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Observation of Chlorine and other RHS Species in the Marine Boundary Layer at Cape Verde Atmospheric Observatory

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Reactive halogen species (RHS) have a significant influence on the marine atmosphere as they react with ozone, change the oxidation capacity and may form particles. However, their release processes, the emissions and concentrations of different RHS species are mostly uncertain. Only a few measurements exist and results are sometimes very different. Most studies focused on iodine and bromine species. Chlorine was mostly not investigated as it is typically more difficult to measure and it was expected that it has a smaller impact on the marine atmosphere and thus less significant. Recent model studies show that this assumption is probably not correct and more information of chlorine is needed to understand the processes in the marine atmosphere. We present results from measurements at the Cape Verde atmospheric research station (CVAO) during the HALOCAVE campaign in 2010 (June to October) using the LP-DOAS technique. Simultaneous measurements of a series of trace gases ranging from RHS like BrO, IO, ClO, OClO and other species like NO_2, O_3, CHOCHO, HCHO, SO_2, HONO, NO_3 have been performed along different measurement paths.

In contrast to previous observations we could not observe IO above the detection limit of 0.5ppt. Also simultaneous CE-DOAS measurements could not observe IO above the detection limit of 1.0ppt. Profile retrievals of IO MAX-DOAS measurements show a concentration between 0.2 to 0.5ppt and thus in agreement with our LP-DOAS observations but not with previous findings. For BrO we found with the LP-DOAS concentrations up to 5ppt, a characteristic daily cycle with high variability from day to day indicating various metrological parameters to be significant for the bromine emission. ClO could not be observed above the relative high detection limit of approx. 25ppt. However, we found significant OClO concentrations in the night of up to 8ppt, which is most likely formed from ClO. This indicates significant chlorine concentrations in the marine atmosphere. Due to missing loss from photolysis, the OClO is relative stable during the night and these observations can be used with model calculations to estimate the ClO levels and chlorine emissions. With basic calculations we retrieve a ClO level during the day of below 7.5ppt and thus below our detection limit. But still chlorine would have a significant influence on atmospheric processes.

We will present results and conclusions of these observations of RHS from LP-DOAS and MAX-DOAS as well as from other trace gases. Spatial variability and vertical profiles will also be addressed. The data suggest that previous conclusion about the RHS chemistry at Cape Verde need to be reviewed. Especially composition and variability from day to day requires a more detailed analysis including meteorology rather than average daily cycles of RHS species.