



Coupling of HO_x, NO_x and halogen chemistry in the antarctic boundary layer

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A modelling study of radical chemistry in the coastal Antarctic boundary layer, based upon observations performed in the course of the CHABLIS (Chemistry of the Antarctic Boundary Layer and the Interface with Snow) campaign at Halley Research Station in coastal Antarctica during the austral summer 2004/2005, is described: a detailed zero-dimensional photochemical box model was used, employing inorganic and organic reaction schemes drawn from the Master Chemical Mechanism, with additional halogen (iodine and bromine) reactions added. The model was constrained to observations of long-lived chemical species, measured photolysis frequencies and meteorological parameters, and the simulated levels of HO_x, NO_x and XO compared with those observed. The model was able to replicate the mean levels and diurnal variation in the halogen oxides IO and BrO, and to reproduce NO_x levels and speciation very well. The NO_x source term implemented compared well with that directly measured in the course of the CHABLIS experiments. The model systematically overestimated OH and HO₂ levels, likely a consequence of the combined effects of (a) estimated physical parameters and (b) uncertainties within the halogen, particularly iodine, chemical scheme. The principal sources of HO_x radicals were the photolysis and bromine-initiated oxidation of HCHO, together with O(1D) + H₂O. The main sinks for HO_x were peroxy radical self- and cross-reactions, with the sum of all halogen-mediated HO_x loss processes accounting for 40% of the total sink. Reactions with the halogen monoxides dominated CH₃O₂-HO₂-OH interconversion, with associated local chemical ozone destruction in place of the ozone production which is associated with radical cycling driven by the analogous NO reactions. The analysis highlights the need for observations of physical parameters such as aerosol surface area and boundary layer structure to constrain such calculations, and the dependence of simulated radical levels and ozone loss rates upon a number of uncertain kinetic and photochemical parameters for iodine species.

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