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Enhanced tropospheric BrO over Antarctic sea ice in mid winter observed by MAX-DOAS on board the research vessel Polarstern

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Abstract. We present Multi AXis-Differential Optical Absorption Spectroscopy (MAX-DOAS) observations of tropospheric BrO carried out on board the German research vessel Polarstern during the Antarctic winter 2006. Polarstern entered the area of first year sea ice around Antarctica on 24 June 2006 and stayed within this area until 15 August 2006. For the period when the ship cruised inside the first year sea ice belt, enhanced BrO concentrations were almost continuously observed. Outside the first year sea ice belt, typically low BrO concentrations were found. Based on back trajectory calculations we find a positive correlation between the observed BrO differential slant column densities (ΔSCDs) and the duration for which the air masses had been in contact with the sea ice surface prior to the measurement. While we can not completely rule out that in several cases the highest BrO concentrations might be located close to the ground, our observations indicate that the maximum BrO concentrations might typically exist in a (possibly extended) layer around the upper edge of the boundary layer. Besides the effect of a decreasing pH of sea salt aerosol with altitude and therefore an increase of BrO with height, this finding might be also related to vertical mixing of air from the free troposphere with the boundary layer, probably caused by convection over the warm ocean surface at polynyas and cracks in the ice. Strong vertical gradients of BrO and O_3 could also explain why we found enhanced BrO levels almost continuously for the observations within the sea ice. Based on our estimated BrO profiles we derive BrO mixing ratios of several ten ppt, which is slightly higher than many existing observations. Our observations indicate that enhanced BrO concentrations around Antarctica exist about one month earlier than observed by satellite instruments. From detailed radiative transfer simulations we find that MAX-DOAS observations are up to about one order of magnitude more sensitive to near-surface BrO than satellite observations. In contrast to satellite observations the MAX-DOAS sensitivity hardly decreases for large solar zenith angles and is almost independent from the ground albedo. Thus this technique is very well suited for observations in polar regions close to the solar terminator. For large periods of our measurements the solar elevation was very low or even below the horizon. For such conditions, most reactive Br-compounds might exist as Br_2 molecules and ozone destruction and the removal of reactive bromine compounds might be substantially reduced.

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