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Atmospheric Environment

Sensitivity of atmospheric models to rate terms within complex chemical mechanisms

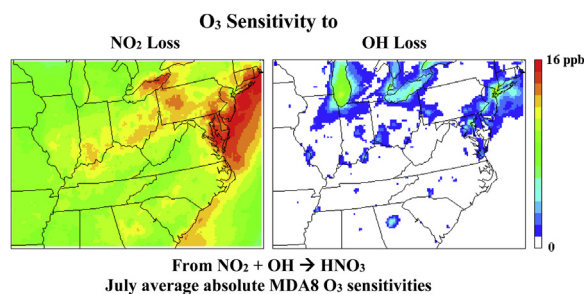Alan M. Dunker [a, *], Bonyoung Koo [b], Greg Yarwood [b]

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HIGHLIGHTS

- The decoupled direct method was extended to chemical production and loss terms.
- Oxidation of reactive VOC's and other processes in Carbon Bond 2005 were studied.
- Isoprene strongly influences O_3 formation in both urban and rural areas.
- NO_2 loss from $OH + NO_2 \rightarrow HNO_3$ is more important than OH loss for O_3 in the eastern U.S.

GRAPHICAL ABSTRACT

O_3 Sensitivity to
NO_2 Loss   OH Loss

From $NO_2 + OH \rightarrow HNO_3$
July average absolute MDA8 O_3 sensitivities

ARTICLE INFO

ABSTRACT

The decoupled direct method for sensitivity analysis was extended to the rate terms for the loss of reactants and formation of products to provide a detailed understanding of the predictions of chemical mechanisms used in atmospheric models. A box-model version and the full three-dimensional (3-D) version of the Comprehensive Air Quality Model with Extensions were used to calculate sensitivities to rate terms in the Carbon Bond 2005 chemical mechanism. The processes studied were formation of products from oxidation of the more reactive organic compounds, removal of NO_x by organic nitrate formation, re-formation of NO_x from organic nitrates, and loss of OH and NO_2 and formation of HNO_3 in the reaction $OH + NO_2 \rightarrow HNO_3$. Simulations of the box model for four scenarios representing urban and rural atmospheres indicated that the largest sensitivities of ozone, formaldehyde and HO_x were to rate terms for certain products of the oxidation of isoprene and to the reactants in $OH + NO_2 \rightarrow HNO_3$. The 3-D model was then applied to calculate sensitivities to these rate terms for an eastern U.S. ozone episode in July, 2008. The 3-D simulation results were better correlated with the more NO_x-limited rural scenario of the box model and showed that the isoprene oxidation products with the greatest impact on O_3 formation are methacrolein, methyl vinyl ketone, HO_2 radical, and species converting NO to NO_2 and organic nitrates. The 3-D results also showed that loss of NO_2 was more important than loss of OH for O_3 formation in most areas of the eastern U.S. This work emphasizes the need for continued experimental work to understand the oxidation of isoprene because the isoprene chemistry influenced modeled ozone predictions for both urban as well as rural areas.

1. Introduction

Photochemical grid models (PGM's) are used to develop emission control strategies for O_3 and particulate matter (PM) in State

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Implementation Plans, to evaluate the impact of proposed federal rules, and to assess the long-range transport of pollutants. A key component of such models is the gas-phase chemical mechanism. Despite several decades of work, there are still important uncertainties in the chemistry, due in part to the large number of volatile organic compounds (VOC's) in emissions and the difficulty of replicating atmospheric conditions in the laboratory. The complexity of atmospheric chemistry and uncertainties in our knowledge are apparent from several recent reviews (Calvert et al., 2008, 2011).

Two methods for understanding and investigating the predictions of chemical mechanisms are Process Analysis (PA) and the decoupled direct method (DDM) for sensitivity analysis. PA gathers information about the chemistry and other processes during a model simulation and makes the data available for post-analysis (Jeffries and Tonnesen, 1994). In a particular form of PA called Chemical Process Analysis (CPA), the post-analysis is moved inside the model for convenience (ENVIRON, 2013). CPA combines integrated reaction rates saved from gas-phase chemistry calculations to quantify chemical processes (e.g., oxidant production and destruction, radical production and destruction) in each grid cell. PA can be used to investigate sources of secondary pollutants such as formaldehyde (Luecken et al., 2012). An advantage of PA is that custom implementations have been developed that focus on chemically meaningful concepts, but a disadvantage is that these implementations are difficult to automate and instead have been re-coded by hand for each new mechanism or update. Another limitation of PA is that chemical species move through the PGM grid whereas the PA results are anchored to grid cells creating a spatial disconnect. PA results are often aggregated over grid cells that contain urban areas or plumes (Henderson et al., 2011) to counter the spatial disconnect between PA results and concentrations.

DDM is a mathematical method for computing sensitivity of model outputs, e.g., concentrations, to perturbations in model inputs, e.g., emission rates, initial and boundary concentrations, and reaction rate constants (Dunker, 1984). Milford et al. (1992) used rate constant sensitivity to compare mechanisms, and recently Cohan et al. (2010) used DDM to assess whether uncertain rate constants influence sensitivity of O_3 to NO_x and VOC emissions. Because DDM maintains spatial coherence between sensitivities and concentrations, its results are not subject to the spatial disconnect limitation of PA. Also, the DDM implementations are accurate, efficient, and easily automated such that changes to the chemistry do not require changes to the code. However, the current implementations in PGM's are less useful than PA for mechanism evaluation.

In this work, we extend DDM in a PGM to calculate sensitivities to chemical rate terms for the production or loss of species. For example, O_3 predictions have generally been found to be very sensitive to the rate constant for the reaction $OH + NO_2 \rightarrow HNO_3$. This reaction contributes rate terms for the loss of OH, loss of NO_2 and production of HNO_3 to the differential equations describing the time evolution of these species. By calculating sensitivities to these rate terms, we can go beyond the sensitivity to the rate constant and determine whether loss of OH or loss of NO_2 by this reaction is more important. Further, by aggregating sensitivities to rate terms for production of the same species (e.g., formaldehyde) by multiple reactions, we can evaluate the relative importance of different products to O_3 formation. Incorporating the sensitivity to rate terms into PGM's may be viewed as improving the DDM implementation to provide information more comparable to CPA.

The next section defines the sensitivities to rate terms and how these sensitivities are related to the sensitivity to the rate constant for the reaction. We investigated the oxidation of VOC's in the Carbon Bond 2005 (CB05) chemical mechanism (Yarwood et al.,

2005) and certain other features of this mechanism and describe which first-order sensitivities were calculated. Lastly, this section gives the inputs to the box-model and three-dimensional (3-D) versions of the Comprehensive Air Quality Model with Extensions (CAMx; ENVIRON, 2013) used to calculate sensitivities. The following section presents a summary of results from the box model, which was used to screen a large number of sensitivities for the relative importance of VOC's and their oxidation products. Then given are detailed results from the 3-D model for the isoprene oxidation chemistry and the $OH + NO_2$ reaction. The final section discusses the implications of the work and recommendations.

2. Methods

2.1. Definition of sensitivities to rate terms

If c_i is the concentration of a species in the model and λ is some parameter in the model, the sensitivity of c_i to λ is $S_{i,\lambda} = \partial c_i / \partial \lambda$. In a Taylor series, this sensitivity provides a first-order or linear representation of the dependence of c_i on λ. Using the reaction $OH + NO_2 \rightarrow HNO_3$ as an example, the net reaction rate terms are:

$$R_{OH} = -\alpha \, \lambda \, k \, c_{OH} c_{NO_2} + \text{terms from other reactions} \tag{1}$$

$$R_{NO_2} = -\beta \, \lambda \, k \, c_{OH} \, c_{NO_2} + \text{terms from other reactions} \tag{2}$$

$$R_{HNO_3} = +\gamma \, \lambda \, k \, c_{OH} \, c_{NO_2} + \text{terms from other reactions} \tag{3}$$

The parameters α, β, and γ scale the rate terms from the reaction and λ scales the rate constant. With these definitions, the following relationship holds (see Supplementary information (SI)):

$$S_{i,\lambda}\big|_{\alpha=\beta=\gamma=\lambda=1} = \left(S_{i,\alpha} + S_{i,\beta} + S_{i,\gamma}\right)\big|_{\alpha=\beta=\gamma=\lambda=1} \tag{4}$$

Thus, the sensitivity to the rate constant can be subdivided into the sensitivities to the rate terms for the reactants and product (if all parameters are at their nominal value of 1). Previous studies of the sensitivity to the chemistry have focused on the left-hand side of eq. (4), the sensitivity to the rate constant. Our focus, and the new feature of this work, is the sensitivities on the right-hand side. These sensitivities allow one to determine which feature of the reaction, e.g., loss of OH vs. loss of NO_2, is more important.

The oxidation mechanism for an individual VOC may have multiple reactions that produce the same product. To determine the sensitivity of c_i to the formation of the product, the rate terms in the different reactions can be scaled by a common parameter α. This sensitivity to α is simply the sum of the sensitivities to the rate terms in the individual reactions:

$$S_{i,\alpha}\big|_{\alpha=\alpha_j=1} = \left(S_{i,\alpha_1} + S_{i,\alpha_2} + \cdots S_{i,\alpha_m}\right)\big|_{\alpha=\alpha_j=1} \tag{5}$$

with $\alpha_j\,(j = 1, \ldots, m)$ being a parameter scaling the rate term for the product in one of the m reactions.

Using the DDM, CAMx was modified to calculate the sensitivity to rate terms from multiple reactions, as in eq. (5). The implementation of the DDM was checked by comparison to the brute-force method using $\pm 10\%$ changes in the scaling parameters (see SI). With our definition, the sensitivity has units of concentration (parts per billion or ppb).

2.2. Sensitivities calculated

We calculated sensitivities to rate terms for various processes in the CB05 mechanism: Formation of products in the oxidation of the