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ANALYSING CONDITIONS LEADING TO HIGH NO_2 CONCENTRATIONS SIMULATED WITH THE DAUMOD-GRS MODEL IN A CONTEXT OF SCARCE MONITORING DATA

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Abstract: In this work, we analysed both input and output variables at the time of occurrence of relatively high hourly NO_2 concentrations (those exceeding 106 ppb) to study the solutions of the DAUMOD-GRS model in the Metropolitan Area of Buenos Aires during the period 2009-2012. While elevated NO_2 concentrations were observed under different atmospheric conditions, all events showed low NO_2/NOx concentration ratios. Statistical comparison with observations at an urban background site showed only a slight underestimation of the ratio, mainly due to an overestimation of NOx. To investigate the influence of chemistry on the modelled hourly NO_2 concentration, sensitivity simulations were performed varying key parameters: reaction time, fraction of NO_2 in NOx emissions (f-NO_2), and background ozone concentration ($[O_3]_r$). Although the overall model performance at the monitoring site remained relatively stable with parameter changes, the area and frequency of hourly NO_2 events were found to be sensitive to f-NO_2, while $[O_3]_r$ had a greater influence on domain-highest annual NO_2 concentrations. These results show that the correct estimation of both parameters is important for the correct assessment of NO_2 events at all relevant time scales.

Key words: *clustering analysis, model evaluation, nitrogen dioxide, sensitivity analysis, urban scale.*

INTRODUCTION

The DAUMOD-GRS model has been developed by coupling the urban atmospheric dispersion model DAUMOD (Mazzeo and Venegas, 1991) and the simplified photochemical scheme GRS (Azzi et al., 1992), in order to improve estimates of nitrogen dioxide (NO_2) concentrations in the Metropolitan Area of Buenos Aires (MABA) (Pineda Rojas and Venegas, 2013). The latest version of the DAUMOD-GRS model shows a good performance in estimating the hourly concentration of NO_2 at the three monitoring stations in the city of Buenos Aires (Pineda Rojas et al., 2022). Given the few air quality monitoring sites in the MABA, there is a need to have a good understanding of model outcomes at locations other than those of the stations.

In this paper, a clustering analysis was performed to study the occurrence conditions of relatively high NO_2 concentrations modelled in the AMBA. The role of chemistry on NO_2 hourly concentrations and events was further explored performing a sensitivity analysis to key parameters. The objective is to understand the behaviour of the model at sites other than those of the monitoring stations to improve its performance in a context of scarce air quality data.

METHODOLOGY

DAUMOD-GRS is a simple semi-empirical model that estimates NO_2 concentrations resulting from a large number of areal emission sources of nitrogen oxides (NOx) and volatile organic compounds (VOCs). As it has a relatively low computational time demand, it allows long simulations (i.e., several years) at high temporal (1 h) and spatial (1 km x 1 km) resolution. In this work, we analysed four years

(2009-2012) of simulations in the MABA, obtained from hourly meteorological information recorded at the Aeroparque station (SMN) and data from the NOx and VOCs emission inventory developed by Venegas et al. (2011). Other conditions of the simulations can be found in Pineda Rojas et al. (2022).

Clustering of NO_2 event leading conditions

For each receptor where the hourly NO_2 concentration exceeds 106 ppb (WHO guideline level, WHO, 2021), the date, time (H) and concentration (CNO_2) value were stored. A k-means algorithm was applied considering as classification variables: H, CNO_2, wind speed (WS) and direction (WD), temperature (T), sky cover (SC), surface solar radiation (TSR), NO_2 to NOx concentration ratio (ratio), etc. The number of clusters (k) was obtained by looking for a uniform distribution of objects between clusters and certain separation in the classification variables. Finally, the differences between clusters in the conditions of the events were analysed.

Sensitivity to key model input parameters

In addition, a sensitivity analysis to key parameter for the chemical module (GRS) or it coupling with the DAUMOD model [reaction time (Δt_r), fraction of NO_2 in NOx emission (f-NO_2) and regional background O_3 concentration ($[O_3]_r$)] was performed. The values of these parameters in the standard simulation (SS) are a variable Δt_r (between 0-60 min), f-NO_2 = 0.1 and $[O_3]_r$ = 20 ppb; while those in the sensitivity are included in **Table 1**.

	Parameter		
Simulation	Δt_r	f-NO_2	$[O_3]_r$
SS	variable	0.10	20 ppb
S1	60 min		
S2	variable	0.15	
S3		0.10	30 ppb
S4			40 ppb

Table 1. Values of key parameters for the chemical module [reaction time (Δt_r), fraction of NO_2 in NOx emission (f-NO_2) and regional background O_3 concentration ($[O_3]_r$)] in the standard (SS) and sensitivity (S1-S4) simulations.

The performance of DAUMOD-GRS to estimate NO_2, NOx and the NO_2/NOx concentration ratio for each simulation, was assessed comparing model results with observations at the urban background site of the city, computing the fractional bias, the normalised mean square error and the fraction of model results that are within a factor of two of observations (Chand and Hanna, 2005).

RESULTS

Hourly concentrations of NO_2 above 106 ppb

Applying the DAUMOD-GRS model in the AMBA in the period 2009-2012, 2335 events were obtained. The maximum frequency of exceedances in the study area varied between 23 (0.26% in 2010) and 37 (0.42% in 2012) events per year, while the area of exceedances varied between 51 km^2 (2009) and 301 km^2 (2012) (not shown). This inter-annual variation can only result from changes in meteorological conditions, as emissions are considered to be unchanged over the period analysed.

Analysis of conditions leading to NO_2 events

The clustering analysis over model input and output variables at the time of events, showed that three clusters are suitable to describe them. **Figure 1** presents the horizontal distribution of the dominant cluster and **Figure 2** shows the curves containing 90% of the data points in different planes of model input variables (T-H, SC-H, CNO_2-T, ratio-WS). In clusters 1 (blue) and 2 (green), the hourly NO_2 concentrations above 106 ppb occur at late evening and night hours; with cluster 1 presenting lower temperature and sky cover values and a slightly larger range of wind speed compared to those of cluster 2. On the other hand, the NO_2 events in cluster 3 (red) occur both during early morning hours with moderate

T and high SC and at night-time with high T and low SC. This cluster presents values of WS around 0.5 m s^{-1} with lower standard deviation and slightly larger NO_2 to NOx concentration ratios (**Figure 2**).

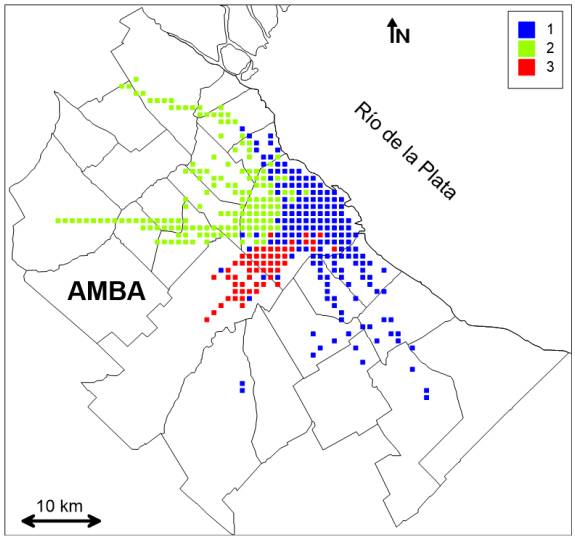

Figure 1. Dominant cluster in the MABA.

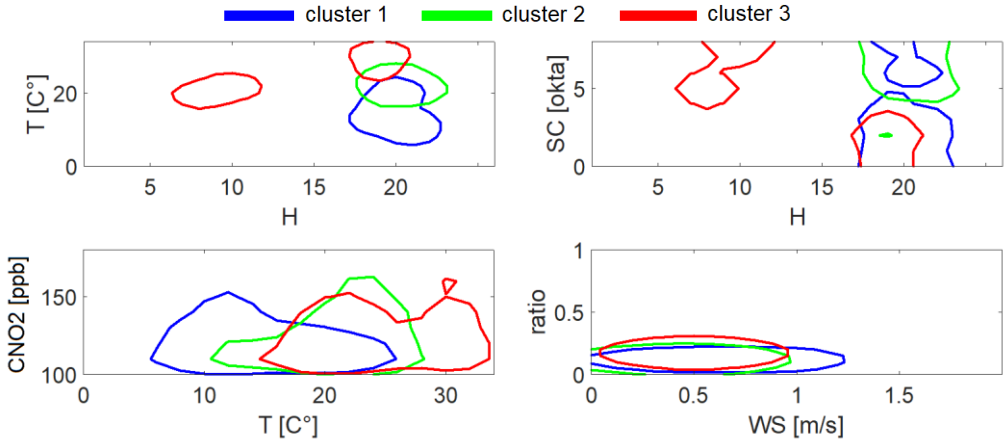

Figure 2. Curves containing 90% of objects of each cluster over different planes.

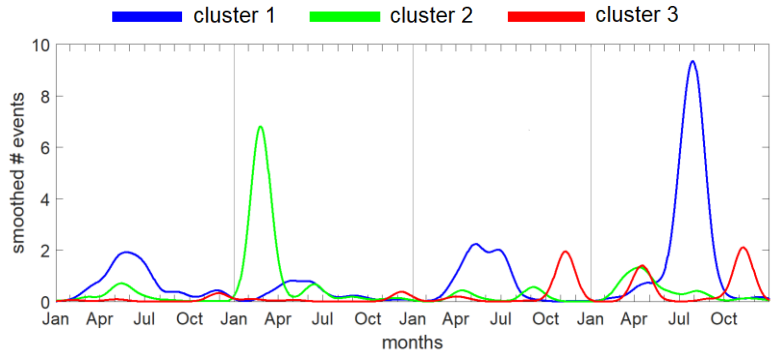

Figure 3. Temporal distribution of the number of events normalized by the total number objects in each cluster by week in the four-year period.

While conditions of the clusters were within expected ranges, the temporal distribution of the clusters (**Figure 3**) highlighted a large number of exceedances concentrated in a few hours. A detailed analysis of those cases revealed a change in the reporting of the low wind speed values from 2010 onwards. After inclusion of this change in the treatment of calm conditions, the annual highest frequency of exceedances was little changed from 23-37 to 23-36 events yr^{-1}. However, the area of exceedances was reduced considerably to 45-56 km^2.

Sensitivity to key model input parameters

The results from the previous section showed that the conditions leading to high hourly NO_2 concentrations (> 106 ppb) are variable, except for the NO_2/NOx ratio which is low (< 0.2) for all events. Analysis of the performance of DAUMOD-GRS in estimating NO_2 and NOx concentrations and the ratio at the UB site showed a slight tendency to underestimate the ratio which appears to be due to some overestimation of NOx (Pineda Rojas et al, 2023). Therefore, in this application the ratio did not provide any information on the performance of the chemistry and sensitivy simulations to key parameters were performed.

The performance metrics obtained for NO_2 under conditions of simulations S1-S4 changed very little compared to SS, except the fractional bias (FB) of S2-S4 which became slightly more negative, indicating a greater overestimation of NO_2 in these cases, although within an acceptable range (abs(FB) < 0.3). However, the relationship of modelled NO_2 with NOx concentrations for simulations S2 and S4 differed from the observed relationship mainly for high NOx concentrations, suggesting an impact of f-NO_2 and $[O_3]_r$ on NO_2 events.

Figure 4 shows the horizontal distributions of the number of NO_2 events in 2009 in simulations SS, S2 and S4. The area and the maximum frequency of exceedances were very sensitive to both parameters f-NO_2 (S2) and background O_3 (S4). The largest impact was observed with simulation S2 where the maximum frequency increased from 36 events (0.4% in SS) to 160 (1.8% in S2). The annual NO_2 concentration fields (not shown) showed similar horizontal variations in all simulations, changing the maximum value of the domain: 28.8 ppb (SS), 34.4 ppb (S2) and 43.6 ppb (S4). The largest difference was observed with S4 where the maximum concentration was 51% higher than in SS.

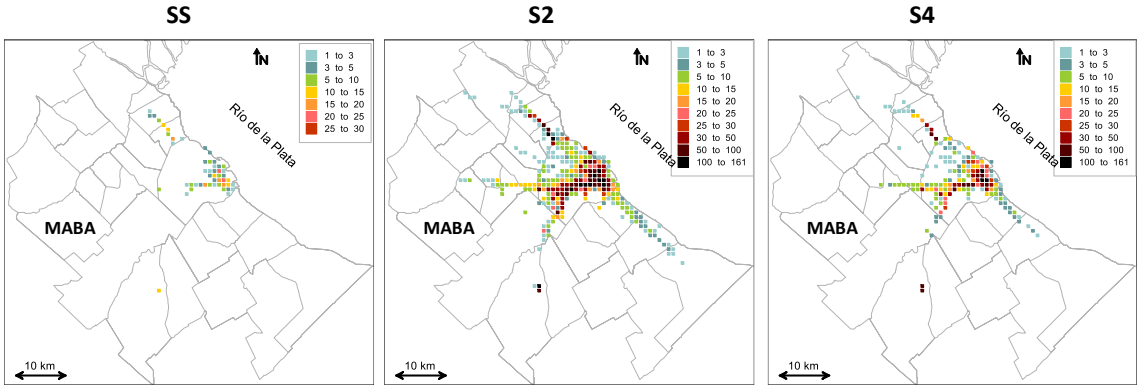

Figure 4. Number of hourly NO_2 concentrations above 106 ppb in 2009, in simulations SS, S2 and S4.

CONCLUSIONS

A clustering analysis was applied to analyse conditions where high hourly NO_2 concentrations (> 106 ppb) occur, aiming to better understand the DAUMOD-GRS model solutions in AMBA in a context of scarce monitoring. The results showed a change in the reporting of low wind speed values, which had not been included in the treatment of calm conditions. After this modification, the area of exceedances was reduced and less variable between years. On the other hand, the occurrence of high hourly NO_2 concentrations with low ratio values suggested a low role of chemistry in such events. Sensitivity simulations to key parameters for chemistry indicate a small effect of the reaction time. In contrast, the

fraction of NO_2 in NOx emissions and the O_3 available to react significantly affect NO_2 events on both hourly and annual scales. These results highlight the importance of their estimation, particularly if the model is to be used to characterise exceedances or to assess the impact of NOx abatement strategies.

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