

Progress in the analysis and interpretation of N₂O isotopes: Potential and future challenges

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In recent years, research on nitrous oxide (N₂O) stable isotopes has significantly advanced, addressing an increasing number of research questions in biogeochemical and atmospheric sciences [1]. An important milestone was the development of quantum cascade laser based spectroscopic devices [2], which are inherently specific for structural isomers (¹⁵N¹⁴N¹⁶O vs. ¹⁴N¹⁵N¹⁶O) and capable to collect real-time data with high temporal resolution, complementary to the well-established isotope-ratio mass-spectrometry (IRMS) method. In combination with automated preconcentration, optical isotope ratio spectroscopy (OIRS) has been applied to disentangle source processes in suburban, rural and pristine environments [e.g. 3, 4].

Within the European Metrology Research Programme (EMRP) ENV52 project “Metrology for high-impact greenhouse gases (HIGHGAS)”, the quality of N₂O stable isotope analysis by OIRS, the comparability between laboratories, and the traceability to the international isotope ratio scales have been addressed. An inter-laboratory comparison between eleven IRMS and OIRS laboratories, organised within HIGHGAS, indicated limited comparability for ¹⁵N site preference, i.e. the difference between ¹⁵N abundance in central (N*NO) and end (*NNO) position [5]. In addition, the accuracy of the NH₄NO₃ decomposition reaction, which provides the link between ¹⁵N site preference and the international ¹⁵N/¹⁴N scale, was found to be limited by non-quantitative NH₄NO₃ decomposition in combination with substantially different isotope enrichment factors for both nitrogen atoms [6].

Results of the HIGHGAS project indicate that the following research tasks have to be completed to foster research on N₂O isotopes: 1) develop improved techniques to link the ¹⁵N and ¹⁸O abundance and the ¹⁵N site preference in N₂O to the international stable isotope ratio scales; 2) provide N₂O reference materials, pure and diluted in an air matrix, to improve inter-laboratory compatibility. These tasks will be addressed in the upcoming European Metrology Programme for Innovation and Research (EMPIR) project “Metrology for Stable Isotope Reference Standards (SIRS)” starting in June 2017.

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References

- [1] S. Toyoda et al., Isotopocule analysis of biologically produced nitrous oxide in various environments, *Mass Spectrom. Rev.*, Doi 10.1002/mas.21459 (2015).
- [2] J. Mohn et al., Site selective real-time measurements of atmospheric N₂O isotopomers by laser spectroscopy, *Atmos. Meas. Tech.* 5(7), 1601-1609 (2012).
- [3] B. Wolf et al., First on-line isotopic characterization of N₂O above intensively managed grassland, *Biogeosci.* 12, 2517–2531, (2015).
- [4] E. Harris et al., Tracking nitrous oxide emission processes at a suburban site with semi-continuous, in-situ measurements of isotopic composition, *J. Geophys. Res. Atmos.*, accepted (2016).
- [5] J. Mohn et al., Interlaboratory assessment of nitrous oxide isotopomer analysis by isotope ratio mass spectrometry and laser spectroscopy: current status and perspectives, *Rapid Commun. Mass Spectrom.* 28, 1995–2007 (2014).
- [6] J. Mohn et al. Reassessment of the NH₄NO₃ thermal decomposition technique for calibration of the N₂O isotopic composition, *Rapid Commun. Mass Spectrom.* 30, 2487–2496 (2016).