Characterization of Nitrogen Isotopic Composition in Fine Aerosol at a Central European Rural Background Station.

Vodička, Petr
2018

CHARACTERIZATION OF NITROGEN ISOTOPIC COMPOSITION IN FINE AEROSOL AT A CENTRAL EUROPEAN RURAL BACKGROUND STATION

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Keywords: PM1 atmospheric aerosols, Total nitrogen, $\delta^{15}N$ isotope ratios, Central Europe, Seasonal trends

INTRODUCTION

Studies of isotope ratios in atmospheric aerosols is relativelly new approach which can provide unique information on source emissions together with physical and chemical processes in the atmosphere (e.g. Kawamura et al., 2004). Here, we present seasonal variations in $\delta^{15}N$ of total nitrogen (TN) in the PM1 fraction of atmospheric aerosols at a rural background site in Central Europe.

EXPERIMENTAL SETUP

Fine aerosol was sampled for 24 h every second day from September 27, 2013 to August 9, 2014 on pre-baked quartz fibre filters at the Košetice rural background site (N49°35, E15°05, 534 m a.s.l..; part of the EMEP, ACTRIS, and GAW networks) in Central Europe (e.g. Schwarz et al., 2016). With some sampling gaps, we collected 146 samples, which were subsequently analyzed by EA-IRMS (elemental analysis - isotope ratio mass spectrometry) for stable nitrogen isotope ratios ($\delta^{15}N$) in total nitrogen (TN).

Nitrogen in collected aerosol was also analyzed for water-soluble ions (NO_3^-, NH_4^+) and content of organic nitrogen (OrgN) was calculated from following equation: $OrgN = TN - 14*[NO_3^-/62 + NH_4^+/18]$

Beside this, for data analysis were also used meteorological data and concentrations of gaseous pollutants measured by Czech meteorological institute on-line on site.

RESULTS AND CONCLUSIONS

Seasonal averages of $\delta^{15}N$ for aerosol TN are depicted in Fig. 1 (left) and showed the maximum enrichment of ^{15}N in summer and the lowest in winer. Similar seasonal patern has been observed also in other studies (e.g., Kundu et al, 2010), however, a large variation of $\delta^{15}N$ at the Košetice site in comparison with other works suggesting bigger diversity of aerosol sources on site, especially in winter and summer.

A comparison of $\delta^{15}N$ with NO_3^-, NH_4^+ and OrgN revealed that although a higher content of NO_3^- was associated with a decrease in $\delta^{15}N$ values in TN, NH_4^+ and OrgN had the opposite influences. The highest concentrations of nitrate, mainly represented by NH_4NO_3, originated from the emissions from biomass burning, leading to lower $\delta^{15}N$ values of approximately 14‰ in winter. During spring, the percentage of NO_3^- in PM1

decreased, and ^{15}N enrichment was probably driven by equilibrium exchange between the gas and aerosol phases ($NH_3(g) \leftrightarrow NH_4^+(p)$) as supported by the increased ambient temperature (Fig. 2).

The majority the yearly data showed a strong correlation between $\delta^{15}N$ and ambient temperature (Figure 2), supporting an enrichment of ^{15}N via isotopic equilibrium exchange between the gas and particulate phases. This process seemed to be one of the main mechanisms for ^{15}N enrichment at the Košetice site, especially during spring. The most ^{15}N-enriched summer and most ^{15}N-depleted winter samples were limited by the partitioning of nitrate in aerosols (see size of circles inn Fig. 2) and suppressed equilibrium exchange between gaseous NH_3 and aerosol NH_4^+. And thus, we observe a seasonal cycle of enrichment and depletion of ^{15}N in aerosol particles.

During winter, we observed an event with the lowest $\delta^{15}N$ values which deviate from temperature dependence in Figure 2. The winter Event was connected with prevailing southeast winds and the lowest $\delta^{15}N$ values were probably associated with agriculture emissions of NH_3 under low temperature conditions that were below 0°C.

Details will be discussed in presentations and curently were also submitted to review (Vodicka et al., 2018).

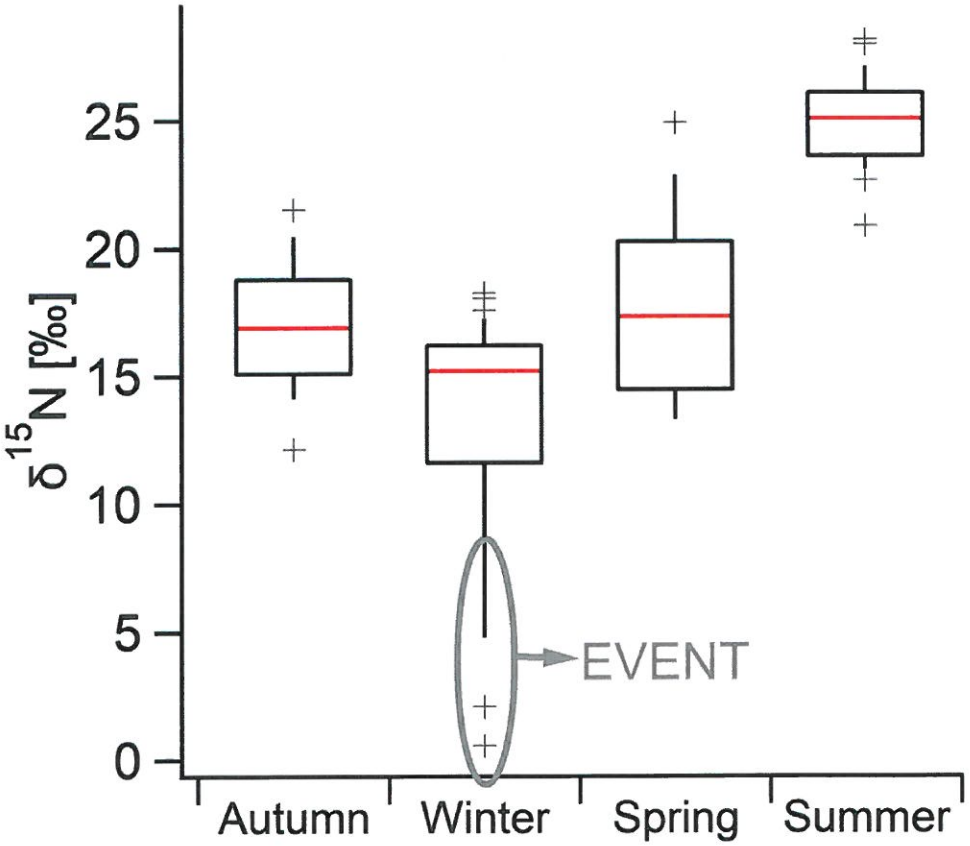

Fig. 1: Seasonal trend of $\delta^{15}N$ in TN. The boxes indicate the 25th percentile (lower edge), median (red line), and 75th percentile (upper edge). The whiskers represent the 10th and 90th percentiles and crosses are outliers.

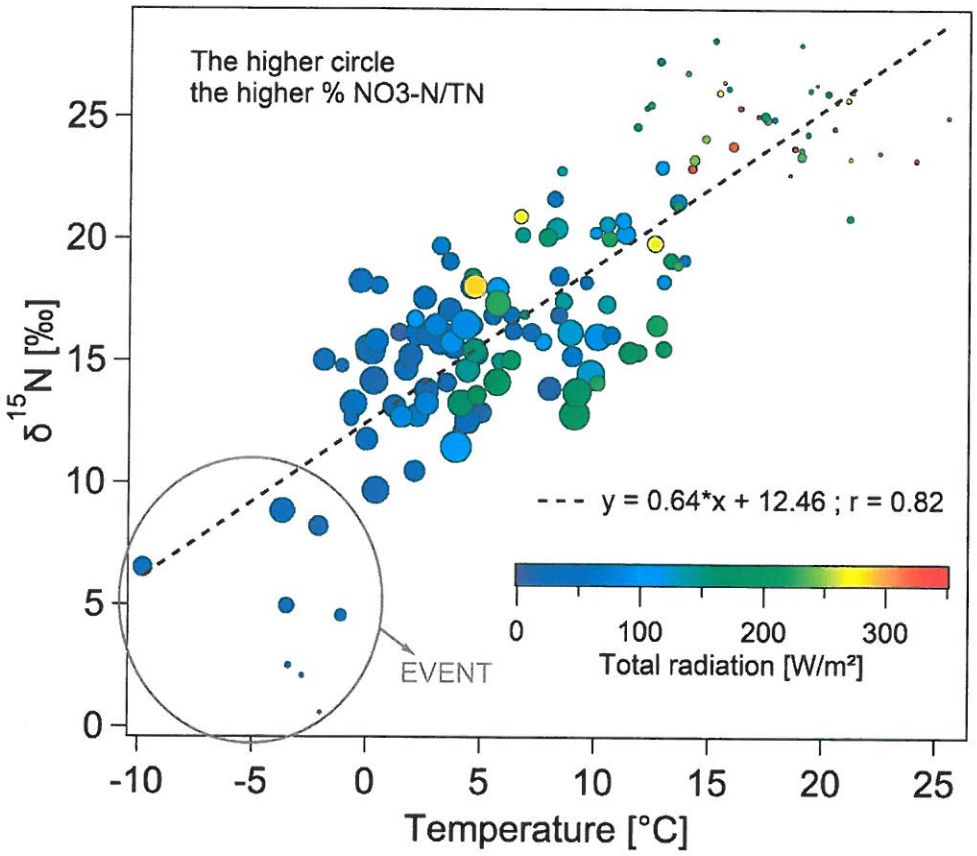

Fig. 2: Relationships between temperature and $\delta^{15}N$ in TN (right). The color scale reflects the total radiation, and the larger circles indicate higher content of NO_3^- in TN.

ACKNOWLEDGEMENT

This conference contribution was supported by the Ministry of Education, Youth and Sports of the Czech Republic under the project No. LM2015037, by the ERDF project "ACTRIS-CZ RI" (No. CZ.02.1.01/0.0/0.0/16_013/0001315) and by the Japan Society for the Promotion of Science (JSPS) through Grant-in-Aid No. 24221001. We appreciate the financial support of JSPS fellowship to P. Vodička (P16760) in Japan.

REFERENCES

Kawamura, K., Kobayashi, M., Tsubonuma, N., Mochida, M., Watanabe, T. and Lee, M.: Organic and inorganic compositions of marine aerosols from East Asia: Seasonal variations of water-soluble dicarboxylic acids, major ions, total carbon and nitrogen, and stable C and N isotopic composition, *Geochemical Soc. Spec. Publ.*, 9(C), 243–265, doi:10.1016/S1.873-9881(04)80019-1, 2004.

Kundu, S., Kawamura, K. and Lee, M.: Seasonal variation of the concentrations of nitrogenous species and their nitrogen isotopic ratios in aerosols at Gosan, Jeju Island: Implications for atmospheric processing and source changes of aerosols, J. *Geophys. Res. Atmos.*, 115(20), 1–19, doi:10.1029/2009JD013323, 2010.

Schwarz, J., Cusack, M., Karban, J., Chalupníčková, E., Havránek, V., Smolík, J. and Ždímal, V.: PM2.5 chemical composition at a rural background site in Central Europe, including correlation and air mass back trajectory analysis, *Atmos. Res.*, 176–177, 108–120, doi:10.1016/j.atmosres.2016.02.017, 2016.

Vodička, P., Kawamura, K., Schwarz, J., Kunwar, B., and Ždímal, V.: Seasonal study of stable carbon and nitrogen isotopic composition in fine aerosols at a Central European rural background station, *Atmos. Chem. Phys. Discuss.*, https://doi.org/10.5194/acp-2018-604, in review, 2018.