

FINAL REPORT PROGRAM LEFE

Two pages to be written in English

Program LEFE/ action(s) AO INSU 2022	Project Title SIMUL-ISONIT	Years 2022 – 2024
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<p>Context</p> <p>Important knowledge gaps about isotopic transfers and fractionations during conversion of nitrogen oxides (NO_x = nitric oxide (NO) + nitrogen dioxide (NO₂)) into nitrate still persist, limiting the interpretation of atmospheric isotopic measurements of reactive N species.</p> <p>Objectives / scientific questions</p> <p>To address the issue of quantifying N fractionation factors in the reactive N cycle, dedicated experiments should be undertaken in controlled atmospheres. SIMUL-ISONIT was designed to study the oxidation chemistry of the NO_x using the CESAM chamber (LISA), focused on reproducing the nocturnal oxidation pathway of NO₂ to nitrate via O₃ through the heterogeneous hydrolysis of N₂O₅. Off-line sampling of the chamber's reactants (NO₂ and O₃) and products (nitrate) was performed, followed by multi-isotopic analysis at IGE.</p> <p>Main results</p> <p>Over the course of the campaign, 10 experiments were carried out under different conditions (e.g. reagent injection order, reagent mixing ratio, humidity, temperature). Measurements from instruments connected to the chamber were used to assess the consumption of the reagents (NO₂, O₃) and to monitor the formation of the desired product (nitrate).</p> <p>One of the main results of this campaign concerned the high quantity of nitrite measured on blank filters dedicated to the collection of NO₂. Variable and high nitrite blanks (from ca. 27 to 106 nmol per ml of extract solution) significantly complicate the interpretation of isotopic measurements. We believe that the oven drying step of the filter to collect NO₂ is mainly responsible for the high amount of nitrite measured in blank filter extractions. Therefore, another protocol with better handling of nitrite blanks needs to be developed for future studies.</p> <p>¹⁵N and Δ¹⁷O values for NO₂ injected into the chamber range from -39.2 ‰ to -12.3 ‰ and from 1.7 ‰ to 15.2 ‰, respectively. Although subject to an elevated blank effect, the mean ± 1 standard deviation of the blank ¹⁵N is (-5.1 ± 2.4) ‰, significantly higher than the sample values. Due to the high nitrite blank, we cannot assess the fractionation factors associated with the reaction reproduced in the chamber, which was the original scientific aim of this project. However, numerous learnings arise from this campaign, which will help to improve the experimental design of future studies, notably those planned as part of the ERC DOC-PAST (supervised by Joël Savarino).</p> <p>With regard to the production of nitrate in the chamber through the hydrolysis of N₂O₅ into sea salt particles, experiments have shown that prior to the injection of O₃, nitrate can be formed in the chamber, likely from the hydrolysis of NO₂ (see Figure 1 for an example). Nitrate for isotopic analysis must therefore be sampled at different stages of the experiment.</p> <p>The amount of NO₃⁻ measured in filter extractions correlates well with the amount of particulate nitrate expected from the an Aerosol Chemical Speciation Monitor (ACSM) of the chamber (R² = 0.96, Figure 2). Interestingly, filter extractions show a higher concentration than that observed by the ACSM. This is likely because the ACSM only measures the particulate fraction of nitrate, whereas the filters collect both gaseous nitric acid and particulate nitrate. The NO₃⁻ contribution from blank filters was very low (< 0.1 nmol per ml of extract solution), representing on average (0.6 ± 0.9) % of sampled NO₃⁻. In addition, the filters collected in parallel showed very good reproducibility, both in terms of nitrate concentration and isotopic composition. These results give us confidence in the efficiency of our nitrate sampling and isotopic analysis methodology. The ¹⁵N and Δ¹⁷O values for nitrate formed in the chamber range from -24.5 ‰ to</p>		

-17.3 ‰ and from 2.2 ‰ to 5.6 ‰, respectively. The ^{15}N values correlate well with the chamber temperature ($R^2 = 0.9$, not shown here). Interestingly, such an effect is expected, with equilibrium isotopic fractionation between NO_2 , NO_3 , and N_2O_5 enhanced at lower temperatures (Walters et al., 2015). The transferable $\Delta^{17}\text{O}$ of O_3 to NO_2 is estimated at about 45 ‰, in very good agreement with previous studies. Therefore, the method used to generate O_3 (i.e., electrical discharge) in the chamber and collect it for isotopic analysis is suitable for our purpose. Although the contaminated NO_2 samples preclude further interpretation, these results are encouraging to reconduct such experiments. With the now funded ERC DOC-PAST, knowledge learned during this unique experiment will greatly help to better set up the upcoming chamber experiments.

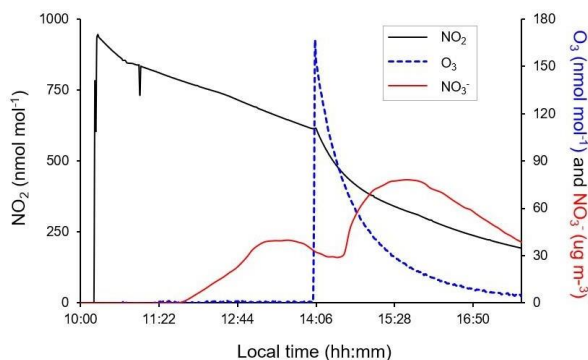


Figure 1. Example of the CESAM chamber monitoring during the SIMUL-ISONIT campaign.

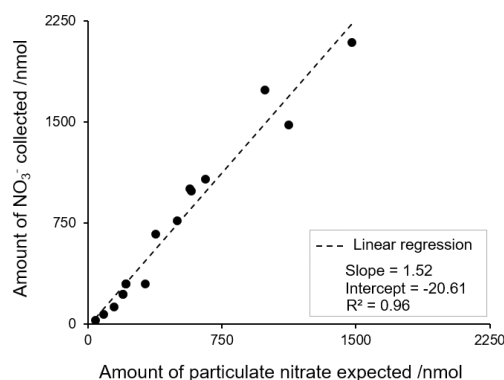


Figure 2. Correlation plot of NO_3^- collected on the first filters as a function of particulate nitrate measured by the ACSM in the chamber during filter collection.

Figure 1 shows a typical experiment performed during the campaign at the CESAM chamber. For this experiment, NO_2 was first injected into the chamber to reach ca. 1 nmol mol^{-1} (at 10:14 LT). We can observe the NO_2 decrease (black line in Figure 1) due to wall absorption and dilution effects. At 10:44 LT, water vapor was injected into the chamber, followed by sea salt (0.1 M NaCl) at 11:03. Using an Aerosol Chemical Speciation Monitor (ACSM) connected to the chamber, we are able to observe nitrate formation after the sea salt injection (red line in Figure 1). This nitrate likely results from the hydrolysis of NO_2 on the salt particles, favored by the high NO_2 concentration in the chamber. At 14:04 LT, O_3 was injected into the chamber (dashed blue line in Figure 1). ACSM measurements show a second nitrate production peak after the O_3 injection, which is thought to be formed by the hydrolysis of N_2O_5 on sea salt particles. Figure 2 shows the amount of nitrate measured in the filter extractions as a function of that expected from the ACSM data. The latter were averaged over each filter sampling period and converted to nmol assuming 100 % collection efficiency.

Future of the project

The project will have a follow up within the ERC DOC-PAST. A full range of chemical reactions to determine their isotopic characteristics is planned at the CESAM and HELIOS chambers for the next 5 years. The aim of the experiments will be to conduct the production of nitrate by different oxidation pathways, including reprocessing the N_2O_5 heterogeneous hydrolysis while better controlling the NO_2 blank in order to quantify the associated isotopic fractionation effect.

Number of publications, communications and theses

N/A. This one-year project was funded on an exploratory basis to submit an ERC. Unfortunately, blank interference prevented any use of the data for publications.

Data availability

Data are stored in personal computers. Given the failure of the experiments, it is not possible to make the data public at this stage.