FINAL REPORT PROGRAM LEFE

Two pages to be written in English

Program LEFE - CHAT	**Project Title: Atmospheric Nitrate Radical Total Reactivity (NITRATE)**	**Years 2019 – 2022**
PI name, email and lab: Véronique Daële, CNRS-ICARE Veronique.daele@cnrs-orleans.fr Other Participating Laboratories: NOAA, Boulder and CSU, Fort Collins, CO (USA)	Other funding sources : Fonds Feder	

Context

The nitrate radical (NO_3) plays an important role in the nighttime tropospheric chemistry as it is among the most important oxidants in the atmosphere, particularly for unsaturated volatile organic compounds (VOCs).

Objectives / scientific questions

The overall objective of this project is to better understand the nighttime chemistry of VOC and NO_3 processing and its implications for air quality and climate change. Scientific questions linked : How this chemistry is important in air masses from different regions of the atmosphere? What are the main chemical processes removing NO_3 radical from the atmosphere? What is the contribution of organics to NO_3 removal in the atmosphere? To gain knowledge on this chemistry, we developed an instrument for the measurement of NO_3/N_2O_5 concentrations. The adaptation of this instrument for the NO_3 total reactivity measurement in ambient air and in laboratory is still under development.

Main results

The instrument to be developed required 1) a sensitive detection for the NO_3 radical at the ppt level based on the cavity ring down spectroscopy (CRDS) technique and 2) the development of a reactor to be coupled to the CRDS for the NO_3 total reactivity studies. Due to Covid-19 pandemic, most of the time was dedicated to the first step, which consisted in modifying the instrument we had in our laboratory to improve its performances for the NO_3 radical detection .

Indeed, to investigate the atmospheric chemistry of NO_3/N_2O_5, a dedicated system for their measurements based on the CRDS has been implemented in our laboratory and has been used for the study of the chemistry of NO_3 reactions with a series of organic and inorganic compounds (Figure 1). The instrument is based on a two-channel cavity ring down spectrometer operating at 662 nm which is used to simultaneously measure the concentrations of NO_3 (1st channel) and N_2O_5 + NO_3 (2nd channel). The second channel is heated to convert N_2O_5 to NO_3 and total NO_3 representing the sum of NO_3 and N_2O_5 is then measured. The air sample entering the CRDS system flows through a filter to remove aerosols, which scatter the 662 nm and tend to enhance the noise in the system. The combined loss of NO_3 and N_2O_5 to the walls of the instrument and the filter located upstream of the device is estimated to be less than 20% and 4%, respectively, for NO_3 and N_2O_5; these losses are accounted for in calculating the concentrations. The uncertainties in the absorption cross section of NO_3 radical at 662 nm and the ratio of the cavity length to the length over which NO_3 and N_2O_5 are present are accounted for in the estimated uncertainties. Based on these factors, the overall (asymmetric) accuracy of the NO_3 and N_2O_5 measurements, are estimated to be +/-10%. The detection sensitivities obtained are: for NO_3: 2 ppt with an integration time of 1 s and 1ppt for an integration time of 30 s; and for N_2O_5: 10 ppt with an integration time of 1 s and 5 ppt for an integration time of 30 s (Figure 2).

The setup of the basis to build up of the reactor to be coupled to the CRDS for the NO_3 total reactivity studies has also been performed. The future planning is the adaptation of the flow reactor to the improved CRDS system. We will use one cavity as a "*Reference channel*" where NO_3 will flow at a constant initial concentration and the other cavity as "*Reactivity channel*" in which, NO_3 will also flow at constant initial concentration in addition to ambient air. This method will allow to gain temporal resolution and will provide a better precision due to simultaneous measurements of the NO_3 concentration.

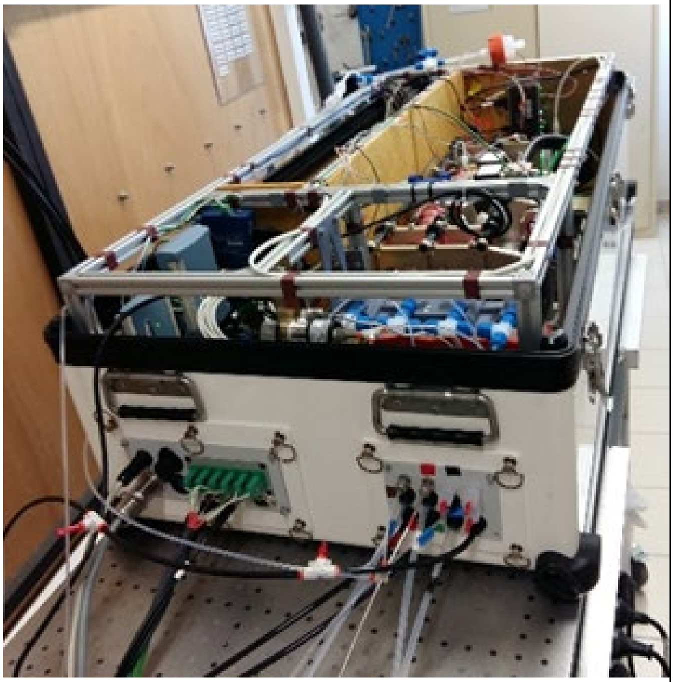

Figure 1

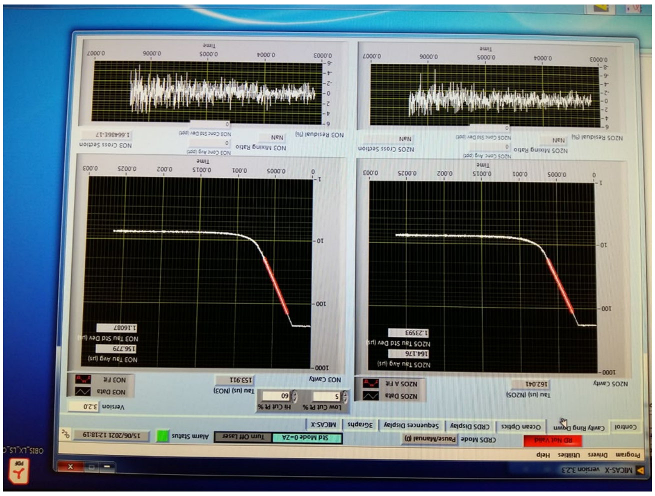

Figure 2

Figure 1 : Instrument based on the cavity ring down spectroscopy (CRDS) technique for the detection of NO_3, on which will be coupled the reactor dedicated to the NO_3 total reactivity studies.

Figure 2: Example of representative signals of NO_3 and N_2O_5 measurement with the CRDS

Future of the project :

The adaptation of the flow reactor to the CRDS system is underway. The two cavities will be used, respectively, as a “*Reference channel*” where NO_3 will flow at a constant initial concentration and the other cavity as “*Reactivity channel*” in which, NO_3 will also flow at constant initial concentration in addition to ambient air. The system will be tested using our atmospheric simulation chamber HELIOS then in the field using the supersite of CNRS campus at Orléans.

Number of publications, communications and theses

Présentation of the instrument at « Ateliers Nationaux INSIS-INSU - Instrumentation pour le suivi environnemental », on September 29, 2021

Data availablility

Not applicable