

Resolving and quantifying ozone contributions from boundary conditions within regional models

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Abstract

In regional model simulations, ozone introduced by boundary conditions (BCs) is important to model performance, model sensitivity and for policy reasons such as transport assessments. Quantitatively tracking the contribution of ozone BCs throughout a regional model is highly desirable. A simple and efficient solution is to add a tracer (O3BC) to the regional model simulation with a source term equal to the ozone BC. However, it is also necessary to model the removal of O3BC by deposition and chemistry. Modeling tracer deposition is relatively straightforward but modeling the photochemical removal of O3BC is complex. We developed a chemical mechanism for the photochemical removal of O3BC that is compact, represents all major removal pathways (i.e., photolysis, reactions with HOx radicals), accounts for important dependencies on NO, and can be implemented as an extension of the main gas-phase chemical mechanism. The method provides great flexibility by permitting O3BC to be factored into components that are then tracked independently. Example components of potential interest are different lateral boundaries segments (north vs. south boundary, etc.), altitude segments (boundary layer vs. free troposphere vs. stratosphere) and geographic origin (e.g., Asia vs. North America vs. Europe). Information about the geographic origin of O3BC can be derived from global model sensitivity simulations. The method is implemented in the CAMx regional model by using an existing model option to add reactive tracers (RTRAC) with complex chemistry. The method is applied and evaluated in simulations for continental North America.

1 Introduction

In regional models like the Comprehensive Air quality Model with extensions (CAMx; ENVIRON, 2013) ozone introduced by boundary conditions (BCs) is important to model performance, model sensitivity and for policy reasons such as transport assessments. Quantitatively tracking the contribution of ozone BCs throughout a regional model is highly desirable. The CAMx ozone source apportionment technology (OSAT; Dunker et al., 2002) probing tool tracks BC contributions to ozone. However, OSAT has limited flexibility in how BC contributions are organized and OSAT tracks ozone contributions from emissions that may not be needed. We have developed and implemented an efficient method for tracking BC ozone contributions using reactive tracers. The new method is flexible because the BC contributions to be tracked are defined using CAMx input files, i.e., specially prepared BC files.

The CAMx reactive tracer (RTRAC) probing tool provides a flexible approach for introducing gas and particulate matter tracers within CAMx simulations (ENVIRON, 2013). Each RTRAC

tracer is influenced by boundary conditions, advection, diffusion, emissions and dry deposition. Gas-phase tracers can also undergo chemical destruction and/or production using either a simpler (RTRAC) or more complex (RTCMC) chemistry interface. The RTRAC Chemical Mechanism Compiler (RTCMC) permits a full chemistry mechanism to be defined through a model input file with no limits on mechanism complexity (within available computer resources). We configured RTCMC to track of ozone from BCs in a manner that is similar to OSAT.

2 Tracking photochemical ozone destruction

Ozone is destroyed by reactions with NO, NO₂, OH, HO₂ and alkenes. Some reactions destroy O₃ permanently and are straightforward to implement in a scheme to track O₃ destruction. Examples are reactions with alkenes (e.g., isoprene) that remove O₃ by forming an ozonide that decomposes to products such as aldehydes. Other reactions may initially destroy O₃ but form products that subsequently re-form O₃. An example is the reaction of O₃ with NO which forms NO₂ that can then photolyze causing O₃ to re-form. In this case, determining whether O₃ is permanently destroyed amounts to deciding whether NO₂ photolyzes to NO or is converted to another NO_y species (e.g., HONO, NO₃, HNO₃, etc.) by complex chemical reactions. During daylight, NO₂ photolysis usually dominates over NO₂ conversion to NO_y species other than NO. At night, O₃ reaction with NO may permanently destroy O₃ if the NO₂ formed is removed before it can photolyze on the following day. The RTCMC scheme assumes zero net destruction of O₃ by reaction with NO and so does not include the O₃ + NO reaction. The reactions of O₃ with OH and HO₂ are simplified for the RTCMC scheme by assuming that: (1) OH and HO₂ inter-convert rapidly and may be treated as a pool (HO_x = OH + HO₂); (2) At high NO, HO_x removal is dominated by HO₂ reacting with NO to form NO₂ which then photolyzes to re-form O₃, resulting in zero net O₃ destruction, and (3) At low NO, HO_x removal is dominated by reactions of HO₂ with HO₂ and RO₂ radicals, resulting in net destruction of one O₃.

The RTCMC scheme for tracking chemical destruction of O₃ tracers is shown in Figure 1 as implemented for use with CB05. The scheme tracks one BC O₃ contribution (O3A) using 15 reactions and 3 RTCMC tracers (i.e., O3A, O1DA and HOXA.) Other chemical species appearing in Figure 1 (i.e., OH, HO₂, NO, XO₂, XO₂N, C₂O₃, CXO₃, ISOP and TERP) are from the CB05 chemical mechanism and their concentrations are provided by CAMx and considered constant within RTCMC. Thus, an RTCMC reaction between O3A and ISOP depletes the RTCMC species O3A but does not change the CB05 species ISOP. CB05 treats the ISOP decay.

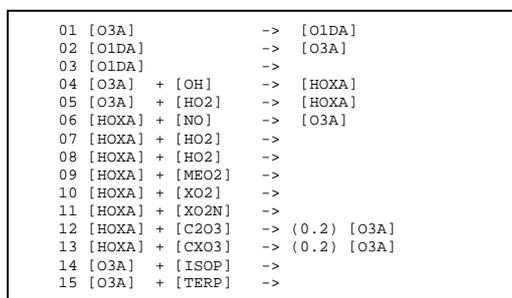


Figure 1. Reaction scheme for tracking chemical destruction of an ozone tracer (O3A) with the CAMx RTCMC probing tool. These reactions are implemented to work with the CB05 chemical mechanism.

3 Contributions of tropospheric and stratospheric ozone

To illustrate how the RTCMC scheme can be applied we used it to quantify contributions of tropospheric and stratospheric O₃ BCs for the continental US (CONUS). The CONUS simulation inputs were for calendar year 2008 with meteorology from WRF, anthropogenic emissions from the 2008 NEI, biogenic emissions from MEGAN and BCs from GEOS-Chem. We classified CAMx layers below ~6 km above ground as tropospheric, layers above ~9 km as stratospheric, and also tracked the contribution from layers between 6 and 9 km. This classification scheme was used for the purpose of demonstrating the method and a more refined classification of BCs into tropospheric vs. stratospheric could be developed.

Contributions to ground-level O₃ of BCs classified as troposphere versus stratosphere are shown in Figure 6 for March 5, 2008. Two areas of stratospheric O₃ influence are apparent on this day, one over northern Mexico and a second over the North Atlantic Ocean. The areas of high stratospheric O₃ influence coincide with areas of low tropospheric influence consistent with air subsiding from near the tropopause to ground level.

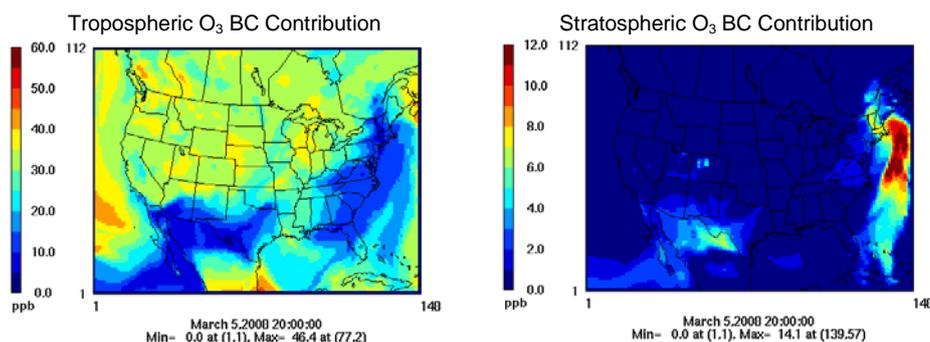


Figure 2. Ground-level O₃ (ppb) from O₃ boundary conditions (BCs) in the troposphere (below 6 km above ground) and the stratosphere (above 9 km) on March 5, 2008. The contribution of O₃ BCs between 6 and 9 km was also tracked but is omitted for brevity. Note that the color scales have different ranges.

We compared the total contribution of BCs to ground level O₃ determined by RTCMC and OSAT, as shown in Figure 3. The spatial patterns of BC O₃ contribution revealed by both methods are nearly identical.

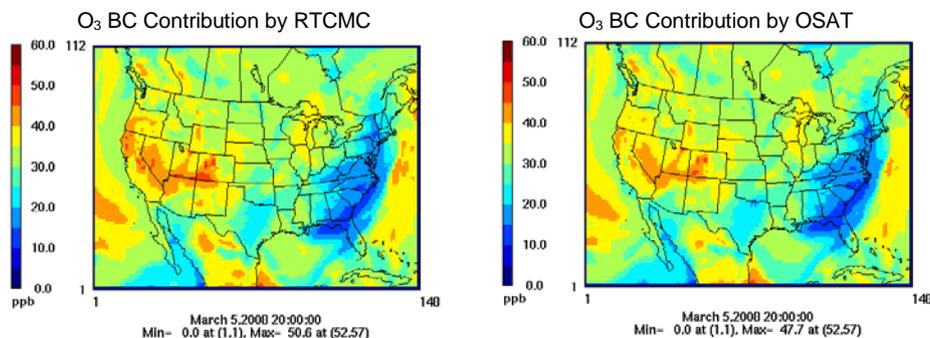


Figure 3. Boundary condition (BC) contribution to ground-level O₃ (ppb) determined by RTCMC and OSAT on March 5, 2008.

The RTCMC scheme is computationally efficient. Tracking three O₃ BC contributions added 9 tracers and 45 reactions in RTCMC and increased CAMx run time by 10%.

3 Summary

We developed and tested a new method for tracking ozone from apportioned BCs within a CAMx simulation by using reactive tracers with the RTCMC probing tool in CAMx. Ozone BC contributions determined by the RTCMC scheme are very similar to those determined by the CAMx OSAT probing tool. The RTCMC scheme is computationally efficient with a 10% increase in CAMx run time to track 3 ozone BC contributions. The RTCMC scheme provides great flexibility by permitting the ozone BCs to be factored into components that are then tracked independently. Example components of potential interest are different lateral boundaries segments (north vs. south boundary, etc.), altitude segments (boundary layer vs. free troposphere vs. stratosphere) and geographic origin (e.g., Asia vs. North America vs. Europe). Information about the geographic origin of ozone BCs can be derived from global model sensitivity simulations.

Acknowledgments

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Questions

Roger Timmis

Q: In the 3-day boundary condition experiment shown in your presentation, is there an explanation for the anomaly (i.e. difference in BC contribution as diagnosed by the RTCMC scheme and OSAT) over the Atlantic Ocean off the Eastern US seaboard? Have you checked whether predict-

ed events with large stratospheric contributions to ground-level ozone are matched to observed events such as tropospheric folds and cut-off lows?

A: Results using the RTCMC scheme and OSAT can differ for two main reasons. First, in areas with sufficient NO_x to support net ozone production OSAT diagnoses more rapid ozone destruction than the RTCMC scheme because OSAT can account more completely for ozone destruction chemistry. Second, falling rain can become saturated with ozone limiting further scavenging and OSAT uses saturation with total ozone to limit scavenging of ozone components (e.g., ozone from BCs) whereas the RTCMC scheme considers each ozone component separately with regard to saturation. The three-day experiment showed a stratospheric ozone contribution over the Atlantic which coincided with a deep low-pressure wave and associated frontal system over the eastern US consistent with deep vertical transport from the tropopause to near ground-level. Emery et al. (2012) have successfully modeled stratospheric ozone intrusions during tropopause folding events.

Rohit Mathur

Q: Please clarify the timescale of ozone model results shown for Gothic, CO. Assuming the modeled BC contributions to ground-level ozone are correct, what fraction do they contribute to the observed ozone or the total modeled ozone?

A: Daily maximum 8-hour average (MDA8) ozone values for April-August 2008 were shown for Gothic, CO, in the central Rocky Mountains. As shown in Figure 5, the percentage of total ozone originating above 9 km (ozone considered to originate from the stratosphere) was up to 52% using MOZART BCs or 51% using GEOS-Chem BCs. The average contributions were 15.3% and 13.7%, respectively. The outlier in Figure 5 (42% MOZART and 6% GEOS-Chem) occurred on July 29, 2008

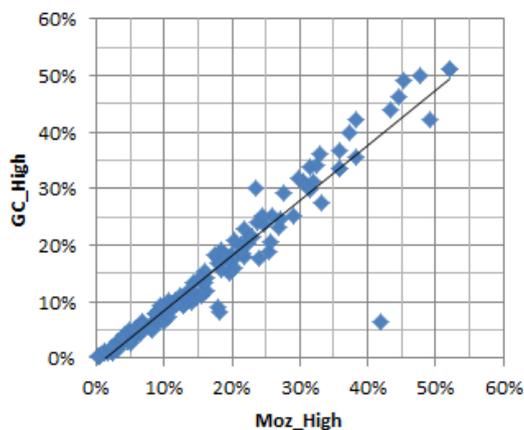


Figure 5. Percent contribution of modeled daily maximum 8-hour ozone concentration at Gothic, CO during April-August 2008 originating from the stratosphere (BCs above 9 km) using the CAMx regional model with BCs from MOZART (Moz_High) or GEOS-Chem (GC_High). Results courtesy of the Western Regional Air Partnership WestJumpAQMS project.