



Simulation of the diurnal variations of the isotope anomaly ($\Delta^{17}\text{O}$) of reactive trace gases (NO_x , HO_x) and implications for the $\Delta^{17}\text{O}$ of nitrate.

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The isotope anomaly of secondary atmospheric species such as nitrate (NO_3^-) has potential to provide useful constraints on their formation pathways. Indeed, the $\Delta^{17}\text{O}$ of their precursors (NO_x , HO_x etc.) differs and depends on their interactions with ozone, which is the main source of non-zero $\Delta^{17}\text{O}$ in the atmosphere. Interpreting variations of $\Delta^{17}\text{O}$ in nitrate requires an in-depth understanding of the $\Delta^{17}\text{O}$ of its precursors taking into account non-linear chemical regimes operating under various environmental settings. In addition, the role of isotope exchange reactions must be carefully accounted for.

To investigate the relevance of various assessments of the isotopic signature of nitrate production pathways that have recently been proposed in the literature, an atmospheric chemistry box model (MECCA, Sander et al., 2005, ACP) was used to explicitly compute the diurnal variations of the isotope anomaly of NO_x , HO_x under several conditions prevailing in the marine boundary layer. $\Delta^{17}\text{O}$ was propagated from ozone to other species (NO, NO_2 , OH, HO_2 , RO_2 , NO_3 , N_2O_5 , HONO , HNO_3 , HNO_4 , H_2O_2) according to the classical mass-balance equation applied at each time step of the model (30 seconds typically).

The model confirms that diurnal variations in $\Delta^{17}\text{O}$ of NO_x are well predicted by the photochemical steady-state relationship introduced by Michalski et al. (2003, GRL) during the day, but that at night a different approach must be employed (e.g. « fossilization » of the $\Delta^{17}\text{O}$ of NO_x as soon as the photochemical lifetime of NO_x drops below ca. 5 minutes). The model also allows to evaluate the impact on $\Delta^{17}\text{O}$ of NO_x and nitrate of the frequently made simplifying assumption that $\Delta^{17}\text{O}(\text{HO}_x)=0$ permil, with and without mass-independent fractionation during the $\text{H}+\text{O}_2 \rightarrow \text{HO}_2$ reaction.

Recommendations for the modeling of $\Delta^{17}\text{O}$ of nitrate will be given, based on the extensive model work carried out. In addition, the link between diurnal variations of the $\Delta^{17}\text{O}$ of nitrate precursors and seasonal variations of the $\Delta^{17}\text{O}$ of nitrate will be explored. Perspectives include the implementation of halogen species in this assessment, and the full incorporation of the developed framework into the CAABA-MECCA box model.