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USING A BOX-GRS MODEL TO STUDY THE ROLE OF INPUT PARAMETERS ON ESTIMATED PEAK O_3 HOURLY CONCENTRATIONS

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Abstract: A local sensitivity analysis was performed using a box model to study the role of each parameter on the maximum ozone (O_3) concentration estimated with the Generic Reaction Set (GRS) under a wide range of conditions. Sensitivity indexes were calculated for small changes in the initial concentrations of O_3 and the precursor species: nitrogen oxides (NO_x) and reactive organic compounds (ROC). Results show that apart from the NO_x-limited region (where the system is extremely sensitive to NO_x), the dominant variable is the initial ozone concentration with sensitivity indexes increasing towards a low NO_x - high ROC regime. Regarding the reaction rate coefficients, the system is the mostly sensitive to (not small) changes in the coefficient corresponding to the pseudo reaction converting ROC to radical species under urban and suburban conditions. When moving towards rural conditions, the reactions corresponding to the removal of NO_x become more important. Results show quantitatively how the most sensitive scheme variables change under different conditions/environments.

Key words: *box-model, Generic Reaction Set, ozone, sensitivity analysis, urban air pollution.*

INTRODUCTION

The Generic Reaction Set (GRS, Azzi et al., 1992) is a simplified photochemical scheme that allows estimation of ozone (O_3) concentrations resulting from emissions nitrogen oxides (NO_x) and volatile organic compounds (VOCs) in urban areas. It represents the thousands of chemical reactions involved in the system NO_x-VOCs-$O_3$with only seven:

$$ROC + h\nu \overset{k_1}{\rightarrow} RP + ROC \quad (1)$$

$$RP + NO \overset{k_2}{\rightarrow} NO_2 \quad (2)$$

$$NO_2 + h\nu \overset{k_3}{\rightarrow} NO + O_3 \quad (3)$$

$$NO + O_3 \overset{k_4}{\rightarrow} NO_2 \quad (4)$$

$$RP + RP \overset{k_5}{\rightarrow} RP \quad (5)$$

$$RP + NO_2 \overset{k_6}{\rightarrow} SGN \quad (6)$$

$$RP + NO_2 \overset{k_7}{\rightarrow} SNGN \quad (7)$$

where ROC represents all VOCs, RP all radicals, SGN and SNGN stable gaseous and non-gaseous nitrogen products, respectively. Therefore, except for reactions (3) and (4) which are exact, the rest are pseudo-reactions. This scheme leads to a set of non-linear coupled ordinary differential equations (ODEs) in which some of the reaction rate coefficients (k_i) depend on air temperature and solar radiation while others are constants.

Due to its acceptable performance, low computational cost and less detailed input data required compared to more complex chemical schemes, the GRS has been included in the algorithms of several atmospheric dispersion models (e.g., Venkatram et al., 1994; Hurley et al., 2005; Pineda Rojas and Venegas, 2013; Malkin et al., 2016). Despite of its simplicity, the sensitivity of the modelled O_3 concentration to the scheme input parameters is hard to anticipate due to the non-linear relationship between O_3 and its precursor species, and because of the number of variables involved which affect both the reaction rate coefficients and the species initial concentrations (emissions, atmospheric transport and dispersion). Understanding the role of input parameters under different conditions is important not only to adequately select parameterizations of specific scheme variables but also to have a better grasp of the propagation of errors within the model in which the scheme is included. In this work, a local sensitivity analysis was performed using a box-GRS model to study the role of each parameter on the maximum ozone concentration achieved under different conditions.

METHODOLOGY

A box model was built including the GRS reactions (1) to (7) with the reaction rate coefficients k_1 proposed for by Venkatram et al. (1994) and k_2-k_7 by Hurley et al. (2005). The set of non-linear coupled ODEs was numerically integrated applying the MATLAB subroutine ODE15s. A large number of one-day simulations (with a time step of 0.01 h) were performed, saving in each run the maximum concentration of ozone reached ($[O_3]_{max}$). Reaction coefficients depending on the temperature and the solar radiation (k_1-k_4) were evaluated considering mean hourly profiles of these variables typical of mid latitudes. Isopleth diagrams were built for combinations of $[NO_x]_0$ varying between 5 and 500 ppb and $[ROC]_0$ between 5 and 1000 ppb, by steps of 5 ppb. The initial NO/NO_x ratio was set to 0.9 and the initial O_3 concentration to 20 ppb. A total of 20,000 simulations were performed. The sensitivity index (SI_S) for each species S (NO_x, ROC and O_3) was assessed computing the average of the differences between the value of $[O_3]_{max}$ obtained for an initial concentration $[S]_0$ and that estimated for $[S]_0 \pm 1$ ppb, keeping constant initial the concentrations of the other two reactants (Turányi, 1990). This was performed for each point ($[ROC]_0$, $[NO_x]_0$) in the isopleths diagram space.

On the other hand, the sensitivity of $[O_3]_{max}$ to the reaction rate coefficients (k_i) was performed considering three scenarios of precursor species initial concentrations that can be considered representative of different environments: urban (UR) with $[ROC]_0 = 200$ ppb, $[NO_x]_0 = 300$ ppb, $NO/NO_x = 0.9$, $[O_3]_0 = 10$ ppb; suburban (SU) with $[ROC]_0 = 300$ ppb, $[NO_x]_0 = 100$ ppb, $NO/NO_x = 0.8$, $[O_3]_0 = 20$ ppb; and rural (RU) with $[ROC]_0 = 500$ ppb, $[NO_x]_0 = 5$ ppb, $NO/NO_x = 0.5$, $[O_3]_0 = 30$ ppb. 234 one-day simulations were run with box-GRS model, considering the standard reaction coefficients k_1-k_7 (base case), and each value of k_i multiplied by different factors varying between 10^{-2} and 10^2, keeping constant the other ones. In this case, the sensitivity of $[O_3]_{max}$ to a given change in k_i was evaluated as the ratio of its value obtained for each simulation over that of the base case.

RESULTS

Figure 1 shows the isopleth diagrams obtained considering an initial NO/NO_x ratio of 0.9 and initial O_3 concentrations of 20 ppb. $[O_3]_{max}$ increases towards the high ROC - low NO_x region of the isopleths diagram, as found in the literature for more complex chemical schemes. According to Tonnesen and Jeffries (1994), the GRS produces more pronounced slopes at the low ROC - high NO_x part of the diagram (compared with the CB4 scheme), implying a lower sensitivity to NO_x at this region. On the other hand, when comparing the isopleth diagram with that obtained for $[O_3]_0 = 40$ ppb (not shown), it is observed that an increase in initial ozone concentration leads to an increase in $[O_3]_{max}$, as expected.

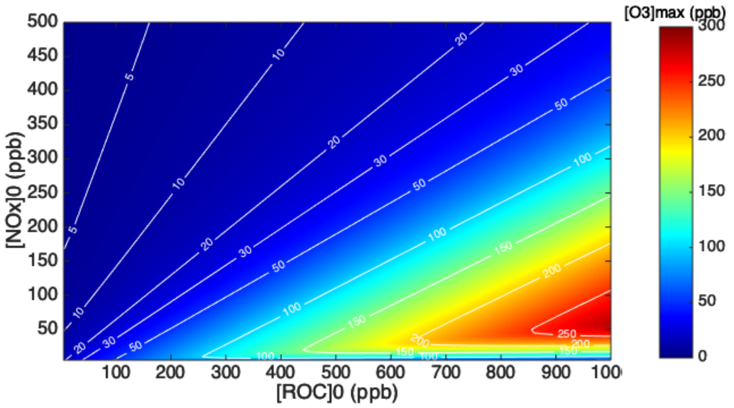

Figure 1. Isopleth diagram obtained for an initial NO/NO_x ratio of 0.9 and $[O_3]_0 = 20$ ppb.

As shown in **Figure 2**, the time of occurrence of $[O_3]_{max}$ during each one-day simulation increases from midday hours at low ROC/NO_x ratios to late evening hours at high ROC/NO_x ratios, showing that t_{max} increases with $[O_3]_{max}$. At the extreme down-right part of the diagram (i.e., large ROC/NO_x ratios), $[O_3]_{max}$ can occur at early morning hours due to the fast and complete elimination of NO_x from the system [reactions (6) and (7)], producing a constant value for O_3 due to the absence of other removal paths.

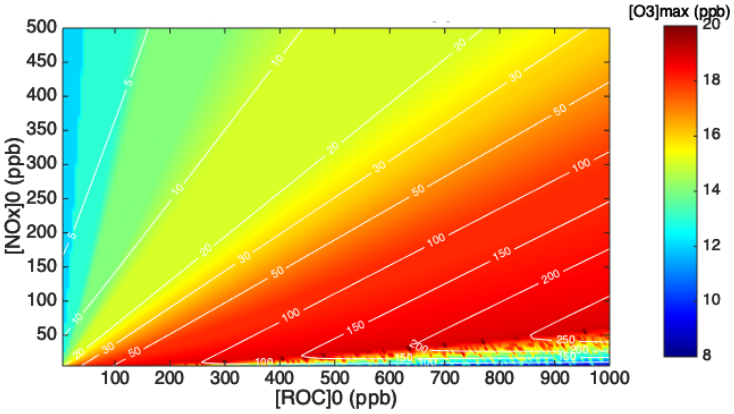

Figure 2. Time of occurrence of $[O_3]_{max}$ (t_{O3max}) superposed to the isopleth diagram shown in Figure 1.

In the isopleth diagram space, the sensitivity indexes (SI_S) obtained for ROC and NO_x reach minimum values lower than 0.01 and maximum values of 0.35 and 11.99, respectively; while that obtained for O_3 is in the range 0.05 - 0.96. Excluding the NO_x-limited region (yellow region in **Figure 3b**), the SI values of the three species increase towards the high ROC/NO_x ratio part of the diagram with the SI_{O3} values being greater than those obtained for ROC and NO_x. The highest SI_{O3} values (>0.9) are found for $[NO_x]_0 < 50$ ppb and $[ROC]_0$ between 25-250 ppb (see **Figure 3.c**) where the modelled peak O_3 concentrations vary between 30-90 ppb. In order to understand the impact of these sensitivity indexes, **Figure 4** shows the average change in $[O_3]_{max}$ caused by a ± 30% change in $[O_3]_0$ relative to the $[O_3]_{max}$. It is observed that the largest changes are found at the low ROC - low NO_x region. Under those conditions, a change of 30% in $[O_3]_0$ leads to changes in $[O_3]_{max}$ up to 25-30%. The relative impact of such change decreases towards the highest ROC/NO_x ratios where the largest peak ozone concentration values are obtained (see **Figure 1**), and it is lower (< 2%) in the NO_x-limited region of the isopleths diagram.

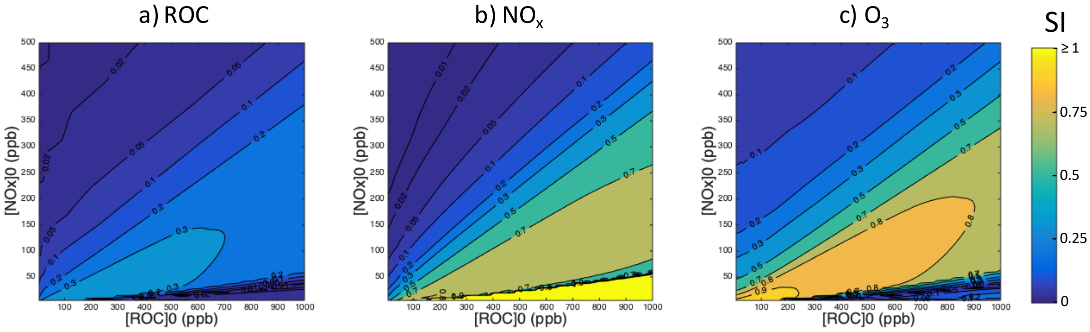

Figure 3. a) ROC, b) NO_x and c) O_3 sensitivity indexes obtained for $NO/NO_x = 0.9$ and $[O_3]_0 = 20$ ppb.

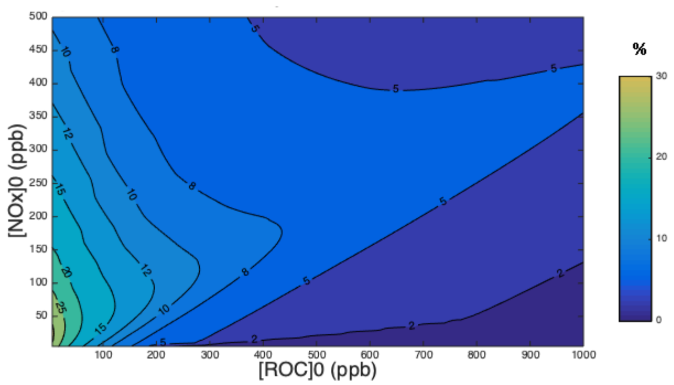

Figure 4. Percentage change in $[O_3]_{max}$ due to a 30% change in $[O_3]_0$, relative to $[O_3]_{max}$.

Figure 5 shows the values of $[O_3]_{max}$ normalized by its base case (BC) value, obtained when each reaction constant k_i is changed keeping constant the other ones, under initial concentration conditions of urban (UR), suburban (SU) and rural (RU) scenarios. Under scenarios UR and SU, $[O_3]_{max}$ is mostly sensitive to k_1, followed by k_3 and k_4. The observed variations are expected since reaction (1) represents the source of radicals (RP), reaction (3) is responsible for the ozone formation and reaction (4) for its sink. The system is less sensitive to other reaction coefficients, while it is completely non-sensitive to k_5 (the removal of RP via its auto-reaction). Under conditions of scenario RU, $[O_3]_{max}$ is less sensitive to changes in all reaction coefficients and k_1 becomes relatively less important. The lesser amount of NO_x (compared to other scenarios) puts the system in the NO_x-limited region, where a small change in k_2 can affect the conversion of NO to NO_2 via RP, and then the $[O_3]_{max}$ produced. Something similar is observed with k_6 and k_7, which are responsible for the removal of NO_2 from the system via RP (reducing the values of k_6 or k_7 allows the system to produce more O_3). Hence, these coefficients may be important under conditions of high ROC (where the amount of generated RP is high enough to remove NO_2 from the O_3 cycle) and explains why $[O_3]_{max}$ increases with k_1 up to a given factor (25, 10 and 0.5 for scenarios UR, SU and RU, respectively) and then decreases.

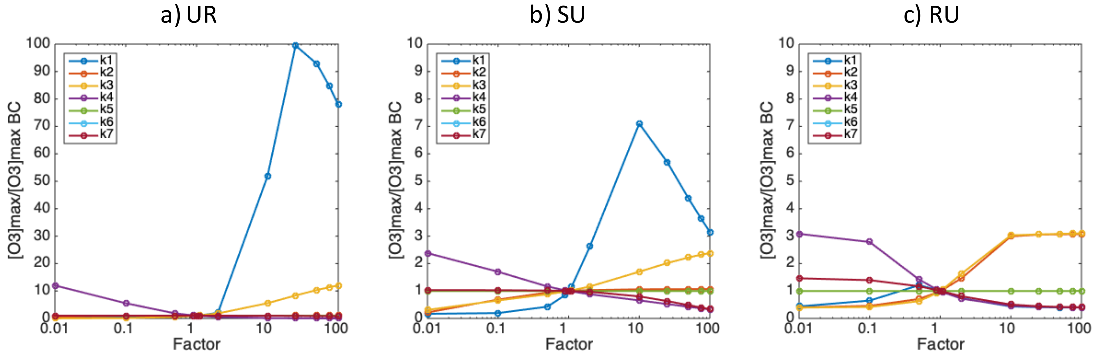

Figure 5. Sensitivity of $[O_3]_{max}$ (normalised by its BC value) obtained with the box-GRS model to variations in the GRS reaction rate constants k_1-k_7 under conditions of scenarios: a) urban (UR), b) suburban (SU) and c) rural (RU).

CONCLUSIONS

A local sensitivity analysis of a box-GRS model was performed in order to quantitatively assess the effect of initial concentrations and reactions coefficients on the maximum ozone concentration ($[O_3]_{max}$). Results show that outside the NO_x-limited region, the modelled peak ozone concentration is more sensitive to its initial concentration value, followed by NO_x and then ROC. The sensitivity indexes of the three species increase with increasing ROC/NO_x ratios (i.e., towards more rural conditions). Regarding the relevance of the reaction coefficients, $[O_3]_{max}$ is more sensitive to k_1, the reaction governing the initial production of radicals. The next relevant reaction rates correspond to k_3 and k_4, which are the only two real constants, representing the NO-NO_2 cycling. Their effects are higher at urban and suburban conditions. When moving towards more rural conditions (higher ROC/NO_x ratios), the relevance of k_1 is reduced and k_2, k_6 and k_7 become more important. These results show quantitatively that, despite of the simplicity of the GRS, the sensitivity of $[O_3]_{max}$ to the scheme input parameters can vary considerably with the precursor species initial concentration.

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