

# Simple atmospheric dispersion model to estimate hourly ground-level nitrogen dioxide and ozone concentrations at urban scale



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## ABSTRACT

Atmospheric nitrogen dioxide (NO<sub>2</sub>) and ozone (O<sub>3</sub>) present potential health risk at large urban centres worldwide. Modelling their ground-level concentrations is a fundamental part of urban air quality assessment studies. Simple atmospheric dispersion models are particularly useful in places lacking detailed input data to run complex models and for applications requiring a large number of simulations, also allowing high spatial and temporal resolution even for long-term calculations. The DAUMOD-GRS urban atmospheric dispersion model has been developed aiming to have these features. This work presents its performance evaluation considering hourly concentrations of NO<sub>2</sub> and O<sub>3</sub> measured at twenty sites across the Metropolitan Area of Buenos Aires (MABA), Argentina. Results show an acceptable model performance, with a small tendency to underestimate NO<sub>2</sub> and to overestimate O<sub>3</sub>. By grouping the monitoring sites in regions having different emission conditions, it is found that the model reproduces well the observed urban-suburban concentration gradients.

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## 1. Introduction

Urban concentrations of nitrogen dioxide (NO<sub>2</sub>) and ozone (O<sub>3</sub>), resulting from anthropogenic emissions of nitrogen oxides (NO<sub>x</sub>) and volatile organic compounds (VOC), may cause adverse effects on human health if they are relatively high (WHO, 2005). Therefore, evaluation of their ground-level concentrations is fundamental in urban air pollution assessment studies, for which modelling plays an essential role. Deterministic urban air quality models (UAQMs) are commonly used to estimate urban background concentrations. They are based on mathematical relationships that describe the processes involved in the formation, transport and dispersion of air pollutants. Since these models provide a link between the emissions of primary species and the concentrations of secondary (formed) compounds, they are useful to identify the various source contributions, and to evaluate the impact of different emission abatement strategies on pollutant levels. In addition, UAQMs provide the input for street canyon models which allow the assessment of human population exposure, and hence they are also an important component of integrated assessment models (e.g., Finardi et al., 2008; Leksmono et al., 2006; Mensink and Cosemans, 2008; Namdeo et al., 2002; Sokhi et al., 2008).

Usually, UAQMs can be classified into comprehensive and simple semi-empirical models (Moussiopoulos, 2003). A detailed representation of simulated processes behind the production/loss of a pollutant may help to understand the interactions among emissions, atmospheric conditions and pollutant chemistry in the urban atmosphere. In this sense, the capabilities and performance of advanced numerical UAQMs have been improved substantially in the last years (Borge et al., 2008). However, increasing the complexity of models can introduce more parameters with uncertain values, decreasing transparency and increasing overall uncertainty (Derwent et al., 2010). The lack of detailed input data is one of the main sources of uncertainty of the deterministic models. For example, the chemical species of the emission inventories must match those of the chemical mechanism included in the UAQM. Thus, a greater number of reactions and species requires a greater knowledge of the pollutants (both their emissions and regional background concentrations) involved in the mechanism, which may not be available. On the other hand, the degree of complexity also influences the number of simulations that can be performed, which is particularly important for regulatory purposes involving hundreds of model runs. In cases like these, simple models provide an acceptable alternative to estimate urban background concentrations. In places where there is not enough available information to run comprehensive models, they may constitute the only tool to gain some insight into the source-receptor relationships. In urban

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areas where the input data are not a limitation, simple UAQMs can be used to obtain a large number of simulations that allow a selection of a few scenarios to be then run with comprehensive models.

The DAUMOD model (Dispersión Atmosférica Urbana, in Spanish) (Mazzeo and Venegas, 1991) is a simple urban atmospheric dispersion model for area sources that was originally designed for inert species. Different versions of DAUMOD were developed during the last two decades to study several aspects of the urban air quality in the Metropolitan Area of Buenos Aires (MABA), Argentina (e.g., Mazzeo and Venegas, 2008; Mazzeo et al., 2010; Pineda Rojas and Venegas, 2009; Venegas and Mazzeo, 2006; Venegas et al., 2011). The MABA, which is composed by the City of Buenos Aires (CBA, ~200 km<sup>2</sup>) and the Greater Buenos Aires (GBA, ~3600 km<sup>2</sup>), is the third megacity of Latin America and the twelfth worldwide (United Nations, 2012). It is located on a flat terrain, mainly surrounded by non-urban areas. A few campaigns carried out in the CBA and air quality modelling studies have shown that urban background concentrations of NO<sub>2</sub> and O<sub>3</sub> are lower than their corresponding air quality standards, but NO<sub>2</sub> hourly levels may exceed the World Health Organisation air quality guideline at some places in the MABA (see Venegas et al., 2011). The DAUMOD-GRS model arises from the need to improve the NO<sub>2</sub> DAUMOD estimations. Based on its structure and taking into account the lack of detailed information available for the MABA (especially in relation to emission data), the DAUMOD model was coupled with a simplified photochemical scheme, the Generic Reaction Set (GRS) (Azzi et al., 1992). The GRS has been included already in some atmospheric dispersion models [e.g., ADMS-Urban (CERC, 2001), TAPM (Hurley et al., 2005), CIT (Lashmar and Cope, 1995), SOMS (Venkatram et al., 1994)] due to its simplicity and ability to reproduce the interactions between NO<sub>2</sub> and O<sub>3</sub> at urban scale. In a previous paper (Pineda Rojas and Venegas, 2013a), the development of the DAUMOD-GRS model and its first application in the CBA was presented. Recently available NO<sub>2</sub> and O<sub>3</sub> concentration data from twenty sites distributed outside the city have allowed a more complete evaluation of its performance in the area. In Pineda Rojas and Venegas (2013b), a study of the model ability to simulate O<sub>3</sub> in the MABA, focussing on the summer maximum diurnal peak concentrations, has been presented. The present work discusses the performance of DAUMOD-GRS to estimate hourly urban background NO<sub>2</sub> and O<sub>3</sub> concentrations considering observations from twenty sites in the MABA. The statistical comparison is carried out by grouping the monitoring stations in regions having different emission conditions, in a way that allows the evaluation of the modelled and observed urban-suburban concentration gradients, and the examination of the validity of the assumption of spatial homogeneity of atmospheric variables for this modelling application.

A brief description of the DAUMOD-GRS structure is presented in Section 2. Section 3 comments on the evaluation procedure and the choice of evaluation metrics and method. Section 4 summarises the data used to perform the statistical evaluation of the model, the running conditions and the results obtained. Finally, a discussion on model assumptions and their likely impact is presented in Section 5, followed by the conclusions in Section 6.

## 2. The DAUMOD-GRS model

The DAUMOD-GRS model was developed by coupling of the DAUMOD model with the GRS scheme. It is written in FORTRAN and due to its simple configuration and low computational demand, it can be run on any personal computer. The description of the two main components (DAUMOD and GRS) and their coupling can be found in Pineda Rojas and Venegas (2013a). Here, its main assumptions and structure are summarised (see Fig. 1).

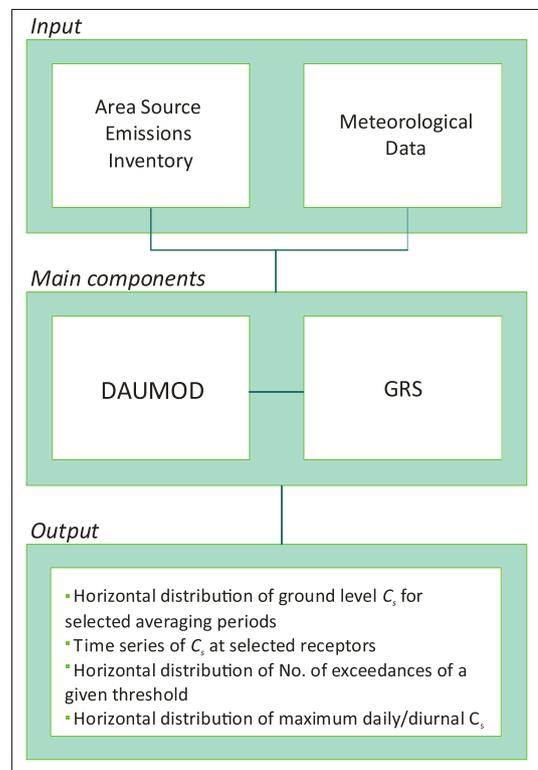


Fig. 1. Structure of the DAUMOD-GRS model ( $C_s$ : concentration of species  $s$ : NO, NO<sub>2</sub>, O<sub>3</sub>).

### 2.1. Input module

The model takes into account information regarding the domain characteristics: grid size, latitude and longitude of the domain centre, meteorological conditions, the distributions of area source emissions of NO<sub>x</sub> and VOC and their speciation, background concentrations of the species involved in the GRS, surface roughness. These data and the running conditions (spatial and temporal resolutions and period of the simulations) are read from an input file.

### 2.2. Transport and dispersion module

Given a horizontal distribution of NO<sub>x</sub> and VOC emissions from multiple area sources, their atmospheric transport and dispersion is first computed by the atmospheric dispersion model DAUMOD (Mazzeo and Venegas, 1991). The DAUMOD model is based on the equation of mass continuity and assumes 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 expression used by the model to estimate the concentration of a species  $s$ , at a down-wind distance  $x$  and ground-level ( $z = 0$ ), due to atmospheric dispersion and transport from an area source  $i$  of uniform emission strength  $Q_{s,i}$  located between  $x = x_{i-1}$  and  $x = x_i$ , is:

$$C_{s,i}(x, 0) = aQ_{s,i} \left[ (x - x_{i-1})^b - (x - x_i)^b \right] / \left( |A_1| k z_0^b u_* \right) \quad (1)$$

where  $k$  is the von Karman 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 (expressions in Venegas and Mazzeo, 2006). It follows that the pollutant ground-level concentration due to a horizontal distribution of  $N$  area sources located upwind the receptor, is given by:

**Table 1**  
Brief description of the GRS chemical scheme and the species involved.

Species	Pseudo-species
NO: nitrogen oxide	ROC: reactive organic compounds (all VOCs)
NO <sub>2</sub> : nitrogen dioxide	RP: radical pool (all radicals)
O <sub>3</sub> : ozone	SGN, SNGN: stable (gaseous and non-) nitrogen compounds
Reaction	Description
ROC + hν → ROC + RP	Photo-oxidation of ROC
NO + RP → NO <sub>2</sub>	Conversion of NO to NO <sub>2</sub> and first RP sink
NO <sub>2</sub> + hν → NO + O <sub>3</sub>	Photo-oxidation of NO <sub>2</sub> to generate O <sub>3</sub> and regenerate NO <sup>a</sup>
NO + O <sub>3</sub> → NO <sub>2</sub>	Reaction of NO with O <sub>3</sub> to generate NO <sub>2</sub> <sup>a</sup>
RP + RP → RP	Second RP sink
NO <sub>2</sub> + RP → SGN	Other sinks for RP through which non-reactive
NO <sub>2</sub> + RP → SNGN	nitrogen compounds are generated

<sup>a</sup> Exact reactions.

$$C_s(x, 0) = a \left[ Q_{s,0} x^b + \sum_{i=1}^N (Q_{s,i} - Q_{s,i-1}) (x - x_i)^b \right] / (|A_1| k z_0^b u^*) \quad (2)$$

where  $Q_{s,0}$  is the emission rate at the receptor. In order to couple the GRS, the computation of the mean travel time ( $\tau_s$ ) of the species  $s$  was included in DAUMOD algorithms as a weighted average of the travel time of the pollutants coming from the source  $i$  ( $\tau_{s,i} = L_{s,i}/U$ , being  $L_i$  the source-receptor distance and  $U$  the wind speed), taking into account its contribution ( $C_{s,i}$ ) to the total concentration in the receptor ( $C_s$ ):

$$\tau_s = \sum_{i=1}^N \tau_{s,i} C_{s,i} / C_s \quad (3)$$

The reaction time ( $\Delta t_c$ ) is then approximated by the minimum value of  $\tau_s$  of both species at each receptor:

$$\Delta t_c = \min(\tau_{NO_x}, \tau_{O_3}) \quad (4)$$

### 2.3. Photochemical module

The GRS scheme (Azzi et al., 1992) was developed aiming to obtain a simplified photochemical scheme that reduced the huge computational time required by detailed chemical mechanisms (Venkatram et al., 1994). The resulting semi-empirical scheme describes the interactions NO<sub>x</sub>–VOC–O<sub>3</sub> with only seven reactions (see Table 1). In this scheme, the formation/loss rate equation for the concentration ( $C_s$ ) of each species  $s$  can be written as:

$$dC_s/dt = p_s - q_s C_s \quad (5)$$

where  $p_s$  and  $q_s C_s$  are its production and loss rates, respectively, which depend on the rate constants  $k$ 's associated to the reactions [see Pineda Rojas and Venegas (2013a) for details on their parameterisations]. In DAUMOD-GRS, the set of coupled Ordinary Differential Equations (ODEs) given by Eq. (5) is solved applying the Quasi Steady State Approximation (QSSA) (e.g., Hesstvedt et al., 1978; Yamartino et al., 1992), assuming that there is a time lapse  $\delta t$  in which  $p_s$  and  $q_s$  are constant, so that Eq. (5) can be easily integrated to obtain:

$$C_s = (p_s/q_s) + [C'_s - (p_s/q_s)] \exp(-q_s \delta t) \quad (6)$$

where the quotation mark indicates the value of the variable at the beginning of  $\delta t$ , which is computed as (Yamartino et al., 1992):

$$\delta t = \epsilon \min [C'_s / (p'_s - q'_s C'_s)] \quad (7)$$

$\epsilon$  represents an acceptable fractional change in the concentration during  $\delta t$ , and the minimum is taken over species  $s$ : NO, NO<sub>2</sub> and O<sub>3</sub>. Once the concentrations of the precursor species ( $C_s$ ) are estimated [Eq. (2)], they can react according to the GRS. At each receptor, the set of equations given by Eq. (6) is numerically integrated during the reaction time  $\Delta t_c$  [Eq. (4)] with the variable time step  $\delta t$ . DAUMOD-GRS includes a corrector step through which (6) is recalculated using  $p_s$  and  $q_s$ , averaged over their values computed at the beginning and the end of  $\delta t$ , leading to errors in the solution of the order of  $\epsilon^3$  (Yamartino et al., 1992).

### 2.4. Output module

Required output results are entered by command line. According with the user selection, the model can produce different results:

- the horizontal distribution of NO, NO<sub>2</sub> and O<sub>3</sub> concentrations averaged during the period of the simulations or at selected hours,
- the temporal series of the species concentrations at selected receptors,
- the horizontal distribution of the number of times that a given threshold value is exceeded, and
- the horizontal distributions of the daily and diurnal maximum hourly concentrations.

### 3. Performance evaluation procedure

Model evaluation is in general a complex procedure involving different steps (e.g., Derwent et al., 2010; Thunis et al., 2012). Two important aspects in the evaluation of model performance are the scientific and the statistical evaluations. The former examines model algorithms, physics and assumptions in detail (Chang and Hanna, 2005). In this sense, both the DAUMOD model and the GRS scheme have been subject to extensive applications, code verification and validations during the past two decades. DAUMOD has been tested for CO and NO<sub>x</sub> species in different cities of Europe, the US and in the City of Buenos Aires (e.g., Mazzeo and Venegas, 1991; Venegas and Mazzeo, 2002; 2006). The GRS has been implemented in the algorithms of several well-known models (e.g., ADMS-Urban, TAPM, CIT, SOMS) and some of their applications gave comparable and sometimes better results than models which had included detailed photochemical mechanisms (e.g., Venkatram et al., 1994; Anh et al., 1998).

The statistical evaluation refers to the comparison of model results with observations and constitutes a critical step in the model performance assessment. Bennett et al. (2013) provide a review of the different available methods to characterise the performance evaluation of environmental models. The choice of an adequate set of metrics depends greatly on the model type. In air quality modelling, commonly used measures of the difference between modelled ( $C_m$ ) and observed ( $C_o$ ) concentrations (i.e., the residuals) are: the fractional bias (FB), the normalised mean square error (NMSE) and the fraction of model estimates that is within a factor of two of the observations (FA2), which are defined as follows:

$$FB = 2(\overline{C_o} - \overline{C_m}) / (\overline{C_o} + \overline{C_m}) \quad (8)$$

$$NMSE = \overline{(C_o - C_m)^2} / \overline{C_o C_m} \quad (9)$$

$$FA2 = \text{fraction of data that satisfies } 0.5 \leq C_m/C_o \leq 2.0 \quad (10)$$

where the overbar denotes the average over the dataset. Scatter plots representing  $C_m$  vs  $C_o$  are also employed to gain a first

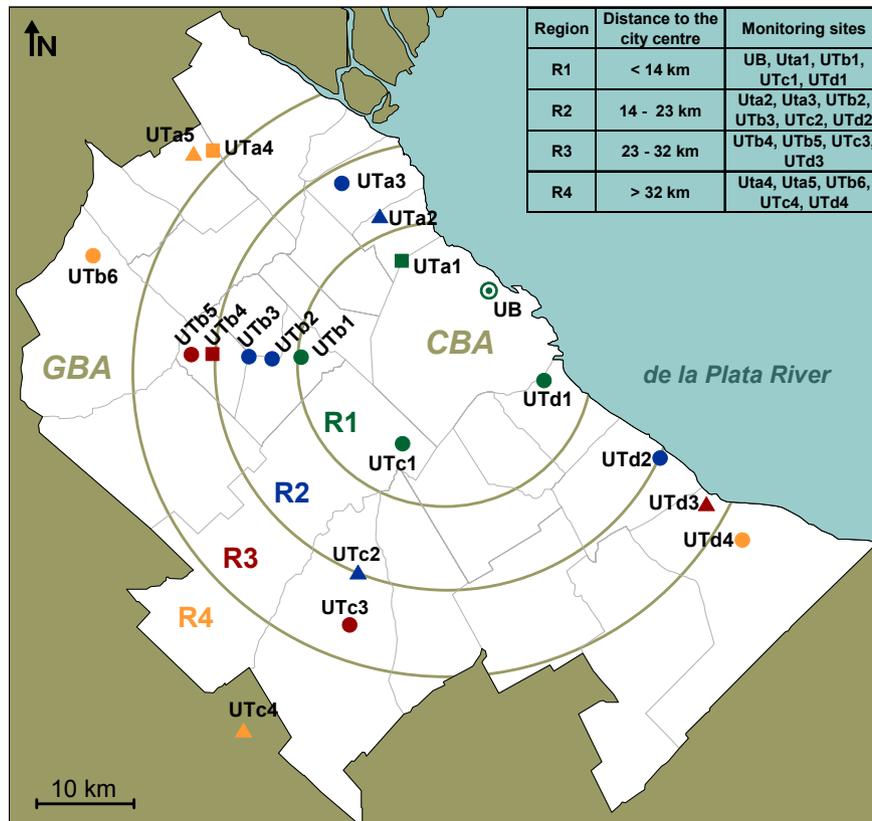


Fig. 2. Measurement sites for  $\text{NO}_2$  (■),  $\text{O}_3$  (▲) and both species (●) within the MABA (CBA + GBA). The UB site is indicated (\*). Selected regions are delimited by curve lines.

overview of the overall model performance. A perfect model would have  $\text{FB} = 0$ ,  $\text{NMSE} = 0$  and all pairs  $(C_o, C_m)$  over the line 1:1 (implying that  $\text{FA2} = 1$ ). However, it is not possible to achieve an exact match between modelled and observed values, because not only the model is a simple representation of the system but also the observational data provide imperfect evidence regarding its true state (Bennett et al., 2013). Based on extensive experience, Chang and Hanna (2004) concluded that an air quality model can be considered to have an acceptable performance if it satisfies:  $-0.3 < \text{FB} < 0.3$ ,  $\text{NMSE} < 1.5$  and  $\text{FA2} > 0.5$ .

It is worth noting that different ways of pairing (i.e., in space, time or both of them) may result in different conclusions. On the other hand, metrics typically calculate a single value for the whole dataset, which can disguise a divergent behaviour over time and/or space (Bennett et al., 2013). To avoid this, the dataset can be partitioned based on knowledge of some property or variable that might influence the model evaluation results. Ideally, the statistical analysis should be performed considering paired values in both time and space, for each measurement site. However, data partitioning must be done aiming to keep a relatively large sample size in order to support the conclusions that might be inferred from the obtained metrics.

Different software packages addressing air quality model performance evaluation have been developed over the past decades (Thunis et al., 2012). In this work, the well-known BOOT software (Chang and Hanna, 2005) is employed to perform the statistical comparison between DAUMOD-GRS estimations of  $\text{NO}_2$  and  $\text{O}_3$  concentrations and observed values in the Metropolitan Area of Buenos Aires. Standard summary statistics (mean, standard deviation and maximum concentration) and the metrics given by Equations (8)–(10) are obtained and analysed for the whole dataset (Section 4.4) and partitioning the data between regions having different emission conditions as described below (Section 4.5).

## 4. Performance evaluation of DAUMOD-GRS in the MABA

### 4.1. Observed concentrations

In order to perform the statistical evaluation of DAUMOD-GRS, modelled urban background  $\text{NO}_2$  and  $\text{O}_3$  concentrations were compared with available observations at several sites in the MABA (City of Buenos Aires + Greater Buenos Aires) (see Fig. 2) from two different data sets. The first one reports measurements from a campaign carried out in the City of Buenos Aires (CBA) during 38 days in winter 2001. This site is located in an urban park (mainly grassland with a few trees) and can be considered as an urban background (UB) site according to previous studies (e.g., Venegas and Mazzeo, 2006). The second data set has been provided recently by the National Office of Public Roads of Argentina and consists of observed concentrations at nineteen urban traffic (UT) sites distributed along the main highways of the Greater Buenos Aires (GBA), in different periods of 2007 and 2008. At these sites, measurements were taken approximately within 50 m from the road during around 1–2 weeks each campaign. All collected data account for a total of 2909 and 3100 hourly concentration values of  $\text{NO}_2$  and  $\text{O}_3$ , respectively.

### 4.2. Running conditions

The DAUMOD-GRS model was applied in the domain of Fig. 2 considering a temporal resolution of 1 h and a spatial resolution of  $1 \text{ km}^2$ . As boundary conditions, a constant regional background concentration of 20 ppb was assumed for  $\text{O}_3$  based on previous works (Bogo et al., 1999; Mazzeo et al., 2005). For other species, clean air concentrations were assumed as initial and boundary conditions due to the lack of available information (e.g., Hurley et al., 2003; Dallarosa et al., 2007) and taking into account that the MABA is surrounded by non urban areas.

#### 4.3. Input data

Hourly surface meteorological data registered at the domestic airport of the CBA and sounding data obtained at the International Airport (30 km towards the SW of the city) were used in calculations.  $\text{NO}_x$  emission data belong to the high resolution (1 h, 1 km<sup>2</sup>) emission inventory developed for the MABA (Venegas et al., 2011). The considered  $\text{NO}_x$  speciation is 90% of NO and 10% of  $\text{NO}_2$  (by mol), following the USEPA (2002) default values. VOC emission rates were obtained for this work using the same activity data base employed to estimate the emissions of  $\text{NO}_x$ . Hourly emissions from residential, commercial and small industry activities, aircraft at the local and international airports of the MABA and road transport, are considered as area source emissions (Fig. 3). Other area sources such as solvent use were not considered in this work. On the other hand, taking into account that urban VOC emissions are dominated by the road transport sector, its speciation was estimated using the MABA vehicle fleet composition, according to the COPERT IV VOC classification. The ROC emission (as a surrogate of VOC) was obtained following the methodology proposed by Venkatram et al. (1994), in which it is computed as the sum of the individual VOCs emissions weighted by their reactivities (see Pineda Rojas and Venegas, 2013a).

#### 4.4. Statistical comparison considering all data

Figs. 4 and 5 present the scatter plots of observed and modelled hourly concentrations of  $\text{NO}_2$  and  $\text{O}_3$ , respectively, including the lines 1:2, 1:1 and 2:1, and Table 2 shows the statistical measures obtained from their comparisons. An apparent regular structure is observed in the centre of the scatter plot of Fig. 5 because  $\text{O}_3$  concentration data from the UT sites were measured at 1 ppb resolution. Considering all hourly ground-level  $\text{NO}_2$  concentration data, observed levels vary between 0.5 and 70 ppb, while modelled values are in the range 0.3–77 ppb (see Fig. 4), with 57.4% of them within a factor of two of the measured ones, and the normalised mean square error (NMSE) is 0.82. The statistical measures presented in Table 2 show an acceptable model performance for  $\text{NO}_2$  with a general tendency to slightly underestimate the observed levels (fractional bias,  $\text{FB} = 0.024$ ) which could be explained by the assumptions made, as discussed below in Section 5. On the other hand, Fig. 5 shows that hourly observed  $\text{O}_3$  concentration values vary between 1.1 and 34 ppb and modelled levels between 0.5 and 35 ppb. In this case, 81.6% of modelled concentrations fall within a factor of two of the observed values and NMSE is 0.22 (see Table 2). The fractional bias ( $\text{FB} = -0.053$ ) shows that the DAUMOD-GRS model overestimates slightly the ozone concentrations in the MABA.

#### 4.5. Sites grouped by regions having different emission conditions

As shown in Fig. 3, the emissions of  $\text{NO}_x$  and VOC from area sources are much higher in the City of Buenos Aires (CBA) than in the Greater Buenos Aires (GBA), showing a decrease pattern towards the suburbs that responds mostly to the reduction of the vehicular traffic as the distance to the city increases, as expected. In order to evaluate the model performance by sectors presenting different emission conditions, four regions were selected. The selection was carried out seeking a nearly equal distribution of stations within areas with decreasing emission rates in the radial direction from the city centre (see Fig. 2), and the statistical comparison was performed for each individual region. Tables 3 and 4 show that the statistical measures obtained from the comparison between observed and modelled

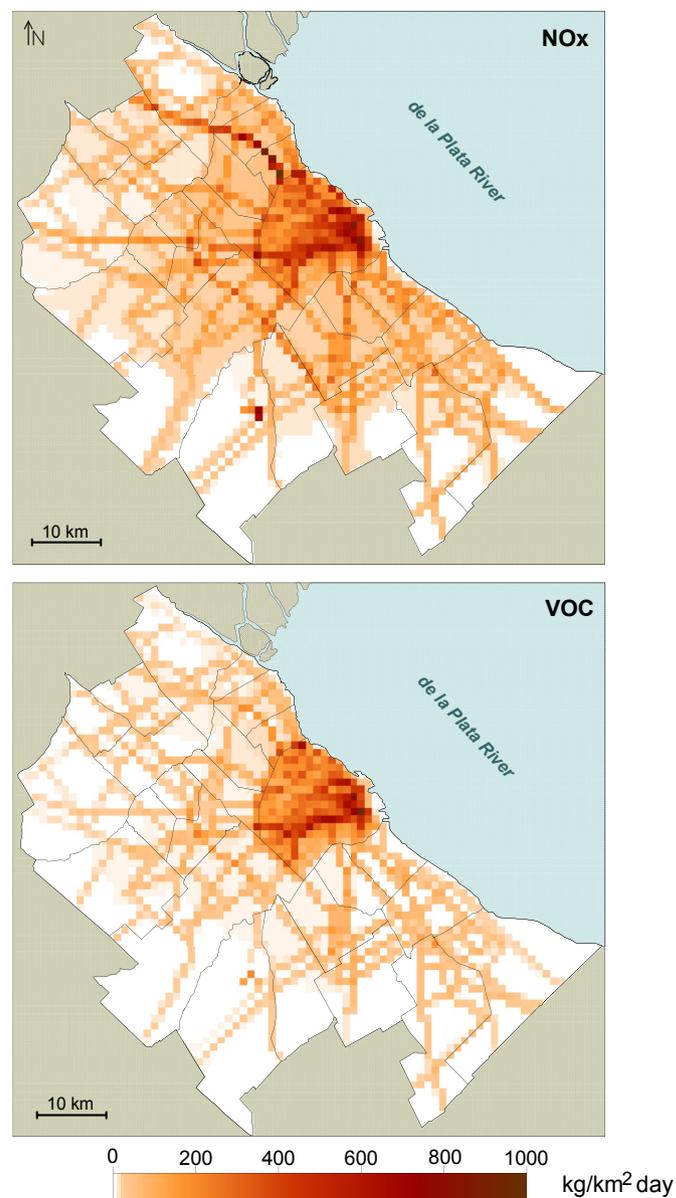


Fig. 3. Estimated  $\text{NO}_x$  and VOC emissions [kg/(km<sup>2</sup> day)] from area sources in the MABA.

concentrations for each species are acceptable within each region.

On the other hand, ground-level  $\text{NO}_2$  usually maximises near the source (e.g., Plejdel et al., 2004) and hence its concentration horizontal distribution is similar to that of the emissions; while  $\text{O}_3$  formation depends also on the VOC/ $\text{NO}_x$  ratio in a way that it maximises further the  $\text{NO}_x$  sources which explains the maximum concentrations commonly observed downwind a city in the prevailing wind direction. Figs. 6 and 7 show that these features are well represented by the model. According to these results, mean observed  $\text{NO}_2$  concentrations decrease from 18.0 ppb in region R1 to 13.0 ppb in R4 (see Table 3), representing a relative decrease of 27.8% across the MABA, while model results estimate a decrease of 29.6%. Mean observed  $\text{O}_3$  levels vary from 10.5 ppb in R1 to 14.4 ppb in R3 (Table 4), indicating a relative increase of 37.1% between the CBA and the second ring of Fig. 2, while DAUMOD-GRS estimates an increase of 38.6% between the same both regions.

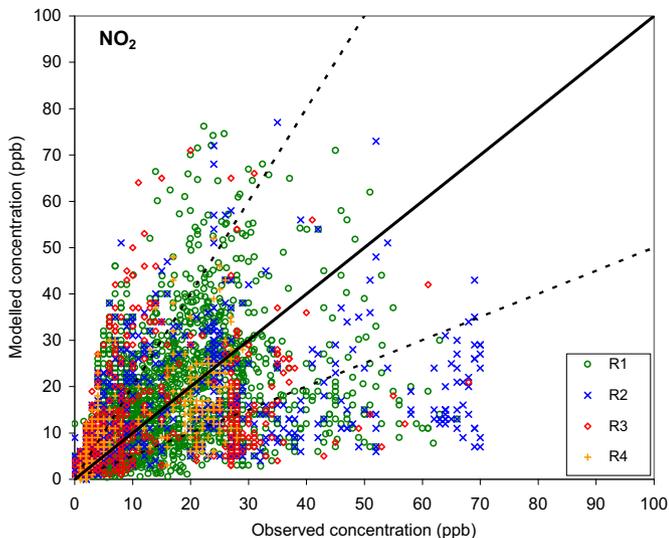


Fig. 4. Scatter plot of observed and modelled NO<sub>2</sub> hourly concentrations (N = 2909).

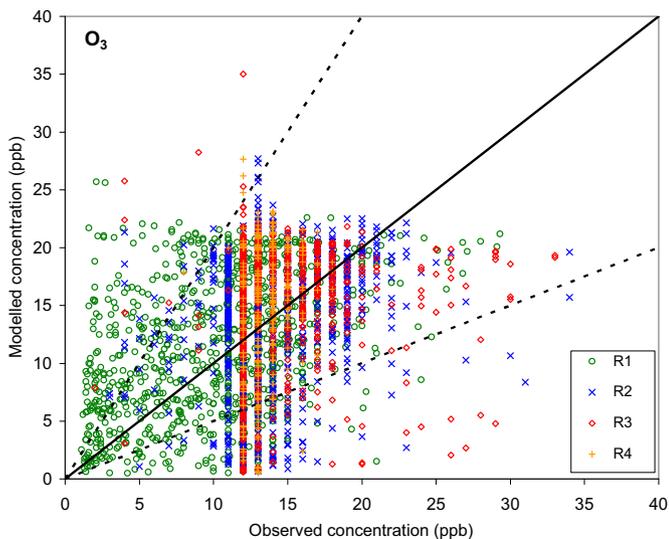


Fig. 5. Scatter plot of observed and modelled O<sub>3</sub> hourly concentrations (N = 3100).

4.6. Examples of DAUMOD-GRS application

As an example of DAUMOD-GRS applicability, Fig. 8 presents the horizontal distribution of annual mean NO<sub>2</sub> urban background concentrations in the MABA, obtained using the emission inventory described in Section 4.3. A large spatial variability across the urban area can be observed. According to these results, annual NO<sub>2</sub> urban background concentrations are expected to be below 30 ppb in

Table 2

Statistical measures obtained from the comparison of observed and modelled concentrations (ppb). [N: number of data; Sigma: standard deviation (ppb); NMSE: normalised mean square error; FA2: fraction of estimations within a factor of two of observations; FB: fractional bias; High: maximum concentration (ppb)].

		Mean	Sigma	NMSE	FA2	FB	High
NO <sub>2</sub>	Observed	16.9	13.6				70
N = 2909	Modelled	16.5	12.7	0.82	0.574	0.024	77
O <sub>3</sub>	Observed	12.8	4.4				34
N = 3100	Modelled	13.5	6.1	0.22	0.816	-0.053	35

Table 3

Statistical measures obtained from the comparison of observed and modelled NO<sub>2</sub> concentrations (ppb) by region. [N: number of data; Sigma: standard deviation (ppb); NMSE: normalised mean square error; FA2: fraction of estimations within a factor of two of observations; FB: fractional bias; High: maximum concentration (ppb)].

Region	N		Mean	Sigma	NMSE	FA2	FB	High
R1	1623	Observed	18.0	11.4				66
		Modelled	18.6	12.9	0.64	0.601	-0.036	76
R2	528	Observed	19.5	19.9				70
		Modelled	15.3	12.9	1.28	0.528	0.242	77
R3	503	Observed	12.8	12.2				68
		Modelled	12.7	11.8	1.20	0.481	0.007	71
R4	255	Observed	13.0	9.5				29
		Modelled	13.1	10.0	0.44	0.678	-0.008	52

most of the CBA and below 20 ppb in the GBA. The greatest concentration values occur near some highways entering the City of Buenos Aires and at downtown, where NO<sub>x</sub> and VOC emissions are the highest (as shown in Fig. 3). Considering the maximum estimated value (36 ppb), all urban background concentration levels are below the corresponding Air Quality Standard for the area (53 ppb).

Other possible applications include the evaluation of the impact of different emission scenarios on NO<sub>2</sub> and O<sub>3</sub> levels (e.g., Pineda Rojas and Venegas, 2013b), and feeding street canyon models (which allow the assessment of human population exposure to a given pollutant). In a recent work, for instance, the DAUMOD-GRS model was used to provide with NO<sub>2</sub> background concentrations for the evaluation of a street canyon model in a busy avenue of the CBA, showing a good agreement with the observed values (Venegas et al., 2014).

5. Discussion on model assumptions and their likely impact

According with the inputs mentioned in Section 4.3, uncertainty in model results can be due to uncertainties in: i) the estimated emissions, ii) the assumed regional background conditions, and iii) the used meteorological data and related parameters.

5.1. Emissions

The DAUMOD-GRS model has been developed for area sources. Due to the lack of available information, the emission inventory for area sources used in this work does not include VOC emissions from the solvent use sector and the vegetation. The possible impact of biogenic VOC (bVOC) emissions is briefly commented in Pineda Rojas and Venegas (2013b), but research is needed to determine whether non-urban areas surrounding the MABA might contribute to O<sub>3</sub> levels in the area. Regarding the NO<sub>x</sub> speciation, a typical

Table 4

Statistical measures obtained from the comparison of observed and modelled O<sub>3</sub> concentrations (ppb) by region. [N: number of data; Sigma: standard deviation (ppb); NMSE: normalised mean square error; FA2: fraction of estimations within a factor of two of observations; FB: fractional bias; High: maximum concentration (ppb)].

Region	N		Mean	Sigma	NMSE	FA2	FB	High
R1	1118	Observed	10.5	4.9				29
		Modelled	11.4	5.7	0.31	0.716	-0.075	26
R2	780	Observed	14.1	3.9				34
		Modelled	13.9	5.8	0.20	0.821	0.015	28
R3	845	Observed	14.4	3.5				33
		Modelled	15.8	5.0	0.17	0.905	-0.093	35
R4	357	Observed	13.5	1.3				18
		Modelled	15.6	5.6	0.16	0.896	-0.147	28

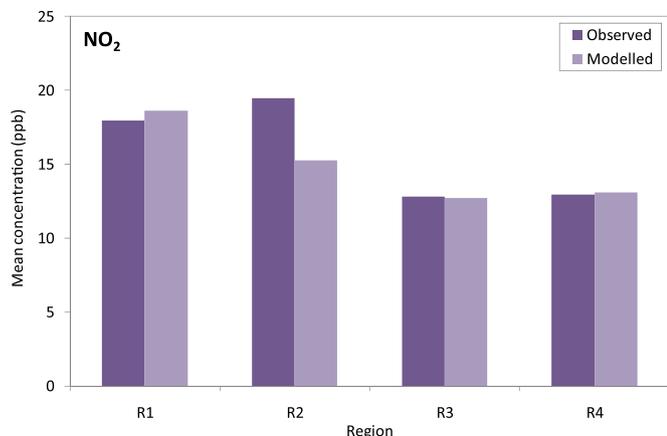


Fig. 6. Comparison of observed and modelled mean NO<sub>2</sub> concentration by region.

fraction of 0.1 is considered for NO<sub>2</sub> emissions following the USEPA defaults. This fraction, which varies with the proportion of diesel cars within the fleet, the actual driving conditions and the vehicle type (e.g., Carslaw et al., 2011), may affect modelled NO<sub>2</sub> and O<sub>3</sub> concentrations and hence future DAUMOD-GRS applications in the MABA will benefit from its evaluation.

### 5.2. Regional background concentrations

Import of pollutants from surrounding areas might be significant based on results obtained for other large urban conglomerations (e.g., Vieno et al., 2010). When modelling photochemical reactions, the use of observations from rural monitoring stations, or values obtained from larger scale models, as background concentration levels is recommended. When none of them are available, it can be assumed that background conditions are constant and equal to clean air concentrations (Dallarosa et al., 2007). In the case of the MABA, which is surrounded by non-urban areas, the assumption of clean air concentrations for regional background NO<sub>x</sub> concentrations seems to be reasonable; however, regional VOC and O<sub>3</sub> levels could be different when the wind comes from the river or from the vegetated land, and they should thus be evaluated in future air quality studies.

### 5.3. Meteorological data and related parameters

Based on the MABA geographic conditions, horizontally homogeneous atmospheric variables and related parameters (such as the

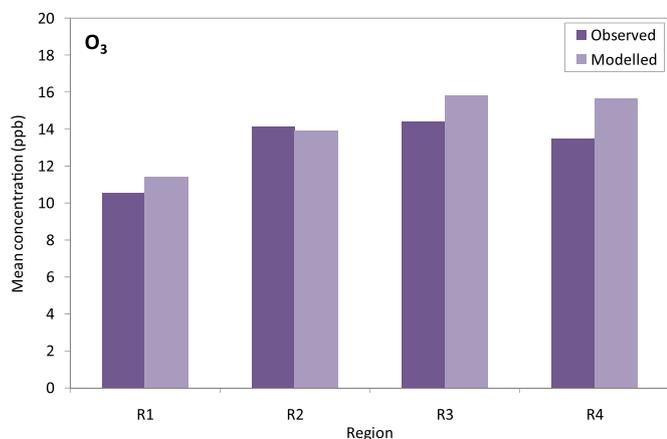


Fig. 7. Comparison of observed and modelled mean O<sub>3</sub> concentration by region.

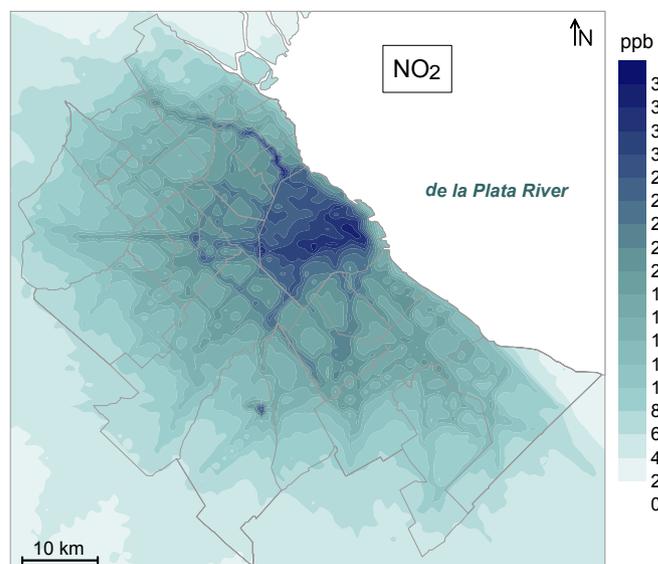


Fig. 8. Modelled annual mean ground-level urban background NO<sub>2</sub> concentration (ppb).

surface roughness,  $z_0$ ) have been assumed. The surface hourly meteorological data used in this work comes from a station that is located at the domestic airport close to the UB site (in R1). These data can therefore be less representatives of the “real conditions” in the suburban area. The results presented in Table 3 show that the DAUMOD-GRS model had a better performance to simulate the urban background NO<sub>2</sub> concentrations in regions R1 and R4 than in R2 and R3. In the case of O<sub>3</sub>, the values of NMSE and FA2 show an improvement of the capacity of the model to estimate its concentrations as the distance to the city increases (see Table 4). This suggests that in the MABA, using surface information from a single meteorological station does not introduce much error in the estimation of NO<sub>2</sub> and O<sub>3</sub> concentrations at the furthest air quality monitoring sites. Sensitivity analysis could help to determine the role of meteorology on the concentrations of these species in the MABA.

Other type of source of uncertainty is that related to the model itself. In this first version of the model, deposition processes are not included. NO<sub>2</sub> and O<sub>3</sub> may be effectively deposited to vegetation rather than to paved surfaces. Then, depositions of these species are expected to be more important in the suburban areas of the MABA, where NO<sub>2</sub> levels are relatively low and O<sub>3</sub> concentrations are high compared to those of the most urbanised part. As discussed in Pineda Rojas and Venegas (2013b), in the case of ozone, the fact that the DAUMOD-GRS performs well in this zone could be due to a compensation of errors (i.e., the O<sub>3</sub> uptake by the vegetation is comparable to that formed by the bVOC emissions, and hence there is no net effect of these two processes on the atmospheric O<sub>3</sub> levels) or because O<sub>3</sub> deposition as well as bVOC emissions are of negligible importance compared to the urban anthropogenic emissions.

## 6. Conclusions

The DAUMOD-GRS model has been recently developed, coupling the DAUMOD urban atmospheric dispersion model with the GRS simplified photochemical scheme, in order to estimate ground-level urban background NO<sub>2</sub> and O<sub>3</sub> concentrations resulting from NO<sub>x</sub> and VOC area source emissions. As with most simple semi-empirical models, the main advantages of DAUMOD-GRS are that it can be run considering high spatial (1 km<sup>2</sup>) and temporal (1 h) resolutions and for long term (i.e., yearly) conditions at low computational cost, and it does not require detailed input data (frequently not available) to be

operated. Its main disadvantages are that it may not be adequate to apply in urban areas presenting severe conditions of photochemical pollution, or in complex terrain requiring simulation of other processes not included in the model. This work discusses the model performance considering observations from twenty sites across the Metropolitan Area of Buenos Aires (MABA). Comparison of model results with observations gives  $NMSE = 0.82$ ,  $FA2 = 0.57$  and  $FB = 0.02$  for  $NO_2$ , and  $NMSE = 0.22$ ,  $FA2 = 0.82$  and  $FB = -0.05$  for  $O_3$ , showing a small tendency to underestimate  $NO_2$  and to overestimate  $O_3$ . Overall, the DAUMOD-GRS model proved a good ability to simulate the ground-level  $NO_2$  and  $O_3$  concentrations observed in the MABA. Considering these results and the simplifications made such as omission of biogenic VOC emissions, depositions processes and point source emissions, it is possible that their errors balance each other, or that they have a small impact on the modelled  $NO_2$  and  $O_3$  concentrations in this area. More studies are required to determine this.

Observed data were grouped in four regions having different emission conditions. Mean observed  $NO_2$  concentrations decrease approximately 28% (5 ppb) from the city towards the suburbs; while in the same direction mean  $O_3$  levels increase around 37% (4 ppb), reaching its maximum value (14.4 ppb) at ~30 km from the downtown. These two spatial variation patterns were well represented by the model. On the other side, statistical measures obtained from the model evaluation at each individual region suggest that the assumption of horizontal homogeneity in the atmospheric variables does not seem to be a significant source of uncertainty. This should be confirmed with further research such as sensitivity analysis. Evaluations of the DAUMOD-GRS model with other experimental data and air quality model results are also recommended.

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