consisting of 12 million public transport and 8.1 million individual transport. On the streets, squares and avenues of the capital, there are around 3 million vehicles circulating per day.

The vehicles are responsible for 97% of CO, 77% of HC, 82% of NO_x, SO_x 36% and 40% of MP emissions. The gasoline cars are the largest emitters of CO (47%). The likely reason is that, besides being the largest fleet they also has high average age (12 years), therefore higher emission factor when compared to current factors.

Currently ozone (O_3) is the main problem of air pollution from MASP, exceeding 98 times the national standards for air quality, 160 μg m^{-3} in 2012. To decrease ozone concentrations in the atmosphere of the city of São Paulo it is necessary to reduce and control ozone precursors which are volatile organic compounds (VOCs) producing pollutant by photochemical processes (CETESB 2013).

Despite considerable reductions in vehicle emissions with improved engine technology programs, there are still frequent days when the concentration of ozone (O_3) in the MASP exceeds national standards for air quality. While the number of exceedances concentration of the CO standard for the MASP decreased from 18 to 0 from 1999 until 2012, the number of days in which the standard of O_3, 1 hour: 160 μg m^{-3} and the attention level: 200 μg m^{-3} was exceeded, decreased from 109 to 98 in the same period, the reduction of O_3 was not significant, this is the worst problem of air pollution in the MASP.

Given the difficulty in reducing the levels of O_3 in the MASP, as in other large urban conglomerates, it is necessary to conduct a detailed study of the main precursors of this pollutant so as to support the development of possible guidelines that may be proposed in an attempt to minimize this problem.

2. Data and Methodology

Samples were realized in CETESB IPEN-USP monitoring station in University City, 800 m of altitude, located in the west of the city of São Paulo during the month of September 2011 until August 2012 on weekdays during the hours from 07:00 to 09:00. Integration of the data were performed for the time period between September 2011 till August 2012 for 66 samples of hydrocarbons, 62 aldehydes and 42 ethanol at two hours due the fact that, this time, the traffic is heavy and the solar radiation is low.

Canisters were used for sampling of hydrocarbons (HCs). The HCs were analyzed by the technique of gas chromatography (GC) with mass spectrometry detector (MS) and flame ionization (FID). Aldehydes were sampled using cartridges coated with C18 silica using the technique of high performance liquid chromatography with ultraviolet detector. The ethanol samples were collected from florisil cartridges and analyzed using GC-FID.

2.1 Trajectory model OZIPR

For this work the trajectory model OZIPR (Ozone Isopleth Package for Research) was used in conjunction with the public domain chemical model SAPRC (Statewide Air Pollution Research Center), they are widely accepted by the international academic community and are applied to study various different cases.

This choice also took into account the fact that these are relatively simple models, ideal for a first job with mathematical modeling in polluted urban areas. Moreover, this model emphasizes the understanding of photochemical reactions of the environment concerned, because its detailed chemical mechanism, similar to the CB-IV and CBM-EX models.

The trajectory model OZIPR (Gery and Crouse, 1990) is a one-dimensional model that requires various data like initial concentrations of CO, NO_x and VOCs , emissions totals, specification of VOCs present in the mixture and meteorological parameters with temporal resolution only without the need for a spatial description of these parameters. This model allows the execution of multiple simulations for various conditions of VOCs and NO_x, providing a graph of a function O_3 isopleths for these two precursors. Moreover, it is a very useful tool for determining scales for VOCs reactivity.

The SAPRC chemical model includes thermal and photochemical reactions, and has been updated in the State University of Rio de Janeiro with a larger number of reactions and currently works with 204 reactions and 83 species (Carter, 2000, Corrêa, 2010). Not all species are treated explicitly. In the model mechanism and a methodology for grouping classes was established. The grouping criteria are two: similarity of structure and reactivity. In this work we used five groups of alkanes, two groups of alkenes and two aromatic.

In the initialization of the models, median concentrations of CO, NO_x, VOCs were used, the samples were perfomed at CETESB IPEN-USP station during the month of September 2011 until August 2012. Sampling of aldehydes, ethanol and hydrocarbons were performed in the same inlet monitors while pollutant gases, CO, NO_x, and O_3 in the CETESB IPEN/USP station. Gases such as CO, O_3 and NO_x were measured by the monitors of pollutants by CETESB (Pretto, 2004; CETESB 2012).

Meteorological data of temperature and relative humidity were obtained from IPEN weather station that is located at the same place where the VOCs were sampled.

Height values of the mixing layer were calculated using data from the Laboratory for Environmental Applications of Lasers - IPEN, which measures the height of the PBL using the sensing system Lidar (Light Detection and Ranging), but depending on the model it represents a period of one season (3 months) and atmospheric conditions which vary greatly from day to day, the actual information used were top of the boundary layer height , time of the maximum and the nearest several days of its evolution throughout the day and supposed for the initial and adjusted the model morning hours.

To calculate the main precursors of ozone the incremental reactivity (IR) was used. This calculation was performed employing the trajectory model OZIPR together with SAPRC mechanism detailed in the work of Orlando et al. (2010).

The calculated IR is the average of the positive IR (IR_+) and negative (IR_-). These were calculated by the increase and decrease, respectively, 0.2% of the total concentration VOCs (ppbC) for each species of VOCs. The variation of the concentration of O_3 was calculated using the maximum concentration of O_3 obtained after the increase or decrease of 0.2% VOCs and subtracted from the base O_3.

3. Results

3.1 Studies of seasonal variation of VOCs Cetesb IPEN USP in 2011-2012

In Table 1 concentrations in ppbv of the 10 most abundant VOCs in the atmosphere of the MASP of the 54 compounds identified in this study referring to the average of 66 samples are shown.

Table 1. Mean concentration of the most abundant VOCs

Compounds	Conc.(ppbv)
Ethanol	36.3
acetaldehyde	28.7
formaldehyde	21.7
acetone	10.9
propane	5.56
ethene	4.84
ethane	2.98
butane	2.94
1-ethyl-4-Methylbenzene	2.85
1,2,4-trimethylbenzene	2.43

Ethanol, acetaldehyde, formaldehyde and acetone were the VOCs found in higher concentrations in 2011/2012. According to global emissions estimates, plants release three times more ethanol than anthropogenic sources. However, considering the atmosphere of the MASP, vehicular emissions are higher than the natural. The ethanol is converted to acetaldehyde atmosphere composed highly reactive to ozone formation and is considered toxic to human health. In a study conducted in Miami, the isotopic ratio $^{13}C/^{12}C$, shows 74.9% ethanol emissions in the atmosphere from the use of this compound as a fuel (Giebel et al., 2011). In the MASP probably the contribution is even greater.

Formaldehyde and acetaldehyde were found in higher amount in VOCs after ethanol. Ethanol vehicles emit more aldehydes than gasoline vehicles. The ratio of formaldehyde/acetaldehyde found in this study was 0.75, with no significant variation during different seasons. This was the lowest ratio found for MASP compared to work done previously by Vasconcellos et al., 2005. The low ratio is due to the use of ethanol as a fuel since the combustion of ethanol produces greater emission of formaldehyde than acetaldehyde. This result shows increased consumption of ethanol as a fuel, because currently at MASP most car sales is comprised of vehicles with "flex-fuel" engines that use gasoline with 25% ethanol or ethanol alone. But according to Branco and Branco (2007) the preferable use of ethanol in the harvesting period reduces to 30% consumption in the off season.

In the year 2011/2012 the aldehydes represented 35.3% of the analyzed VOCs concentration in the MASP atmosphere, followed by ethanol with 22.6%, 15.7% aromatics, alkanes 13.5%, acetone 6.8%, alkenes 6.0% and alkadienes less than 0.1%. It was observed in the year 2011/2012 the percentage increase is aromatic, and this group is the second most reactive to ozone formation.

3.2 Major VOCs ozone precursors in studies of 2011/2012

The model OZIPR was run separately for each climate station and was initiated with the average concentrations of CO, NO_x and VOCs for the period from 07:00 h to 09:00 h, corresponding to the the years 2011/2012. An hourly data for the same period from 06:00 h to 18:00 h for temperature, relative humidity of the Meteorological Station of IPEN was also used. The concentrations of VOCs used for speciation in the model were the results of sampling conducted for one year in CETESB IPEN/ USP station in University City, from September 2011 until August 2012. 66 samples of hydrocarbons, were analyzed in the laboratory for atmospheric chemistry (LQA) in the IPEN, and 62 aldehydes and 42 ethanol, analyzed University of the State of Rio de Janeiro in Resende.

The hourly emissions of CO, VOCs and NO_x were based on information of inventory by CETESB and mobile sources inventory: retrospective and prospective analysis of the benefits of PROCONVE to air quality from 1980 to 2030, considering the time distribution of miles slowness which is proportional to the vehicle traffic (Branco and Branco, 2007; CETESB 2012).

Data from initial concentrations of CO, NO_x and VOCs for the seasons of spring, summer, autumn and winter of 2011/2012 are shown in Table 2 for the period from 7:00 h until 9:00 h.

TABLE 2 - Initial concentration of VOCs (ppmC), NOx and CO (ppm) in CETESB IPEN / USP Station

Compounds	Spring	Summer	Autumn
VOCs	0.74	0.74	0.67
NO_x	0.04	0.06	0.04
CO	0.47	0.36	0.30

Meteorological data of temperature and relative humidity were obtained from IPEN weather station, located in the same location of VOCs sampling. The values of the PBL height for the time from 6:00 to 18:00, inserted in OZIPR model for the seasons of 2011/2012, were modified using information from Orlando et al. (2010), but most of the CLP was increased to 2000 m, using observations of the Laboratory for Environmental Applications of Lasers - IPEN, using the sensing system Lidar (Light Detection and Ranging) were considered in adjusting the characteristics of each season, with their variations in temperature.

After loading the OZIPR model and setting it up with all the above mentioned parameters, data was generated for the pollutants CO, NO_x and O_3 in a file with hourly concentrations from 06:00 to 18:00. These results from the simulation were compared with the average of the measured values for the seasons of 2011/2012, in CETESB IPEN/USP Station.

The simulation results show that the alternative to decrease ozone in the atmosphere would be reduceing the emission of VOCs. However, it appears that a reduction of up to 30% VOC reduce only of around 3-7% of O_3. Already a reduction of CO and VOCs simultaneously would be a slightly more effective alternative, with the 30% decrease of VOC and CO, while maintaining current levels of NOx, O_3 reduce the concentration to around 4-7%. The results of these simulations show that a decrease in the emission rates of NO_x would not be effective for reducing ozone levels, however, this reduction would result in elevated ozone concentrations.

Since on reducing VOCs in general there was a significant reduction in the concentration of O_3, it was decided to remove the class of the most important aldehydes in the formation of ozone to study its reduction. Starting with spring time scenerio, reduction of acetaldehyde to a negligible concentration in the atmosphere, 16% lower ozone concentration was obtained. Doing the same process with acetaldehyde and formaldehyde, O_3 reduction was 22%, and reducing all aldehydes ozone depletion was 26%. Performing the reduction of aldehydes to all the other stations yielded a decrease in ozone concentration of 30% in summer, 28% in winter and 25% in autumn.

With data output of the simulator it was possible to construct graphs of ozone isopleths for the seasons, shown in Figure 1 for the spring season.

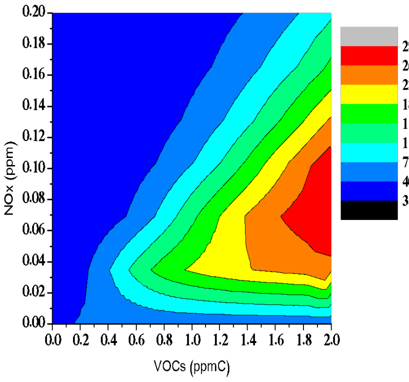

FIGURE 1 - Isopleths of ozone (in ppb) for various concentrations of VOCs (ppmC) and NO_X (ppm) for the campaign in the year 2011/2012 during the spring in CETESB IPEN/USP station.

The Figure 1 reinforces the above results, showing that an increase of VOCs would provide an increase of ozone and a decrease of VOCs would occur too decrease of ozone.

The Figure 1 shows that the decrease in the concentration of VOCs in the MASP will lead to ozone depletion. The ratios of VOCs/ NO_x found during this study for the spring, summer, autumn and winter season were 4, 3, 3 and 2 respectively. In places with relative abundance of NO_x compared with VOCs, the ratio VOCs/NOx is low and the ozone formation is dependent on the concentration of VOCs. In the literature ratios 8 to 15, characterized intermediates locations where both the control of VOCs, NO_x are as effective in decreasing and ratios above of 15 are considered limiting NO_x (Finlayson-Pitts and Pitts 2000). The Figure 2 shows the mean increments of positive reactivity for 4 seasons of the year, yielding an annual average of 19 ozone precursors VOCs found in this study.

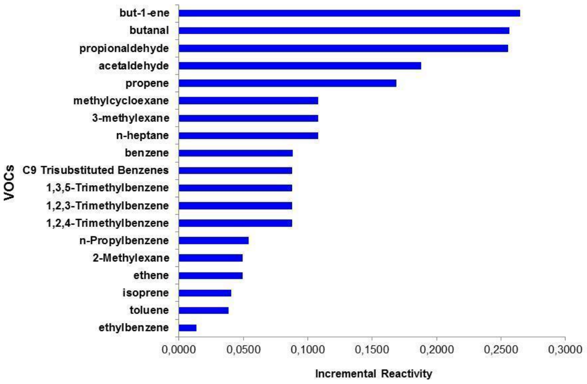

FIGURE 2 - Incremental reactivity (ppbv of O_3/ppbC VOCs) for the 19 major precursors of ozone in the atmosphere of the MASP - CETESB IPEN/USP station.

Considering the potential to form ozone (IR), for this study in the year 2011/2012, the five major compounds were: but-1-ene, butanal, propionaldehyde, acetaldehyde, propylene and methylcycloexane. However, when considering their potential to form ozone, multiplied by its concentration in the atmosphere, results in the real participation that each species has played in the formation of ozone, Table 3.

Considering the abundance of VOCs analyzed and incremental reactivity determined by OZIPR model, shown in Figure 2, acetaldehyde was responsible for forming 61.2% of the ozone in the atmosphere MASP in the year 2011/2012 . This result is important to point out what measures would be effective in controlling the formation of ozone in the atmosphere. The aldehydes were responsible for 74% of the ozone formation in the atmosphere, followed by 14.5% aromatics, 10.2% alkenes, 1.3% alkanes and 0.03 % alkadienes (isoprene). Despite alkanes represent 13.5 % by mass in the atmosphere, they were responsible for the formation of only 1.3 % of ozone due to its low reactivity.

TABLE 3 - Potencial of each VOCs in ozone formation in the year 2011/212 in CETESB IPEN/USP Station.

Compounds	**Conc x IR**	**% of O_3**
acetaldehyde	5.40	61.2
propionaldehyde	0.61	6.92
butanal	0.52	5.85
1-butene	0.42	4.74
C9 disubst. benzene	0.40	4.59
propylene	0.24	2.75
ethylene	0.24	2.70
1,2,4-TMB[a]	0.21	2.41
1,3,5-TMB	0.20	2.32
1,2,3-TMB	0.20	2.27
n-propylbenzene	0.12	1.37
toluene	0.08	0.86
benzene	0.04	0.45
n-heptane	0.04	0.43
methylcycloexane	0.03	0.38
3-methylexane	0.03	0.34
ethylbenzene	0.02	0.21
2-methylexane	0.01	0.16
isoprene	0.003	0.03

[a] TMB (Trimethylbenzene)

This shows that it is important to work with the local scenario for determining the incremental reactivity. The incomplete combustion of ethanol issues various gases such as his own, which is less reactive to ozone formation when compared to aldehydes and several other species of unsaturated hydrocarbons, which are also products of combustion of the ethanol .

In analyzing the results of simulations it was found that the reduction in NO_x and/or VOCs together with data produced for the isopleths shown that MASP alternative to reduce the levels of O_3 in the region is the reduction in VOCs, concluding that the most effective measure for reducing this pollutant would be the reduction of the emission of aldehydes. The simulations indicate that the 30% reduction in VOCs emissions result in total reduction of 3 -6.5 % in the concentration of O_3, depending on the season. Reducing compounds such as acetaldehyde and formaldehyde, a negligible concentration in the atmosphere, the reduction of O_3 for the spring season would be 22%, reducing other pollutants from the class of aldehydes occur a decrease of 26% of O_3 in the atmosphere MASP. Moreover, 30% decrease in NO_x emissions would increase the concentration of O_3 by 7-22 % depending on the season.

4. Summary

The 10 most abundant VOCs in the atmosphere found in the study conducted in 2011/2012 in CETESB IPEN/USP season, were: ethanol, acetaldehyde, formaldehyde, acetone, propane, ethylene, ethane, butane, 1-ethyl-4-methylbenzene and 1,2,4-trimethylbenzene. In the year 2011/2012 the aldehydes represented 35.3% of the analyzed VOCs, followed by ethanol with 22.6%, aromatics 15.7%, alkanes 13.5%, acetone 6.8%, and alkenes 6.0% and alkadienes less than 0.1%.

The main precursors of ozone found in the study year 2011/2012 belongs to the class of aldehydes which accounted for 74% of the ozone formation in the atmosphere, followed by 14.5% aromatics, 10.2% alkenes, 1.3 alkanes and 0.03%. alkadienes (only isoprene) These results are important to point out what measures would be effective in controlling the formation of ozone in the atmosphere.

Reducing all aldehydes quantified in this study by a negligible concentration in the atmosphere occurs a reduction in the concentration of ozone around 26% in spring, summer 30%, 28% in winter and 25% in the autumn.

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