



Modeling reactive halogen species based on measurements at the Irish West Coast

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We performed model studies based on measurements of reactive halogen species at Mace Head and Mweenish Bay at the Irish West Coast. The measurements were made using Differential Optical Absorption Spectroscopy (DOAS) and showed a strong heterogeneity for the spatial distribution of molecular iodine and iodine oxide.

The model study was performed in order to get a better understanding of the spatial distribution of the trace gases, the mechanisms that lead to the formation of new particles and the impact of iodine emissions on atmospheric chemistry. We used the one-dimensional model MISTRA to obtain a better understanding of the related processes. The model was initialized based on the conditions for the Irish West Coast, the iodine flux (from macro algae) was adjusted so that the model reproduces the observed IO mixing ratios. A number of different model runs were performed to be able to quantify the impacts of iodine chemistry on local and regional photochemistry under different meteorological conditions.

The model suggests that inorganic iodine is rapidly mixed vertically: About 75% of the inorganic iodine is transported upwards, which is in good agreement with field measurements using multi-axis DOAS that indicate a significant amount of IO in higher layers of the lower troposphere. Furthermore the model was able to reproduce the field measurements of IO and molecular iodine during day and night. Not only the modeled mixing ratios, but also the spatial distribution of the iodine species was in good agreement with the field studies. The model also reproduced qualitatively the nucleation of aerosol particles that was observed during the field campaigns. The model results also suggest that IO_2^- in sulphate as well as in sea salt particles gets oxidized to IO_3^- during the model runs. Most interestingly, the model showed strong indications of for rapid multiphase cycling of halogen species and an exciting link between the chemistry of bromine and iodine: Iodine is taken up on the particles in form of HOI, which acts as a source of I^- to the aqueous phase. This then leads to the release of ICl , IBr and later Br_2 into the gas phase. These species get photolysed quickly and yield bromine atoms, which then rapidly react with ozone to form bromine monoxide BrO . During this process a significant amount of ozone is destroyed (0.6 ppt/h), surprisingly not as a direct result of the iodine source, but as an indirect effect via bromine chemistry.