APPLICATION AND INTERCOMPARISON OF THE RADM2 AND RACM ATMOSPHERIC CHEMISTRY MECHANISM INCLUDING A NEW ISOPRENE DEGRADATION SCHEME WITHIN THE ONLINE-COUPLED REGIONAL METEOROLOGY CHEMISTRY MODEL MCCM

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INTRODUCTION

Since the huge number of chemical species and reactions involved in the degradation of organic compounds does not permit an explicit treatment of these reactions, the use of condensed mechanisms in regional models is necessary. Such mechanisms are for example the RADM2 (Stockwell et al., 1990) or the RACM (Stockwell et al., 1997) mechanism, which are widely applied in regional air chemistry models. With increased knowledge about biogenic VOC's chemistry, updates of the description of organic chemistry may be necessary. Geiger et al. (2003) introduced a new mechanism based on RACM with improved isoprene and biogenic VOC chemistry.

To understand the behavior of the three mechanisms for the application within regional air chemistry models, two case studies were performed for the three mechanisms: A box-model-inter-comparison and a cross-validation of the simulations with the three-dimensional online-coupled regional air chemistry model MCCM (Grell et.al. 2001).

AIR CHEMISTRY MODELING

The case studies for the inter-comparison were carried out using the RADM2, RACM and the new mechanism from Geiger et al. (2003) called RACM-MIM.

RADM2 was developed by Stockwell et al. (1990) from the RADM Model by Chang (1989). It treats 63 chemical species, which contain real species like NO, NO_2, or O_3 and several condensed species classes like hydrocarbons HC_3, HC_5 and HC_8. RADM2 contains 21 photolysis reactions and 136 chemical reactions of higher order.

RACM was developed by Stockwell et al. (1997) from the RADM2 mechanism. RACM applies a more detailed description of the air chemistry of biogenic ozone precursors. It treats 77 chemical species (as real species and condensed species classes) and contains 23 photolysis reactions and 214 chemical reactions of higher order.

RACM-MIM was developed by Geiger et al. (2003). It is based on the RACM mechanism combined with the MIM isoprene mechanism (Mainzer Isopren Mechanismus, Poeschl et al. (2000)) and reflects an advanced description of the air chemistry of biogenic ozone precursors like isoprene and others. It treats 84 chemical species (as real species and condensed species classes) and contains 23 photolysis reactions and 221 chemical reactions of higher order.

For both studies, the box model and the online-coupled three-dimensional meso-scale simulations with MCCM, the three mechanisms were numerically integrated using an implicit and reasonable accurate integration method from Hairer et al. (2000). In both cases the forth order integration method of Rosenbrock-type ROS4 was applied.

BOX MODEL SIMULATIONS

The box-models for the three mechanisms were constructed using the KPP chemistry preprocessor from Damian et al. (2002). For the inter-comparison of the box-model simulations the scenario URBAN from Poppe et al. (2001) was selected. The scenario describes a predefined initial state and typical urban emissions for an episode of 5 days (120

hours) to be simulated. Fig. 1 shows the resulting concentrations for selected species in parts per million [ppm] over the simulated 120 hours period starting at moon.

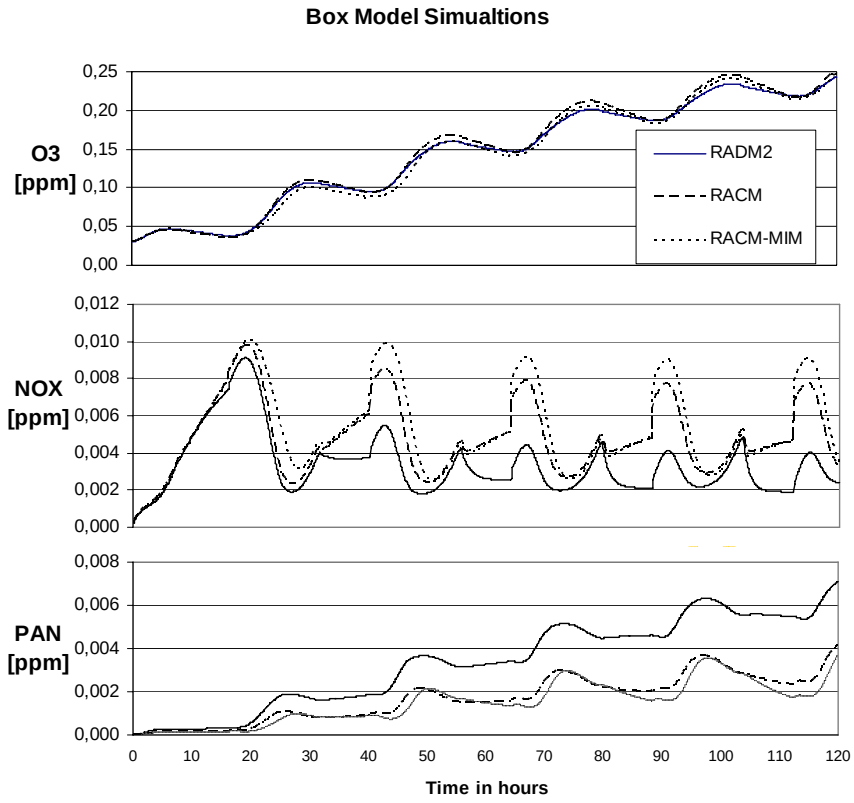

Fig. 6; Concentrations for selected species in ppm over the simulated period of 120 hours starting at moon.

The box-model simulation results in more O_3 for the RACM mechanism, specially during daytime compared to the two others. The RADM2 first follows the RACM, but after 48 hours it results in less maximum O_3 while the nighttime local minimum corresponds with the RACM. The RACM-MIM produces for the first 72 hours noticeable less O_3 and for the following 48 hours the O_3 concentrations are for the daytime maximum between the RACM and the RADM2, whereas the nighttime local minimum corresponds with the two others.

REGIONAL AIR QUALITY SIMULATIONS WITH MCCM

MCCM is based on the NCAR/Penn State University meso-scale meteorological model MM5. In addition to MM5 the modeling system of MCCM includes online coupled gas phase chemistry, computation of photolysis frequencies, anthropogenic and biogenic emissions, and deposition. MCCM incorporates the RADM2 and RACM gas phase chemistry. In order to investigate the effect of an updated isoprene degradation mechanism with the RACM-MIM, the new mechanism was implemented into MCCM as well. To make the simulations with the three gas phase chemistry mechanisms comparable, the same numerical integration method used for the box-model simulation was applied. This new implementation, which uses a Rosenbrock-type solver is also based on the KPP pre-processor (Damian et al. 2002).

The selected test case scenario is a four day photo-smog episode from August 12th to 15th (GMT) in southern Germany with moderate near ground ozone concentrations. The simulation was performed using AVN global meteorological input data with a nesting strategy

of four domains with 27, 9, 3 and 1 km grid resolution. The coarse domain was using typical artificial distributions for the chemical species as initial and boundary conditions. Domain D1 was initialized at August 12th at midnight and domain D2 was started 8 hours later in order to nest down realistic initial and boundary conditions from the coarse to the finer grid. Finally the domain D4 simulated the sub-urban region around the city of Augsburg for 3 days from August 13th to 15th. The anthropogenic emissions were based on a spatial and temporal high resolution emission inventory for the year 1998 containing 37 different species and the type of emission (point, line or area source). The biogenic emissions were calculated online by the MCCM model. For the validation of the quality of the simulations, ground measurement data from the regional environmental authorities (Bayerisches Landesamt für Umwelt) were available for NO_2 and O_3.

REGIONAL AIR QUALITY SIMULATION

The MCCM simulation of the photo-smog episode in southern Germany with the RADM2 mechanism resulted in an approximately 5 % lower mean ozone concentration as compared to the runs with the two RACM mechanisms. For peroxyacethylnitrate (PAN) the difference during day time can be up to 50 %, whereas NO is about 10% lower and NO_2 up to 8 % higher when the RACM type mechanisms were applied. In comparision to the original RACM, the RACM-MIM with updated isoprene chemistry yields significantly higher concentrations of methacrolein. Also the concentrations of formaldehyde tend to higher values while the concentrations of organic nitrate are always lower when the new isoprene scheme was applied compared to the original RACM mechanism.

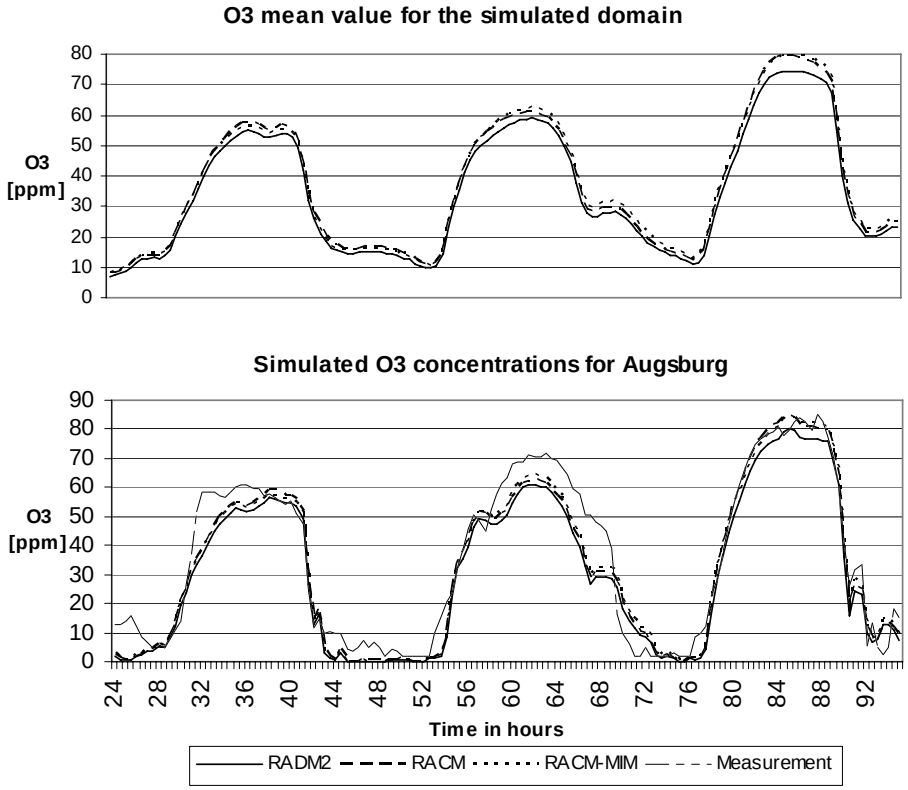

Fig. 7; Simulated and measured near ground concentrations of O_3 and NO_2 for the simulated domain and the city of Augsburg.

CONCLUSION

Due to the short simulation period an exact estimation of the differences between the three chemistry mechanisms is hard to retrieve, but in general the results show major differences in the simulated concentrations for the simulated three day episode. Further analysis of the differences when applying any of the three mechanisms for regional air quality modeling has to be performed for the exact interpretation of any simulated results.

For the near future, a transient simulation of an episode of several months with the given configuration is in preparation. This simulation should result in an amount of data, which allows to draw a statistiscally safe conclusion about the behaviour of the three mechanisms when applied to problems of regional air quality modeling.

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