

COST Report

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In the framework of my PhD thesis, I performed field measurements of reactive halogen species at Mace Head and Mweenish Bay at the Irish West Coast. The measurements were made using Long-Path Differential Optical Absorption Spectroscopy (DOAS). At Mace Head the reactive halogen species IO, I₂ and BrO could be detected, whereas at Mweenish Bay only IO and BrO could be identified. At Mace Head it was possible to compare our path-averaged results to in-situ techniques: For IO a comparison with laser-induced fluorescence (LIF) was performed and I₂ was compared to a denuder technique and broad band cavity enhanced absorption spectroscopy (BB-CEAS). At Mweenish Bay two light paths with different lengths were established to obtain information about the spatial distribution of the trace gases of interest and also measurements of ultrafine particles were performed. The results of both measurement sites support the so-called “hot-spot-theory” according to which the reactive iodine species have to be inhomogeneously distributed to explain the observed particle formation. However, to get a better understanding of the spatial distribution of the trace gases and the mechanisms that lead to the formation of new particles, it is necessary to implement the data in a model. The aim of this STSM is to implement the experimental results in the model MISTRA to obtain a better understanding of the related processes and also to be able to make global estimates for both, emission of reactive halogen species and particle formation in coastal environments. Since the reactive halogen species are involved in several atmospheric processes and particle formation can affect local climate, this tasks are of great relevance.

In the first step of the STSM, the iodine flux necessary to explain the observed formation of iodine oxide IO was determined. Therefore, iodine emissions corresponding to a seaweed abundance similar to that at the measurement sites were varied in the model until the obtained mixing ratios of IO matched the observations. In the next step more iodine sources were included in the model run, to make the runs more realistic and to study the impact of more sources on the obtained mixing ratios. It turned out, that when including more sources the iodine emissions in the model had to be reduced in order to reproduce the observed mixing ratios with the model. With the final iodine emission three model runs were performed: In run 1 a daytime model run over 4 hours starting at noon with an output every minute was performed. In an attempt to make the model set-up as close to reality as possible, the seaweed abundance implemented was based on seaweed maps of the area around Mace Head. Run 2 was a nighttime model run over 8 hours with an output every minute to compare model results to night time measurements and to study nighttime chemistry. In run 3 a high-resolution run with an output every 10 seconds and just crossing one seaweed bed was performed to test if the model is able to reproduce the high heterogeneity that was in the framework of the field measurements.

Results:

First we discovered that there is a strong vertical transport of inorganic iodine. 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 showed the formation of fresh particle, which was observed during the field campaigns. However, the formation of fresh particles as it is implemented in the model, is more of qualitative than quantitative nature. The model also showed that the IO_2^- in sulphate as well as sea salt particles gets oxidized to IO_3^- during the model runs. Most interestingly the model showed strong indication for aqueous cycling: The 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 back into the gas phase. These species get photolyzed quickly and yield bromine atoms, which then rapidly react with ozone to form bromine monoxide BrO. In this process a significant amount of ozone is destroyed (0.6ppt/h). Surprisingly not as a direct result of the iodine source, but as an indirect effect via bromine chemistry (see Figures 1 and 2).

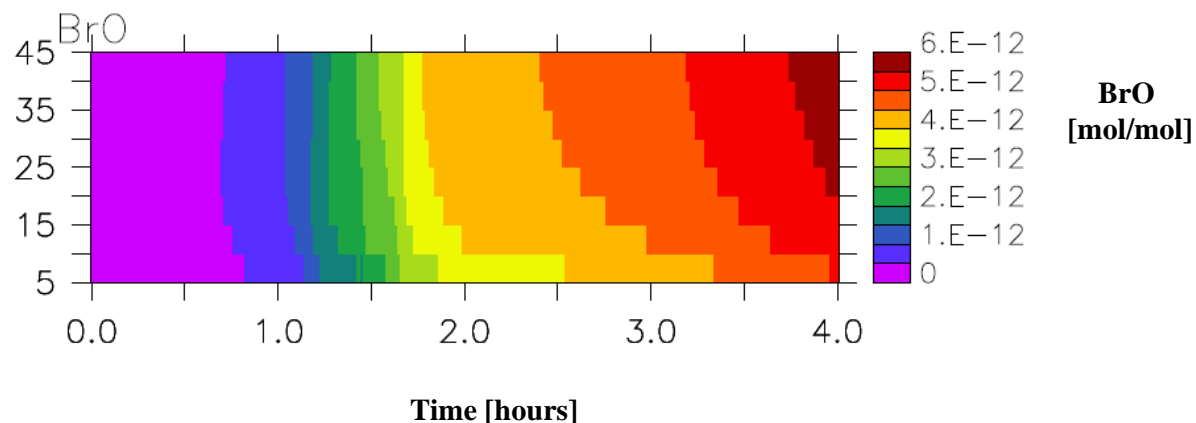


Figure 1: Iodine induced increase of BrO

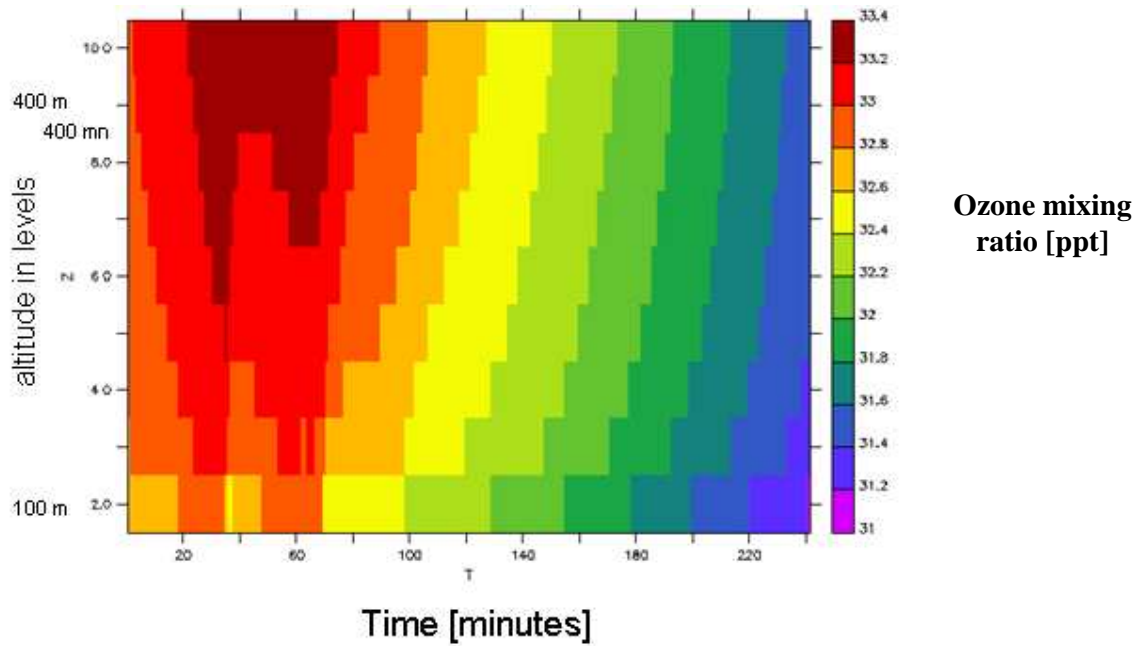


Figure 2: Decrease of ozone mixing ratio due to enhanced bromine atoms

The results of this STSM are new and will- together with results from field measurement- be part of a publication.