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

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## Introduction

The Generic Reaction Set (GRS) [1] 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. 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 [2-5]. Despite of its simplicity, the sensitivity of the modelled $O_3$ concentration to the scheme input parameters is hard to anticipate because of the number of variables affecting both the reaction rate coefficients and the species initial concentrations, and the non-linear relationship between them. Sensitivity studies can help to identify the variables that can be improved to obtain better model results and 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-GRS model was built including the reaction rate coefficients summarized in the Table below. 60,903 one-day simulations (time step = 0.01 h) were performed, saving in each run the maximum concentration of ozone reached ($[O_3]_{max}$). Reaction coefficients ($k_i$) depending on the temperature (T) and the solar radiation (TSR) 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 5-500 ppb and $[ROC]_0$ between 5-1000 ppb, by steps of 5 ppb, an initial $O_3$ concentration of 20 ppb and a $NO/NO_x$ ratio of 0.9.

### GRS reaction set

$$ROC + h\upsilon \xrightarrow{k_1} RP + ROC$$
$$RP + NO \xrightarrow{k_2} NO_2$$
$$NO_2 + h\upsilon \xrightarrow{k_3} NO + O_3$$
$$NO + O_3 \xrightarrow{k_4} NO_2$$
$$RP + RP \xrightarrow{k_5} RP$$
$$RP + NO_2 \xrightarrow{k_6} SGN$$
$$RP + NO_2 \xrightarrow{k_7} SNGN$$

-ROC represents all VOCs
- RP all radicals
- SGN and SNGN stable gaseous and non-gaseous nitrogen products, respectively

| Coefficient | Expression | Source |
|---|---|---|
| $k_1$ ($min^{-1}$) | $k_3 \times 10^4 \times e^{-4700\left(\frac{1}{T}\right)}$ | [2] |
| $k_2$ ($ppm^{-1}\ min^{-1}$) | $\frac{3.58\times10^6}{T}$ | [3] |
| $k_3$ ($min^{-1}$) | $10^{-4}\times\delta\times TSR$<br>$\delta = \begin{cases} 4.23 + \frac{1.09}{\cos Z} & 0 \le Z \le 47 \\ 5.82 & 47 \le Z \le 64 \\ -0.997 + 12\times(1-\cos Z) & 64 \le Z \le 90 \end{cases}$<br>$Z$ : zenith angle in degrees<br>$TSR$ : solar radiation in $Wm^{-2}$ | [3] |
| $k_4$ ($ppm^{-1}\ min^{-1}$) | $\frac{9.24\times10^5}{T} e^{\left(-\frac{1450}{T}\right)}$ | [3] |
| $k_5$ ($ppm^{-1}\ min^{-1}$) | $10^4$ | [3] |
| $k_6$ ($ppm^{-1}\ min^{-1}$) | $1.2 \times 10^2$ | [3] |
| $k_7$ ($ppm^{-1}\ min^{-1}$) | $1.2 \times 10^2$ | [3] |

- Sensitivity indexes ($SI_S$) for each species S ($NO_x$, ROC and $O_3$) were computed as [6]: $SI_S = \left|\overline{\Delta[O_3]_{max}}/\Delta[S]_0\right|$

  where $\Delta[S]_0$ = 1 ppb and the overbar indicates the average of $\Delta[O_3]_{max}$ over both an increase and a decrease of 1 ppb in $[S]_0$.

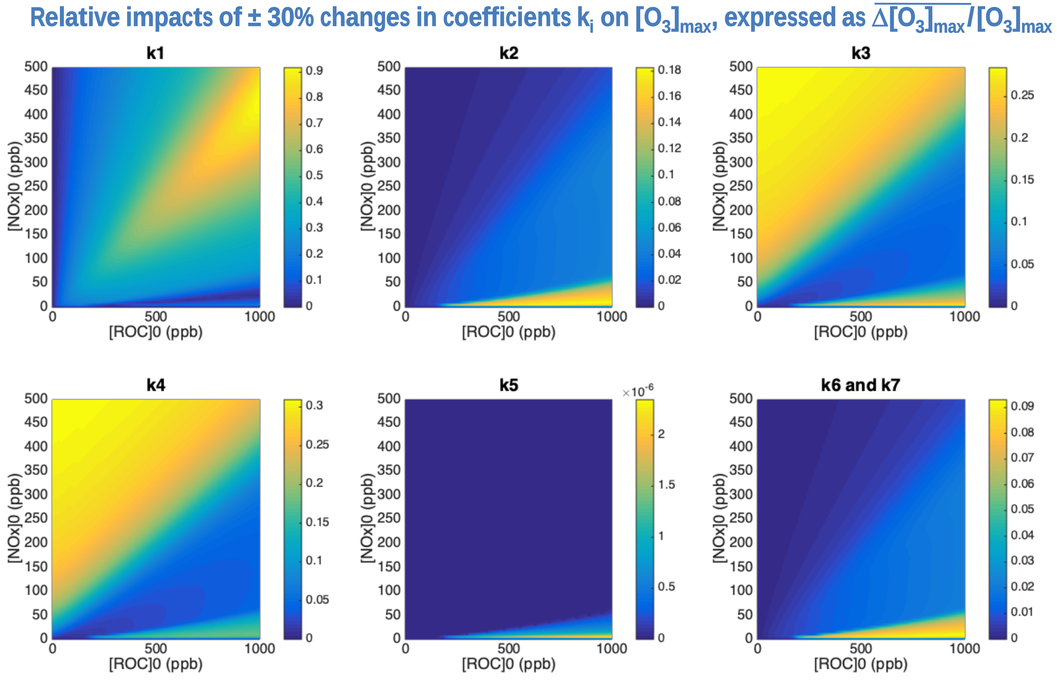
- Sensitivity of $[O_3]_{max}$ to each reaction rate coefficient was performed considering ±30% changes in $k_i$ for each point ($[ROC]_0$, $[NO_x]_0$) in the isopleths diagram space.

- In addition, the impact of not small changes in $k_i$ (factors varying between $10^{-2}$ and $10^2$) was assessed in order to consider the potential effect of using different parameterisations of the reaction rate coefficients, for three scenarios of initial concentration condition:

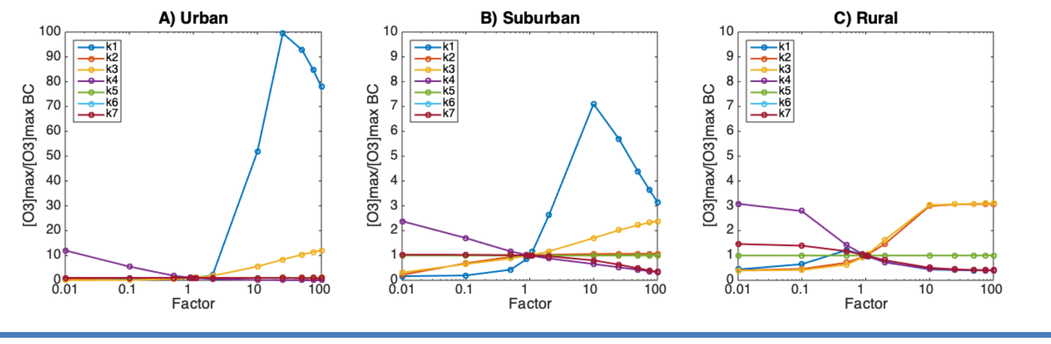
| Species | Scenario | | |
|---|---|---|---|
| | A | B | C |
| $[ROC]_0$ | 200 | 300 | 500 |
| $[NO_x]_0$ | 300 | 100 | 5 |
| $NO/NO_x$ | 0.9 | 0.8 | 0.5 |
| $[O_3]_0$ | 10 | 20 | 30 |

## Sensitivity to Reaction Coefficients

### Relative impacts of ± 30% changes in coefficients $k_i$ on $[O_3]_{max}$, expressed as $\overline{\Delta[O_3]_{max}}/[O_3]_{max}$

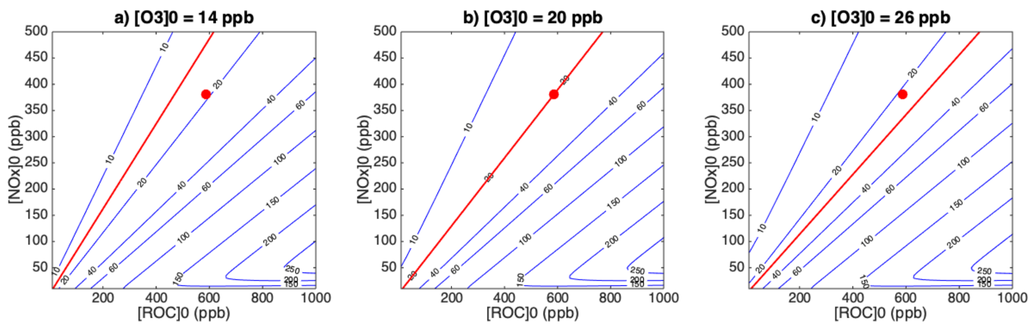



### Change in $[O_3]_{max}$ [expressed as its value normalised by that obtained for the base case (BC)] due to a given change factor in coefficient $k_i$, under conditions of scenarios A, B and C




## Results

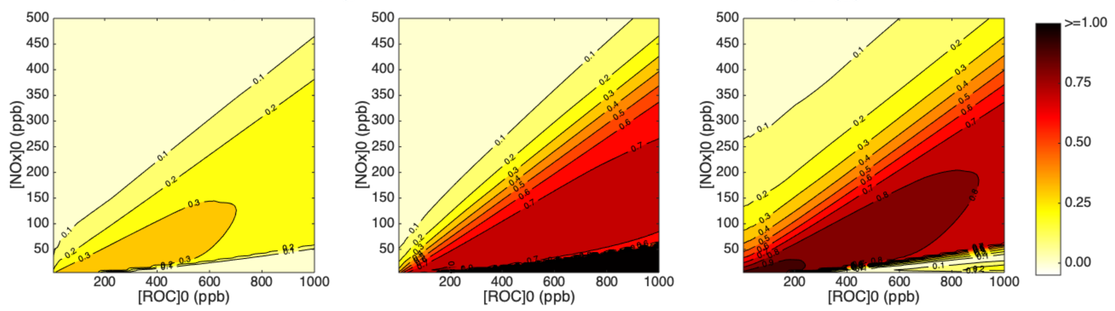
### Isopleth diagrams obtained an initial $NO/NO_x$ ratio of 0.9 and three values of $[O_3]_0$



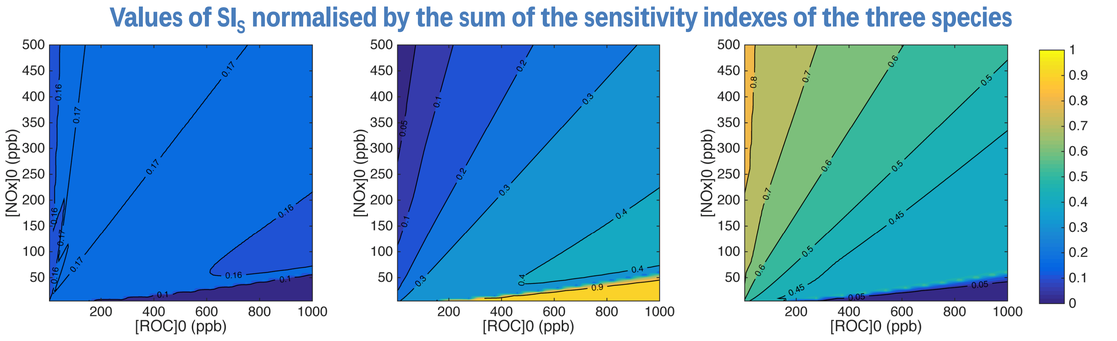

### Sensitivity to Initial Concentrations

ROC | $NO_x$ | $O_3$

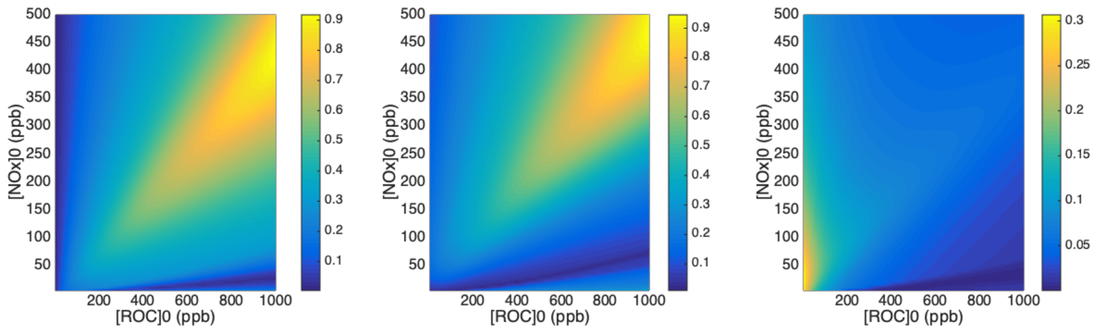
### Sensitivity index ($SI_S$) obtained for each species S considering $[O_3]_0$ = 20 ppb



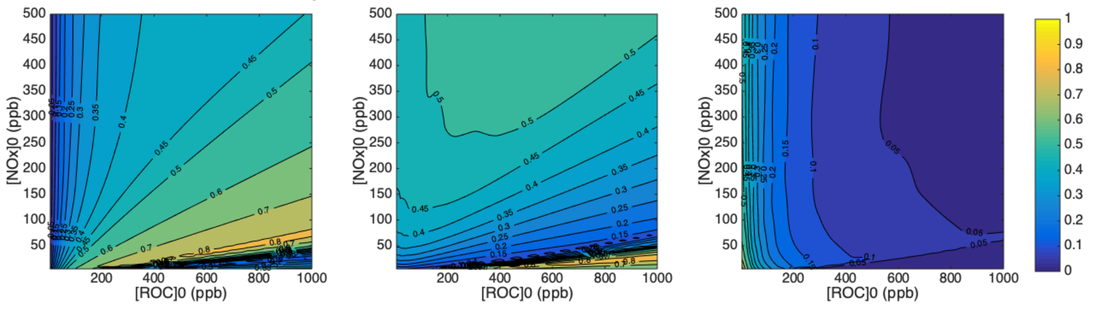

### Values of $SI_S$ normalised by the sum of the sensitivity indexes of the three species




### Relative impact ($RI_S$) of ± 30% changes in $[S]_0$ on $[O_3]_{max}$ expressed as $\overline{\Delta[O_3]_{max}}/[O_3]_{max}$




### Values of $RI_S$ normalised by the sum of the values of the three species




## Conclusions

- The 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 concentrations.
- Outside the $NO_x$-limited region, $[O_3]_{max}$ is more sensitive to its initial concentration value, followed by $NO_x$ and then ROC, with SI values increasing towards high $ROC/NO_x$ ratios.
- The relative impacts of the species initial concentrations on $[O_3]_{max}$ change considerably in the isopleth diagram space, and suggest that for low values of $[ROC]_0$ the parameterisation of its emission could contribute to determine the sensitivity conditions.
- Small changes in the reaction coefficients ($k_i$) may cause an impact on $[O_3]_{max}$ depending on the initial concentration conditions, as expected. In general, the scheme is more sensitive to $k_1$, the reaction governing the initial production of radicals. Under low $ROC/NO_x$ ratios (urban conditions), the system is more sensitive to $k_3$ and $k_4$.

## References

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