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Unexpected autumnal halogen activity in the lower troposphere at Neumayer III/Antarctica

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The influence of Reactive Halogen Species (RHS, like IO, BrO, ClO, etc.) on the lower polar troposphere has been subject of intense research for several decades. Ozone Depletion Events (ODEs) caused by the catalytic reaction of tropospheric ozone with inorganic halogen species or the oxidation of gaseous elemental mercury are well observed phenomena that occur during the respective springtime in both Arctic and Antarctica.

Chlorine atoms also react more efficiently with hydrocarbons than e.g. OH radicals and all reactive halogen species can furthermore influence the atmospheric sulphur or nitrate cycles. While an autocatalytic release mechanism from salty surfaces, the so called bromine explosion, has been identified to rapidly increase inorganic bromine mixing ratios many aspects of atmospheric halogen chemistry in polar regions remains unclear.

Since January 2016, we are operating an active Long Path DOAS instrument at Neumayer III on the Antarctic Ekström shelf ice designed for autonomous measurements. This instrument is able to detect a wide range of trace gases absorbing in the UV/Vis including ClO, BrO, OClO, IO, I_2, OIO, ozone, NO_2, H_2O, O_4, and SO_2 at a temporal resolution of 5-30 minutes.

The analysis of the first year of observations shows several surprising findings which give new insights into polar halogen chemistry. E.g. we observe surprisingly strong bromine activity in late summer and autumn (in addition to well-known springtime events) with mixing ratios often higher than 20 pptv. We could even observe peak mixing ratios of 110 pptv. The observed BrO levels could be the result of local/regional chemistry rather than long-range transport and modulated by the stability of the boundary layer. Also, there are hints for NO_x - driven halogen activation. Furthermore, chlorine monoxide (ClO) and OClO mixing ratios of several ten pptv could be detected on a number of days, however the source mechanism for reactive chlorine remains unclear. We will give an overview of the entire time series and discuss interesting case studies with regard to chemistry, atmospheric conditions and transport.