Scenarios for Modeling of Multi-Phase Tropospheric Chemistry

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Chemical transformation of reactive trace compounds in the troposphere includes gas phase, liquid phase and heterogeneous processes on the surfaces of water droplets and aerosol particles. The oxidation of most gaseous compounds is initiated by gas phase processes. Aqueous phase chemistry plays a substantial role in the subsequent oxidation and the formation of acidic species. Heterogeneous processes influence also the budget of reactive trace gases. It has been shown in case of nitrogen compounds that uptake on aerosol surfaces can be an important loss. Also formation of aerosol particles may act as a sink for higher weighted organic compounds.

A quantitative understanding of the fate of primary and secondary pollutants in the tropo-sphere is mandatory for science-based reduction strategies for environmentally important pollutants like the photooxidants, nitrogen oxides, acids, and peroxides.

We have developed several test cases (hereafter called scenarios) that will improve our knowledge on multi-phase chemistry.

The scenarios are designed to serve three purposes:

1. They can be used as base cases for sensitivity analysis with respect to rate constants, mixing ratios of compounds, emissions strength, new chemical processes, etc. To be useful with any reaction scheme, the scenarios do not refer to a particular chemical reaction mechanism.
2. Comprehensive chemical reaction schemes have too many reactions and compounds to be operationally useful in threedimensional CTMs. Reduction of mechanisms is necessary based on scientific objectives and with a quantified error relative to the reference reaction scheme. Since the scenarios cover environmentally relevant situations in the atmosphere, they can serve as input for reduction schemes.
3. To evaluate chemical schemes that are currently in use in box models and CTMs for prediction purposes and the development of reduction strategies.

The scenarios describe mixing ratios in the gas phase, the liquid phase, and the aerosol distributions as well as meteorological parameters which can be used as initial conditions

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and parameters for model calculations.

To keep things as simple as possible a few approximations are necessary:

- The scenarios are limited to a zerodimensional (box) treatment. While this may be for example adaquate for sensitivity studies for gas phase rate constants, it is a severe approximation if heterogeneous processes and hence transport is involved.
- Meteorology is incorporated by prescribed time dependencies for temperature, humidity, and pressure. Cloud events with uptake of gaseous compounds and subsequent evaporation are included.
- Photolysis frequencies and their diurnal cycles are prescribed for gas phase and liquid phase compounds. Aerosols are also specified by their chemical composition and size distribution. To facilitate the numerical treatment also an approximation of the size distributions by three monodisperse modes is given.

The scenarios are summarized in the table. The gas phase part of the cases LAND, MARINE, BIO, FREE, and PLUME (= PLUME/1) are identical to those discussed in the final report of the Chemical Mechanism Working Group (CMWG) of EUROTRAC(M. Kuhn et al., Atmos. Environ. **32**, 693-709, 1998).

SCENARIOS:

scenario	**short description**	**emissions**
LAND	continental planetary boundary layer with a low burden of pollutants	no
MARINE	marine boundary layer	no
FREE	middle troposphere	no
PLUME	moderately polluted PBL	yes
URBAN	polluted PBL	yes
URB/BIO	URBAN plume with biogenic impact (first 60 h identical to URBAN)	yes

The scenarios are similar (but not identical) to the corresponding cases in the IPCC intercomparison 1994 (Olsen et al., J. Geophys. Res. **102**, 5979-5991, 1997). The cases URB/BIO and URBAN refer to more polluted situations downwind industrialized areas with and without biogenic emissions. Initial conditions for the liquid part and the aerosol distributions are under development in the scenarios group of MPM.

The description of the scenarios is intended to provide the necessary information to perform such calculations in an unambigous way, such that numerical simulations by different scientists with the same reaction scheme come up with the same answers.

The status and future work is summarized as follows:

- A preliminary version of the scenarios has been completed. The final version will be avail- able in spring 1999.
  (Web-page: http://www.kfa-juelich.de/icg/icg3/ALLGEMEIN/cmdform.html)
- The scenarios are currently tested by members of the MPM group with the gas phase chemistry reaction scheme RADM2 (Stockwell et al., J. Geophys. Res., **95**, 16343, 1990), aqueous phase chemistry (Walcek et al., Atmos. Environ., **31**, 1221, 1997), and a newly developed heterogeneous chemistry module. Calculations will be done for a period of 5 days using the full scenarios as well as gas phase chemistry only to investigate the impact of multi phase chemistry. Once the scenarios are finalized, the results of the model simulations will be available on the web for intercomparisons with other reaction schemes, for check of numerical solvers, etc.
- Work has been started to implement a box model on the web for interactive calculations of multi-phase chemistry using the scenarios (see contribution by P. Biggs). A first version addressing gas phase chemistry is already in operation (CMD Photochemical Box Model). (Web-page : http://physchem.ox.ac.uk/sbox/)