Validation of Chemical Mechanisms for the Atmospheric Degradation of Isoprene and α-Pinene – Regional Modeling of Isoprene Degradation

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Introduction and Objectives

Isoprene plays a major role in the formation of tropospheric ozone and other photooxidants. Within chemistry transport models the processes involved in isoprene oxidation are described by highly condensed mechanisms. Since the knowledge about the oxidation of biogenic VOC has increased significantly over the last years, a re-evaluation of the chemical mechanisms used within chemistry transport models seems to be necessary.

Within the subproject ´Chemical Mechanisms´ of ValCheM, an updated isoprene degradation mechanism was implemented into the RACM (Regional Atmospheric Chemistry Mechanism, Stockwell et al., 1997). Comparison of this updated mechanism (Geiger et al., 2003) against smog chamber measurements has indicated that the revised mechanism reproduces the measured concentrations in a better way than the original RACM.

This poster shows the application of the updated RACM within a regional chemistry transport model in comparison with results obtained with the original version of RACM.

Methods

The updated isoprene degradation mechanism for RACM was implemented into the regional meteorology-chemistry model MCCM (Grell et al., 2000). MCCM is based on the NCAR/Penn State University mesoscale 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 the updated isoprene degradation mechanism within the RACM, the new mechanism was implemented and its performance compared with the original RACM.

To facilitate the implementation of new additional atmospheric chemistry mechanisms into MCCM a new solver was added as an additional option to MCCM. This new implementation, which uses a Rosenbrock4 solver allows the automatic generation of the code by the KPP pre-processor (Damian-Iordache, 1996) from a list of the chemical reactions.

Results

As an example, the effect of the two different descriptions of the isoprene chemistry on the regional scale is shown for a simulation with MCCM with 20 km horizontal resolution over 5 weeks in summer 2001.

The spatial distributions (Figure 1) for the mean maximum daily ozone concentration show only very small differences on the order of 2% between the results obtained with the original and the updated mechanism. Areas with higher concentrations of MACR (methacrolein and MVK) and of H_2O_2 correlate with high isoprene emission. For PAN and organic nitrates (not shown) lower concentrations are found throughout the whole modeling domain when the updated mechanism is applied.
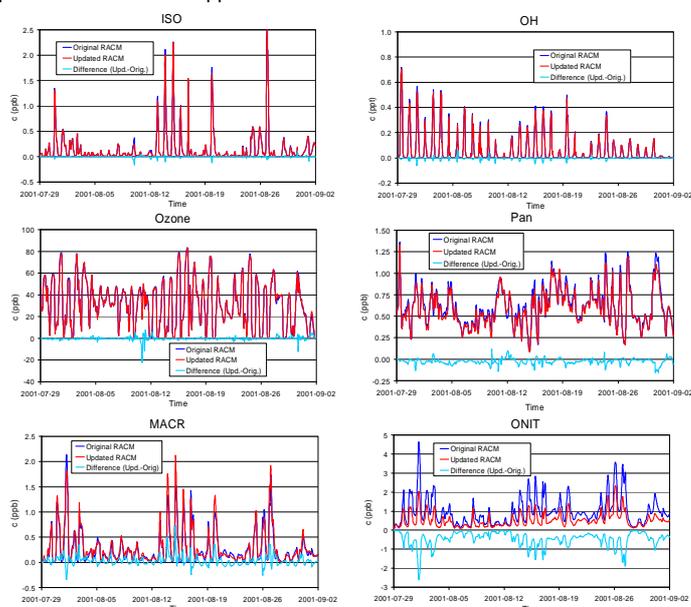

Fig. 1: Differences between updated RACM and original RACM for near surface mean maximum values of ozone, MACR (methacrolein + MVK), H_2O_2, and PAN.

Fig. 2: Diurnal course of near surface values of isoprene, OH, ozone, PAN, MACR (methacrolein + MVK), and ONIT (organic nitrate) for a grid point near the center of the modeling domain, corresponding to an area west of Augsburg.

The diurnal courses of isoprene and the OH radical show only small deviations between the original RACM and the RACM with updated isoprene scheme. Similar to the area distributions mostly negative deviations occur for ozone and PAN, whereas for MACR higher values dominate in the case of the updated mechanism. The strongest deviation occurs for ONIT (organic nitrates), where the production of organic nitrates through the reaction of NO with peroxy radicals formed from isoprene is mainly replaced by a higher production of MACR and formaldehyde in the updated mechanism.

Generally, the features shown above are observed for all scales ranging from the urban to the continental scale. Only for cases with NO_2 concentrations around 5 ppb a significantly higher ozone production was simulated with the updated mechanism in the presence of isoprene emissions.
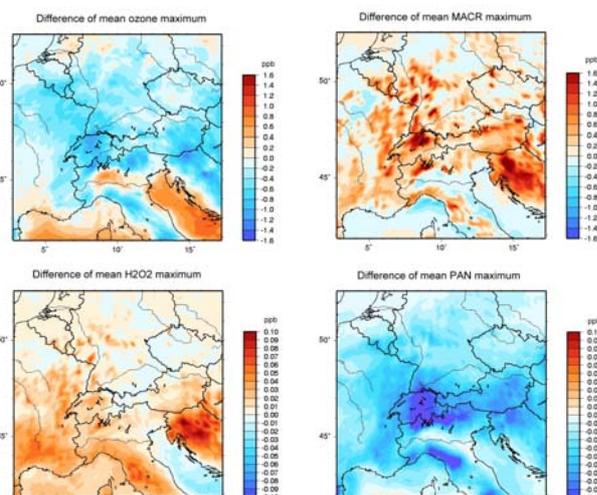
Summary and Conclusions

An updated and validated isoprene degradation mechanism for RACM was implemented into the coupled meteorology-chemistry model MCCM. Applications for different weather situations and different scales over Europe were performed and compared with results from simulations with the original RACM. The following results were obtained:

- Small differences in isoprene and OH
- Slightly lower ozone concentrations for most situations and locations
- Higher concentrations of methacrolein and H_2O_2 at locations with significant isoprene emissions
- Significantly lower concentrations of organic nitrates.

In regions where anthropogenic emissions of NO_x are important, only minor differences of the ozone concentrations were found. However, the new mechanism is recommended for the investigation of other products and for applications with significant isoprene emissions and moderate advection of NO_2.

References

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Validation of chemical mechanisms for the description of isoprene and α-pinene degradation within 3-dimensional CTMs

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