Nitrogen's stable isotopes as a proxy to determine ammonium sources in PM using a Monte Carlo's simulation

S. Weber[1], B. Golly[1], O. Favez[2], S. Conil[3], J. Savarino[1], J-L Jaffrezo[1]

[1]LGGE-CNRS, Univ. Grenoble Alpes, Grenoble, 38000, France
[2]INERIS, Verneuil-en-Halatte, 60550, France
[3]ANDRA, Châtenay-Malabry, 92298, France
Keywords: ammonium, isotope, Monte Carlo, $\delta^{15}N$
Presenting author email: samuel.weber@ens.fr

During cold periods (from November to April) in France, PM concentrations regularly exceed the standard prescribed 50 µg.m^{-3} limit, which about 50 % in mass is composed on ammonium nitrate (NH_4NO_3) (Rouïl et al. 2015). The continental scale of such events is a threat to human health and decrease significantly the quality of our environment. The ammonium (NH_4^+) is suspected to come from different sources, especially from the agricultural ammonia (NH_3) but there is no direct evidence of it. The INACS program aims to investigate the sources proportion in the PM using several methods. This work tries to distinguish and quantify the source apportionment using nitrogen stable isotopes from ammonium nitrate in the PM since previous studies (Felix et al. 2014) highlighted the high level of correlation between the NH_4^+ concentration and the $\delta^{15}N$ of NH_4^+.

From 2011 to 2013, PM were collected at 7 stations in France at daily sampling rate. $\delta^{15}N$ of NH_4^+ was measured at these sites, ranging from ambient rural to urban background. Besides these isotopic measurements on ambient aerosol samples, the isotopic characterization of different emissions sources (traffic, biomass burning, and agricultural activities) was performed to obtain their specific source isotopic signatures. To the best of our knowledge, this database constitutes probably the most extensive dataset studied so far, with more than 500 $\delta^{15}N$ of NH_4^+ aerosols' observations.

In order to take into account the isotopic variability of the sources, a stochastic Monte Carlo's simulation (MCS) was conducted. This approach has in the past demonstrated its applicability for source apportionment method (Sheesley et al. 2011). Applying MCS to our dataset gives a probability distribution function (PDF) for each source and observation day as shown in Fig. 1 for the 2nd March 2013 in a French rural background site.

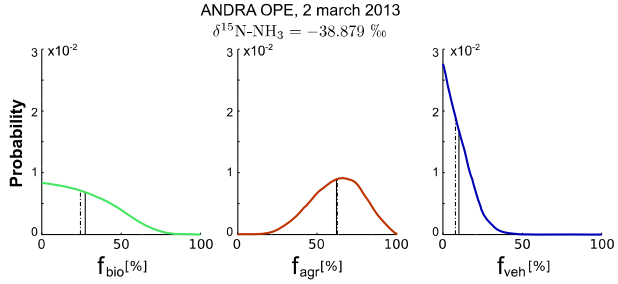

Fig. 1: PDF of the biomass combustion (green), agriculture (red) and vehicle (blue) contribution in the total NH_4^+ of the PM. The doted line is the median and the black one the mean of the PDF.

The three different sources are well separated for all observation but the ammonium concentration attributed to the biomass burning ($NH_4^+{}_{bio}$) has an important uncertainty due to its intermediate isotopic signature. During presentation this limitation will be discussed in more details. Nevertheless the contributions of the three factors are significantly different between the spring events and the atmospheric background. Long time series analysis shows that the contribution of the NH_3 emission source have an important variability in the total NH_4^+ concentration over the year. The vehicular emission ($NH_4^+{}_{veh}$) is the main source emitter during summer while during the spring pollution events the agricultural $NH_4^+{}_{agr}$ makes up to 65±12 % of the total NH_4^+ mass whereas it is around 10 % for the rest of the year. It also appears that during some high concentration PM events, vehicle exhaust emissions can be the main source of ammonium with $[NH_4^+]_{veh} > 5$ µg.m^{-3}.

The geographical areas of origins for NH_4^+ in the PM are also investigated using the Potential Source Contribution Function (PSCF). It shows that in the north part of the France during the spring events $NH_4^+{}_{agr}$ is mainly coming from the E-NE whereas $NH_4^+{}_{veh}$ is more of local origin. However in some stations the origins may differ and highlight local or regional processes for agricultural or biomass NH_4^+.

Those results are also coupled with a detailed PMF approach at the French rural background site in order to link the isotopic and chemistry tracers. The main interest is to improve understanding of the dynamics of the source factors' during spring events according to the isotopic information in the PMF.

This work was supported by the INACS and INACS2 programs funded by the ADEME. The authors wish to thank all of staff from the AASQA and ANDRA for the samples and CARA's program from the LCSQA.

References

Rouïl et al, (2015), *Pollution atmosphérique*.

Felix et al, (2014), *Atmos. Environ.* **(95),** 563-570.

Sheesley et al, (2011), *Atmos. Environ*, **45 (23)**, 3874-3881.