

Overview of Reactive Halogen Species in the Marine Boundary Layer observed with different DOAS techniques

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Reactive halogen species (RHS) in the in the marine boundary layer have the potential to influence the ozone budget on a global scale, but their release processes are partly uncertain and measurements on global scale with the required precision are rare. Their direct dependence on halogenated compounds as precursors is uncertain as well as the precursors' fluxes. To clarify these interdependencies various campaigns during the last years with a broad range of different measured species were performed in the Mauretanian Upwelling, Cape Verde and the eastern tropical Pacific between 2009 and 2014 mostly within the SOPRAN project (BMBF Förderkennzeichen 03F0611F). They are used to obtain a picture of the global distribution of reactive halogen species (RHS) in the marine boundary layer (MBL) and their driving mechanisms. Cavity-Enhanced (CE) and MAX-DOAS measurements were performed on several ship and land campaigns. In the later case they were also accompanied by Longpath (LP)-DOAS measurements. An overview of the measurement results will be presented.

Iodine monoxide measurements over the open tropical ocean show agreement for different measurements, most measurement techniques and different campaigns. Especially during SOPRAN M91 in the Peruvian upwelling region very good agreement for MAX-DOAS and CE-DOAS inferred IO mixing ratios was found. The good agreement between the retrieved NO₂ and water vapor mixing ratios of the MAX-DOAS and CE-DOAS measurements further confirms the applied aerosol and trace gas retrieval. Values for BrO volume mixing ratios in the marine boundary layer apart from so-called 'BrO-events' in the upwelling regions of the eastern tropical Atlantic remain challenging. The limiting factors were often not instrumental limitations, but could rather be found in measurement errors of literature cross-sections and the way in which spectral data was analyzed. For coastal studies on Cape Verde LP-DOAS measurements as well as MAX-DOAS measurements agreed on BrO volume mixing ratios of 2-3ppt, while MAX-DOAS measurements on the open ocean regularly showed lower values. This indicates that observations at Cape Verde are likely not representative for open ocean conditions. A reanalysis of ship-borne MAX-DOAS data over the Atlantic and the Pacific will be presented including first conclusions. Furthermore, upper limits for glyoxal volume mixing ratios were calculated for two months of MAX-DOAS data in the tropical Atlantic and eastern tropical Pacific. These 2σ upper limits were found at $4 \cdot 10^{14}$ and $7 \cdot 10^{14}$ molec/cm², corresponding roughly to 20-30ppt, which is a factor of four smaller than previous observations on the tropical Pacific.