Environmental Pollution 183 (2013) 159-165

Contents lists available at SciVerse ScienceDirect

Environmental Pollution

journal homepage: www.elsevier.com/locate/envpol



Spatial distribution of ground-level urban background O₃ concentrations in the Metropolitan Area of Buenos Aires, Argentina



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ARTICLE INFO

Article history: Received 15 August 2012 Received in revised form 5 October 2012 Accepted 16 November 2012

Keywords: Air quality modelling Ozone Urban air quality Nitrogen oxides Volatile organic compounds Metropolitan Area of Buenos Aires

ABSTRACT

In this work, a recently developed urban-scale atmospheric dispersion model (DAUMOD-GRS) is applied to evaluate the ground-level ozone (O_3) concentrations resulting from anthropogenic area sources of NO_x and VOC in the Metropolitan Area of Buenos Aires (MABA). The statistical comparison of model results with observations (including new available data from seventeen sites) shows a good model performance. Estimated summer highest diurnal O_3 1-h concentrations in the MABA vary between 15 ppb in the most urbanised area and 53 ppb in the suburbs. All values are below the air quality standard. Several runs are performed to evaluate the impact of possible future emission reductions on O_3 concentrations. Under all hypothetical scenarios, the maximum diurnal O_3 1-h concentration obtained for the area is slightly reduced (up to 4%). However, maximum diurnal O_3 concentrations could increase at some less urbanised areas of MABA depending on the relative reductions of the emissions of NO_x and VOC.

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1. Introduction

Ground-level ozone (O_3) is formed through reactions involving nitrogen oxides (NO_x) and volatile organic compounds (VOC) in presence of sunlight. Although it is a common compound of the troposphere, human activities have increased their levels considerably (e.g., Alvim-Ferraz et al., 2006), and nowadays it constitutes an atmospheric pollutant of increasing concern worldwide. Elevated O_3 concentrations can damage lung tissue, make people more susceptible to respiratory infections, or aggravate existing respiratory disease. It may also inhibit plant growth and cause widespread damage to crops and forests.

Despite the great efforts made to reduce the anthropogenic emissions of its precursor species (NO_x and VOC), ground-level O₃ is still above the air quality standards in many cities of the world (e.g., de Miranda et al., 2005; EEA, 2012; Elshorbany et al., 2009; Shan et al., 2008; USEPA, 2012). Ozone concentrations are usually lower in the urban atmosphere than in rural areas. However, in a recent study, their levels were found to be increasing at both urban and rural sites, with a faster rate of increase for urban centres and an overall trend for convergence between urban and rural O₃

levels (Paoletti et al., 2012). These trends strengthen the need for the evaluation of its ground-level concentrations in urban areas.

The Metropolitan Area of Buenos Aires (MABA) is comprised by the city of Buenos Aires (CBA) and the 24 Districts of the Greater Buenos Aires (GBA). It is located on a flat terrain, surrounded by non-urban areas, including the Río de la Plata on its east side. With a population of 12 801 364 inhabitants in 3830 km², the MABA is considered the third megacity of Latin America and the tenth worldwide. A few campaigns carried out at three urban sites have shown that O₃ concentrations in the CBA are low (Bogo et al., 1999; Mazzeo et al., 2005). Bogo et al. (1999) suggested that photochemical processes could play a minor role in whole urban area, but no data regarding ozone pollution in the GBA have been reported.

The DAUMOD model, a simple urban-scale atmospheric dispersion model that has been extensively used to study the air quality in this region, has recently been coupled with the Generic Reaction Set (GRS), a widely used simplified scheme of the most complete photochemical mechanisms. In this work, the coupled DAUMOD-GRS model (Pineda Rojas and Venegas, 2013) is applied to estimate the ground-level urban background O_3 concentrations resulting from high resolution (1 km², 1 h) area source NO_x and VOC anthropogenic emissions in the Metropolitan Area of Buenos Aires. Modelled hourly ozone concentrations are tested against observations in the CBA and new measurements from sixteen urban traffic sites in the GBA. The horizontal distribution of the maximum



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^{0269-7491/\$ –} see front matter \odot 2012 Elsevier Ltd. All rights reserved. http://dx.doi.org/10.1016/j.envpol.2012.11.013

diurnal O_3 levels in the MABA during summer conditions as well as their sensitivity to possible future emission reductions is evaluated.

2. Brief description of the DAUMOD-GRS model

The DAUMOD-GRS has been recently developed coupling the model DAUMOD (Dispersión Atmosférica Urbana – MODelo) with the Generic Reaction Set (GRS). It is a simple urban-scale atmospheric dispersion model that allows the estimation of ground-level urban background concentrations of nitrogen oxide (NO), nitrogen dioxide (NO₂) and ozone resulting from multiple area source emissions of NO_x and VOC. A complete description of the DAUMOD-GRS model can be found in Pineda Rojas and Venegas (2013). Here, its main features and assumptions are summarised.

DAUMOD (Mazzeo and Venegas, 1991) is an atmospheric dispersion model that was originally developed to estimate the concentrations of inert pollutants in urban areas. The model is based on the equation of mass continuity and considers the *x*-axis in the mean wind direction, the *z*-axis vertical and no transport of mass through the upper boundary of the pollutant plume. The ground-level (z = 0) concentration [C(x,0)] due to a horizontal distribution of *N* area sources of intensity Q_i located upwind a receptor *x*, is estimated by:

$$C(x,0) = a \left[Q_0 x^b + \sum_{i=1}^{N} (Q_i - Q_{i-1})(x - x_i)^b / (|A_1| k z_0^b u^*) \right]$$
(1)

where *k* is the von Karman's constant (=0.41), u^* is the friction velocity, z_0 is the surface roughness length and *a*, *b* and A_1 are coefficients that depend on the atmospheric stability. The DAUMOD model has been tested in different cities of Europe and USA (Mazzeo and Venegas, 1991; Venegas and Mazzeo, 2002). In the MABA, it has been used during the last two decades to study some aspects of the air quality and the impact of urban emissions on surrounding areas (e.g., Pineda Rojas and Venegas, 2009, 2010; Venegas and Mazzeo, 2006; Venegas et al., 2011).

The GRS (Azzi et al., 1992) is a simplified parameterisation of the most complete photochemical schemes. It was developed at the Division of Coal & Energy Technology, Commonwealth Scientific and Industrial Research Organisation (CSIRO) of Australia, and represents the thousands of reactions involving NO_x , VOC and O_3 with just seven reactions:

 R_1 . ROC + $h\nu \rightarrow$ ROC + RP

 R_2 . $RP + NO \rightarrow NO_2$

R₃. NO₂ + $h\nu \rightarrow$ NO + O₃

 $R_4. \text{ NO} + \text{O}_3 \rightarrow \text{NO}_2$

$$R_5. RP + RP \rightarrow RP$$

 $\text{R}_{6}\text{. NO}_{2} + \text{RP} \rightarrow \text{SGN}$

$$R_7$$
. $NO_2 + RP \rightarrow SNGN$

where ROC represents all VOC compounds, RP all radicals, SGN the stable gaseous nitrogen products and SNGN the stable non-gaseous nitrogen products. Therefore, the model describes the interaction between NO, NO₂ and O₃ explicitly (through reactions R₃ and R₄) but represents the photochemical generation of NO₂ with just one reaction for the generation of RP from emitted ROC. Due to its simplicity and ability to reproduce the interactions between NO–NO₂–O₃ at urban scale, the GRS has been widely adopted in urban air quality assessment studies (e.g., Anh et al., 1998; Hurley et al., 2005; Lashmar and Cope, 1995; McHugh et al., 1997; Venkatram et al., 1994; Zlatev et al., 1992).

The set of coupled differential equations describing the variation of the concentration (C_s) of each species *s* involved in reactions R_1 – R_7 , is of the form:

$$dC_s/dt = p_s - q_s C_s \tag{2}$$

where p_s and q_sC_s are its production and loss rates, respectively, depending on the reaction constants k_n that are associated to each of the reactions R_n . Eq. (2) is analytically solved applying the Quasi Steady State Approximation (QSSA) (e.g., Yamartino et al., 1992):

$$C_{s} = (p_{s}/q_{s}) + [C_{s0} - (p_{s}/q_{s})]\exp((-q_{s} \,\delta t)$$
(3)

where C_{s0} is the initial concentration at the beginning of the temporal integration step δt :

$$\delta t = \varepsilon \min[C_{s0}/(p_{s0} - q_{s0}C_{s0})] \quad \forall s \tag{4}$$

being ε an acceptable fractional change in the concentration so that p_s and q_s are approximately constant during δt .

In DAUMOD-GRS, the concentrations of the precursor species (NO_x and VOC) due to the atmospheric transport and dispersion are first computed by Eq. (1). During daylight hours, these species can react following reactions R_1 – R_7 for which the solutions given for C_s [Eq. (3)] are numerically integrated during a reaction time that accounts for the mean travel time of both species from their sources to the receptor. At night, since almost all NO present reacts with O₃ to produce NO₂ (Seinfeld and Pandis, 2006), only reaction R_4 is allowed in the model.

3. Testing of DAUMOD-GRS in the Metropolitan Area of Buenos Aires

3.1. Observed ozone concentrations

In order to test the performance of the DAUMOD-GRS model to estimate ground-level urban background O_3 concentrations, two sets of data accounting for a total of 3100 hourly ozone concentration values are used.

The first one has been obtained from a winter campaign performed in an open green area within the CBA (see Fig. 1), where O₃ concentrations were continuously measured from 11 August to 17 September 2001. The monitoring station is surrounded by the domestic airport (located at ~ 800 m to the NW), two Thermal Power Plants (2 km to the E, on the coastline), and two avenues, one extending from SE to WNW (at distances varying between 80 and 900 m) and the other one from SW to NNE (at distances between 180 and 800 m). At this site pollution level is not determined significantly by any single source or street, but by the integrated contribution from all sources upwind of the station, therefore it can be considered as an urban background site (Larssen et al., 1999: Venegas and Mazzeo, 2006). Ozone concentrations were measured using a cross-flow modulated ultraviolet absorption method (Equipment: Horiba, APOA-360, Japan). The results from these measurements have been analysed in detail in Mazzeo et al. (2005).

The second data set has become available recently from several campaigns carried out by the National Office of Public Roads of Argentina at sixteen urban traffic sites, mostly distributed along the main highways of the Greater Buenos Aires (GBA), in different periods of 2007 and 2008. Ozone concentrations were measured approximately within 50 m from the traffic line, with a Thermo Scientific Ozone Analyzer, Model 49i, a dual cell photometer



Fig. 1. Values of mean \pm standard deviation of observed ground-level O₃ concentrations (ppb) at each measurement site in the MABA (CBA + GBA).

certified by the US EPA (United States Environmental Protection Agency) which measures the amount of ozone in the air with a precision of 1 ppb. To our knowledge, these campaigns provide the first observations of ground-level O_3 concentrations in the Greater Buenos Aires.

Fig. 1 presents the observed O_3 concentrations at each measurement site, averaged during its sampling period. Regardless the fact that the two sets of data were obtained in different years, mean ozone levels vary between (9.3 ± 5.5) ppb at CBA and (21.8 ± 5.1) ppb at GBA, showing a typical variation pattern with lower mean concentrations in the most urbanised area (CBA) and greater ones in the suburbs (GBA).

3.2. Comparison between estimated and observed O_3 concentrations

The DAUMOD-GRS model was applied to estimate O_3 hourly concentrations at each monitoring site during its sampling period. The runs were performed considering temporal and spatial resolutions of 1 h and 1 km², respectively.

Input hourly surface meteorological data registered at the domestic airport of the CBA and sounding data obtained at the international airport (located in the GBA, 30 km to the SW of the city) were used for calculations. Input NO_x emission data belong to the high resolution (1 h, 1 km²) emission inventory recently developed for the MABA for year 2005 (Venegas et al., 2011). The assumed speciation for the NO_x species is 90% of NO and 10% of NO_2 (by mol), following the USEPA defaults (USEPA, 2002), VOC emission rates were obtained using the same activity data base employed to estimate the emissions of NO_x. Emissions from the residential, commercial and small industry activities, the aircraft operations at the local and international airports and the road transport in the MABA, are considered all together as area source emissions. Taking into account that among these categories, VOC emissions are dominated by the road transport sector, its speciation has been estimated using the MABA vehicle fleet composition and the COPERT IV VOC classification. Other sources such as solvent use or biogenic emissions are not considered in this work. ROC emissions were obtained from those of VOC, following the methodology proposed by Venkatram et al. (1994). The details of this estimation can be found in Pineda Rojas and Venegas (2013). On the other hand, as initial condition, a regional background concentration of 20 ppb was assumed for O₃ based on the previous measurements performed in the CBA (Bogo et al., 1999; Mazzeo et al., 2005). For other species, clean air concentrations were used as boundary conditions.

Fig. 2 shows the scatter plot of observed and modelled hourly O₃ concentrations and Table 1 summarises the statistical measures (Chang and Hanna, 2005) obtained from their comparison. The observed hourly values vary between 1 and 34 ppb, while the modelled ones are in the range 1–35 ppb, with their mean levels differing by less than 1 ppb. 82.1% of modelled O₃ concentrations are within a factor of two of the observed values, being slightly overestimated according to the fractional bias (-0.066). On the other hand, when comparing the daily maximum ozone concentrations (N = 169), it is found that the observed and modelled values vary between similar ranges (8-34 ppb and 9-35 ppb, respectively) with 97.6% of modelled daily peaks being within a factor of two of the observed levels (see Fig. 3), a NMSE of 0.11 and a FB of -0.139. Note that they do not necessary occur at the same hour but represent the maximum concentration reached at each measurement day. From Fig. 3, 85.7% of modelled daily peak O₃ levels fall within $\pm 50\%$ of the observed values. The percentage of model results within this relative error varies among the monitoring sites between 33.3% and 100.0%, but no pattern is observed

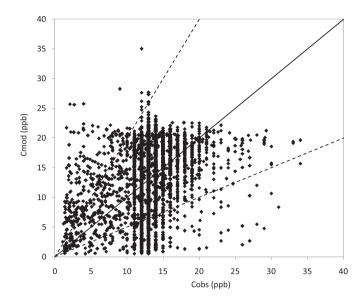


Fig. 2. Scatter plot of observed and modelled hourly O_3 concentrations (N = 3100), including the lines 2:1, 1:1 and 1:2.

with the distance from the city. In summary, all statistical measures show a general good performance of the DAUMOD-GRS model to simulate ground-level O₃ concentrations in the MABA, with a good ability to reproduce the maximum daily levels.

4. Horizontal distribution of maximum diurnal O₃ levels in the MABA

Often, in urban areas ozone ground-level concentration presents a double peak pattern with one maximum occurring after midday (due to the greatest photochemical activity of the atmosphere) and the other one at night-time hours (due to other factors such as reduced mixing height). The highest daily peak may be reached at either nocturnal or diurnal hours. According to the observations, maximum O₃ concentrations in the MABA occur mostly during daylight hours. Therefore, the following analysis focuses on the maximum diurnal levels.

4.1. Present conditions

In order to assess the spatial distribution of O_3 maximum 1-h ground-level concentration in the MABA and its surroundings, the DAUMOD-GRS model was applied for summer 2007 (taking this year as representative of the present conditions), considering a horizontal resolution of 1 km². During that summer, the hourly wind speed varied between calm conditions (16%) and 8.2 m s⁻¹, the sky was clear during 52% of the time, the air temperature was in the range 15.1–33.4 °C, and the estimated total solar radiation varied between 2.9 and 895.2 W m⁻². Fig. 4 presents the spatial distribution of the estimated highest diurnal 1-h ground-level concentration of O_3 in the area. From this Figure, it can be seen

Table 1

Statistical measures obtained from the comparison of hourly observed and modelled O_3 concentrations (N = 3100). [SIGMA: standard deviation (ppb); NMSE: normalised mean square error; FA2: fraction of estimations within a factor of two of observations; FB: fractional bias].

	Mean	Sigma	NMSE	FA2	FB
Observed	12.8	4.4			
DAUMOD-GRS	13.7	5.8	0.21	0.821	-0.066

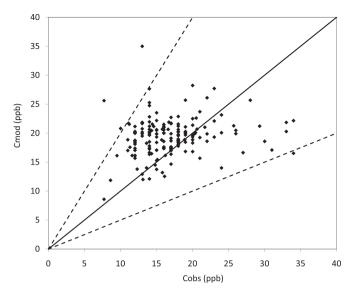


Fig. 3. Scatter plot of observed and modelled daily maximum hourly O_3 concentrations, including the lines 2:1, 1:1 and 1:2.

that the diurnal peak values vary between 14.9 ppb in the areas of highest vehicular traffic and 52.8 ppb in surrounding areas outside the MABA, as expected. All 1-h concentrations are therefore well below the Air Quality Standard (120 ppb) established for the MABA.

Fig. 5 presents the daily variation of the MABA diurnal highest O_3 concentration, while Fig. 6 shows the histogram of values shown in Fig. 5. It is observed that most of the time (73% of summer days), the maximum O_3 levels are lower than 30 ppb, while nearly 17% of the time the maximum values are in the range 30–40 ppb. According to model results, concentrations of ozone above 40 ppb occur 10% of the summer days, between 6 and 8 h in the morning, during conditions of low wind speed (<2 m s⁻¹), clear sky (<2 oktas), relatively high temperatures (19–25 °C) and solar radiation ranging between 14 and 357 W m⁻². Therefore, O_3 concentrations greater than 40 ppb obtained in the suburbs of MABA could be explained by relatively stagnant conditions occurring during early morning hours of some sunny days. On the other hand, the absence of strong ozone-

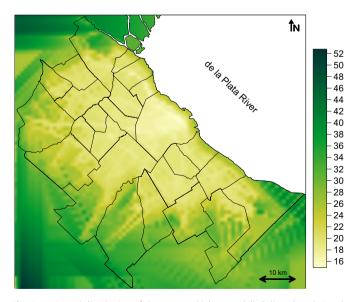


Fig. 4. Horizontal distribution of the summer highest modelled diurnal peak O_3 1-h concentration (ppb).

destroying mechanisms (e.g., titration with local NO_x emissions) is known to result in higher ozone concentrations, particularly at night-time (Syri et al., 2001). Since O₃ diurnal peaks above 40 ppb occur outside the MABA (Fig. 4) relatively far from the NO_x emissions, this could also help explaining these higher levels, although further studies such as process analysis are required to determine which of these factors (i.e., physical or chemical) is dominating.

4.2. Impact of possible future NO_x and VOC emission reductions

In large urban areas, ground-level O_3 concentrations depend greatly on the vehicle emissions of its precursor species NO_x and VOC (e.g., Borge et al., 2008; Gao, 2007), which in turn depend on a variety of factors (e.g., vehicular traffic, vehicle fleet, mileage and age, mean driving speed). Despite that in general the number of vehicles is increasing, NO_x and VOC emissions are being reduced in many cities due to improvements in engines and fuels forced by stricter legislations and fleet renewals (e.g., Wang et al., 2010; Zamboni et al., 2009).

Therefore, the following arising question is how sensitive the maximum O_3 levels in the MABA could be to possible future NO_x and VOC emission reductions. Projections of emission inventories are key to evaluate their likely impact. Unfortunately, at present there is not enough available information to estimate them for the MABA. For this reason, different scenarios of emission reductions have been considered (see Table 2), taking into account the general trends and projections that have been obtained in recent years for the road transport sector at several countries (e.g., Borge et al., 2008; Grice et al., 2009; Lumbreras et al., 2008; USEPA, 2008; Zamboni et al., 2009). The scenarios shown in Table 2 assume NO_x and VOC emission reductions ranging between 30 and 50%. Given that the VOC/NO_x emission ratio is another important factor affecting the O_3 formation in the urban atmosphere, the NO_x and VOC reductions have been selected/combined so as to include all its possible variations: no change (scenarios E2 and E3), a reduction (E4 and E5), and an increase (E6 and E7). On the other hand, some authors have reported a positive trend in the fraction of NO₂ with respect to NO_x emissions (f-NO₂), which may also affect O₃ levels in urban areas (Jacobson et al., 2004). Therefore, an increase of the f-NO₂ value is also considered (see Table 2).

The DAUMOD-GRS model was applied considering the emission reductions shown in Table 2 and no change in the atmospheric conditions. For each summer day, the diurnal maximum O₃ 1-h concentration obtained in the area was stored and compared with the highest peak obtained for that day at present conditions (scenario E1). The results obtained for each scenario are presented in Table 3. The lowest day-to-day maximum concentration (C_{max}) ratio to case E1, varies very little among different scenarios. The minimum ratio obtained (0.927 for case E4) indicates that the greatest decrease among these hypothetical emission conditions would be of 7.3%. This was obtained for 15th January, when the highest diurnal peak in the area, 40.8 ppb (see Fig. 5) would be decreased to 37.9 ppb. On the other hand, the highest day-to-day C_{max} ratio to case E1 varies between 1.074 (E4) and 1.185 (E7), showing a maximum increase of 18.5% on the basis of the day-today variation. In this case, the C_{max} value estimated for 2nd February, 42.8 ppb (Fig. 5) would be increased to 50.7 ppb. If the analysis is performed independently of the day, the lowest diurnal O₃ peak concentration (21.7 ppb) is almost not affected by the emission reductions: its highest difference was obtained with scenario E7 and shows a maximum increase of only 0.2 ppb (0.9%). On the other hand, in all scenarios, the maximum O₃ level reached in the MABA is slightly lower than the one obtained at present conditions (52.8 ppb). As shown in Table 3, this level could be

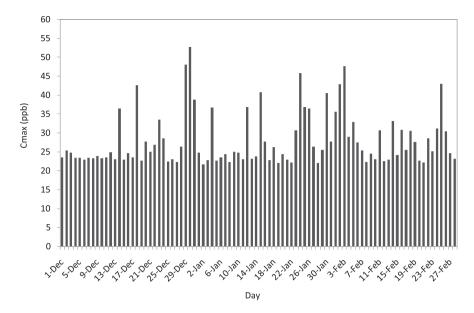


Fig. 5. Daily variation of the highest modelled diurnal peak O₃ 1-h concentration (ppb) in the area (Fig. 1) in summer.

reduced up to 50.7 ppb (under the emission conditions of scenario E7) representing a maximum decrease of 4%.

By comparing the maximum diurnal O₃ levels estimated for present conditions (presented in Fig. 4) with the corresponding values for scenarios E4 (the "best" case of Table 2) and E7 (the "worst"), it is found that the response varies spatially, as expected. Under both situations, the summer maximum diurnal O3 concentrations would experience an increase in most of the MABA and a decrease in some surrounding areas up to 36% (17.4 ppb), as shown in Fig. 7. For scenario E4, the increase in the urban area would be mostly lower than 5%, between 5 and 10% in a large area of the CBA where O_3 peak levels are the lowest, and up to 35% (10.7 ppb) in some less urbanised areas of the MABA. On the other hand, if the emissions were reduced as in scenario E7, the increase of O₃ peaks would be between 10 and 20% in most of the CBA (meaning still a very low impact) and could reach a 50% increase (13.0 ppb) in the suburbs of the GBA. This greater increase responds to the fact that scenario E7 assumes a greater reduction in the emissions of NO_x than in those of VOC, and also an increase in f-NO₂. Regardless the differences in the methodologies employed (the applied models, the analysed statistics, etc.), similar results

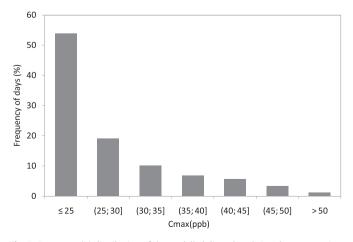


Fig. 6. Frequency (%) distribution of the modelled diurnal peak $\rm O_3$ 1-h concentrations shown in Fig. 5.

have been obtained for other urban areas (e.g., Che et al., 2011; Roustan et al., 2011).

5. Discussion

The results presented in Section 4 must be considered within a context that takes into account the common limitations of modelling studies. In particular, the approximations under which the study is based: those related to the model itself (the processes that are included and how they are simulated), and the ones regarding the model run conditions (the spatial and temporal resolutions, input data, etc.). Furthermore, projections of given conditions only constitute a likely alternative; and hence, the results of what may occur under those conditions must be consider as such.

DAUMOD-GRS is a simple model that simulates the concentrations of NO, NO₂ and O₃ resulting from area source emissions of NO_x and VOC in an urban area. The model includes the processes of atmospheric transport, dispersion and photochemical reactions on the gaseous phase, in a simple way. Thus, the main advantages of the DAUMOD-GRS model are the simplified input information required and that it can be applied to a large number of area sources (typical of urban areas) for long time periods (i.e., yearly) using short computation time. In this way, the model can be particularly useful in providing urban background concentrations for smallscale local models (e.g., street canyon models) to assess population exposure to O₃ in urban areas. On the other side, its main drawback is that it may not be adequate to use in places whose

Table 2

 NO_x and VOC anthropogenic emission reduction scenarios considered in calculations [f-NO₂: fraction of NO_2 in NO_x emission speciation].

Scenario	Emission reduc	f-NO ₂	
	NO _x	VOC	
E1	Present conditi	ons	0.1
E2	30	30	0.1
E3			0.2
E4	30	50	0.1
E5			0.2
E6	40	30	0.1
E7			0.2

Table 3

Highest modelled diurnal peak O_3 1-h concentrations in the area (C_{max}) during the summer season, for each scenario.

	Scenario								
	E1	E2	E3	E4	E5	E6	E7		
Day-to-da	Day-to-day C _{max} ratio to case E1								
Lowest	1	0.928	0.928	0.927	0.928	0.928	0.929		
Highest	1	1.078	1.134	1.074	1.130	1.136	1.185		
Daily C _{max}	Daily C _{max} (ppb)								
Lowest	21.7	21.8	21.8	21.7	21.8	21.8	21.9		
Highest	52.8	52.4	51.0	52.4	51.0	50.8	50.7		

photochemical pollution conditions are severe, or in complex terrain where other mechanisms of transport (not included in the model) can be important.

As mention before, the MABA is located on a flat terrain and is mostly surrounded by non-urban areas. According to previous

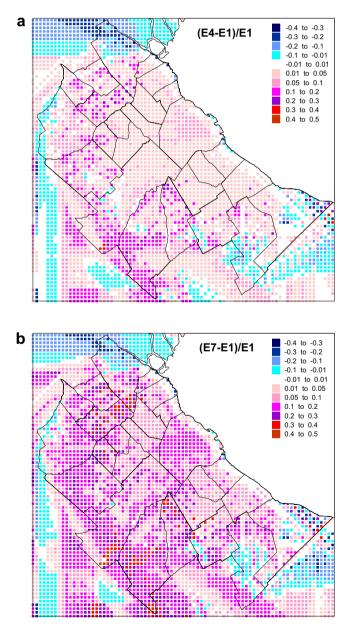


Fig. 7. Relative difference of the summer highest modelled diurnal peak O_3 1-h concentration (ppb) estimated for scenarios E4 and E7 and that obtained for present conditions (E1): (a) (E4–E1)/E1; (b) (E7–E1)/E1.

studies on the air quality in the area (carried out mostly in the CBA), the MABA does not seem to present significant pollution episodes (e.g., Bogo et al., 1999), which supports the use of a simple model such as the DAUMOD-GRS. Then, the next question is to what extent it was correct to have neglected the biogenic emissions of VOC (bVOC). The vegetated ground might be an important contributor to total VOC emissions. Depending on the plant species. different VOC compounds having a specific potential of O₃ formation (POF), can be emitted (Calfapietra et al., 2009). Therefore, some vegetated areas of the MABA could have some effect on O₃ levels through both the magnitude and POF of bVOC emissions. The fact that the observed ozone concentrations are well reproduced by the model in this region, suggests that either the bVOC emissions are small compared to the anthropogenic ones, are not small but have a low POF, or the error for its omission is counteracted by other errors (for example, deposition processes have been neglected in this work). Recent findings show higher ozone uptake by VOCemitting trees as compared to non-emitting ones (Calfapietra et al., 2012), which would support the last hypothesis. But more studies are required to elucidate this.

6. Conclusions

This work applies the DAUMOD-GRS atmospheric dispersion model to evaluate the spatial distribution of ground-level urban background O_3 concentrations resulting from high resolution (1 km², 1 h) area source NO_x and VOC anthropogenic emissions in the Metropolitan Area of Buenos Aires (MABA). The statistical comparison of modelled hourly ozone concentrations with recently available observations from 17 monitoring sites shows that the model performs well in the area. Considering all data (N = 3100), both modelled and observed hourly O_3 concentrations at the measurement sites are lower than 35 ppb. As expected, mean ozone levels are lower in the most urbanised areas and greater in the suburbs.

Maximum diurnal O₃ 1-h concentrations are estimated at each square kilometre of the MABA and its surroundings during present summer conditions. According to model results, daily O₃ peaks occur approximately at 50–60 km downwind downtown and vary between 22 and 53 ppb. Therefore, all hourly ozone concentrations are below the Air Quality Standard (120 ppb). Values greater than 40 ppb were obtained in sunny mornings under stagnant atmospheric conditions, during 10% of the days.

Based on current trends of anthropogenic NO_x and VOC emissions, the sensitivity of O₃ peak levels to different scenarios of possible future emission reductions is also evaluated. Results show that the summer highest 1-h concentrations estimated for the area (53 ppb) would be slightly diminished (up to 4%) under all considered emission conditions. On the other hand, a situation in which NO_x emissions were reduced more than those of VOC (with a resulting increase in the VOC/NO_x ratio) and the fraction of NO₂ in NO_x emissions was enhanced would lead to an increase of diurnal O₃ peak levels in the MABA, being small in the most urbanised zone and considerable in the suburbs (up to 13.0 ppb, representing a maximum increase of 50%). The same hypothetical emission conditions could decrease maximum ozone levels in the outer region (up to -17.4 ppb, meaning a maximum decrease of 36%).

Acknowledgements

This study has been supported by CONICET Project PIP0304. The authors are particularly grateful to the "Organo de Control de Concesiones Viales (OCCOVI)" of Argentina, for provided concentration data which greatly contributed to the development of this work.

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