

Ozone Air Quality Modeling. A Case Study: A Heavily Vehicle Impacted Urban Avenue in Rio de Janeiro, Brazil

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As concentrações de ozônio para um área urbana, com alto fluxo veicular, no centro da cidade, foram simuladas usando um modelo cinético empírico. Foi desenhado um caso base usando dados experimentais, do mês de dezembro de 1999, para a Avenida Presidente Vargas, Rio de Janeiro. O acordo entre os resultados calculados e os dados experimentais é satisfatório. O pico de ozônio calculado acontece às 15:15 horas (23,0 ppb). Foi realizada uma análise de sensibilidade e incertezas e desenhados alguns cenários hipotéticos para ilustrar a capacidade preditiva do modelo.

An empirical kinetic modeling approach is used in order to simulate ozone concentrations for an urban downtown area with high vehicular traffic. A base case was designed using experimental data for December 1999 in Presidente Vargas Avenue, Rio de Janeiro. The agreement between experimental and simulated results was quite good. The simulated ozone peak was obtained at 3:15 PM (23.0 ppb). A sensitivity-uncertainty analysis was performed and hypothetical scenarios were designed to illustrate the predictive potential of Air Quality Models.

Keywords: air quality modeling, urban air pollution, ozone concentrations

Introduction

For the last couple of decades one of the most challenging problems tackled by atmospheric scientists has been the accurate depiction of photochemical processes taking place in the open atmospheres, with emphasis on the forecast of secondary air pollutants production. Due to the importance of its associated impacts, special efforts have been devoted to study the formation of tropospheric ozone (O_3).¹ Secondary air pollutants, such as ozone, are formed in the troposphere by chemical reactions of primary pollutants (e.g. nitrogen oxides, NO_x , and volatile organic compounds, VOC) that are emitted directly into the atmosphere. In urban environment, primary pollutants are mainly caused by anthropogenic activities associated with energy production and utilization. For a good prediction of secondary pollutants it is necessary to describe in detail the emission of precursor compounds, their transport, dispersion, mixing and chemical reactions. Simulation studies have attempted

to reproduce as closely as possible the actual composition of urban atmospheres by modeling the combined effects of physical and chemical processes. Air Quality Models (AQMs) are mathematical descriptions of the atmospheric transport, diffusion, deposition, emissions and chemical reactions of pollutants. They operate on sets of input data that characterize the emissions, topography and meteorology of a particular location, thus producing outputs which describe its regional air quality characteristics.²

The challenge for mathematical simulations has always been to establish the best in-balance possible between the simplified portrait and the actual view, thus optimizing the generalization, distortion and deletion in the mathematical formulation of the models. By averages of increasingly more powerful hardware resources, which in turn allow more detailed computer codes, sophisticated numerical solutions may be achieved throughout the work on the descriptive equations of a given reactive system.

Basically, there are two kinds of models: three-dimensional urban airshed models (UAM) and EKMA (empirical kinetic modeling approach).² UAM are grid-based

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models and are recommended for simulating ozone over urban areas since they are physically detailed and suited for modeling multiple days in extended areas (up to 400 km). Their main limitations are their sensitivity to boundary conditions and the need of detailed input data (information about meteorology and emissions) for each grid cell. The choice of the modeling domain and the dimension of each grid cell will depend on the resolution of the data. Besides, the spatial resolution of the concentrations predicted by a grid-based model corresponds to the size of the grid cell (usually the covered area is at least 15-20 km²). Thus, effects that have spatial scales smaller than those of the grid cell can not be resolved, as local ozone depletion near strong sources of NO_x, such as high traffic density urban highways. EKMA-type models are easy to apply, require a limited set of input data and are chemically detailed, their main limitations being a very simple description of physical processes and failure to accurately simulate multiple-day events or long-range transport. Nevertheless, when the available experimental data is highly limited, these models are considered an acceptable approach.

Smog chamber and modeling studies have shown that the atmospheric chemistry of NO_x and VOC leading to ozone and other secondary pollutants exhibits significant non-linearity. A decrease in precursors concentrations may or may not lead to a decrease in the formation of ozone and, in some circumstances, such decrease may lead to increases in ozone. Mainly due to the highly non-linear behavior of the atmospheric formation of secondary oxidants, environmental authorities are often forced to resort to mathematical models in order to forecast the more likely effects of control strategies. AQMs can be used to illustrate compliance with current Air Quality Standards (AQS) and are also helpful tools to estimate the magnitude of emissions abatement or control needed to attain ozone AQS. AQMs are also important to help planners to predict the probable response to control strategies.¹

Secondary pollutant formation is highly dependent on the emissions specific to the region studied. In this respect, Brazil is unique in the world for its reliance on ethanol, which is used both as a vehicle fuel and as an oxygenated additive to gasoline.³⁻⁹ In this paper, some of the results of the computer simulation of a base case and some hypothetical scenarios are discussed. The base case was designed on the basis of experimental data obtained at Presidente Vargas Avenue, Rio de Janeiro (Brazil), during December 1999, using the continuous monitoring equipment of FEEMA. The hypothetical scenarios were designed to illustrate the predictive potential of AQMs and to analyze the consequences of changes in the input data of the model.

Computational Procedure

Methodology

Computer simulations were performed using an empirical trajectory model implemented in OZIPR.¹⁰ In this model a well-mixed box is moved at average wind speed along a trajectory through the urban area. As the box moves, its height increases due to the mixing height rise from the sun's heating. This rise results in a decrease in the concentrations of the species in the box. At the same time, fresh emissions are added through the bottom of the box increasing the concentrations of primary species.

It was not possible to use a sophisticated urban airshed model, which requires very detailed information as input data, including meteorology and emissions resolved in time and space, that is not available for Rio de Janeiro. Therefore the use of an airshed (3D) model would not yield averageingful results.

The photochemical mechanism SAPRC¹¹ was used. This model has been extensively studied and validated and has been used in many computer simulations of urban air quality in the United States and elsewhere.¹² Reactions of ethanol and MTBE were included and stoichiometric coefficients and rate constants were re-calculated for a VOC mixture characteristic of Brazilian cities.¹³ The model represents explicitly the inorganic compounds and their chemistry. The model species is intended to have exactly the same properties as the real species and to undergo the same reactions in the model as those of the real species. Organic compounds are described using the lumped-species approach. The model species characteristics are determined by a mole fraction weighting of the characteristics of the individual explicit mechanisms for the species that are being lumped together. In this work, the lumped species include two groups of alkanes, two groups of aromatics, three groups of alkenes and one group of non-reactive compounds. Some compounds, as ethylene, acetylene, propane, benzene, MTBE, ethanol, formaldehyde and acetaldehyde are described explicitly.¹³

The model may be used to describe three types of scenarios: individual days (in general, days in which AQS were exceeded), base cases (*i.e.* representative scenarios) and hypothetical scenarios. The simulation of base cases is of special interest since it uses a combination of input data that may be chosen to be relevant and representative of Rio de Janeiro urban area. The analysis of the results may explain the impact of hydrocarbons and NO_x on ozone air quality in Rio de Janeiro. Additionally the base case may serve as a reference to examine the effect of changing the input parameters (*e.g.* temperature, emissions, solar radiation, *etc.*) on the calculated concentrations.

Table 1. Input parameters for the simulation of the base case. Temperature and relative humidity are average experimental values for December 1999. Mixing heights and emission values are estimated parameters (see text for details)

Time	Relative Humidity (%)	Temperature (°C)	Mixing height (m)	COV (kg/h)	NOX (kg/h)	CO (kg/h)
8:00 a.m.	69.18	24.74	500	68.68	62.33	397.0
9:00 a.m.	65.13	25.72	500	89.80	81.02	516.1
10:00 a.m.	63.46	26.76	700	43.51	39.49	251.55
11:00 a.m.	60.80	27.54	850	99.13	89.96	573.0
12:00 a.m.	57.12	28.65	1300	32.18	29.20	186.0
1:00 p.m.	54.56	29.16	1600	22.02	19.98	127.3
2:00 p.m.	51.93	29.50	2500	4.13	3.75	23.9
3:00 p.m.	51.46	29.54	1900	3.18	2.88	18.4
4:00 p.m.	50.81	29.17	1650	3.55	3.22	20.5
5:00 p.m.	51.62	28.59	1420	3.51	3.18	20.3
6:00 p.m.	54.50	27.81	1380	3.51	3.18	20.3
7:00 p.m.	57.31	27.05	1200	3.51	3.18	20.3

Description of the base case

The metropolitan area of Rio de Janeiro is located on the Atlantic coast of Brazil with about 6 million inhabitants distributed over a 6500 km² area. The main source of pollution in the central area is the vehicular fleet fueled with gasohol (gasoline with 24% v/v of ethyl alcohol), ethanol, diesel and, in minor extent, natural gas.

Presidente Vargas Avenue carries fourteen lanes of traffic, seven in each direction. It is representative of downtown vehicle fleet because the traffic includes light duty vehicles which use ethanol (17.5%) and gasohol (66.0%) as well as diesel (16.5%) fueled heavy duty vehicles, with diurnal fluxes (from Mondays to Fridays) between 6000 and 8000 vehicles/hour, depending on the time of the day.¹⁴

Experimental data used to set the model initial conditions were collected by FEEMA¹⁵ at the monitoring station located at 22°54' S and 43°10' W, between December 1 and December 29, 1999. Rainy days were not taken into account because in those conditions the main effect is the wash out of the atmosphere. The input parameters are listed in Table 1.

To maximize simulated ozone formation, the solar actinic flux was set at the highest level, *i.e.*, that for December 21 in Rio de Janeiro. Meteorological parameters (temperature and relative humidity) are hourly average values for the same period. The initial and final mixing heights were set as 500 m and 1200 m, respectively. The initial value was set according to the information of atmosphere temperature and pressure profiles available at IAG-USP¹⁶ home page. Diurnal variation and final value were recommended by the Meteorological Department (IGEO/UFRJ),¹⁷ since there were no available experimental data. The main effect of the mixing height is the dilution of gases. Since, in this work, the absolute value of CO emissions was used as an adjustable parameter, an error in

the mixing height may be corrected by changing the emissions.

The VOC/NO_x/CO emission ratios were calculated in consistence with the vehicle emission inventory for Rio de Janeiro city¹⁸ and the local vehicle flux (VOC/CO = 0.173 and NO_x/CO = 0.157, both on mass basis).¹⁴ This ratio was kept constant during the day and was considered as a non-adjustable parameter. CO emissions were set using measured ambient concentrations (the average hourly values for the month of December 1999) as a rough guide.

Initial concentrations are shown in Table 2. The initial concentration of CO, NO and NO₂ were based on the average hourly concentrations measured at 8 a.m. during the month of December 1999. Since there is no information regarding speciated VOC in vehicle emissions in Rio de Janeiro, speciated ambient VOC values (averaged data 46 samples collected in downtown Porto Alegre between March 1996 and April 1997) were used.¹⁹⁻²² This approach assumes that ambient VOC composition are similar for Rio de Janeiro and Porto Alegre, where vehicle emissions are predominant. This may not be rigorously valid since vehicle fleet composition may not be equal and, mainly, because in 1996-1997 Porto Alegre was using gasoline with 15% of methyl-tert-butyl-ether (MTBE) as oxygenate additive. The main product of MTBE oxidation is formaldehyde while the main product of ethanol oxidation is acetaldehyde. Using experimental data obtained at the same location of the simulations in 1998 and 1999,

Table 2. Initial concentrations for the simulation of the base case. Data are average values for 8:00 a.m. during December 1999, at the FEEMA monitoring station of Presidente Vargas Avenue

Compound or group	Concentration
VOC	0.4 ppmC
NOx	0.16 ppm
CO	1.7 ppm

formaldehyde and acetaldehyde initial concentrations were set to more reliable values.^{23,24} Also MTBE was set as zero and ethanol was increased by a factor of *c.a.* two, to account for increased exhaust and evaporative emissions. Since MTBE and ethanol have a low photochemical reactivity, this last assumption has no significant impact on modeling results. Values used in the simulation are presented in Table 3.

Results (base case)

As previously noted, emissions were set to fit experimental CO concentrations for December 1999. This approach is valid since CO has the lowest reaction rate constant in the VOC mixture. Figure 1 shows average experimental values and calculated results for CO concentrations. The fit is quite good. A further adjust was

considered unnecessary since the main goal of this work was to model a representative case of downtown Rio de Janeiro, and not to exactly reproduce a particular day and scenario.

The simulated ozone peak was obtained at 3:15 p.m. (23.0 ppb). As shown in Figure 2, both calculated and experimental data for ozone concentrations are in reasonable agreement for the diurnal variations, considering the 8:00 a.m.-8:00 p.m. time slot, throughout the whole period. This indicates that the constructed base case is representative of average summer time air quality at Presidente Vargas Avenue, Rio de Janeiro.

Solar flux, temperature and relative humidity impact on ozone concentrations

Solar fluxes were varied to consider a clean atmosphere (attenuation factor = 1.0) and a cloudy, polluted atmosphere

Table 3. Average composition of volatile organic compounds used for the simulation of the base case (units are ppbC in 1 ppbC total)

Compound or group	fraction (on a ppmC basis)	Compound or group	fraction (on a ppmC basis)	Compound or group	fraction (on a ppmC basis)
Alkanes 1 (C2-C6)	0.172	aromatics 2 (toluene and mono-substituted benzenes)	0.136	formaldehyde	0.014
Alkanes 2 (C ≥ C7)	0.111	aromatics 2 (xylenes)	0.049	acetaldehyde	0.028
ethene	0.075	aromatics 3 (reactive aromatics of higher molecular weight)	0.049	non-reactive	0.006
propene and higher terminal olefins	0.081	higher aldehydes	0.008	acroleine	0.011
acyclic alkenes C ≥ C4 (non-terminal)	0.075	butadiene	0.075	ethanol	0.062

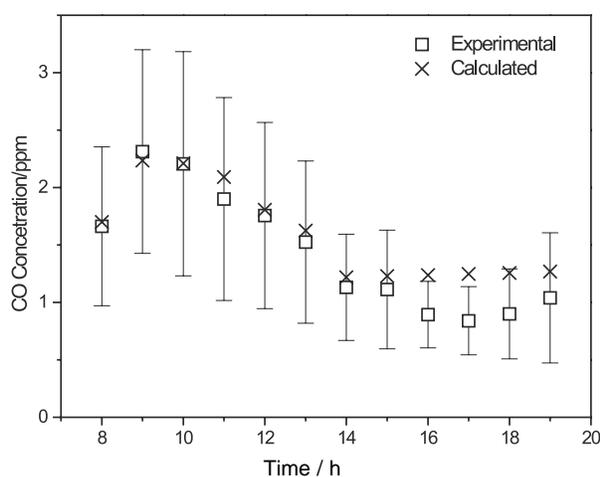


Figure 1. Calculated CO time profile for the base case and average experimental values for December 1999, at the FEEMA-Presidente Vargas monitoring station

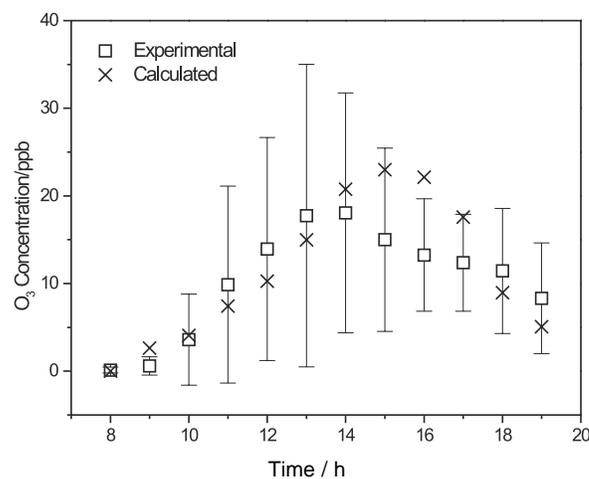


Figure 2. Calculated O₃ time profile for the base case and average experimental values for December 1999, at FEEMA-Presidente Vargas monitoring station

Table 4. Minimum and maximum experimental values for temperatures and relative humidity registered during December 1999, at the FEEMA monitoring station of Presidente Vargas Avenue, Rio de Janeiro

Time	Maximum temperature (°C)	Minimum Temperature (°C)	Maximum relative humidity (%)	Minimum relative humidity (%)
8:00 a.m.	27.3	22.3	85.0	31.0
9:00 a.m.	29.4	22.2	82.5	33.0
10:00 a.m.	30.1	22.8	83.0	44.0
11:00 a.m.	31.7	23.0	84.0	42.0
12:00 a.m.	33.1	22.9	87.5	36.0
1:00 p.m.	33.8	22.9	86.0	32.0
2:00 p.m.	33.8	22.8	86.0	27.0
3:00 p.m.	27.3	27.3	86.0	22.0
4:00 p.m.	34.5	21.7	86.0	20.0
5:00 p.m.	27.3	21.6	85.0	22.5
6:00 p.m.	33.9	21.8	80.0	24.0
7:00 p.m.	32.9	22.3	77.0	30.0

(attenuation factor =0.3). Temperature and relatively humidity were varied within their minimum and maximum values for December 1999 (see Table 4). The calculated values for ozone concentrations are shown in Table 5 and may be explained on the basis of the known ozone chemistry in urban areas.

Ozone can be considered as the main product of tropospheric chemistry.^{1,2} The only significant source of ozone in the atmosphere is the NO₂ photolysis in the presence of molecular oxygen:



As usually, M is an inert species.

Table 5. Sensitivity uncertainty analysis for ozone peak values calculated for the base case

Scenarios	Maximum O ₃ concentration, ppb (b)
Base case (a)	23.0
Solar flux (factor = 0.3)	6.22 (-72.95%)
Solar flux (factor = 1.0)	34.21 (48.74%)
Maximum temperatures	25.18 (9.47%)
Minimum temperatures	20.39 (-11.34%)
Maximum relative humidity	24.72 (7.48%)
Minimum relative humidity	21.65 (-5.87%)
Lower mixture height (-20%)	22.81 (-0.83%)
Higher mixture height (+20%)	23.28 (1.21%)

(a) Solar flux factor = 0.7

Temperature: average values for December 1999 (Table 2)

Relative humidity: average values for December 1999 (Table 2)

Mixture height: recommended values (Table 2)

(b) Values in parentheses were calculated as follows: (O₃ hypothetical case - O₃ base case)/O₃ base case x 100

Once formed, ozone may react with NO to regenerate NO₂ or may photolyse to produce both ground state and excited singlet oxygen atoms:



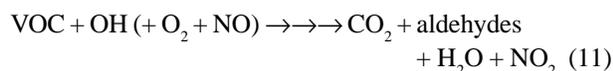
Tropospheric ozone concentration levels commonly achieved at urban environments can not be explained solely on the basis of reactions 1-7. In fact, the ozone production would be indeed very limited, unless another chemical route would take place, thus providing the oxidation of NO to NO₂ through an alternative path, competing with reaction 3.

Heicklen *et al.*²⁵ (1969) and Stedman *et al.*²⁶ (1970) explained the chain processes, involving OH and HO₂ radicals, that are responsible for both the oxidation of organic species and the oxidation of NO to NO₂. The basic process may be illustrated through the oxidation of CO:



In urban troposphere a large number of anthropogenic pollutants are present (organic compounds and enhanced

levels of NO_x over those in the background atmosphere). Tropospheric gas-phase chemistry can be summarized as the complex chain reactions triggered by sun light, in which organic molecules and nitrogen oxides play the most important role. The hydroxyl radical is the key reactive species in the chemistry of ozone formation. The VOC-OH reaction initiates the oxidation sequence. For the higher VOC species, the chemical steps involve alkyl radical (RO) and alkyl peroxy radicals (RO_2) formation, generation of OH, oxidation $\text{NO}-\text{NO}_2$ and formation of aldehydes, CO_2 and H_2O .



Since sunlight drives atmospheric chemistry by initiating some of the most important reactions and radical cycles involving ozone (mainly, reactions 1,4 and 5) it is expected that the results may depend on the actinic solar flux. The actinic solar flux is the photon flux incident on the molecule from all directions and depends on the latitude, date, hour and, also, on surface reflection (*i.e.* albedo), the cloud cover and the concentration of particulate matter and ozone which scatter and/or absorb light.¹ The effect is not linear, since solar radiation both contribute to the formation and consumption of ozone. The net effect is an increase in the maximum calculated value for higher solar fluxes. Values in Figure 1 (base case) were calculated considering an attenuation factor in the solar flux incident at ground level of 0.7. That attenuation factor is a typical value for urban, light polluted atmospheres, where the absorption of radiation by pollutants and the effect of clouds are not very severe.¹ In Table 5, two extreme conditions were considered: a perfectly clean cloudless sky atmosphere (attenuation factor = 1.0) and a cloudy and/or heavily polluted atmosphere (attenuation factor = 0.3). The ozone mixing ratio, at the peak, is 48.7% higher for a factor of 1.0 and 72.9% lower for a factor of 0.3. Clearly, the effect of radiation is very important. There are no instruments that measure actinic flux and its computation in the urban environment is a complex process. Because of that, the uncertainty in the calculations due to this factor may be relatively high.

The main effect of temperature is on the values of temperature dependent rate constants, in particular rate constants for the oxidation of VOC by OH radicals and the chemical equilibrium of peroxyacetyl nitrate (PAN), which may be considered a reservoir of NO_x and affects the NO_x and reactive species concentration. Calculated ozone concentrations using the higher values of temperature

registered by the monitoring station are 9.5% higher than base case results. The values calculated using the lower temperature data are 11.3% lower. These results may be explained by the fact that rate constants increase for higher temperatures (usually activation energies are all positive values) and so do the equilibrium constant for peroxyacetyl nitrate (PAN) decomposition in NO_2 and acyl peroxy radical.

The impact of relative humidity is still lower. In rural atmospheres, the removal of ozone is more effective at low latitudes and low altitudes where the radiation is intense and the humidity is high. This fact can be explained considering the reactions 5, 6 and 7. In urban atmospheres, the reaction of OH radicals with VOC becomes relevant to the formation of ozone and reaction 7 responsible for the increase in ozone concentrations with the increase in relative humidity.

VOC composition impact on ozone concentrations

In this section the contribution to ozone formation by individual VOC is analyzed. Each of the groups in the base case mixture was varied and the change in the peak ozone levels resulting from the additional or incremented organic is simulated. Results of these calculations are summarized in Table 6. The results depend on the chemical mechanism, on the conditions of the base case, on the VOC mixture and on NO_x concentrations. The relative reactivity of compounds is in agreement with the data for other scenarios.²⁷⁻²⁹

Different ranking scales of photochemical reactivity may be built. In a kinetic scale, the reaction with OH is evaluated by multiplying the reactive species concentration by the corresponding specific OH reaction rate constant. This is portrayed by the third entry in Table 6 and is indicative of the efficiency of OH removal by the reactive species, leading to carbonyls and radicals.

Another approachment is the MIR scale, which is based upon the concept of Maximum Incremental Reactivity (MIR), developed by Carter.²⁸ The MIR coefficient is the amount (in grams) of ozone formed per gram of VOC added to a reference atmosphere. In fact, it depends on the details of the mechanism in use. Since similar values have been reported by Carter,²⁸ Bowman and Seinfeld²⁹ and Derwent and Jenkin,³⁰ it is usual to report reactivities calculated using Carter²⁵ coefficients. In this work, Carter's coefficients were re-calculated for each group by weighting each individual coefficient (for each compound) by the compound relative composition in the group. The product of the MIR coefficient and the average group concentration indicates how much the group may contribute to ozone formation in the air mass.

Table 6. VOC composition impact on ozone concentrations. Four different analyses were performed: rate of reaction with OH (third column), MIR method (fifth column), (ppbO₃)/(ppbO₃ base case) x 100 for an increase of 50% (in ppbC units) in the group (sixth column) and (ppbO₃)/(ppbO₃ base case) x 100 for an increase of 1 ppb in the group (last column)

Compound ^a	$k_{OH} \times 10^{-4}$ (ppm ⁻¹ min ⁻¹)	reaction rate with OH, at 8:00 a.m. (min ⁻¹) ^b	MIR	ozone productivity (MIR scale) ^d	ozone productivity 50% increase in ppmC units (ppbO ₃ /ppbO ₃ base case) x 100 for	ozone productivity an increase of 1 ppb (ppbO ₃ /ppbO ₃ base case) x 100 for
alkanes 1 (C2-C6)	0.475	65.2	1.2	16.4	- 3.04	0.08
alkanes 2 (C ≥ C7)	0.911	55.5	1.1	6.7	0.74	0.13
ethene	1.258	188.7	7.4	111.0	8.91	0.43
propene and higher terminal olefins	3.883	427.1	9.4	103.0	11.52	1.08
acyclic alkenes C ≥ C4, non-terminal	9.405	705.4	7.5	56.2	16.74	1.74
aromatics 1 (toluene, mono-substituted benzenes)	0.913	62.1	3.9	26.5	3.34	0.52
aromatics 2 (xylenes)	3.618	86.8	7.7	18.5	8.43	2.69
aromatics 3 (reactive aromatics of higher molecular weight)	9.157	182.3	8.0	16.8	15.30	4.91
formaldehyde	1.442	80.7	7.2	40.0	8.39	1.21
acetaldehyde	2.326	130.2	5.5	30.8	5.82	0.83
higher aldehydes	2.923	32.2	6 ^c	6.6	1.34	1.00
ethanol	0.478	59.3	1.3	16.1	1.17	0.04

(a) Individual compound or group (see text for details)

(b) Reaction rate calculated as: k_{OH} x species concentration at 8:00 a.m. The true value should be multiplied by the mixing rate of OH radicals (2.75×10^{-5} ppm)

(c) Estimated value

(d) ppb x MIR

The (ppbO₃)/(ppbO₃ base case) x 100 scale was calculated by incrementing each group in 50% (in a ppbC basis). The results (sixth column in Table 6) represent the overall effect of a change in an individual VOC (or group) on the reaction mixture. This includes both the amount of ozone produced directly by the additional VOC that has been added to the mixture as well as changes in ozone production by other VOC as a result of changes in the mixture chemistry upon adding the individual VOC (or group).

Finally, the last entry in Table 6 was calculated by adding to the mixture 1 ppb of each species. This small change is not relevant on an absolute basis, thus imposing no relevant impact on the overall mixture composition. The results may be interpreted as the isolated effects of a change imposed on a given individual VOC.

Results in Table 6 show that ranking the VOC with respect to ozone production yields results that are substantially different from those for removal of OH.

The majority of organic degradation is through OH attack. The rate of this process depends both on rate coefficients and VOC concentrations. As known, the rate

constant for removal of OH by carbon monoxide is very low in comparison to other constants in Table 6 (3.544×10^2 ppm⁻¹ min⁻¹). Usually CO is considered within the least reactive species because its own mixing ratio does not alter significantly due to chemical reactions (the main effect on CO concentrations may be attributed to emissions and dilution). The rate of removal ($[OH] \times 602.5$ min⁻¹ at 8:00 a.m. and $[OH] \times 435.2$ min⁻¹ at 3:00 p.m.) is higher than rates for other species, mainly due to the larger mixing ratio of CO relative to VOC throughout the simulation. This averages that although CO concentration remains nearly constant during the simulation, its contribution to OH removal, with the consequent formation of CO₂ + H, is as important as the contribution of more reactive species, on an absolute mass basis. At 8:00 a.m., the more effective compounds in removing OH are acyclic alkenes (C ≥ C4), propene, higher aromatics, ethene, acetaldehyde and xylenes. This order varies during the simulation due to the change in the individual concentrations. Since the reactive mixture has a low VOC/NO_x ratio, VOC concentrations tend to deplete during the day, especially for the more reactive species. At 3:00 p.m. CO, acetaldehyde, formaldehyde and

propene are found to be the most reactive species. Ethanol is of minor importance: its rate constant is comparable to the constant for the lower alkanes but its mixing ratio is considerable lower.

For most VOC, when they are added to the base case mixture, significant ozone formation is observed. Exceptions to this pattern are the low alkanes group and low reactive compounds (not shown in Table 6). This result is due to changes in the reactive mixture (*i.e.* a decrease in the mixing ratio of the other species).

The relative amount of ozone formed by each species was evaluated using the three approaches described above. Results are not exactly the same because they use different scales (grams of O₃/gram of VOC, a ppbC basis and a ppb basis). In any case, it is clear that the more productive species are higher aromatics and alkenes, followed by formaldehyde and lower aromatics. Alkane and ethanol contribute little to ozone production. The species with the highest ozone productivities are not merely species that directly produce more ozone themselves, but are those that increase the radical flows, which then lead to an increase of ozone. New radicals are created through photolysis of ozone, aldehydes and other species. Under the NO_x-rich conditions of this scenario, an increase in the organic precursors increases the fraction of OH radicals that are converted to RO₂ and HO₂ radicals. These pathways lead to the re-creation of OH through reaction with NO. As a result, OH radicals can cycle through the radical propagation chain more times before combining to form terminal products such as HNO₃, nitrates and PAN. Since the calculated ranking depends on the reaction mixture, VOC/NO_x ratio and on the parameters of the model, different results would be obtained for other scenarios. Anyway, the present results are similar to those reported for other cities.²⁸⁻³⁰

Vehicular flux impact on ozone concentrations

Emissions (in kg h⁻¹ km⁻²) depend on the number of vehicles. In this section, the effect of an increase and a decrease in the vehicular flux was analyzed. In all calculations the VOC / NO_x / CO ratio was kept constant since this ratio is independent of the vehicular flux and is characteristic of the type and composition of fuel and vehicle distribution.

As shown in Table 7, an increase in vehicular flux leads (as expected) to an increase in CO concentrations. The effect is non-linear because part of CO reacts or dilute (for example, an increase of 100% in the vehicular flux will cause an increase of 43% in CO concentrations). For ozone an increase in emissions leads to a small increase in the

Table 7. Vehicular flux impact on calculated ozone and CO concentrations for the base case. Numbers in first column are the multiple factors for emissions. Numbers in parenthesis are referred to the base case (factor = 1.0)

factor ^a	Maximum O ₃ (ppb) ^b	CO(ppm) ^{c,d}
2.0	26.12 (13.6%)	1.757 (43.3%)
1.5	24.70 (7.4%)	1.508 (23.0%)
1.25	23.88 (3.8%)	1.367 (11.5%)
1.0 (base case)	23.00	1.226
0.75	22.06 (-4.1%)	1.084 (-11.6%)
0.50	21.09 (-8.3%)	0.943 (-23.1%)
0.25	20.18 (-12.3%)	0.8018 (-34.6%)

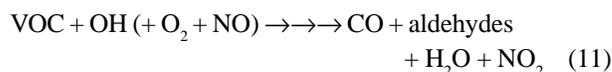
(a) Emission rates were multiplied by these factors

(b) Values in parentheses were calculated as: (O₃ hypothetical case - O₃ base case)/O₃ base case x 100

(c) Calculated at the time of O₃ maximum

(d) Values in parentheses were calculated as: (CO hypothetical case - CO base case)/CO base case x 100

calculated concentrations. This effect can be rationalized on the basis of the knowledge of the chemistry involved in ozone formation. As discussed beforehand the VOC + OH reaction initiates the oxidation sequence. There is a competition between VOC and NO_x for the OH radical:



At high VOC/NO_x concentration ratio, OH will react mainly with VOC; at low concentration ratio, the NO₂ reaction can predominate. At ambient conditions, the second order rate constant for reaction 12 is about 1.7 x 10⁴ ppm⁻¹ min⁻¹. Considering an average urban mix of VOC, an average VOC + OH rate constant is about 3.1 x 10³ ppm C⁻¹ min⁻¹. Using these values, the ratio of the OH+NO₂ / VOC+OH rate constants is about 5.5. Thus, when the VOC/NO₂ concentration ratio is approximately 5.5:1.0, with the VOC concentration expressed on a carbon atom basis, the rates of the reactions of VOC and NO₂ with OH are equal. If the VOC/NO₂ concentration ratio is less than 5.5:1.0, the reaction of OH with NO₂ predominates over the reaction of VOC with OH. The OH+NO₂ reaction removes OH radicals from the active VOC oxidation cycle, retarding the further production of ozone. On the other hand, when the concentration ratio exceeds 5.5:1.0, OH reacts preferentially with VOC. Also, the reaction of O₃ with NO (reaction 3) contributes to the consumption of ozone at high ratios NO_x/VOC.

At the VOC/NO_x concentration ratio considered for the simulations (VOC/NO_x = 2.5), an increase in NO_x

concentration levels would inhibit ozone production in two ways: 1) OH propagation is reduced because increased NO_2 mixing ratios cause increased termination of OH radicals, 2) a larger fraction of the total O_3 production is required to oxidize the larger mass of NO. A simultaneously increase in VOC concentrations produces more ozone. This fact may be seen in the ozone isopleth displayed in Figure 3. For VOC/ NO_x ratios lower than *c.a.* 8, reducing VOC and NO_x simultaneously leads to a slight decrease in the ozone maximum and, eventually, for higher NO_x concentrations may result in a slight increase in the ozone mixing ratio. This area of the diagram is known as the “hydrocarbon-limited” region. Whereas, in general, increasing VOC concentrations averages more ozone, increasing NO_x may lead to either more or less ozone, depending on the prevailing VOC/ NO_x ratio. Thus, the rate of ozone production is not simply proportional to the amount of NO_x present. For Brazilian cities the VOC/ NO_x ratio is generally low, due to the use of ethanol (which reduces VOC and CO emissions) and diesel (which highly contributes to NO_x emissions). This fact explains the apparently anomalous result of higher concentrations of ozone as a consequence of the reduction of the global emissions.¹⁸ It should be noted that this effect may not be valid in locations far from the emission sources (for example, downwind) where the VOC/ NO_x ratio may not be necessary the same.

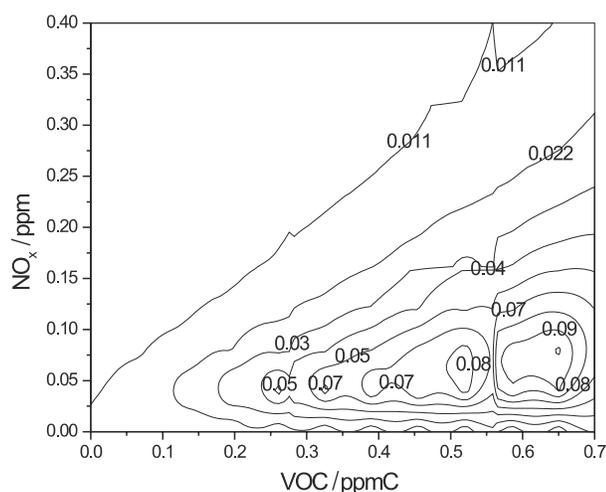


Figure 3. Ozone isopleth diagram calculated for the base case

Conclusions

It is currently established that ozone is a secondary pollutant formed by reactions of NO_x and VOC, known as ozone precursors. So it is widely accepted that control strategies targeting ozone attainment must necessarily be

based upon the control of its precursors. As the science of atmospheric photochemistry evolved, it became clear that complex, non-linear, feedback control processes relate NO_x and VOC precursors mixing ratios to ozone mixing ratios. This fact led regulators to adopt mathematical models that include the best representation of the non-linear chemistry as the basis of needed control computations. The model used in this work shows quite a good agreement with experimental data.

Sensitivity-uncertainty analysis stresses the importance of solar flux evaluation for the correct calculation of the photochemical coefficients, which determines ozone concentrations.

The amount of ozone attributable to each reaction species was estimated using different reactivity scales. Examining ozone formation after an increase of 1ppb in the mixing ratio on an individual species, the most productive compounds are higher aromatics, xylenes, higher alkenes, formaldehyde, propene and other olefins. Incremental reactivity calculations, on a per carbon basis showed the contribution to the ozone change as a result of changes in individual concentrations and in the reaction mixture. On this basis the more reactive species are alkenes and higher aromatics, followed by formaldehyde and lower aromatics.

Reduction in the vehicular flux leads to a decrease in CO concentration and very small changes in ozone mixing ratios. It may be concluded that reductions of VOC always lead to reductions of secondary pollutants, mainly ozone. In a joint reduction strategy (NO_x and VOC), reduction of emissions may result in an increase of ozone mixing ratios and a larger reduction of VOC is needed to reach a reduction of ozone.

These results show the potencial of AQMs to describe and predict the probable response to control strategies. However for simple EKMA models, like the model presented in this paper, the results are only valid for the local of the simulation. Control strategies derived from the isopleths generated under the constraint of constant VOC/ NO_x ratio, for an upwind location, often do not reflect the conditions in downwind areas, where the VOC/ NO_x ratio is different. For this reason, this kind of model provides useful information and may be used to explain the main aspects of air pollution, but in general, is not a good approach to design control strategies for an air basin.

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