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Development of a Microscale Gas-Phase Chemistry Mechanism for Implementation in the Microscale Model MITRAS

A contribution to subproject SATURN

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Problems and aim of the project

For defining efficient air pollution abatement strategies it is essential to understand the fundamental mechanisms of transport and transformation of air pollutants at extremely high concentrations. Since a significant fraction of precursor substances for the formation of ozone and other photo-oxidants are emitted within European cities, the transport and transformation processes need to be studied in street canyons, in addition to the mesoscale processes. Pollutants emitted by traffic and other local sources contain substances which are very reactive and consequently are transformed within the city forming secondary substances which are transported into the boundary layer. Emerging secondary flows can prolong the residence time of pollutants in the urban canopy. Therefore, the flux of pollutants from the urban canopy into the atmosphere, which consists of a mixture of emitted and secondary formed substances, can differ significantly, depending on the meteorological conditions, from the calculated traffic emission inventories which are generally used as input data for mesoscale models. The oxidation of pollutants within cities can cause the mesoscale model to predict grid average concentrations which differ significantly from the real atmospheric concentrations.

In order to describe the urban photo-chemistry it is mandatory to include chemical modules in microscale dispersion models. An appropriate mechanism is the Regional Atmospheric Chemistry Mechanism (RACM) by Stockwell *et al.* (1997), which is an updated and improved version of the older RADM2 mechanism (Stockwell *et al.*, 1990) used in many photochemical transport/transformation models. The latter mechanism has been developed for

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the application in regional air quality models, but is not recommended for use in small-scale models. Therefore it is necessary to adapt this mechanism for describing the fast urban chemistry in order to achieve the aims of the project.

The project is carried out within the frame of the German Tropospheric Research Programme in collaboration with the Meteorological Institute of the University of Hamburg, the Alfred-Wegener-Institute for Polar and Oceanic Research in Bremerhaven and the Institute for Tropospheric Research in Leipzig. The scientific issues are:

* the development of a gas-phase chemistry module, which is adapted to the microscale and using an emission inventory including heterogeneous reactions on particles,
* the development of a general module for determining photolysis rates for any time period, which is adapted to the gas-phase chemistry module and which is directly coupled with MITRAS,
* the development of a prepocessor for determining emission rates for single VOCs from the emission inventory, and
* the evaluation of the chemistry module with experimental data from smog chambers.

First results

Reduced gas-phase mechanism

The modification of the RADM2 gas-phase mechanism for microscale applications is based on a timescale (τ) analysis of each chemical species. With the assumption of an urban high emission scenario, chemical lifetimes are calculated from average loss rates at mid-day (12:00 CET) and during the night (2:00 CET). Species with lifetimes at 12:00 CET much greater than the transport time in the model ($\tau > 2$ h) are removed from the reaction equation system and are calculated as passive tracers. The microscale mechanism is further enlarged by the compound benzene (BZL) with regard to § 40/2 of the Bundes-Immissionsschutzgesetz (BImSchG).

Table 1 lists calculated chemical lifetimes of selected species. A number of species are chemically reactive in microscale domains and can form secondary substances, especially during the day. An important transforming process close to traffic emissions is the NO–NO_2 conversion via ozone and peroxy radical reactions. Therefore, in street canyons very low ozone concentrations can be found. With the NO–peroxy radical reaction, formaldehyde (HCHO) is formed, and NO reacts with the high concentrations of HO radicals to produce nitrous acid (HONO). Other compounds, like CO, SO_2, ethane, ketones, alkanes with low reaction rates, as well as benzene have chemical lifetimes during day and night-time which are much longer than the transport time to a receptor within the small area. The calculations show that the flux of pollutants from the urban canopy layer differs significantly from the traffic emission inventories in mesocale model.

Table 1: Calculated averaged chemical lifetimes τ of selected RADM2 species plus benzene (BZL) at 12:00 CET and 2:00 CET under an urban high emission situation. Definition of reactive or inert compounds in the microscale version of the mechanism.

Species (Symbol)	τ (12:00 CET)	τ (2:00 CET)	reactive	inert
NO_2	2 min	96 min	×	
NO	24 s	42 s	×	
O_3	3 min	3 min	×	
HONO	9 min	∞	×	
HNO_3	46 h	19 days		×
HCHO	42 min	9 h	×	
HC_8 (high reactive alkanes)	44 min	8 h	×	
BZL (benzene)	7 h	70 h		×

Photolysis frequencies

The photodissociation of only a small number of atmospheric molecules drives the important radical chain reactions during daytime. Since the photolysis of many species is very rapid it has to be considered in microscale applications. In the MITRAS model photolysis frequencies are calculated by integrating the product of the spectral actinic flux, the spectral absorption cross section and the photodissociation quantum yield over the tropospheric wavelength interval from 255 nm to 730 nm using the delta Eddington method (Joseph *et al.*, 1976; Madronich, 1987). For every species, tables of cross sections and quantum yields for 130 discrete photolysing wavelengths from DeMore *et al.* (1994) are used. The actinic flux on a molecule is subdivided into a direct part (parallel solar radiation) and a diffusive part. For flux calculations the knowledge of the atmospheric optical depth is necessary. It depends on scattering by air molecules, ozone absorption, extinction by aerosol particles and cloud droplets.

Photolysis frequencies will be strongly modified in the presence of clouds (Fig. 1). The optical depth of water clouds is calculated with a simple

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parameterisation of the number of cloud droplets and the equivalent droplet radius as well as the calculated cloud water content from the MITRAS model.

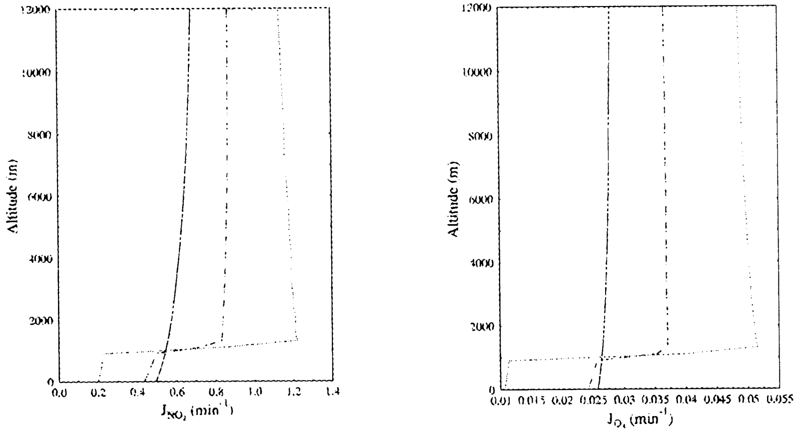

Fig. 1: Photolysis frequencies (J) under clear sky condition (solid line) and including a cloud of 200 m thickness at 1 km height. The cloud water content amounts to 0.5 gm^{-3} (dotted line) and 0.1 gm^{-3} (dashed line). NO_2 photolysis frequencies (left) and O_3 photolysis frequencies (right).

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