

Impact of inert organic nitrate formation on ground-level ozone in a regional air quality model using the Carbon Bond Mechanism 4

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Abstract. A regional air quality model is used to assess the impact of inert organic nitrate formation on ground-level ozone in the eastern United States during summer. The chemical mechanism used is the Carbon Bond Mechanism 4 (CBM4), which is widely used by regulatory agencies in the United States in air quality modeling applications. Recently, modifications were made to the reaction mechanism involving the organic peroxy radicals which form inert organic nitrates without a critical scientific review of the effects of these changes. In this study, we demonstrate for the first time that the simulated large-scale distribution of ground-level ozone is extremely sensitive to these mechanism changes. Inclusion of radical-radical reactions involving the organic peroxy radicals suppresses inert organic nitrate formation, and leads to significant increases in nitrogen oxide levels over large parts of the model domain. As a consequence of increased rates of ozone photochemical production, ozone mixing ratios are enhanced by as much 10-25 ppbv when these additional radical termination pathways are considered in the model.

Introduction

The United States Environmental Protection Agency (USEPA) has recently proposed sweeping changes in the National Ambient Air Quality Standards (NAAQS) for ground-level ozone (O_3) [USEPA, 1997]. These changes are motivated primarily by concerns that the existing NAAQS for O_3 does not provide adequate protection for human health. The proposed change reflects a shift from a 1-hour standard to a longer-term standard based on an 8-hour average. From a regulatory perspective, it is projected that this change will cause designated non-attainment U.S. counties to approximately triple in number (Wolff, 1996). Furthermore, the problem of non-attainment will change from one which is primarily urban and suburban in character, to one which affects large parts of the rural eastern United States as well (Chameides et al., 1997).

In recent years, it has become increasingly apparent that regional processes such as long-range transport of O_3 and its precursors may play a significant role in urban non-attainment (e.g., Seinfeld et al., 1992). Moreover, the need to develop a regional picture of the O_3 distribution will likely be enhanced under the proposed new NAAQS since the problem of non-attainment itself will be more regional in character (Chameides et al., 1997). In this context, regional emissions-based air quality modeling will be an important component of the regulatory process for assessing regional effects and managing O_3 pollution. Clearly, the effective use of air quality models (AQMs) for this purpose will require a

through evaluation of model performance not only for urban and suburban conditions but for rural conditions as well. It will also be important to understand the sensitivity of model results to the algorithms used to represent various physical and chemical processes in the model.

In this paper, we focus on a model sensitivity study with reference to a particular chemical mechanism, namely the Carbon Bond Mechanism 4 (CBM4), which is widely used by regulatory agencies in the United States in urban and regional air quality modeling applications. Most recently, CBM4 has been used in regional air quality modeling studies conducted by the Ozone Transport and Assessment Group (OTAG) to develop strategies for controlling ground-level O₃ pollution in the eastern United States (LeClair, 1997). CBM4 is a condensed chemical mechanism derived from a more extensive and explicit mechanism using a structural lumping approach (Gery et al., 1989). Our study specifically focuses on the treatment of organic peroxy radical chemistry in CBM4 as currently being implemented in regulatory air quality modeling applications.

In CBM4, two universal peroxy radical operators, XO2 and XO2N, are used as surrogates for organic peroxy radicals that are produced by the oxidation of anthropogenic and biogenic hydrocarbons (for details see discussion by Gery et al. [1989]). Each XO2 oxidizes one nitric oxide (NO) molecule to nitrogen dioxide (NO₂), and in addition can react with another XO2 radical to form unreactive products. A widely used modification to the Gery et al. (1989) mechanism includes a reaction between HO₂ and XO2 radicals (Dodge, 1989). In contrast, XO2N only reacts with NO to form unreactive organic nitrates. Under certain conditions the XO2N+NO reaction can be the dominant photochemical sink for nitrogen oxides (NO_x=NO+NO₂). Since there are no radical termination pathways for XO2N other than reaction with NO, the photochemical loss rate of NO_x will then be determined by the rate of XO2N production. In regions characterized by relatively high hydrocarbon and low NO_x emissions, XO2N can strongly suppress O₃ photochemical production by rapidly converting NO_x to inert organic nitrates.

In 1994, modifications to the original XO2N reaction scheme were implemented in the Urban Airshed Model (which is one of USEPA's recommended AQMs for regulatory applications). Specifically, the rate coefficient for the XO2N + NO reaction was increased by a factor of 12 and three additional radical termination reactions for XO2N (XO2N+HO₂, XO2N+XO2, XO2N+XO2N) were included in the Urban Airshed Model as part of CBM version 4.2 (G. Yarwood, private communication, 1997). These changes were based on the premise that both XO2 and XO2N represent organic peroxy radicals in CBM4, and only differ in the products they form upon reaction with NO. On this basis it was argued that both XO2 and XO2N should undergo similar radical termination reactions, and the XO2N reaction scheme was therefore modified to achieve consistency with the XO2 reaction scheme in CBM4.

The motivation for our study stems from the fact that the large-scale regional impact of these modifications on model results has not been thoroughly assessed. In this study, we examine the effect of the above-mentioned changes on the simulated regional-scale distribution and budget of O₃. We will show that changes in the XO2N reaction scheme can have an extremely large impact on the ground-level ozone distribution simulated by a regional AQM and identify the reasons for this impact. We emphasize that we

are not proposing new modifications to the XO₂N reaction scheme. On the contrary, our goal is to examine the impact of actual changes that have already been implemented in CBM4 by the developers of the Urban Airshed Model. Our study is significant because these modifications are already being used in regulatory air quality modeling applications without a critical review of the full scope of these changes by the larger scientific community.

Description of the Regional Air Quality Model Simulations

The AQM used in this study is the nonhydrostatic version of the three-dimensional Multiscale Air Quality SIMulation Platform (MAQSIP), developed at MCNC/Environmental Programs in a co-operative agreement with the USEPA (Odman and Ingram, 1996). In the present application, the model is used to simulate the distribution of O₃ and related species over the eastern United States (see Figure 1 for the horizontal extent of the model domain) during July 7-16, 1995, using a horizontal resolution of 54 km and 22 sigma layers in the vertical extending up to 100 mb. The AQM is driven using meteorological fields derived from the Mesoscale Meteorological Model 5 (MM5) [Grell et al., 1995]. From an operational perspective, the MM5 model is exercised in a four-dimensional data assimilation (FDDA) mode, using analysis nudging with re-initialization every 5 days.

Temporally and spatially-varying emissions of carbon monoxide, volatile organic compounds and NO_x are specified in the AQM. The anthropogenic emission inventory is the Ozone Transport Assessment (OTAG) inventory for 1995, which in turn was grown from the recently-developed national inventory for 1990 (Houyoux et al., 1996). Biogenic emissions are calculated using the USEPA Biogenic Emission Inventory System 2 (BEIS2) [Geron et al., 1994].

In order to examine the effect of changes in the XO₂N reaction scheme on the simulated regional-scale distribution and budget of O₃, two model simulations were performed. The first simulation was initialized at 0700 EST on July 7, 1995 and was run for a period of 10 days. The chemical mechanism used in this simulation is from Gery et al. (1989), modified to include updated kinetic data for the CO + OH reaction (DeMore et al., 1994) and for PAN chemistry (Chang et al., 1996). The additional XO₂+HO₂ reaction proposed by Dodge (1989) was also included. Since the version of CBM4 used in this simulation is similar to CBM Version 4.1 in the Urban Airshed Model, this version of the model will be referred to as MAQSIP-CBM4.1.

The second simulation was initialized at 0700 EST on July 12, 1995 using the spun-up results at this hour from MAQSIP-CBM4.1, and was run for a period of 5 days. In this simulation, three additional XO₂N reactions (XO₂N+HO₂, XO₂N+XO₂, and XO₂N+XO₂N) were considered, and the rate coefficient for the XO₂N + NO reaction was increased by a factor of 12 relative to that in MAQSIP-CBM4.1. In this second simulation, the reaction rate constants for the XO₂N+NO, XO₂N+HO₂, XO₂N+XO₂, and XO₂N+XO₂N reactions are 8.1×10^{-12} , $7.6 \times 10^{-14} e^{1300/T}$, $3.4 \times 10^{-14} e^{1300/T}$, and $1.7 \times 10^{-14} e^{1300/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, respectively. These kinetic parameters were chosen so as to be the same as those used in CBM Version 4.2 (G. Yarwood, private communication, 1997), and hence this version of the model will be referred to as MAQSIP-CBM4.2. Since the MAQSIP-CBM4.1 and MAQSIP-CBM4.2 simulations are both characterized by identical

spun-up trace gas distributions at 0700 EST on July 12, 1995, we can examine the consequences of chemical mechanism changes on model results by comparing the two simulations from this point in time onwards.

Model Results

We first focus on model results during the July 14-16, 1995, time period. Afternoon-average (1300-1700 hours) surface O_3 mixing ratios from the two simulations are shown in Figure 1, and the difference between the two O_3 fields is shown in Figure 2. O_3 mixing ratios are highest near large anthropogenic emission regions along the Ohio river valley, in the northeastern United States, and along the Great Lakes region. O_3 mixing ratios from both simulations are less than 35 ppbv in the northern and northwestern parts of the model domain due to the influence of boundary conditions. Away from the boundaries, O_3 mixing ratios are 5-15 ppbv higher in MAQSIP-CBM4.2 than in MAQSIP-CBM4.1 over a widespread region. The most striking difference between the two simulations is in parts of the southeastern and midwestern United States. In MAQSIP-CBM4.1, simulated O_3 levels in these regions are less than 35 ppbv. By contrast, O_3 levels in these regions are generally higher by 10-20 ppbv, and by as much as 20-25 ppbv, in MAQSIP-CBM4.2.

Also, shown in Figure 1 are the afternoon-average surface NO_x mixing ratios from the two simulations. Simulated NO_x concentrations are of the order of 1 to 5 ppbv in regions where NO_x emissions are largest. However, simulated NO_x concentrations are extremely low in parts of the southeastern and midwestern United States in MAQSIP-CBM4.1, a feature not seen in the MAQSIP-CBM4.2 results. The difference between the afternoon-average surface NO_x concentration fields is shown in the bottom panel of Figure 2. Differences of the order of 0.1-0.4 ppbv occur in much of the model domain away from the boundaries, with largest differences occurring in parts of the midwest, southeast, and northeast.

The relatively large increases in NO_x occur despite the increase in the $XO_2N + NO$ reaction rate coefficient due to the fact that the additional termination reactions for XO_2N have a dramatic effect on its lifetime and reduce its ability to consume NO_x chemically. In regions where significant differences are seen between the MAQSIP-CBM4.1 and MAQSIP-CBM4.2 NO_x fields, XO_2N lifetimes decrease from 30 min or greater to 0.5-1 min when additional XO_2N termination reactions are considered. Thus, simulated XO_2N concentrations decrease from 0.1-1 ppbv (in MAQSIP-CBM4.1) to 0.005-0.01 ppbv (in MAQSIP-CBM4.2) in these regions. The spatial NO_x -enhancement pattern is the result of spatial variability in the efficiency of the XO_2N+NO sink mechanism for NO_x , which in turn depends on the spatial distribution of hydrocarbon and NO_x emissions. In our model, the largest effect on NO_x is generally in regions where the daytime isoprene emissions exceed NO_x emissions by at least a factor of 10 on a molar basis.

While the spatial O_3 -enhancement pattern does not always reflect the spatial NO_x -enhancement pattern shown in Figure 2 due to the non-linear nature of O_3 photochemistry, it is evident that the largest O_3 enhancements in the southeast and midwest correspond to regions of significant NO_x enhancement. In these regions, we find that the O_3 photochemical tendencies calculated in MAQSIP-CBM4.1 generally range from 0 to -10 ppbv/day during

July 14-16, 1995, while the corresponding O₃ photochemical tendencies calculated in MAQSIP-CBM4.2 are higher by about 5 to 15 ppbv/day.

Averaged over the continental boundary-layer, we find that the difference between the O₃ burden simulated in the two models is about 8 ppbv after about 60 hours of simulation. However, the change in photochemical production is even greater, and is of the order of 21 ppbv after four days. The enhancement due to chemistry is partially compensated for by increased dry deposition and transport out of the continental boundary-layer.

We have performed an additional simulation which is identical to the MAQSIP-CBM4.2 simulation, except for the fact that the XO₂N + NO rate constant is lower by a factor of 12 (corresponding to the value used in MAQSIP-CBM4.1). For this case, simulated ground-level O₃ concentrations are generally 5-10 ppbv higher than those calculated by MAQSIP-CBM4.2 in parts of the midwestern and southeastern United States. Thus, while one would expect the rate constant used for the XO₂N + NO reaction to have only a minor effect on model results in the absence of additional termination reactions for XO₂N, we find that model results are somewhat sensitive to the magnitude of this rate constant when additional XO₂N termination reactions are considered.

Summary

We find that the simulated O₃ distribution using CBM4 can be profoundly changed over large regional-scales when the XO₂N reaction scheme is changed. An earlier unpublished study suggested that changing the XO₂N reaction scheme would lead to very modest changes of only 2-5 ppbv in the daily maximum O₃ (Yarwood, private communication, 1997). However, that study focussed on the New York/Philadelphia corridor alone. In our study, we find that the effect in the New York/Philadelphia region is of the order of 5-10 ppbv (see Figure 2), which is roughly consistent with the previous study. However, we find a much more pronounced effect (10-25 ppbv) in parts of the midwestern and southeastern United States. In these regions, the changes to the XO₂N reaction scheme have a significant effect on the lifetime (and thus on the concentration) of XO₂N, which in turn leads to significant changes in the simulated concentrations of NO_x and O₃.

Our results demonstrate that the efficiency with which relatively inert organic nitrates are formed can have a significant impact on ground-level O₃ in NO_x-limited regions over large spatial scales. Detailed measurements of speciated organic nitrates in rural environments are needed to fully understand the formation and fate of these species, and to elucidate their role in O₃ photochemistry. It may also be useful to conduct detailed and systematic intercomparisons of the chemical modules in various AQMs to shed light on the uncertainties associated with O₃ photochemistry in rural environments.

Furthermore, our results show that a seemingly minor change in the chemical mechanism used in an AQM can in reality have a major effect on the model's results. Given these findings, it would seem prudent that the implementation of any changes in the chemical mechanisms used in regulatory AQMs be preceded by comprehensive evaluation and discussion of these changes in the open scientific literature. On a more general note, it is critical that the theoretical underpinnings of the various components of regulatory AQMs be carefully reviewed and documented in the peer-

reviewed literature so as to provide a sound scientific basis for air quality management policy decisions.

Acknowledgments. We gratefully acknowledge the support and expertise provided by MCNC/Environmental Programs in performing and analyzing the model runs. Computational support for this work was provided by the North Carolina Supercomputing Center. This work was funded in part by the Southeastern States Air Resource Managers (SESARM) and by the Southern Oxidants Study (SOS). We also acknowledge the helpful discussions with Dr. G. Yarwood. We are also grateful to Dr. Malcolm Ko and two anonymous reviewers for their comments on the original version of this manuscript.

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(Received April 28, 1997; revised October 14, 1997;
accepted November 7, 1997.)

Figure 1. Simulated afternoon-average surface O₃ and NO_x mixing ratios (ppbv) during July 14-16, 1995, from the MAQSIP-CBM4.1 and MAQSIP-CBM4.2 models.

Figure 2. Differences between MAQSIP-CBM4.2 and MAQSIP-CBM4.1 afternoon-average surface O₃ and NO_x mixing ratios (ppbv) during July 14-16, 1995.

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