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Simulation of the isotope anomaly (Δ^{17}O) of NOx and nitrate during ozone depletion events in the Arctic boundary layer after polar sunrise

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The first measurements and modelling of the seasonal variations in the isotope anomaly (Δ^{17}O) of atmospheric nitrate (measurements performed in coastal California (La Jolla, CA, USA (33°N)) for one year starting in March 1997) showed a clear link with the relative proportions of chemical reaction pathways leading to the formation of nitrate (Michalski et al., 2003). These authors concluded that the isotope anomaly of nitrate was mainly induced by the isotope anomaly of NO_2 (primarily originating from mass-independent fractionation during the formation of ozone), and modulated by changes in the proportions between reaction pathways leading to nitrate from NOx, on seasonal timescales.

More recently, in spring 2004 at Alert, Nuvanut, Canada (82°N), simultaneous measurements of O_3 mixing ratio and the isotopic composition of atmospheric inorganic nitrate were carried out during Ozone Depletion Events (ODE) (Morin et al., 2007). Analysis of these samples showed short-term variations of $\Delta^{17}O(NO_3^-)$ (days to weeks), and a significant correlation between the variations of atmospheric ozone mixing ratio and of the isotope anomaly of nitrate ($\Delta^{17}O(NO_3^-)$). From mass balance equations, Morin et al. (2007) suggested that this correlation originates from variations in $\Delta^{17}O(NO_2)$, brought about by changes in the relative importance of the three oxidation channels of NO : oxidation by O_3, RO_2 and BrO.

In order to better constrain the analysis, we present here numerical simulations of the

photochemistry of these events using the photochemical box model CiTTyCAT (Cambridge Tropospheric Trajectory model of Chemistry And Transport). Heterogeneous reactions on aerosols are also considered in order to simulate correctly the ozone depletion events. The model is integrated along retro-trajectories that are calculated from ECMWF analyses and that originates from the measurement points. The model is able to calculate the temporal variations of the isotope anomaly of NO_2. The results of the simulations underline the rapid temporal variations of the relative importance of the three oxidation channels of NO and confirm that they are the main drivers in the variation of $\Delta^{17}O(NO_2)$. They also bring new information on the major pathways for nitrate formation.

References: Morin et al., ACP, 7, 1451, 2007 - Michalski et al., GRL, 30(16), 1870, 2003.