Measuring mesoscale horizontal and vertical distributions of reactive halogen oxides in Antarctica

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Motivation
Halogen compounds have an important influence on the atmosphere of the Earth. In the polar troposphere chlorine, bromine and iodine released from sea salt particles or produced by photolysis of halocarbons, I2, can be emitted by the ocean. These compounds destroy ozone which strongly influences the equilibrium of tropospheric chemistry. Especially sudden increases in reactive bromine in polar springtime can cause nearly complete ozone destruction in the boundary layer over areas of several million square kilometers. The origin of these elevated concentrations are heterogeneous, autocatalytic reactions on sea ice surfaces and sea salt aerosols exponentially increasing the reactive bromine (bromine explosion).

Model results also indicate that even small concentrations of iodine species in the range of a few parts per trillion (ppt) could have important consequences for tropospheric chemistry: increased ozone destruction, possible particle formation with impact on the (local) climate and change of the oxidation properties of the troposphere resulting for example in elevated mercury deposition with according consequences for the local biosphere.

Despite major scientific efforts many details of polar halogen chemistry such as distribution, vertical profiles, sources and sinks and key processes are still not completely understood.

Objectives
• Retrieval of vertical BrO and IO profiles over the Antarctic Weddell Sea under different conditions using ship - and helicopter borne measurements.
• Investigation of the sources and release mechanisms of reactive bromine.
• Study of possible sources and atmospheric release mechanisms of IO.
• Comparison of results from active and passive measurements in order to explain discrepancies in past measurements.

Instrumentation

Differential Optical Absorption Spectroscopy (DOAS)
DOAS is based on the separation of narrowband differential absorption structures from broadband absorption and scattering. The differential absorption structures are characteristic for each species which allows a reconstruction of the measured spectrum to determine the different concentrations. One main advantage for atmospheric chemistry measurements is that it is a contact free technique that does not influence chemistry.

\[
I(\lambda) = I(\lambda)_{\text{exp}} - I(\lambda)_{\text{cal}} = \sum_n (c_n \lambda_n - I_n \lambda_n) - \sum I(\lambda)_{\text{cal}} - \sum I(\lambda)_{\text{cal}} \cdot P(\lambda)
\]

where, \(I(\lambda)\): measured optical depth

Multi-Axis DOAS
MAX-DOAS is a passive measurement technique that uses scattered light as light source. It measures slant column densities (SCDs) i.e. concentrations integrated along the light path. By scanning several elevation angles or at different flight altitudes, vertical profiles of absorbing trace gases and aerosols for heights up to several kilometers can be computed.

The retrieval of vertical profiles (Yilmaz, 2012) is based on the optimal estimation method and uses a Monte Carlo radiation transport model.

Measurement Campaigns ANT XXIX-6/7
Measurements will be performed during two expeditions of the German Research ice breaker RV Polarstern:
ANT XXIX-6 (8.6.-12.8. 2013): from Cape Town into the sea ice, along the Greenwich meridian, crossing the Weddell Sea from South to North and arriving in Punta Arenas/Chile.
ANT XXIX-7 (14.10.-16.10. 2013): departing from Punta Arenas, several transects into the sea ice and back into the open ocean, 3 ice camps of ca. 8 days.

 Instruments deployed: two MAX-DOAS, one ship- and one helicopter borne; a Longpath-DOAS from aboard the ship and a Cavity Enhanced-DOAS aboard the ship and on the ice (operated by Johannes Zieckle)

Fig. 1: Bromine Chemistry modified

Iodine oxide strongly enhances ozone destruction. Even small concentrations of iodine have a strong impact due to coupling mechanisms with reactive Br and Cl. Oxidized iodine can lead to formation of ultra-fine particles. Although not yet completely confirmed, indications show that atmospheric IO abundance are due to the photodegradation of organic and inorganic precursors released by macroalgae and phytoplankton in the ocean and at the bottom of sea ice.

Fig. 2: Iodine chemistry in the marine boundary layer, modified

References

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