OZONE FORMATION POTENTIAL IN THE MEGACITY OF SÃO PAULO.

Leila Droprinchinski Martins[*] and Maria de Fátima Andrade.

Department of Atmospheric Sciences, Institute of Astronomy, Geophysics and Atmospheric Sciences,

University of São Paulo.

1. Introduction

In Brazil, since 1989 was implemented the PROCONVE (Brazilian Program for the Control of Air Pollution Emission by Motor Vehicles) that established limits to emissions from new vehicles. A decrease in pollutants levels was observed associated to these emissions control, mainly for CO. However Ozone and Inhalable Particulate Matter (PM_{10}) levels routinely exceed the 160 μg m^{-3} ($\cong$ 82 ppbv) hourly and 150 μg m^{-3} daily of Brazilian National Ambient Air-Quality Standard, respectively. São Paulo is classified as a megacity with about 10.6 millions inhabitants. The footprint of a megacity encompasses not only the area physically occupied, but also the area that contributes resources and, in turn, is affected by wastes and pollutants (Molina and Molina, 2004). The main sources of pollutants in São Paulo are associated to the production, transportation and burning of vehicular fuel. São Paulo has a complex topography, localized 50 km away from the Atlantic Ocean. In some events during the winter, low relative humidity of air, low wind speed and sunny days promoted by high-pressure systems, which hinder the entrance of cold fronts in São Paulo, provide conditions for occurrence of ozone episodes and consequently poor air quality. The control of ozone is not only important for Sao Paulo but also for other neighbor cities that are impacted by the photochemical precursors and ozone from the megacity.

Previous studies have shown that in many areas of world the ozone standard cannot be met without significant reductions in both NO_x and VOC emissions. The ability to identify which emissions reductions would most effectively reduce pollution would help in minimizing costs. Recently a study performed for São Paulo region identified for episode studied, that the ozone production is limited by VOC (Sánchez-Ccoyllo et al., 2006a). However, RHC reactivity rates vary, and it is important to determine which RHCs should be reduced in order to better control ozone levels in São Paulo region. In this study, 3-D organic reactivities are calculated for São Paulo region and the sensitivity of ozone to NO_x and VOC for two periods with different meteorological and levels of pollutants

2. Period of study

Simulations of meteorology and chemistry for two different periods (summer and winter) were performed for the Metropolitan Area of São Paulo (MASP) with different emission scenarios. Base case (BC) simulations were conducted from August 22, 2000 to August 24, 2000 and from March 13, 2000 to March 15, 2000 for MASP.

During the period of August 22 to 24 the synoptic conditions were dominated by the South Atlantic High Pressure, a high-pressure system centered over the Atlantic Ocean and extending into the continent over MASP, favorable to days

[*] Corresponding author address: Leila Droprinchinski Martins, Rua do Matão, 1226 Universidade de São Paulo, IAG, departamento de Ciências Atmosféricas; e-mail: leiladro@model.iag.usp.br

without clouds. The wind speed varied from calm winds to 3 km h^{-1} and prevailed from ESE. In the second period the conditions for dispersion of pollutants were favorable and the levels of pollutants were below the air quality standard. The synoptic situation was characterized as pos frontal with winds prevailing from SE. The synoptic situation, together with its interaction with local circulation, influences airflow, which plays an important role in pollutant transport in all seasons (Silva Dias et al., 1995, Silva Dias and Machado, 1997).

3. Model description

In this study was employed the CIT urban airshed model, which is an eulerian photochemical model developed jointly by the California Institute of Technology and Carnegie Mellon University. McRae et al. (1982), Russell et al. (1988) and Harley et al. (1993) present detailed descriptions of the CIT model.

The eulerian grid-based CIT urban airshed model describes the formation and transport of chemically reactive species in the turbulent planetary boundary layer. The model consists of three basic modules: the meteorological module, the chemistry module and the emission inventories module (including spatial and temporal distribution). The chemistry module evaluates three basic types of chemical species: inorganic species, explicit organic species and organic species lumped according to the reactivity and structure of compounds. A detailed description of the model, including a list of enhancements and an evaluation of its performance, is presented in Harley et al. (1993).

The chemical mechanism employed was the 1999 California Statewide Air Pollution Research Center (SAPRC99) photochemical mechanism developed by Carter (2000), which is the recommended chemical mechanism for reactivity assessment. In the present study, this mechanism was expanded to include, explicitly, the chemistry of methane, methanol, ethanol, isoprene, hydrogen peroxide, and sulfur dioxide.

4. Input data

In the present study, the Regional Atmospheric Modeling System (RAMS), a prognostic (dynamic) meteorological model, output was used to create input for the CIT model, together with observational data provide by network air quality stations from CETESB (Sao Paulo State Environmental Protection Agency). The meteorological and photochemical models had the same horizontal resolution. RAMS model was run with variable resolution up to 1000 m level, starting with 70 m resolution and increasing by a factor of 1.2 and with a 1-h time resolution. Above 1000 m level, the vertical spacing was kept constant up to the rigid top of the model. The RAMS model features for the MASP are described in more detailed by Silva Dias and Machado (1997), Freitas (2003) and Sánchez-Ccoyllo et al. (2006b).

The meteorological input fields for CIT are wind speed and direction, mixing height, humidity and air temperature. The ultraviolet radiation is calculated by CIT from astronomy formulation as well the total radiation that is correct by a sky cover factor. The prognostic values together with the observational data were interpolated based on the weighted average procedure described by Goodin et al. (1979). Initial and boundary conditions were based on pollutant concentrations measured at CETESB air quality stations (CETESB, 2001). Also hourly concentrations of routinely monitored gas phase pollutants (O_3, NO, NO_2, SO_2, CO, and

hydrocarbons) were interpolated for initial and surface boundary conditions based on the weighted average procedure.

Emission inventories for total hydrocarbons, NO_x, CO and SO_2 were compiled for the year 2000. These inventories were spatially and temporally distributed throughout the MASP and adjusted. These adjusts were based, for both periods, on pollutants concentrations measured on air quality stations, localized in MASP. The ratio among the pollutants concentration was considered as a factor of correction in the emission profile considered in the model. Should be remarked that the emission inventory available for MASP is relative to total emission of pollutants for one year and therefore it does not account for daily variability.

The split of total hydrocarbons was compiled from measurements performed inside tunnels in São Paulo, from analyses of fuel liquid (gasohol, diesel and alcohol) and from literature

(Martins et al., 2006; Pretto, 2005; Andrade et al., 2004; Harley et al., 2000; Murgel 1990; Chuí et al. 1975).

5. Results and discussion

5.1 Base case

Base case simulations were performed for both period and the comparison between simulated and observed data was done for two groups of air quality stations. The grouping of the stations was based on results of cluster analysis, previously accomplished. One group was composed of stations localized in downtown area (G1) and the other by the stations localized in a southeastward of São Paulo (G2) which, have earlier the influence of sea breeze.

Figures 1 (a-b) and 2 (a-b) present the time series of simulated and observed ozone concentrations for the two surface group stations during the two periods. The bars represent the maximum and minimum values observed in relation to average values.

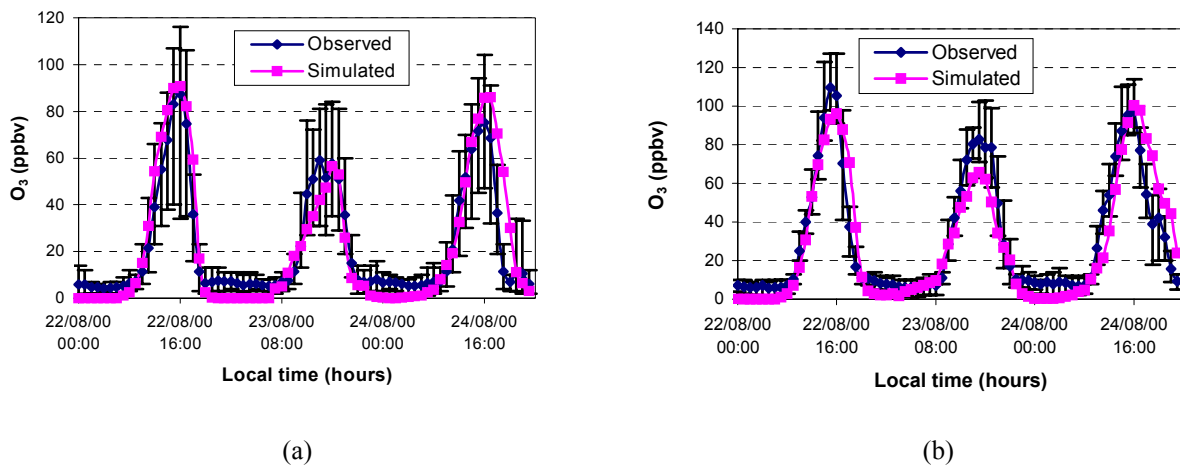(a)   (b)

Figure 1: Comparison between simulated and observed ozone concentrations (ppbv) for two groups of air quality stations inside MASP, during the period of August 22, 2000 and August 24, 2000. (a) G1 stations, (b) G2 stations.

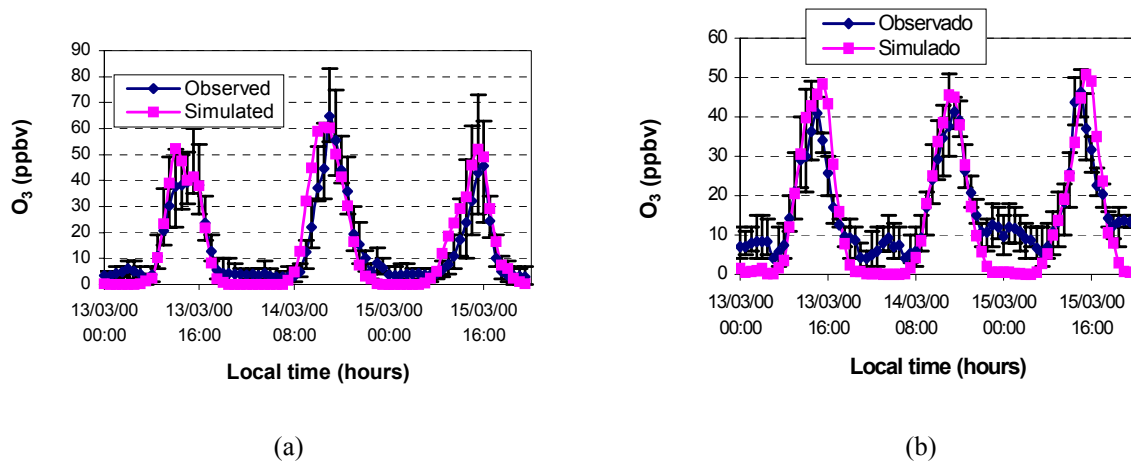(a)   (b)

Figure 2: Comparison between simulated and observed ozone concentrations (ppbv) for two groups of air quality stations inside MASP, during the period of March 13, 2000 and March 15, 2000. (a) G1 stations, (b) G2 stations.

The time series plot of ozone concentrations (figures 1 and 2) shows consistency between observed and predicted at the two groups of stations for both periods. The peak and behavior of ozone predicted is in agreement with the observations. However at nighttime simulated ozone was predicted to be near zero, whereas the observed ozone concentrations were about 10 ppbv at this time.

In the Table 1 and 2 are presented the statistical analysis of the predicted and observed pollutants concentrations for the periods. The Mean Normalized Bias (MNB), Mean Normalized Gross Error (MNGE) and the index of agreement (d) are calculated respectively as:

$$MNB = \frac{1}{N}\sum_{i=1}^{N}\left(\frac{(P_i - O_i)}{O_i}\right).100\% , \qquad (1)$$

$$MNGE = \frac{1}{N}\sum_{i=1}^{N}\left(\frac{|P_i - O_i|}{O_i}\right).100\% , \qquad (2)$$

$$d = 1 - \frac{\sum_{i=1}^{N}(P_i - O_i)^2}{\sum_{i=1}^{N}(|P_i - O| + |O_i - O|)^2} , \qquad (3)$$

where: P_i is the predicted value; O_i is the observed value; N is the number of valid data and O is the observed average value.

Table 1

The statistical analysis of the predicted and observed pollutants concentrations from period of August 22 to 24 of 2000.

Statistical parameters	Group 1				Group 2			
	CO (ppmv)	O_3 (ppbv)	NO_x (ppbv)	NMHC (ppmC)	CO (ppmv)	O_3 (ppbv)	NO_x (ppbv)	NMHC (ppmC)
Stand. dev. (σ_{obs})	1.0	24.3	188.4	0.8	-	31.4	72.9	2.0
Stand. dev. (σ_{sim})	1.1	28.9	166.5	0.6	-	31.9	92.7	0.5
Correlation coefficient (r_{xy})	0.88	0.93	0.91	0.66	-	0.91	0.71	0.44
Mean Normalized Bias (MNB)	1.3	-27.0	-1.2	-37.3	-	-23.8	13.5	-18.5
Mean Normalized Gross Error (MNGE)	16.5	62.9	23.2	43.9	--	50.9	36.3	43.0

	CO (ppmv)	O₃ (ppbv)	NOₓ (ppbv)	NMHC (ppmC)	CO (ppmv)	O₃ (ppbv)	NOₓ (ppbv)	NMHC (ppmC)
Index of agreement (d)	0.94	0.96	0.95	0.69	-	0.96	0.82	0.48
Root Mean Square Error (RMSE)	0.5	10.2	76.1	0.9	-	12.7	66.6	2.1
Peak of O₃ (%)								
Paired	-3.5				-10.8			
Unpaired	4.7				-9.9			

Table 2

The statistical analysis of the predicted and observed pollutants concentrations from period of March 13 to 15 of 2000.

Statistical parameters	Group 1				Group 2			
	CO (ppmv)	O₃ (ppbv)	NOₓ (ppbv)	NMHC (ppmC)	CO (ppmv)	O₃ (ppbv)	NOₓ (ppbv)	NMHC (ppmC)
Stand. dev. (σ_{obs})	0.46	15.7	23.6	0.19	-	11.5	11.1	0.4
Stand. dev. (σ_{sim})	0.37	19.5	23.0	0.16	-	16.8	8.3	0.12
Correlation coefficient (r_{xy})	0.94	0.92	0.90	0.56	-	0.93	0.68	0.16
Mean Normalized Bias (MNB)	17.5	-26.3	8.3	-12.1	-	-40.2	33.2	-33.2
Mean Normalized Gross Error (MNGE)	20.4	66.8	19.3	32.7	-	54.4	48.9	44.7
Index of agreement (d)	0.95	0.96	0.95	0.7	-	0.93	0.81	0.45
Root Mean Square Error (RMSE)	0.18	7.2	9.7	0.18	-	1.0	8.1	0.49
Peak of O₃ (%)								
Paired	-0.2				5.7			
Unpaired	11.1				12.4			

The results of statistical parameters calculated for both periods of study are, in general, within the error considered acceptable by the recommendations of Environmental Protection Agency (USEPA, 2005; Elbir, 2003; Freitas, 2003). The results of these applied tests indicate that the results of simulations are consistent.

5.2 Scenarios of Perturbation cases

Simulations to evaluate the individual ozone potential formation of VOCs were performed considering variations of ±15% in the emissions, which produce stable and close-to-linear responses (Hakami et al., 2004). These perturbations were performed equally for all the VOCs individually and for CO, NOₓ and VOCs.

The sensitivity of ozone to incremental of individual VOC mass was analyzed using reactivity scales written as:

$$MIR_{3D_i} = \max\left(\frac{\Delta C_{O_3}}{\Delta E_{VOC_i}}\right), \qquad (4)$$

and

$$POIR_{3D_i} = \frac{\Delta C_{O_3}}{\Delta E_{VOC_i}}\Big|_{\max(O_3)}, \qquad (5)$$

where: C_{O_3} is the ozone concentration in ppm and ΔE_{VOC_i} is the emission perturbation for each individual VOC in units of gVOC/cell min (Hakami et al., 2004). The variation of ozone concentration is analyzed in relation base case and in whole surface domain and time of day.

Additionally sensitivity of ozone to VOC and NOₓ emissions were calculated. These sensitivities according to Cohan et al. (2005) can be obtained with the brute force method thought of the finite different approximation for first-order coefficient as:

$$S^{(1)} \approx \frac{C_{+\Delta E_j} - C_{-\Delta E_j}}{2\Delta E_j} \qquad (6)$$

where: $C_{+\Delta E}$ is the ozone concentration of perturbation case (+15%) and $C_{-\Delta E}$ is the ozone concentration of perturbation case (-15%). The fractional perturbation in the parameter is denoted by $\Delta E_j = (E_j - 1)$.

In the Table 3 is presented the higher values of reactivity obtained for August 22 to 24. The reactivities are evaluated by the calculation of the MIR_{3D} and $POIR_{3D}$ indices. The organic species are representing by a code as: ACET (Acetone); ARO1 (aromatics with kOH < $2x10^4$ ppm^{-1} min^{-1}); BALD (aromatic aldehydes); BUTD (butadiene); CCHO (acetaldehyde); HCHO (formaldehyde); ISOP (isoprene); MEK (Ketones and other non-aldehyde oxygenated products which react with OH radicals); OLE1 (alkenes, other than ethene with kOH < $7x10^4$ ppm^{-1} min^{-1}) and UNID (non identified species).

Table 3

Three-dimensional incremental reactivity scales MIR_{3D} and $POIR_{3D}$ for August 22 to 24, 2000.

Species	MIR_{3D} (ppm O$_3$/g VOC)			$POIR_{3D}$ (ppm O$_3$/g VOC)		
	22/08	23/08	24/08	22/08	23/08	24/08
BUTD	2,4E+00	1,0E+00	1,0E+00	-3,2E-01	-2,6E-01	0,0E+00
ARO1	1,6E-01	7,5E-02	3,9E-02	6,4E-02	3,1E-02	6,8E-04
ISOP	1,5E-01	8,5E-02	2,3E-01	-3,5E-02	-7,1E-03	1,5E-01
HCHO	1,3E-01	3,7E-02	1,5E-02	4,1E-02	1,5E-02	9,5E-03
BALD	8,8E-02	5,0E-02	1,3E-01	-1,0E-02	0,0E+00	0,0E+00
ACET	8,4E-02	6,0E-02	2,6E-02	1,7E-02	2,6E-02	0,0E+00
OLE1	7,9E-02	2,0E-02	1,2E-02	5,6E-02	1,0E-02	1,7E-03
MEK	7,6E-02	5,3E-02	3,3E-02	-1,0E-02	4,1E-03	0,0E+00
UNID	6,6E-02	2,2E-02	2,9E-02	-3,9E-03	0,0E+00	0,0E+00
CCHO	5,6E-02	3,6E-02	1,8E-02	9,1E-03	2,3E-02	1,1E-03

MIR and POIR values presented in Table 3 are for whole day and domain and it represents the absolute reactivities. The MIR indices can be defined as the maximum incremental reactivity and it represents conditions where VOC control has the greatest effect on ozone. Therefore, the species with high MIR are the species more effective on ozone control in conditions of low VOC-to-NO$_x$ ratios.
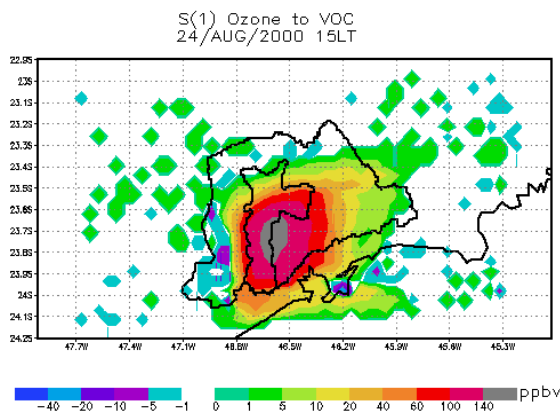
On the other hand the POIR (Peak Ozone Incremental Reactivity) indices represent the optimum conditions for ozone formation or where ozone is NO$_x$ limited.
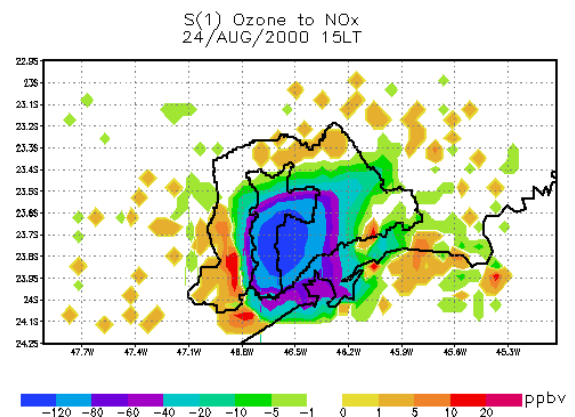
Figure 3 show the peak of ozone concentrations and their sensitivity to VOC and NO$_x$ anthropogenic emission for the wintertime period.
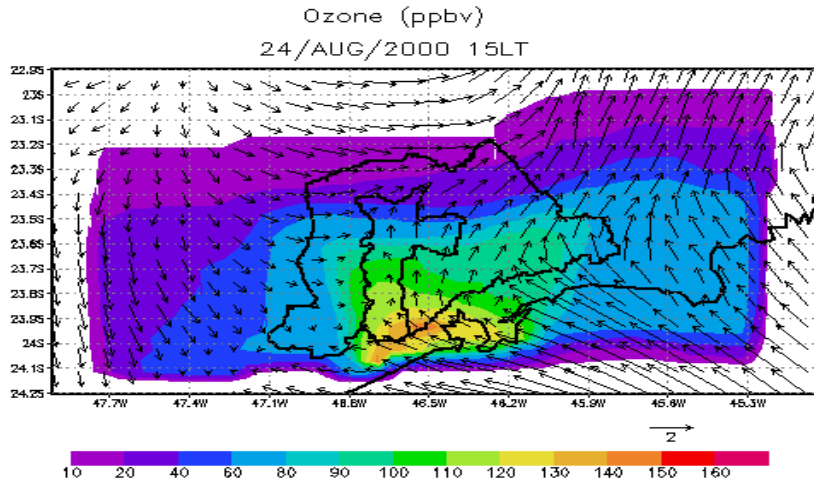
Figure 3: Peak of ozone concentrations on August 24 (a) and their sensitivity (first-order) to domain-wide anthropogenic emissions of VOC (b) and NO_x (c).

In the Figure 3 a large sensitivity of ozone to VOC can be observed on São Paulo region, where is localized the majority of source emission. The sensitivity of ozone to NO_x can be observed only in neighbor cities of São Paulo. The average sensitivity of ozone to VOC for whole domain and period was 1.3 ppbv in 1-hour and 2.8 ppbv in 8-hour. For NO_x the average in 1-hour was of −2.0 ppbv and in 8-hour of −3.4 ppbv.

In the second period (not showed the figure here) the peak of ozone was observed far of São Paulo and is happening later. This is result of the different meteorological situation

presented during winter and summer. In particular periods of study the intensity of sea breeze front and consequently the regime of winds was the important factor to promote the different levels of pollutants in São Paulo region. Although, it presents significant differences between the two periods the sensitivity of ozone is demonstrated to be much larger to VOC than NO_x for both periods in domain-wide.

6. Conclusions

The CIT model is a valuable tool to estimate the ozone concentration in the MASP. The estimated statistical indices showed that the results are in accordance to what is expected in

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terms of air quality modeling. The analysis of perturbations for all the VOCs individually and for CO, NO$_x$ and VOCs showed that ozone formation in MASP is more sensitivity to VOCs variation emission for both periods studied. In addition considering the composition of VOCs in São Paulo the preliminary results indicate that species represent by BUTD, ARO1, ISOP and HCHO are those with higher ozone potential formation in the region studied.

7. References

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