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Isotopic composition of atmospheric nitrogen mono- and dioxide

Sarah Albertin, Joël Savarino, Nicolas Caillon, Jean Martins, and Albane Barbero

Institut des Géosciences de l'Environnement (IGE), Université Grenoble Alpes, 38 000 Grenoble, France (albertin.sarah@gmail.com)

Stable isotopes have demonstrated their ability to reveal the transformation processes of chemical compounds in the atmosphere, beyond just as tracers of source emitters. Nitrate (NO_3^-) is an emblematic compound of this approach for which its nitrogen and oxygen stable isotope composition result also from transformation mechanisms occurring in the atmosphere. However, there are still some difficulties to interpret the isotopic composition of the nitrate, mainly due to an unclear understanding of the link between the oxygen and nitrogen isotopic composition of the nitrogen oxides (NO_x = NO + NO_2), the precursors of nitrate in the atmosphere, and the chemical state of the atmosphere. Indeed, oxides of nitrogen are a masterpiece of the oxidative capacity of the atmosphere as they strongly interact as source or sink of ozone and other oxygenated radicals in the atmosphere. Based on ^{17}O-excess (i.e. Δ^{17}O) mass balance, it is expected that Δ^{17}O of NO_2 represent a subtle indicator of the O_3 to peroxyl ratio, in other words an indicator of the chemical activity of the atmosphere.

Demonstrating this causal link between NO_2 isotope composition and the chemical activity of the atmosphere will have a double objective: firstly, the use of the Δ^{17}O of NO_2 as a probing tool of the reactivity of the atmosphere and secondly establishing the isotopic link between NO_2 and nitrate. As nitrate is preserved in snow and ice contrary to NO_2, establishing such isotopic link will allow to use the isotopes of nitrogen and oxygen of nitrate as a tool for probing the chemical reactivity of the present and past atmosphere in a more quantitative way than is done today.

In this perspective, this work aims to develop a high selective and sensitive method to collect NO and NO_2 using honeycomb denuders. The protocol must both ensure a complete collect of the nitrogen oxides and preserve their singular oxygen isotopic composition until mass spectrometer analysis.

Using NO_x generator and monitors and isotope standards, we will show how efficient our system works and present the first in situ Δ^{17}O NO_x measurements performed in the urban area of Grenoble city.