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Linking the GRS photochemical scheme with the DAUMOD urban atmospheric dispersion model

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Abstract: The DAUMOD model is a simple urban scale atmospheric dispersion model which was originally developed to estimate inert air pollutant ground-level background concentrations resulting from a great number of area emission sources. The model has been tested against observations from Buenos Aires and different cities of Europe and the US, and has been extensively used during the past two decades to study the air pollution related to NO_x species in the city of Buenos Aires and surrounding areas. The Generic Reaction Set (GRS) constitutes a simplified scheme of the most complete photochemical mechanisms. Due to its simplicity and its ability to reproduce the interactions between NO, NO_2 and O_3 at urban scale, the GRS has been widely adopted in air quality assessment studies. In this work, we present the coupling of the DAUMOD model with the GRS. The developed coupled model DAUMOD-GRS is applied to estimate the ground-level concentrations of NO_2 and O_3 resulting from high resolution (1h, 1km^2) NO_x and VOC emissions in the Metropolitan Area of Buenos Aires (MABA). Modelled hourly concentrations are tested against observed values at several sites. The statistical measures obtained are satisfactory. The comparison of model estimations with air quality data measured at twenty sites across the MABA shows that for NO_2 (N=2909), the normalised mean square error (NMSE) is 0.83, the fraction of two within observations (FA2) is 0.575, and the fractional bias (FB) is 0.034; while for O_3 (N=3100), NMSE=0.21, FA2=0.821 and FB=-0.066.

***Keywords**:* DAUMOD-GRS model; NO_x and VOC emissions; Metropolitan Area of Buenos Aires; NO_2 and O_3 air pollution.

1 INTRODUCTION

In large urban areas, anthropogenic emissions of nitrogen oxides (NO_x) and volatile organic compounds (VOC) to the atmosphere may lead to concentration levels of nitrogen dioxide (NO_2) and ozone (O_3) which may produce adverse effects on human health. Hence, the evaluation of their ground level concentrations constitutes a fundamental part in air quality assessment studies. This task is usually achieved through the application of air quality models (AQMs) including photochemical processes.

Usually, AQMs can be classified into comprehensive and simple semi-empirical models. The former include very detailed photochemical schemes allowing for a more complete description of main processes behind the production/loss of a pollutant in the urban atmosphere. However, their applications are frequently limited by all the input data that is required to operate them; while their high computational cost limits considerably the temporal and spatial resolutions of the

simulations. Simpler models become an acceptable alternative to estimate urban background concentrations (at 1km^2-level) in places where the air quality is not seriously constrained and/or there is not enough available information to run more complex ones. In urban areas where the input data are not a limitation, simple AQMs 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 [Mazzeo and Venegas, 1991] is within this category of simple urban atmospheric dispersion models. Originally, it was developed to estimate urban background concentrations of inert species. The model has been validated using observations from Buenos Aires and different cities of Europe and the US [Mazzeo and Venegas, 1991; Venegas and Mazzeo, 2002, 2006], and has been extensively used to study the air quality of the urban atmosphere in Buenos Aires and its impact on surrounding areas [e.g., Mazzeo and Venegas, 2008; Mazzeo et al., 2010; Pineda Rojas and Venegas, 2009, 2010; Venegas et al., 2011].

In order to allow the photochemical formation of NO_2 and O_3 concentrations resulting from NO_x and VOC emissions in an urban area, the DAUMOD model has been coupled to the Generic Reaction Set (GRS) [Azzi et al, 1992] which is a simplified scheme of the most complete photochemical mechanisms. Due to its simplicity and its ability to reproduce the interactions between NO_2 and O_3 at urban scale, the GRS has been widely adopted in urban air quality assessment studies [eg., Venkatram et al., 1994; Anh et al., 1998; Hurley et al., 2003].

A previous paper [Pineda Rojas and Venegas, 2011] presents the first application of the DAUMOD-GRS model in which the simulated NO_2 and O_3 concentrations were consistent to those obtained with the CALGRID model, considering an hypothetical scenario for a range of atmospheric and emission conditions typical of urban areas in summer. Recently available concentration data have allowed the testing of the application of DAUMOD-GRS in the Metropolitan Area of Buenos Aires (MABA). In this work, we describe the coupling between the DAUMOD model and the GRS photochemical scheme, and we present the first evaluation of the DAUMOD-GRS model performance considering observations of NO_2 and O_3 concentrations from several campaigns carried out in the Metropolitan Area of Buenos Aires.

2 METHODOLOGY

A complete description of the DAUMOD model can be found in Mazzeo and Venegas [1991]; while the detailed development of the GRS scheme is presented in Azzi et al. [1992]. Here we summarise their main assumptions and focus on the coupling of the DAUMOD-GRS model.

The DAUMOD model is based on the equation of mass continuity and has been originally developed to estimate 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, the expression used by the model to estimate the pollutant ground level concentration at a downwind distance *x*, due to an area source *i* of uniform emission strength Q_i located between $x=x_{i-1}$ and $x=x_i$, is estimated by:

$$C_i(x,0)= a\, Q_i\, [(x - x_{i-1})^b - (x - x_i)^b\,] / (\,|\, A_1 \,|\, k\, z_0^{\,b}\, u_*) \qquad (1)$$

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 concentration due to a horizontal distribution of *N* area sources located upwind the receptor, is then obtained by summing up all their contributions:

$$C(x,0)= a\ [\ Q_0\ x^b + \sum_{i=1}^{N}\ (Q_i - Q_{i-1})(x - x_i)^b\ ]\ /\ (\ |\ A_1\ |\ k\ z_0^{\ b}\ u_*) \qquad (2)$$

The GRS scheme was developed at the Commonwealth Scientific and Industrial Research Organisation (CSIRO) Division of Coal & Energy Technology (Australia) from a systematic analysis of the principal reactions that produce photochemical smog [Azzi et al., 1992]. It is a simplified semi-empirical scheme that represents the thousands of reactions involving NO_x, VOC and O_3 with just seven reactions:

R_1. ROC + *hv* → ROC + RP

R_2. RP + NO → NO_2

R_3. NO_2 + *hv* → NO + O_3

R_4. NO + O_3 → NO_2

R_5. RP + RP → RP

R_6. NO_2 + RP → SGN

R_7. NO_2 + RP → SNGN

Except for R_3 and R_4 that are exact, the above are pseudo-reactions. The four "representative species" are ROC (which represents all VOC compounds), RP (all radicals), SGN (stable gaseous nitrogen products) and SNGN (stable non-gaseous nitrogen products). In this scheme, the formation/loss rate equation for the concentration (C_s) of each species *s* can be written as:

$$dC_s/dt = p_s - q_s C_s \qquad (3)$$

where p_s and $q_s C_s$ are its production and loss rates, respectively, which depend on the reaction constants k_n (associated to the reactions R_n). (3) can be solved applying the Quasi Steady State Approximation (QSSA) [e.g., Hesstvedt et al., 1978; Yamartino et al., 1992], which assumes that there is a time lapse δt in which p_s and q_s are constant, so that they can be easily integrated to give solutions of the form:

$$C_s = (p_s/q_s) + [C_{s0} - (p_s/q_s)]\ \exp(-q_s\ \delta t) \qquad (4)$$

subscript "0" indicates the value of the variable at the beginning of δt.

The coupling of the two models is performed as follows. Once precursor species are transported and dispersed by the wind and the atmospheric turbulence, they can react according to the GRS scheme. During daylight hours, O_3 formation requires the presence of both species NO_x and VOC (represented by ROC). Then, for a given a horizontal distribution of emission sources, the reaction time (Δt_c) at each receptor is given by the minimum value of the average ages (τ) of both pollutants:

$$\Delta t_c = \min[\tau(NO_x),\ \tau(ROC)] \qquad (5)$$

where τ is computed for each species as:

$$\tau = \sum_{i=1}^{N} \tau_i C_i\ /\ \sum_{i=1}^{N} C_i \qquad (6)$$

being τ_i the time it takes the species coming from the source *i* to reach the receptor:

$$\tau_i = L_i/U \qquad (7)$$

L_i is the source-receptor distance and *U* is the wind speed.

The set of equations given by (4) are then numerically integrated during the reaction time Δt_c, with a variable time step δt [Yamartino et al., 1992]:

$$\delta t = \varepsilon\ \min[C_{s0}\ /(\ p_{s0} - q_{s0}\ C_{s0}\ )] \quad \forall s \qquad (8)$$

where ε represents an acceptable fractional change in the concentration during δt. DAUMOD-GRS includes a corrector step through which (4) 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, NO_2 does not photolyze and the chemistry of the NO_x family is therefore entirely different from that during daytime: any NO present reacts rapidly with O_3 through the reaction NO + O_3 → NO_2. As a result, almost all NO_x at night is converted to NO_2 [Seinfeld and Pandis, 2006]. In the DAUMOD-GRS model, the nighttime chemistry of these species is included by allowing computation of (4) for reaction R_4 only.

3 EVALUATION OF THE MODEL PERFORMANCE

3.1 Concentration data

Two data sets are used to compare model results with observations: (i) one from an urban background (UB) site located in the City of Buenos Aires (CBA) where NO_2 and O_3 were measured from 11 August to 17 September 2001 and whose results are studied in detailed in Mazzeo et al. [2005], and (ii) other recently available from several campaigns carried out by the National Office of Public Roads of Argentina at nineteen urban traffic (UT) sites across the Greater Buenos Aires (GBA) in different periods during 2007 and 2008. The spatial distribution of the twenty sites in the MABA (CBA+GBA) is shown in Figure.1.

The UB site is located at an urban park (mainly grassland with a few trees), surrounded by the domestic airport at 800 m (towards the NW), two thermal power plants at 2 km (E), two major avenues extending from distances between 80 m (SW) and 900 m (SE), and between 180 m (SW) and 800 m (NNE), respectively, and de la Plata River at ~1 km (NE). The UT sites are mostly distributed along the main highways of the GBA accessing to the CBA, and the measurements were taken approximately within 50 m from the traffic line. All collected data account for a total of 2909 and 3100 hourly concentration values of NO_2 and O_3, respectively.

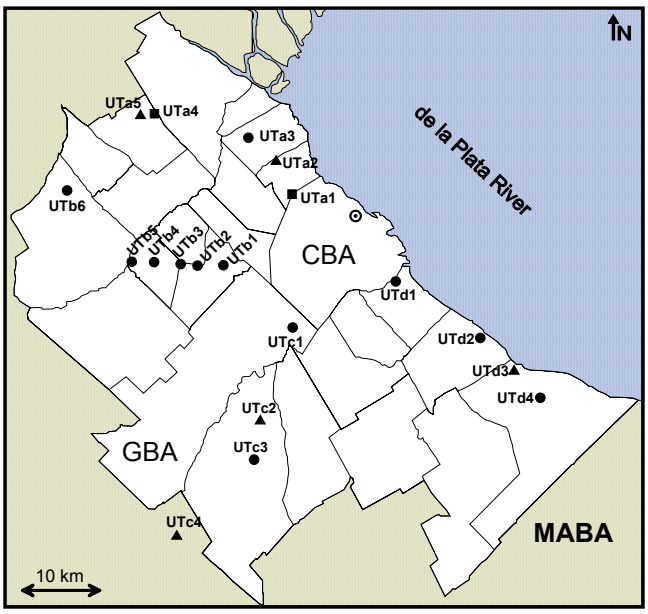

Figure 1. Measurement sites for NO_2 (■),O_3 (▲) and both species (●) within the MABA [the City of Buenos Aires (CBA) + the Greater Buenos Aires (GBA)]. The UB site is indicated (⊙).

3.2 Running conditions

The DAUMO-GRS model was applied to estimate NO_2 and O_3 hourly concentrations at each monitoring site during its sampling period. The runs were performed considering temporal and spatial resolutions of 1h and 1km^2, respectively.

Input hourly surface meteorological data registered at the domestic airport of the City of Buenos Aires and sounding data obtained at the International Airport (30 km towards the SW of the CBA) were used for calculations. Input NO_x emission data belong to the high resolution (1h, 1km^2) emission inventory developed recently for the MABA [Venegas et al., 2011]. The speciation for the NO_x species considered in calculations is 90% of NO and 10% of NO_2 (by mol), according with the data from this inventory and the EMEP/CORINAR methodology [EMEP/CORINAIR, 2007]. VOC emission rates have been obtained for this work using the same activity data base employed to estimate the emissions of NO_x. Emissions from residential, commercial and small industry activities, aircraft at the local and international airports of the MABA and road transport, are considered all together as area source emissions. Other area sources such as solvent use are not considered in this work. On the other hand, taking into account that VOC emissions are dominated by the road transport sector, its speciation has been estimated using the MABA vehicle fleet composition, according to the COPERT IV VOC classification.

Based on previous O_3 measurements performed in the CBA [Bogo et al., 1999; Mazzeo et al., 2005], a regional background concentration of 20 ppb is assumed as initial condition for ozone. For other species, clean air concentrations are used as boundary conditions [e.g., Hurley et al., 2003; Dallarosa et al., 2007].

3.3 Results

Table 1 presents the statistical measures obtained for the comparison of hourly ground-level NO_2 concentrations. Considering all data (N=2909), observed NO_2 varies between 0-70 ppb, while modelled values are in the range 0.3-77 ppb (as shown in Figure 2), with 57.5% of them within a factor of two of the measured ones. The mean observed level is 16.9 ppb and the standard deviation is 13.6 ppb. The modelled mean concentration for NO_2 is 16.3 ppb and its standard deviation is 12.7 ppb. As can be seen in Table 1, the obtained normalised mean square error (NMSE) is 0.83 and the fractional bias (FB) is 0.034. These statistical measures show an acceptable model performance for NO_2 with a small general tendency to underestimate the observed levels which could be explained by the fact that the used NO_x and VOC emission inventories do not include some sources, as mentioned above.

Table 1. Statistical measures obtained from the comparison of observed and modelled NO_2 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; Cmax: maximum concentration]

Sites	N		MEAN	SIGMA	NMSE	FA2	FB	Cmax
All	2909	Observed	16.9	13.6				70
		DAUMOD-GRS	16.3	12.7	0.83	0.575	0.034	77
UB	859	Observed	17.2	9.1				62
		DAUMOD-GRS	19.0	14.4	0.49	0.676	-0.097	76
UT	2050	Observed	16.8	15.1				70
		DAUMOD-GRS	15.3	11.7	1.00	0.532	0.096	77

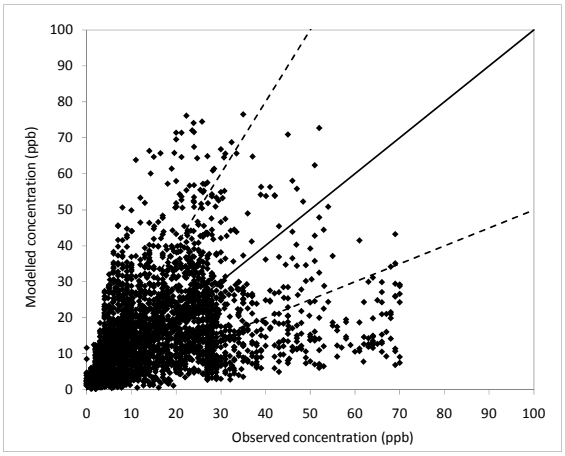

Figure 2. Scatter plot of observed and modelled hourly NO_2 concentrations (N=2909). The lines 2:1, 1:1 and 1:2 are included

The scatter plot of observed and modelled hourly O_3 concentrations is presented in Figure 3. The statistical measures obtained for the comparison of O_3 (Table 2) show that 82.1% of modelled concentrations fall within a factor of two the observed values. In this case, hourly observed values vary between 1.1-34 ppb with a mean level of 12.8 ppb and a standard deviation of 4.4 ppb. Hourly modelled O_3 concentrations are in the range 0.5-35 ppb, have an average value of 13.7 ppb and a standard deviation of 5.8 ppb. These statistics compare very well to those of the observed values. The NMSE for the O_3 comparison is 0.21 and FB=-0.066, showing that ozone concentrations tend to be slightly overestimated by the DAUMOD-GRS.

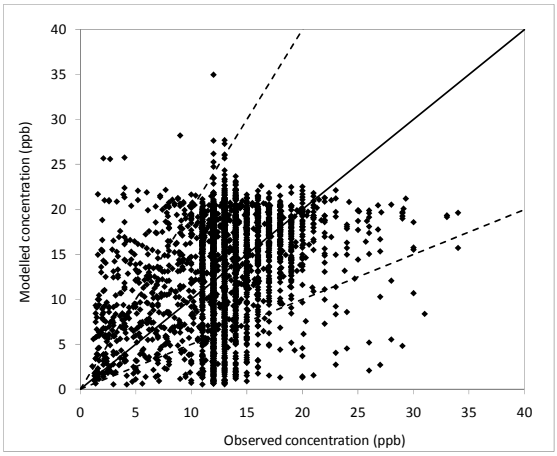

Figure 3. Scatter plot of observed and modelled hourly O_3 concentrations (N=3100). The lines 2:1, 1:1 and 1:2 are included

Table 2. Statistical measures obtained from the comparison of observed and modelled O_3 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; Cmax: maximum concentration]

Sites	N		MEAN	SIGMA	NMSE	FA2	FB	Cmax
All	3100	Observed	12.8	4.4				34
		DAUMOD-GRS	13.7	5.8	0.21	0.821	-0.066	35
UB	684	Observed	9.3	5.5				29
		DAUMOD-GRS	11.6	6.0	0.38	0.684	-0.225	26
UT	2416	Observed	13.8	3.4				34
		DAUMOD-GRS	14.3	5.7	0.19	0.859	-0.032	35

At the UB site, the performance of the model is similar for both species regarding the NMSE (0.49 for NO_2 and 0.38 for O_3) and the FA2 (0.676 for NO_2 and 0.684 for O_3) measures; however, the fractional bias shows considerable overestimation for O_3 (FB=-0.225) compared to NO_2 (FB=-0.097). On the other hand, considering all the UT sites, both species present comparable FB (0.096 for NO_2 and -0.032 for O_3). The fractions of modeled concentrations that are within a factor of two of observations are 53.2% for NO_2 and 85.9% for O_3.

Figure 4 presents the comparisons between modelled and observed mean NO_2 and O_3 concentrations at each measurement site (see Figure 1). The ratios modelled-to-observed of NO_2 mean concentrations vary across the MABA between 0.50 (at the site UTd1) and 2.13 (UTb3). The modelled mean NO_2 concentration compares very well with the observed one in the city (in the UB site); while in the GBA, the comparison improves as the distance to the CBA increases (at the UT sites in the suburbs). In the case of O_3, all modelled mean concentrations are within a factor of two of the observed values, with modelled-to-observed ratios varying between 0.57 (UTb5) and 1.46 (UTc4). The results show an underestimation of mean values at the N and W suburban zones, and an overestimation at the SW and S of the GBA. Further analysis of the positions of the monitoring sites, the emission conditions and the meteorological conditions during the measurement periods is required to better understand these results.

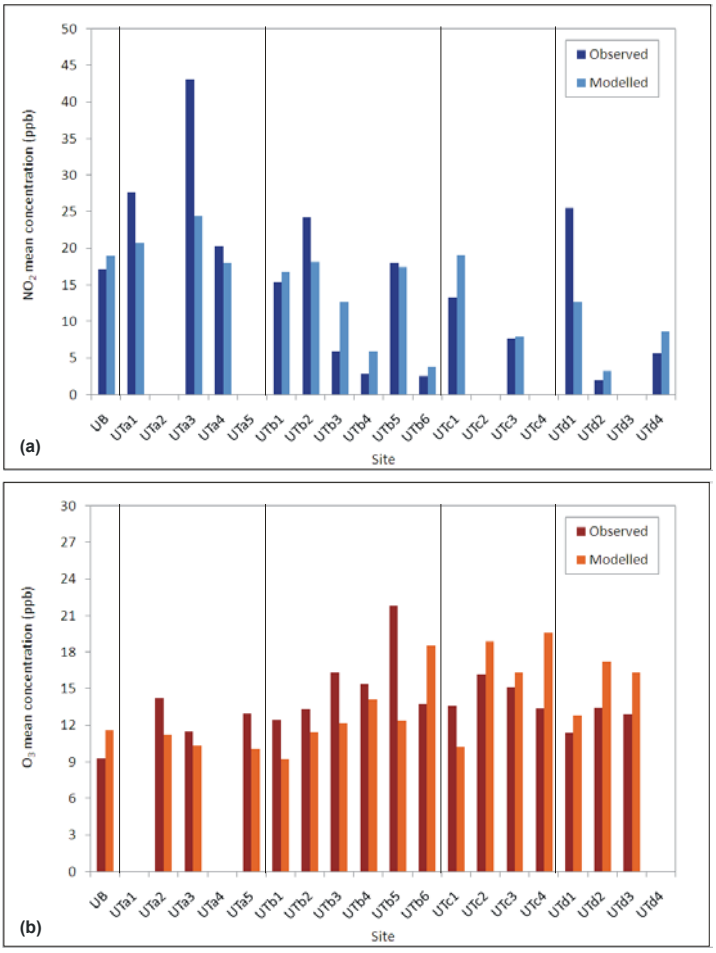

Figure 4. Comparison between observed and modelled mean concentrations: (a) NO_2 and (b) O_3.

As an example of the temporal variations, Figure 5 shows the observed and modelled time series of NO_2 and O_3 during 4 working days at the UB site. It can be seen that for both species, modelled concentrations follow the general temporal

variation of the observed values. In this period, the minimum and maximum values were very well represented most of the times, except at some hours that the model was not able to reproduce the observed peaks of NO_2. The greatest difference obtained in the last day of the period (Friday 7-Sep-01) could result from its proximity to the weekend when real emissions rates could be lower than the estimated.

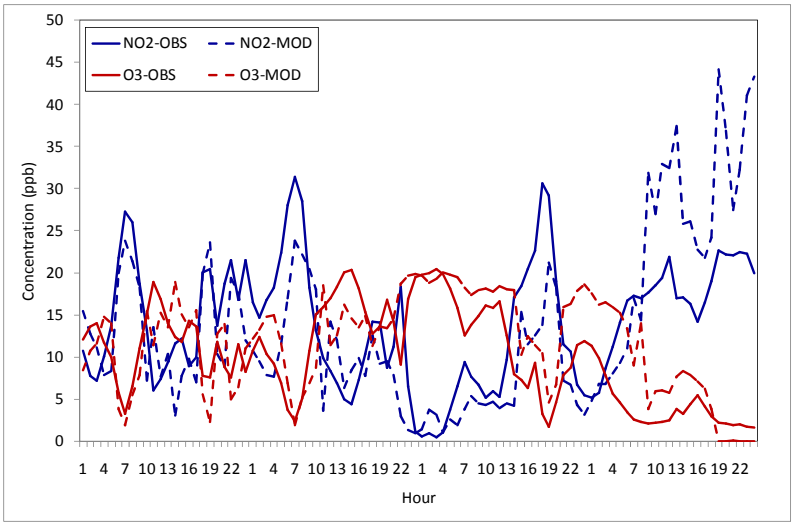

Figure 5. Time series of observed and modelled NO_2 and O_3 concentrations (ppb) during four days (4-7 September 2001) at the UB site.

4 CONCLUSIONS

The DAUMOD urban atmospheric dispersion model has been coupled to the GRS simplified chemical scheme in order to include the photochemical formation of NO_2 and O_3 resulting from NO_x and VOC area source emissions in an urban area.

Modelled concentrations of NO_2 and O_3 have been compared with observations from several campaigns carried out in the Metropolitan Area of Buenos Aires (MABA) in different periods of 2001, 2007 and 2008. The statistical measures obtained for NO_2 are: a normalised mean square error (NMSE) of 0.83, a fraction of two within observations (FA2) of 0.575, and a fractional bias (FB) of 0.034, showing a small underestimation which is mostly observed in the urban traffic sites and could be due to the contribution of other sources not included in this work. For O_3, NMSE=0.21, FA2=0.821 and FB=-0.066, indicating a slight overestimation that is more pronounced in the urban background site. Overall, the DAUMOD-GRS model proved a good performance in simulating the ground level NO_2 and O_3 concentrations observed in the MABA, although further model evaluations such as an analysis of its sensitivity to key input variables, are recommended.

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