Application of the CAPRAM Halogen Module 2.0 in mixed urban and maritime coastal areas

Peter Bräuer, Erik Hoffmann, Andreas Tilgner, Ralf Wolke, and Hartmut Herrmann
Leibniz Institute for Tropospheric Research (TROPOS), Permoserstr. 15, D-04318 Leipzig, Germany

braeuer@tropos.de

Introduction and Motivation

It is well known that halogen multiphase chemistry plays an essential role in the marine boundary layer. In coastal regions, which cover ~20% of the Earth’s surface, they directly influence marine and urban air masses. Marine halogens play an important role in the atmospheric evolution of clouds, aerosols, and gases. The presence of marine inorganic halocycles, such as 

\[ \text{Br}_2 \] 

and 

\[ \text{I}_2 \] 

in the boundary layer can have a significant impact on the climate and air quality of coastal and maritime areas. The in situ chemistry of halogens in the marine boundary layer is complex and depends on a variety of factors, including the presence of marine aerosols, halocycles, and trace gases. The interactions of maritime and continental urban influenced air masses in coastal regions are also crucial, as they can affect the chemical composition of aerosols and the ozone concentration levels. Thus, it is of great interest to understand the interactions of maritime and continental urban influenced air masses in coastal regions.

Model Description

Application of the CAPRAM Halogen Module 2.0 together with the multi-phase chemical mechanism RACM-MMIDCAPRAM 3.0 (with and without HOX) has been performed to investigate the complex chemistry of halogens in coastal areas. Two scenarios have been applied with an urban populated air mass moving over the coastal ocean and a marine air mass moving over a coastal city. The simulations have shown that the influence of the air mass origin is most important on the first day. Thereafter, the emissions of the new environment dominate the multiphase chemistry. The scenario C_U showed the influence of halogen multiphase chemistry on NOx species. The production of Cl atoms is mainly triggered by production during night-time and photolysis of ClNO2 over the whole simulation time (see Fig. 1). The production of Cl is mainly triggered by production during night-time and photolysis of ClNO2 over the whole simulation time (see Fig. 1).

Results and Discussion

Chlorine chemistry

The scenario Coastal — Urban

- Modelled concentrations for ClNO2 over the urban area show a good agreement with measurements, e.g. of Philipps et al. [10], with maximum concentrations of 2 - 10^12 molecules cm^-3.
- The ozone production rate in the cloud period is in contrast to the scenario C_U.
- Increased production of Cl atoms due to NO3 chemistry in clouds.

The scenario Urban — Coastal

- Modelled Cl concentrations in both sensitivity studies (with and without iodine) show a good agreement with measurements [10] and measured 2 – 6.1012 molecules cm^-3 (see Fig. 3).
- Main source for the iodine is the iodide of NOx species which is produced in the particle phase. Clouds suppress the formation of chlorine atoms due to different cycles.
- The influence of the urban air mass is identified on the first model day.

Iodine chemistry

The scenario Coastal — Urban

- The reactions of IO with NOx species form the largest sources for gaseous iodine.
- Cloud periods suppress the iodine production.

The scenario Urban — Coastal

- Modelled concentrations of IO are in better agreement with measurements in scenario without iodine, than with iodine emissions (see Fig. 4), but concentrations of IO coincide well with the scenario with iodine emissions.
- The influence of the urban air mass is identified on the first model day.
- After the first day, cloud periods decrease the concentration of gaseous iodine and accumulate iodate in the aqueous phase.

Interactions with organics

In urban areas, VOC degradation by OH is dominant, however, during night-time ClNO2 over the whole simulation time (see Fig. 5), the formation of Cl atoms is triggered by the process ClNO2 + HO2, which is formed during the reaction of HO2 with NO2. The production of Cl in these reactions is mainly triggered by the formation of ClNO2 over the whole simulation time (see Fig. 5).

Bromine chemistry

The scenario Coastal — Urban

- The reactions of Br and BrO with NOx species form the largest sources for gaseous Br species.
- Cloud periods suppress the bromine production.

The scenario Urban – Coastal

- Modelled concentrations of bromine species do not agree well with measurements.
- The influence of the urban air mass is identified on the first model day.
- Clouds suppress the concentration of bromine species significantly due to increased IO concentration levels (see Fig. 4 and Fig. 5).
- A peak in several bromine species is caused by the photolysis of Br2 in the gas phase. The reaction of Br2 with NOx species forms the largest sources for gaseous Br species.

Summary and Outlook

Box model studies with a detailed multiphase chemistry mechanism (RACM-MMID/CAPRAM 3.0 + HOX) have been performed to investigate the complex chemistry of halogens in coastal areas. Two scenarios have been applied with an urban populated air mass moving over the coastal ocean and a marine air mass moving over a coastal city. The simulations have shown that the influence of the air mass origin is most important on the first day. Thereafter, the emissions of the new environment dominate the multiphase chemistry. The scenario C_U showed the influence of halogen multiphase chemistry on NOx species. The production of Cl atoms is mainly triggered by production during night-time and photolysis of ClNO2 over the whole simulation time (see Fig. 5).

References