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Calibration strategy, precision and long term stability of real-time analysis of N_2O isotopomers and the ^{18}O-N_2O isotopologue by laser spectroscopy

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Regional scale estimations of N_2O budgets using process oriented biogeochemical models are usually calibrated and validated by investigating the deviation from measured total N_2O emission. Differentiation between fluxes originating from nitrification or denitrification is commonly not considered as in-situ measurements capable of source partitioning are not available. Therefore, it is unclear if the relative source strengths of nitrification and denitrification are represented adequately in process oriented models.

The analysis of the four main isotopic species ($^{14}N^{15}N^{16}O$ / $^{15}N^{14}N^{16}O$ / $^{14}N^{14}N^{18}O$ / $^{14}N^{14}N^{16}O$) has been suggested as a powerful tool to trace the biogeochemical cycle of N_2O and to allocate its emission sources. In microbial pure culture studies and mixed population systems (Wunderlin et al. 2012) characteristic isotopic signatures have been identified for the most important bacterial production processes. These have been applied to identify relevant sources at different scales (Park et al. 2012). However, current studies suffer from limited spatial and temporal resolution due to the combination of discrete flask sampling with laboratory-based mass spectrometric analysis. Recently, a quantum cascade laser based spectrometer capable of simultaneously measuring the three main N_2O isotopomers has been presented (Waechter et al. 2008). Furthermore, its potential for in-situ measurements in conjunction with a liquid nitrogen-free pre-concentration unit has been proven (Mohn et al. 2012).

Here we present the latest results obtained from a state-of-the-art laser spectrometer employing recently available cw-QCL and a novel astigmatic absorption cell with a 200 m optical path length. The adequate selection of the spectral range allows us to simultaneously measure all four main isotopic species of N_2O with 0.04‰ and 1‰ precision in pre-concentrated ambient and ambient air respectively.

We introduce an efficient and accurate calibration strategy for the simultaneous analysis of the N_2O isotope ratios $\delta^{15}N^{\alpha}$, $\delta^{15}N^{\beta}$ and $\delta^{18}O$. Sample gas pre-treatment and N_2O pre-concentration were optimized with respect to reproducibility and minimization of fractionation effects. The long-term accuracy of the instrument for isotope ratios will be addressed and extended by first in-situ measurements from a field campaign starting in spring 2013 in Central Switzerland. The results will be discussed in relation to requirements for background air monitoring at remote locations.

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