FINAL REPORT PROGRAM LEFE

Program LEFE/CHAT	Project Title: NH3-IDF Ammonia measurements in coincidence in Ile-de-France region: integrated and in situ	Years 2019 – 2020

PI: **Pascale CHELIN** pascale.chelin@lisa.ipsl.fr LISA (Créteil, France) Participating Laboratories : LISA, IMT Nord Europe, LSCE, LATMOS	Contribution to: ACROSS (MOPGA, ANR, LEFE-CHAT) Other funding sources : UPEC

Context

Ammonia (NH_3) plays an important role in springtime smog events in Europe, including France and the Ile-de-France region, as precursor of ammonium particles. Monitoring the atmospheric concentrations of NH_3 is essential for improving air quality models and for quantifying the fluxes characterizing the nitrogen cycle. The measurement of atmospheric ammonia concentrations is not yet subject to regulation (in the sense of the European directives) and is really challenging.

Objectives / scientific questions

In the project, we proposed to combine different independent and complementary measurements of atmospheric ammonia: vertically integrated column and *in situ* in the Paris megacity, in order to give information regarding the representativeness of NH_3 vertically integrated measurements to estimate surface concentrations.

Main results

First of all, a measurement campaign was carried out at Creteil in spring 2019 including an *in situ* analyzer for measuring NH_3 at the surface (PICARRO G2103 from IMT Nord Europe based on Cavity Ring Down Spectroscopy), combined with measurements of NH_3 total columns using the OASIS ground-based remote sensing observatory of the LISA (**Figure 1**). Unfortunately, no peak concentration of NH_3 is measured during this period, since we probably missed the manure spreading time in rural areas. This induced that combining measurements of ammonia with different techniques implies to have all the instruments operational for a long period in springtime. However, those first results showed a clearly different diurnal behavior of atmospheric ammonia concentrations at the surface and those vertically integrated over the total atmospheric column.

Then LISA got an *in situ* analyzer in early 2020 (AP2E based on Optical Feedback Cavity Enhanced Absorption Spectroscopy), but unfortunately no measurement campaign could be planned during the first lockdown in March 2020 due to COVID pandemic. Moreover, we could not perform in 2020 an intercalibration campaign for measuring NH_3 at the surface, to check the time response and the potential bias of our *in situ* analyzer. The intercalibration campaign (AMICA) was postponed and done in autumn 2021 at the INRAE Grignon site, and implicated 8 different institutes.

Additionally, we did a detailed analysis of the diurnal evolution of ammonia as observed in the OASIS total columns from ground-based remote sensing and at the surface from an *in situ* analyzer in Paris (LSCE at SIRTA site), France, during a major pollution event in late March 2012. The original aspect is the characterization of the diurnal variation of atmospheric ammonia, analyzing both the link with the formation and volatilization of ammonium particles and the vertical dilution in the atmospheric boundary layer. Spring 2012 was one of the most polluted periods since 2007, with a succession of persistent pollution events (Petit et al., 2015, 2017). Despite a wide variety of factors influencing ammonia, our study distinctly identifies the crucial role of vertical mixing within the atmospheric boundary layer for explaining the difference between the evolution of ammonia at the surface and that integrated over the total column (**Figure 2**). Indeed, the increase of the mixing boundary layer entrains vertical dilution of atmospheric pollutants within the boundary layer and thus a relative reduction of air pollutant concentrations near the surface (but not over the total atmospheric column).

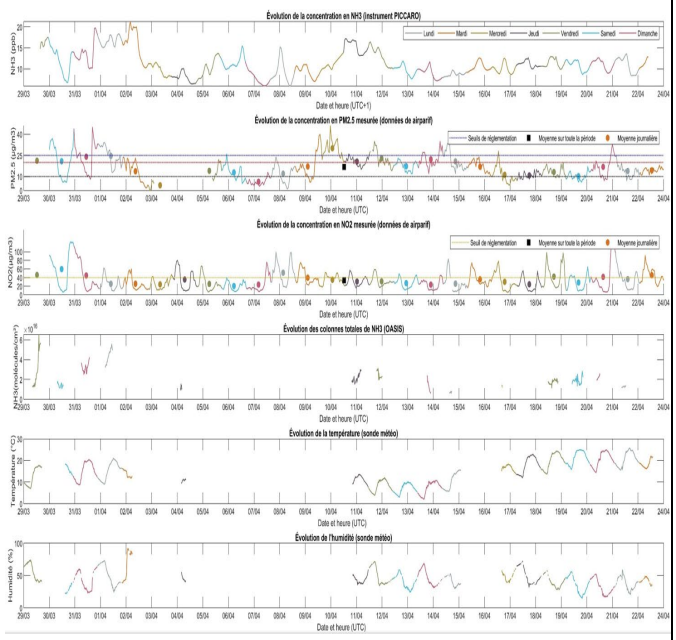

Figure 1: Time series of pollutant concentrations (at the surface and integrated for NH_3 measured by OASIS observatory) and meteorological parameters between 29th March and 23rd April 2019 at Créteil.

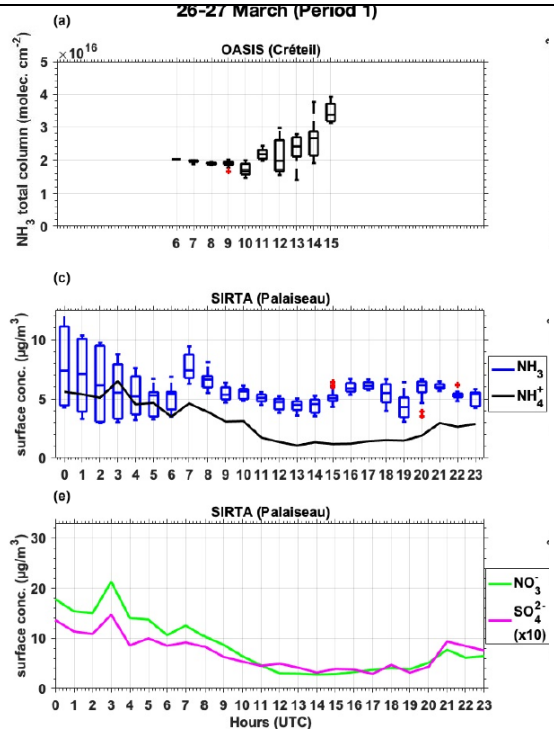

Figure 2: Average diurnal evolution of total column NH_3 (a), surface NH_3 and NH_4^+ (c) hourly median surface measurements of NO_3^- and $SO_4^{(2-)}$ (e) for period 1. Hourly boxplots of NH_3 total column retrieved from OASIS (a) and hourly boxplots of NH_3 from surface measurements show within the boxplot the median as a line in the plot, the 25th and 75th percentile as the lower and upper border of the box, and whiskers that extend to the most extreme data points, whereby outliers are separately marked with a "+".

Future of the project:

A key achievement of this project is the coordination aspect since experts for ammonia measurements were brought together for the first time and a national consortium on NH_3 has emerged.

In order to fully exploit all the results obtained during this multi-instrumental project, a better chemical characterization for comprehensive understanding of gas–particle partitioning over the column in needed. A quantitative ammonia–ammonium equilibrium throughout the atmospheric column (as a function of altitude) should be considered from dedicated *in situ* measurements field campaigns. This is our next project with the development of innovative spectroscopic instrumentation aboard tethered balloons, capable of simultaneously measuring the vertical distribution of ammonia and particle components, in combination with chemistry–transport models.

Publications and communications

Tournadre, B., Chelin, P., Ray, M., Cuesta, J., Kutzner, R. D., Landsheere, X., Fortems-Cheiney, A., Flaud, J.-M., Hase, F., Blumenstock, T., Orphal, J., Viatte, C., and Camy-Peyret, C.: Atmospheric ammonia (NH_3) over the Paris megacity: 9 years of total column observations from ground-based infrared remote sensing, *Atmos. Meas. Tech.*, 13, 3923–3937, https://doi.org/10.5194/amt-13-3923-2020, 2020.

Kutzner, R. D., Cuesta, J., Chelin, P., Petit, J.-E., Ray, M., Landsheere, X., Tournadre, B., Dupont, J.-C., Rosso, A., Hase, F., Orphal, J., and Beekmann, M.: Diurnal evolution of total column and surface atmospheric ammonia in the megacity of Paris, France, during an intense springtime pollution episode, *Atmos. Chem. Phys.*, 21, 12091–12111, https://doi.org/10.5194/acp-21-12091-2021, 2021.

Kutzner, R. D.: Evolution of Ammonia and Ammonium Particles analyzed by Remote Sensing from the Ground and Space, PhD dissertation, University of Paris Est, France, Dec. 2021.