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Upgrade of the DAUMOD atmospheric dispersion model to estimate urban background NO₂ concentrations

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ABSTRACT

Ambient concentrations of nitrogen dioxide (NO₂) resulting from the emissions of nitrogen oxides (NO_x) and volatile organic compounds (VOCs) in an urban area may cause adverse impacts on the human health and the natural environment if they exceed the air quality standards. The evaluation of NO₂ can be achieved through the application of air quality models including photochemical reactions. DAUMOD is a simple urban scale atmospheric dispersion model which was originally developed to estimate urban background concentrations of inert species. In order to allow the estimation of NO₂ concentrations in an urban atmosphere, the DAUMOD model has been recently coupled to the Generic Reaction Set (GRS), a simplified photochemical scheme. This work presents the development of the DAUMOD-GRS model and its first application in the city of Buenos Aires considering high resolution area source NO_x and VOC emissions recently obtained for the area. Estimated hourly NO₂ concentrations are compared with the observations from a campaign carried out at a green open area within the city in winter 2001. Results show a good model performance, with NMSE = 0.49, FA2 = 0.676 and FB = −0.097. DAUMOD-GRS is applied to obtain the spatial distribution of annual NO₂ concentrations in the city. The maximum value is 36 ppb, indicating that annual NO₂ concentrations in Buenos Aires are below the Air Quality Standard (53 ppb). In addition, hourly ozone concentrations estimated by DAUMOD-GRS are compared with observed values, giving NMSE = 0.38, FA2 = 0.684 and FB = −0.225.

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1. Introduction

The production of photochemical pollutants is a complex process involving thousands of reactions in the presence of sunlight. Their precursors, nitrogen oxides (NO_x) and volatile organic compounds (VOCs), are greatly emitted by anthropogenic activities at urban zones, and lead to the formation of nitrogen dioxide (NO₂) and ozone (O₃) which are very important constituents of air pollution, producing adverse effects on human health (WHO, 2005). The evaluation of NO₂ and O₃ concentrations in the urban atmosphere

can be achieved by combining observations and results from air quality models (e.g., Taghavi et al., 2005; Lasry et al., 2005; Astitha et al., 2008; Shan et al., 2009; Misenis and Zhang, 2010). The latter can be classified into comprehensive and simple semi-empirical models (Moussiopoulos, 2003). The former include very detailed photochemical schemes allowing a more complete description of main processes behind the production/loss of smog related species in the urban atmosphere. However, their applications require large sets of detailed input data (i.e., local scale three-dimensional wind field, land use type, NO_x and disaggregated VOC emission distributions, and initial conditions for their regional background concentrations). Also the high computational cost required to solve detailed photochemical schemes limits considerably the temporal and spatial resolutions of the simulations. At the urban scale, when the air quality is not seriously constrained and/or there is not enough

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available information to run complex models, simpler models may be an acceptable alternative (e.g., Varotsos et al., 1992; McHugh et al., 1997; de Leeuw et al., 2001; Mensink et al., 2008).

DAUMOD (Mazzeo and Venegas, 1991) is a simple urban scale atmospheric dispersion model that was originally developed to estimate pollutant concentrations of inert species. This model has been validated using observations from the city of Buenos Aires (CBA) and different cities of Europe and the United States (Mazzeo and Venegas, 1991; Venegas and Mazzeo, 2002, 2006), and has been extensively used to study the air quality of the urban atmosphere in the Metropolitan Area of Buenos Aires (MABA) (Mazzeo et al., 2010; Pineda Rojas and Venegas, 2010; Venegas and Mazzeo, 2006). In order to upgrade the DAUMOD model to allow the estimation of urban background NO₂ concentrations, it is coupled to the Generic Reaction Set (GRS) (Azzi et al., 1992). The GRS scheme constitutes a simplified parameterisation of the most complete photochemical mechanisms which has allowed a considerable reduction of the computing time (Venkatram et al., 1994), making its application for regulatory (yearlong) purposes possible. Given its ability to reproduce the photochemical loss/production of NO, NO₂ and O₃ at urban scale in a very simple and accessible way, the GRS has been widely adopted in urban air quality assessment studies. Some atmospheric dispersion models including GRS are the Danish Eulerian Model (DEM) (Zlatev et al., 1992), the Simplified Ozone Modelling System (SOMS) (Venkatram et al., 1994), the California Institute of Technology (CIT) Photochemical Airshed Model (Lashmar and Cope, 1995), the Atmospheric Dispersion Modelling System for urban environments (ADMS-Urban) (McHugh et al., 1997), the Semi-empirical Reaction Model (SEGRS) (Kim et al., 2005) and The Air Pollution Model (TAPM) (Hurley et al., 2005).

In this work, we present a complete description of the DAUMOD-GRS model and its first application to obtain NO₂ concentrations in the CBA considering recently obtained high resolution (1 km², 1 h) NO_x and VOC emissions for the area. Hourly NO₂ concentrations modelled with DAUMOD-GRS are statistically compared with the observed values at a green open area within the city in a 2001 winter campaign. The model is applied to estimate the surface distribution of annual NO₂ concentrations in the city of Buenos Aires. In addition, hourly O₃ concentrations computed by DAUMOD-GRS are also statistically compared with the values registered during the monitoring campaign.

2. Development of the DAUMOD-GRS model

The atmospheric dispersion model DAUMOD-GRS has been developed to estimate background concentrations of NO₂ in an urban area, considering area source emissions of NO_x and VOCs. The physical and chemical components as well as their coupling into the DAUMOD-GRS model are described below.

2.1. Brief description of the Urban Atmospheric Dispersion Model (DAUMOD)

The DAUMOD model is based on the equation of mass continuity and has been originally developed to estimate urban background concentrations of inert pollutants emitted to the atmosphere from multiple area sources in an urban area.

Considering 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 ($z = h$), the expression used by the model to estimate the pollutant concentration is given by (Mazzeo and Venegas, 1991):

$$C(x, z) = C(x, 0) \sum_{j=0}^6 A_j (z/h)^j \quad (1)$$

where $C(x, 0)$ is the ground level concentration and h is given by:

$$h/z_0 = \beta (x/z_0)^b \quad (2)$$

z_0 is the surface roughness length and β , b and A_j are coefficients that depend on the atmospheric stability (Mazzeo and Venegas, 1991) whose expressions can be found in Pineda Rojas and Venegas (2008). Ground level concentration at a downwind distance x , due to an area source emission of a uniform strength Q_i located between $x = x_{i-1}$ and $x = x_i$, is estimated by:

$$C_i(x, 0) = \beta Q_i \left[(x - x_{i-1})^b - (x - x_i)^b \right] / \left(A_1 \backslash k z_0^b u_* \right) \quad (3)$$

where k is the von Karman's constant ($= 0.41$) and u_* is the friction velocity. The concentration due to a horizontal distribution of N area sources upwind the receptor, is obtained by summing up all their contributions:

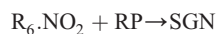
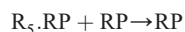
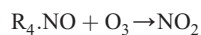
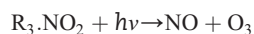
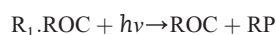
$$C(x, 0) = \beta \left[Q_0 x^b + \sum_{i=1}^N (Q_i - Q_{i-1}) (x - x_i)^b \right] / \left(A_1 \backslash k z_0^b u_* \right). \quad (4)$$

The performance of the model in estimating air pollutant concentrations has been evaluated comparing modelled concentration values with observations in different cities of the United States, Germany, Denmark, and in the city of Buenos Aires, Argentina. Results of these evaluations, presented in Mazzeo and Venegas (1991) and Venegas and Mazzeo (2002, 2006), show that the ability of the DAUMOD model to estimate pollutant concentrations for short averaging time (hourly and daily) is good and it improves when estimating values for long averaging time (monthly and annual).

2.2. The Generic Reaction Set (GRS)

The GRS scheme (Azzi et al., 1992) was developed at the Commonwealth Scientific and Industrial Research Organisation (CSIRO) Division of Coal and Energy Technology (Australia), by identifying the most important reactions in the process of photochemical smog formation, using outdoor smog chamber data for a range of hydrocarbon mixtures and different VOCs/NO_x ratios. It is a semi-empirical scheme that

represents the thousands of reactions involving VOCs–NO_x–O₃ with just seven reactions:



where ROC, RP, SGN and SNGN are “pseudo-species” representing a group of species. ROC represents of all (reactants and products) VOCs, RP all radicals, SGN stable gaseous nitrogen products and SNGN stable non-gaseous nitrogen products. Therefore, except for R₃ and R₄ that are exact, the above are pseudo-reactions. R₁ represents the photo-oxidation of all ROCs. It is the most important reaction because it is considered the “starting point” in the smog formation process and is the source of RP (Azzi et al., 1992). R₂ is fast and constitutes the first fate for RP, converting NO to NO₂. The NO₂ produced is ready to be photolysed, producing O₃ and regenerating NO through R₃. In R₄, the O₃ formed can then react with NO to generate back NO₂. R₅ represents the second sink for RP; while R₆ and R₇ constitute other sinks through which non-reactive nitrogen compounds are generated.

The formation/loss rates for each of these seven species can be written as:

$$d[\text{ROC}]/dt = 0 \quad (5)$$

$$d[\text{RP}]/dt = k_1[\text{ROC} - k_2\text{RP}][\text{NO}] - (k_6 + k_7)[\text{RP}][\text{NO}_2] \quad (6)$$

$$d[\text{NO}_2]/dt = k_2[\text{RP}][\text{NO}] + k_4[\text{NO}][\text{O}_3] - k_3[\text{NO}_2] - (k_6 + k_7)[\text{RP}][\text{NO}_2] \quad (7)$$

$$d[\text{NO}]/dt = k_3[\text{NO}_2] - k_2[\text{RP}][\text{NO}] - k_4[\text{NO}][\text{O}_3] \quad (8)$$

$$d[\text{O}_3]/dt = k_3[\text{NO}_2] - k_4[\text{NO}][\text{O}_3] \quad (9)$$

$$d[\text{SGN}]/dt = k_6[\text{RP}][\text{NO}_2] \quad (10)$$

$$d[\text{SNGN}]/dt = k_7[\text{RP}][\text{NO}_2] \quad (11)$$

where k_n ($n = 1, \dots, 7$) is the reaction rate constant of reaction R_n, and in Eq. (6) it has been assumed that the concentration of RP is sufficiently small so that $[\text{RP}]^2 \sim 0$ (Kim et al., 2005). Besides, given that the representative species RP has a short life time; it is possible to assume that its concentration rapidly falls to its equilibrium value (Kim et al., 2005; Venkatram et al., 1994). Therefore, $d[\text{RP}]/dt \approx 0$ and Eq. (6) reduces to a simple algebraic equation.

The reaction constants in DAUMOD-GRS are parameterised as follows. The calculation of the reaction constant k_3 is an important component of air quality photochemical models, given that the photo-dissociation of NO₂ (reaction R₃) contributes significantly to the tropospheric ozone formation. The parameterisation of k_3 (min^{-1}) included in the DAUMOD-GRS model is the one proposed by Schere and Demerjian (1978) and corrected by Wratt et al. (1992):

$$k_3 = \begin{cases} [4.23 + 1.09/\cos \chi] \times 10^{-4} \text{ TSR} & 0 \leq \chi < 47^\circ \\ 5.83 \times 10^{-4} \text{ TSR} & 47^\circ \leq \chi < 64^\circ \\ [-0.997 + 12(1 - \cos \chi)] \times 10^{-4} \text{ TSR} & 64^\circ \leq \chi < 90^\circ \end{cases} \quad (12)$$

being χ the solar zenith angle and TSR the total solar radiation (W m^{-2}), which is estimated according to the following expression (Holtslag and van Ulden, 1983):

$$\text{TSR} = (990 \sin \theta - 30) (1 - 0.75 \text{CL}^{3.4}) \quad (13)$$

where θ is the solar elevation angle and CL is the fraction of sky covered by clouds.

On the other hand, since k_1 is the rate at which a given mixture of VOCs (represented by ROC) produces radicals (RP), its original expression is a function of a weighted activity coefficient $\bar{a}_{\text{ROC}} = (\sum_{i=1}^M a_i C_i) / (\sum_{i=1}^M C_i)$, where a_i is the reactivity coefficient for the emitted VOCs species i and C_i its concentration. Thus, k_1 depends on the emission of each VOC (Q_i). In order to separate the treatment of the chemistry from the emission conditions, Venkatram et al. (1994) present a method in which this dependence of k_1 on the ability of each VOC species to produce radicals, is “moved” or “passed” to the ROC emission rate (Q_{ROC}) through the expression:

$$Q_{\text{ROC}} = \sum_{i=1}^M a_i Q_i \quad (14)$$

and the reaction constant k_1 (min^{-1}) can be therefore estimated as a function of the air temperature T (K) and k_3 only (Venkatram et al., 1994):

$$k_1 = k_3 1\text{E} + 04 \exp[-4700/T] \quad (15)$$

The considered expressions for k_2 and k_4 (both in $\text{ppm}^{-1} \text{ min}^{-1}$) are (Azzi et al., 1992; Hurley et al., 2003):

$$k_2 = 3.58\text{E} + 06/T \quad (16)$$

$$k_4 = (9.24\text{E} + 05/T) \exp(-1450/T) \quad (17)$$

and $k_6 = k_7 = 120 \text{ ppm}^{-1} \text{ min}^{-1}$ (Azzi et al., 1992).

The GRS scheme has been validated with CSIRO outdoor smog chamber data using a range of hydrocarbon mixtures and different ROC/NO_x ratios (Azzi et al., 1992). In addition, several applications of air quality models including the GRS chemical mechanism (e.g., ADMS-Urban, CIT, SEGRS, SOMS, TAPM) showed that in the urban scale it gives comparable or better results than other photochemical models. For example, Venkatram et al. (1994) incorporated the GRS mechanism into the SOMS model and applied it to an ozone episode in the San Joaquin Valley of California (US) in August 1990.

By comparing model results with the observations, these authors showed that the GRS had comparable performance in explaining peak ozone concentrations and reproducing the diurnal variation to a detailed version of the same model including the SAPRC mechanism. They also found that the replacement of the SAPRC scheme by the GRS resulted in a reduction of the computing time in a factor of 5. Lashmar and Cope (1995) applied the CIT model for a two day oxidant event in Sydney (Australia) and obtained that predicted maximum smog concentrations were comparable with the observations. Anh et al. (1998) showed that the performance of GRS for the ROC/NO_x ratios characteristic of large Australian cities was far superior to that of CBM-IV, pointing out that the GRS mechanism does not include inorganic processes that may be important for the description of photochemical smog production in a NO_x-rich region (i.e., for low ROC/NO_x emission ratio). Hurley et al. (2003) applied the TAPM to simulate one year of hourly averaged air pollution concentrations in Melbourne (Australia) and showed that the GRS scheme can be applied for regulatory applications. In particular, the model performed very well for estimations of extreme smog and particle concentrations. Also, Kim et al. (2005) ran the SEGRS model to simulate ground-level O₃ concentrations over the Seoul metropolitan area (Korea) for days of high ozone levels. The simulated diurnal trend and maximum values of O₃ concentration were quite reasonably compared with observations.

2.3. Linking the GRS chemical scheme with the DAUMOD model

Once precursor species (NO_x and ROC) are transported and dispersed by the wind and the atmospheric turbulence, they can react according to the GRS (reactions R₁–R₇). Since this scheme is driven by the presence of both species, the reaction time (Δt_c) is determined by the minimum value of the average ages (τ) of both pollutants:

$$\Delta t_c = \min[\tau(\text{NO}_x), \tau(\text{ROC})]. \quad (18)$$

To estimate τ , the time it takes each species coming from the source i to reach the receptor is first computed as:

$$\tau_i = L_i/u \quad (19)$$

where L_i is the source–receptor distance. τ can then be calculated as the average of τ_i taking into account the contribution of the source i to its concentration in the receptor:

$$\tau = \frac{\sum_{i=1}^N \tau_i C_i}{\sum_{i=1}^N C_i} \quad (20)$$

where N is the number of sources located upwind the receptor and C_i is given by Eq. (3).

Eqs. (19)–(20) are evaluated for each receptor and determine the temporal interval Δt_c for the integration of the chemical Eqs. (5)–(11). Note that the latter can be written as:

$$dC_s/dt = p_s - q_s C_s \quad (21)$$

where p_s and $q_s C_s$ are the production and loss rates for the species s , respectively. This non-linear and coupled Ordinary Differential Equation Systems (ODES) requires a numerical

integration scheme to be solved. A widely used method to solve such a system is the Quasi Steady State Approximation (QSSA) (e.g., Hesstvedt et al., 1978; Yamartino et al., 1992; Taghavi et al., 2005). This technique assumes that there is a time lapse δt in which p_s and q_s are constant, so that Eq. (21) can be easily integrated to give the algebraic solution:

$$C_s = (p_s/q_s) + [C_{s0} - (p_s/q_s)] \exp(-q_s \delta t) \quad (22)$$

where subscript “0” indicates the value of the variable at the beginning of δt .

The precision of this method depends on the careful choice of δt so that the concentration change in that interval is not too large. The time step δt included in the DAUMOD-GRS model is (Yamartino et al., 1992):

$$\delta t = \varepsilon \min[C_{s0}/(p_{s0} - q_{s0} C_{s0})] \forall s \quad (23)$$

where ε represents an acceptable fractional change in the concentration during δt . DAUMOD-GRS includes a corrector step through which Eq. (22) is recalculated using p_s and q_s averaged over their values computed at the beginning and the end of δt . This correction leads to errors in the solution of the order of ε^3 (Yamartino et al., 1992).

At night, NO₂ does not photolyse and the chemistry of the NO_x family is therefore entirely different from that during daytime: any NO present reacts rapidly with O₃ through the reaction $\text{NO} + \text{O}_3 \rightarrow \text{NO}_2$. As a result, almost all NO_x at night is converted to NO₂ (Seinfeld and Pandis, 2006). In the DAUMOD-GRS model, the night-time chemistry of these species is included by allowing computation of reaction R₄ only.

3. Results and discussion

The DAUMOD-GRS model is applied to estimate NO₂ concentrations in the city of Buenos Aires (CBA). High resolution emission inventories have been proved to give better results, particularly for primary species like nitrogen oxides (e.g., Astitha et al., 2008; Taghavi et al., 2005). Calculations are performed considering a high spatial (1 km × 1 km) and temporal (1 h) resolution NO_x emission inventory (Venegas et al., 2011) for area sources (i.e., road transport; residential, commercial and small industry activities; aircrafts operations at the local and international airports) in the Metropolitan Area of Buenos Aires (MABA). The assumed NO_x speciation is 90% of NO and 10% of NO₂ by mol. Point sources (given mainly by the stacks of the Power Plants located in the coastline) are not considered in calculations, since their contribution to ground level concentrations in the city is much lower than that of area sources. The VOC emission rates have been obtained using the same activity database employed to estimate the emissions of NO_x (other sources of VOCs, such as solvent product use or biogenic sources, are not considered). Given that VOC emissions in urban areas are mostly dominated by motor vehicles (e.g., Lau et al., 2010; Nesamani, 2010) the speciation of VOC classes has been estimated using the MABA vehicle float composition, in accordance with the VOC classification of COPERT III. The ROC emission rate required by the GRS scheme is computed via Eq. (14) using the

coefficients a_i obtained by Venkatram et al. (1994). On the other hand, when modelling photochemical reactions, the use of observations from monitoring sites as background concentration values is recommended. Alternatively, values obtained from larger scale models can be employed (e.g., Lasry et al., 2005). 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). Due to the lack of information on regional background concentrations in the area, it has been assumed that background conditions are constant and equal to those of clean air for all species except for ozone. Based on the results obtained by Mazzeo et al. (2005), a regional background ozone concentration of 20 ppb is assumed.

Surface hourly meteorological data for this study are obtained from the Argentine Meteorological Office weather station located at the domestic airport in the CBA. Sounding data are obtained from the Argentine Meteorological Office weather station located at the international airport in the MABA, at 30 km from the city.

The results of DAUMOD-GRS are compared with available observations of hourly concentrations obtained during a campaign carried out in a green open area of the city of Buenos Aires from 11 August to 17 September 2001. A description of this campaign (monitoring site, methodology and data) can be found in Mazzeo et al. (2005).

3.1. The DAUMOD-GRS reaction constants

According to the expressions (12)–(17), the reaction constants depend on the air temperature (T) and the total solar radiation (TSR). The air temperature directly influences k_1 , k_2 and k_4 , while the total solar radiation determines k_3 and also affects k_1 . Hourly values of TSR estimated using Eq. (13) for the period of study vary between 57.3 and 777.2 W m⁻². In diurnal hours (i.e., when $TSR > 0$) the air temperature varies between 6.2 and 17.3 °C, giving rise to values of k_2 and k_4 in the ranges 12,053.9–12,817.8 ppm⁻¹ min⁻¹ and 18.4–23.6 ppm⁻¹ min⁻¹, respectively. The photo-dissociation constant of ROC (k_1) varies between 1.0E-04 min⁻¹ and 5.0E-04 min⁻¹, and that of NO₂ (k_3) between 0.06 and 0.40 min⁻¹. These modelled values of k_3 agree with winter-time estimations reported by other authors. For example, using observations from the above mentioned campaign and following a different methodology, Mazzeo et al. (2005) obtained that NO₂ photo-dissociation constant varies between 0.02 min⁻¹ and 0.81 min⁻¹ with a mean value of 0.19 min⁻¹. On the other hand, de Miranda et al. (2005) estimated values of k_3 in the range 0.34–0.41 min⁻¹ for the Metropolitan Area of Sao Paulo, Brazil.

3.2. Nitrogen dioxide concentrations in the city of Buenos Aires

Fig. 1 shows the scatter plot of observed and modelled hourly NO₂ concentrations. Hourly observed values vary between 0.5 and 61.9 ppb, while modelled ones are in the range 0.3–76.2 ppb. The following statistical measures have been computed to assess the agreement between estimated and observed concentrations: the mean value (MEAN), the standard deviation (SIGMA), the normalised mean square error (NMSE), the fraction of estimations within a factor of two of

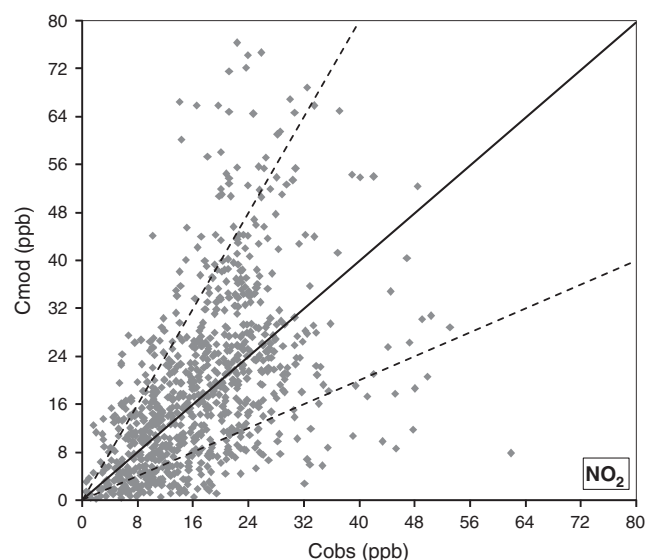


Fig. 1. Scatter plot of observed and modelled hourly NO₂ concentrations (N=859). The lines 2:1, 1:1 and 1:2 are included.

observed values (FA2) and the fractional bias (FB). The obtained values of these statistical measures are included in Table 1. The mean observed NO₂ concentration is 17.2 ppb while the mean value of DAUMOD-GRS estimations is 19.0 ppb; the NMSE is 0.49; and 67.6% of modelled values are within a factor of two of the observations. These results show an acceptable model performance for NO₂ at this site, with a slight overestimation of observed values (FB = -0.097). Having neglected the contribution of point source emissions does not seem to introduce much error in the modelled hourly NO₂ concentrations. Fig. 2 displays the histograms of both observed and modelled hourly NO₂ concentrations. The distributions of frequencies are, in general, similar; although modelled values present a slightly higher frequency of low (≤ 10 ppb) and high (> 30 ppb) concentrations, and a lower occurrence of values between 10 and 30 ppb.

Fig. 3 shows the hourly variation of mean modelled and observed concentrations. In general, this variation is well reproduced and it is also consistent with the mean daily NO₂ cycles that are commonly observed in urban areas (e.g., Im et al., 2008; Notario et al., 2012; Pudasainee et al., 2010). Both observed and modelled NO₂ hourly mean concentrations present a double peak pattern with the second maximum being higher than the early morning one, probably due to more O₃ available to produce NO₂ via reaction R₄, as noted at some other places (e.g., Notario et al., 2012). Mean observed

Table 1

Statistical measures obtained from the comparison of observed and modelled NO₂ 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].

	N	Mean	Sigma	NMSE	FA2	FB
NO ₂						
Observed	859	17.2	9.1	–	–	–
DAUMOD-GRS		19.0	14.4	0.49	0.676	-0.097
O ₃						
Observed	684	9.3	5.5	–	–	–
DAUMOD-GRS		11.6	6.0	0.38	0.684	-0.225

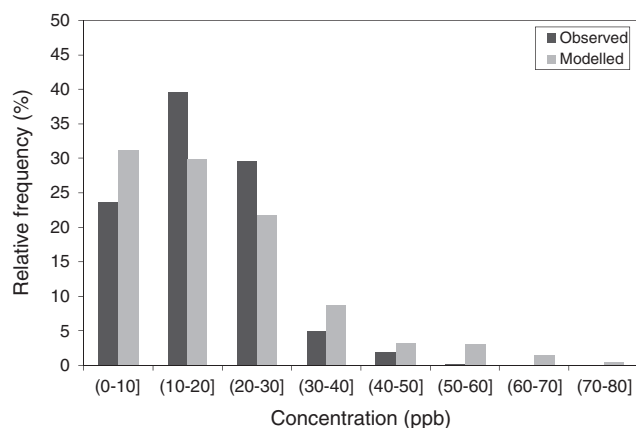


Fig. 2. Histogram of observed and modelled hourly NO₂ concentrations.

hourly values vary between 11.2 ppb (at 4 h) and 25.9 ppb (at 19 h). Mean modelled hourly NO₂ concentrations vary between 11.7 ppb (at 14 h) and 28.7 ppb (at 20 h). The relative difference (i.e., the modelled to observed ratio) varies between 0.76 (at 17 h) and 1.52 (at 3 h). From this figure, a better performance of DAUMOD-GRS in diurnal hours (when the GRS is active) can be expected. At night-time hours, greater differences between modelled and observed values may appear because the nocturnal chemistry included in DAUMOD-GRS is highly simplified. At early morning hours, the GRS has still little influence on the concentrations due to the reduced photochemical activity of the atmosphere, and other reactions (not included in DAUMOD-GRS) could be playing an important role.

The DAUMOD-GRS is applied to one year of hourly input data to obtain the horizontal distribution of annual NO₂ ground-level concentrations in the city of Buenos Aires (Fig. 4). Annual concentrations of NO₂ in the city vary between ~10.0 ppb and 36.1 ppb. Higher concentrations can be found near the areas with dense traffic. According to these results, annual NO₂ concentrations in the city lower than the air quality standard (53 ppb) (Res. 198/06, city of Buenos Aires) are expected.

3.3. Ozone concentrations

The application of DAUMOD-GRS also gives estimations of ozone concentrations in the urban area. Hourly ozone concentrations estimated by DAUMOD-GRS are compared with observed values registered during the mentioned monitoring campaign. The scatter plot of modelled and observed hourly O₃ concentrations is presented in Fig. 5. Measured values vary between 1.1 and 29.3 ppb and estimated ones between 0.5 and 25.7 ppb. Observed ozone concentrations present a mean level of 9.3 ppb and a standard deviation of 5.5 ppb; while modelled concentrations have a mean value of 11.6 ppb and a standard deviation of 6.0 ppb. The statistical measures obtained for the comparison of estimated O₃ hourly concentrations are also shown in Table 1. Results indicate that 68.4% of modelled concentrations fall within a factor of two the observed values, the NMSE for the O₃ comparison is 0.38 and FB = −0.225. In this case, ozone concentrations are somewhat overestimated by the DAUMOD-GRS model. The fact that in the city of Buenos

Aires, the modelled O₃ hourly levels are comparable and even greater than the observed values suggests that other contributions, such as the biogenic VOCs emissions, could be negligible in the studied area.

Fig. 6 shows that both observed and modelled hourly O₃ concentrations present higher frequencies of values between 5 and 15 ppb: 61.2% and 52.3%, respectively. Modelled values show lower frequency than observations in the ranges 0–5 ppb and 25–30 ppb, and higher frequency in the range of concentrations between 15 and 25 ppb in which the greatest difference between observations (11.9%) and estimations (31.6%) is obtained. On the other hand, both observed and modelled O₃ levels are mostly lower than 20 ppb (i.e., its assumed regional background concentration). From Fig. 6, it can be seen that only 3.8% of observations and 10.7% of estimations are above this value, reflecting a low net O₃ production at the site. Taking into account that the measurements have been carried out in winter at a site located within the city, a low production of ozone at the study area is expected. Considering that O₃ concentrations usually maximise downwind the large urban centres, measurements in the suburbs during summer time would be more appropriate to evaluate the performance of DAUMOD-GRS in estimating net ozone formation.

4. Conclusions

In this work, the DAUMOD urban atmospheric dispersion model has been updated incorporating the simplified GRS photochemical scheme, developing the DAUMOD-GRS model to estimate NO₂ concentrations in an urban atmosphere. The development of the DAUMOD-GRS model and its first application to evaluate annual NO₂ concentrations in the city of Buenos Aires (CBA) are presented. The model is applied considering recently obtained high resolution NO_x and VOC emissions for the area. Modelled concentrations of NO₂ and O₃ are compared with the observations from a 38-day winter campaign carried out at a green open area of the CBA. It is found that both species are well simulated by the model at the site.

Hourly NO₂ concentrations (N = 859) present a mean observed level of 17.2 ppb while the modelled mean concentration is 19.0 ppb. The obtained statistical measures are as follows: a normalised mean square error (NMSE) of 0.49, a factor of two within observations (FA2) of 0.676 and a fractional bias (FB) of −0.097. Modelled mean hourly NO₂

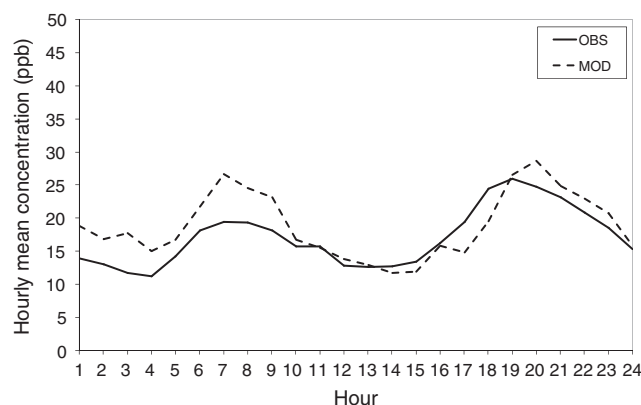


Fig. 3. Hourly variation of mean modelled and observed NO₂ concentration at the monitoring site.

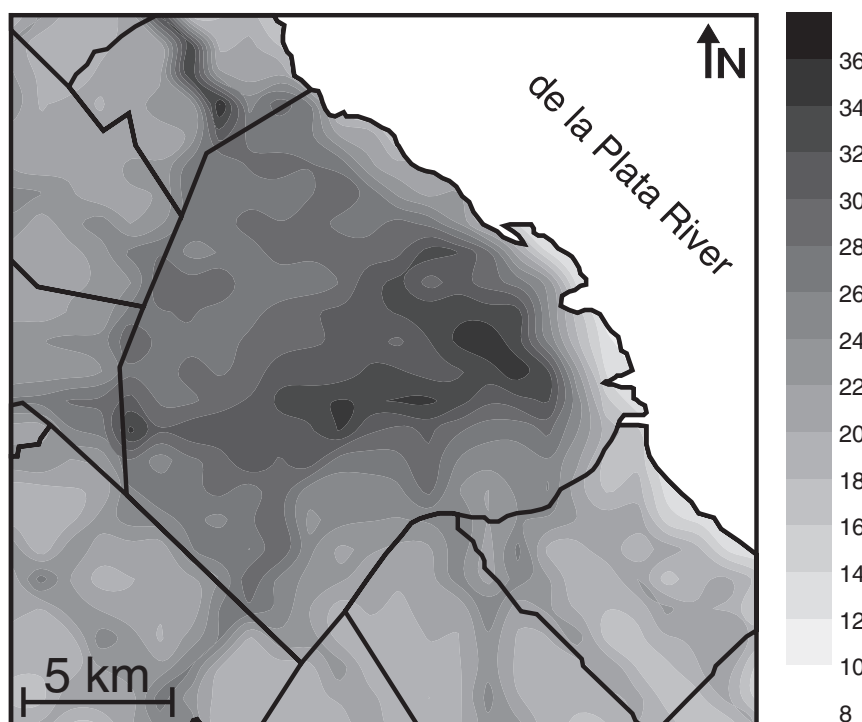


Fig. 4. Horizontal distribution of modelled annual mean NO_2 ground-level concentration (ppb) in the city of Buenos Aires.

concentrations compare well with the observed ones, especially during diurnal hours when the GRS is active. Greater differences between observed and modelled mean hourly NO_2 levels are found at night and early morning hours. According to the model results, annual NO_2 concentrations in the CBA are below the air quality standard (53 ppb). The maximum annual NO_2 concentration in the city reaches 36.1 ppb.

On the other hand, the observed and modelled mean hourly O_3 concentrations are 9.3 ppb and 11.6 ppb, respectively. The comparison between estimated and observed hourly O_3 concentrations ($N = 684$) indicates that $\text{NMSE} = 0.38$, $\text{FA2} =$

0.684 and $\text{FB} = -0.225$, showing some overestimation of observations. Considering the low formation of O_3 observed at the measurement site, more evaluations of ozone simulation with DAUMOD-GRS at sites located downwind the city, are recommended. In a future work, the performance of the DAUMOD-GRS model may be improved further by including deposition processes. However, the estimation of air concentrations taking into account the deposition of both species will be possible if high resolution data on the land use type distribution for the MABA becomes available.

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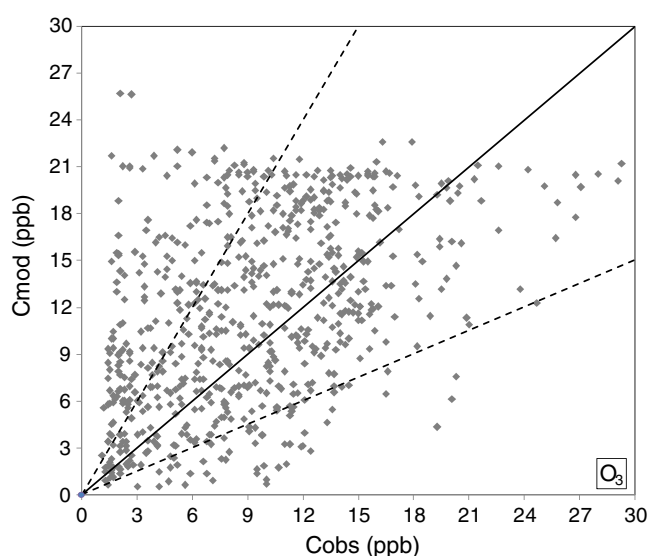


Fig. 5. Scatter plot of observed and modelled hourly O_3 concentrations ($N = 684$). The lines 2:1, 1:1 and 1:2 are included.

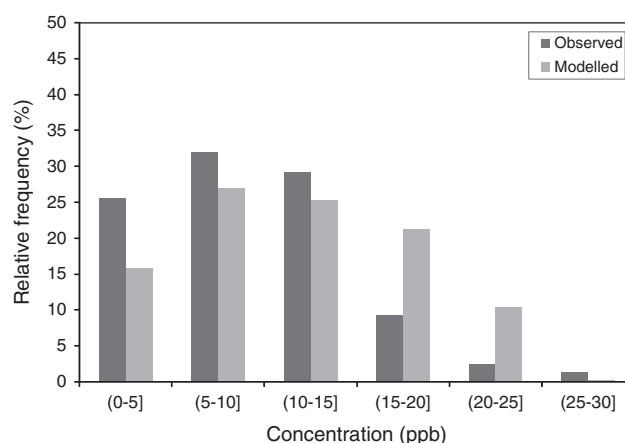


Fig. 6. Histogram of observed and modelled hourly O_3 concentrations.

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