



Spectroscopic measurements of reactive halogen compounds at the Cape Verde Islands, over the Eastern Tropical North Atlantic and at the Mauritanian coast

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Reactive Halogen compounds like the halogen oxides BrO and IO play an important role in tropospheric Chemistry. BrO and IO can destroy ozone in catalytic reaction cycles, also they influence the concentration of hydrogen radicals and can thus strongly influence the atmospheric oxidation capacity. IO is also involved in the formation of new aerosol particles and oxidizes dimethyl sulfide..

Reactive halogen species originate from biogenic and abiotic sources. A biogenic source of Bromine in the MBL are volatile halogenated hydrocarbons, like CHBr₃. They are emitted by marine algae and accumulate in the troposphere. This source is most relevant in coastal and in upwelling regions. Organohalogens are also emitted by halophytes, i.e. plants (e.g. mangroves in tropical regions) growing in areas with high salt concentrations like salt marshes for instance at the Mauritanian coast. As an example for an abiotic source, halogens reach the MBL as sea salt aerosols, from which Br₂, BrCl or I₂ can be released and become photolysed, thus yielding Br or I atoms. It is not clear yet, how important abiotic halogen release is on a global scale. But considering the huge sea surface even a small open ocean halogen release will have a significant global impact.

In our efforts to elucidate the sources of the RHS measured at the Cape Verde Atmospheric Observatory, several Differential Optical Absorption Spectroscopy (DOAS) measurements in the Eastern Tropical North Atlantic region were performed during the last four years as a part of the SOPRAN (Surface Ocean Processes in the ANthropocene) project. We compare the results of three ship-borne MAX-DOAS measurements (January 2007, January 2008 and Mai June 2010) with the long term measurements of the MAX DOAS instrument hosted at the Cape Verde Atmospheric Observatory. Furthermore the results of active Long Path DOAS (LP-DOAS) vertical profile measurements with four light paths are presented for the trace gases BrO, IO and O₃. These measurements were performed simultaneous to the Ship campaign in June 2010 and additionally also long term LP-DOAS observations were made between July and November 2010..For the intensive measurement period in June 2010 also several measurements with a newly developed Cavity Enhanced (CE) – DOAS instrument were performed to observe in-situ IO concentrations.

The LP-DOAS results show BrO peak concentrations of up to 5 ppt in the morning and the evening and strong diurnal variations. The absolute BrO concentration also varies considerably for different meteorological conditions. IO concentrations seem to be lower than reported so far and are typically below the detection limit of ~0.8ppt. These results are in agreement with our CE-DOAS measurements. But surprisingly we observed regularly very high concentrations of formaldehyde of up to 4 ppb, peaking at noon.

The known, potential spectral evaluation problems due to cross section correlation between water vapour and IO and the correlation of formaldehyde with BrO will be discussed.

Furthermore, measurement results from LP-DOAS and MAX-DOAS from the Mauritania coast are presented which could not observe IO and BrO. The derived upper limits for their concentration indicate that the continental influence is probably not important for the halogen concentration at the open ocean.