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# Isotopomer analysis of soil derived $N_2O$ – comparative measurements using QCLAS and IRMS techniques

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The analysis of the intramolecular $^{15}N$ distribution in the linear nitrous oxide ($N_2O$) molecule is an upcoming tool for $N_2O$ source identification. Isotopomer studies on soil-derived $N_2O$ emissions are mainly based on flask sampling in combination with laboratory based isotope ratio mass spectrometry (IRMS). Here we present the first on-line analysis of site-selective $\delta^{15}N$ $N_2O$ of soil-derived $N_2O$ at high temporal resolution applying quantum cascade laser absorption spectroscopy (QCLAS; Wächter *et al*., 2008; *Opt. Express* 16: 9239; Mohn *et al*., 2010; *Atmos. Meas. Tech.* 3: 609). Results are compared to IRMS analysis which is at present state of the art.
The experiment was performed in a laboratory setup with incubation vessels filled with sieved soil. The headspace was purged with a slow but constant flow of pressurized air. In one treatment soil was amended with sucrose and nitrate (sucrose-nitrate treatment); in the control treatment soil was supplemented with nitrate only. The effluent gas of three replicates of each treatment was combined and continuously analyzed by Fourier transform infrared (FT-IR) spectroscopy for trace gas concentrations over four days. Additionally, the site-selective isotopic composition of $N_2O$ emitted from the sucrose-nitrate treated soil was analyzed online by QCLAS at 1 Hz resolution. For an intercomparison between QCLAS and IRMS gas samples from both treatments were pooled continuously in Tedlar® bags integrating over twelve and 24 hours (for sucrose-nitrate treatment and control treatment, respectively).
In the sucrose-nitrate treatment the $\delta^{15}N^{bulk}$ $N_2O$ increased by about +50‰ and the SP by about +7‰ within three days, indicating a shift in the isotope composition of the soil nitrate pool due to fractionation during denitrification and a gradual increase in $N_2O$ reduction. In contrast, in the control treatment the $^{15}N$ $N_2O$ was slightly more depleted and the change in $\delta^{15}N^{bulk}$ $N_2O$ was clearly less pronounced which we attribute to low nitrate consumption due to low organic carbon availability. Interestingly, the SP in the control treatment was higher in the beginning but exhibited only a marginal increase during the experiment.
In summary, we showed that QCLAS is very well suited for high precision $N_2O$ isotopomer analysis in soil incubation studies, especially when continuous monitoring or high temporal resolution is required.