Protocol development for continuous nitrogen-15 measurement of N_2O and its isotopomers for real-time greenhouse gas tracing

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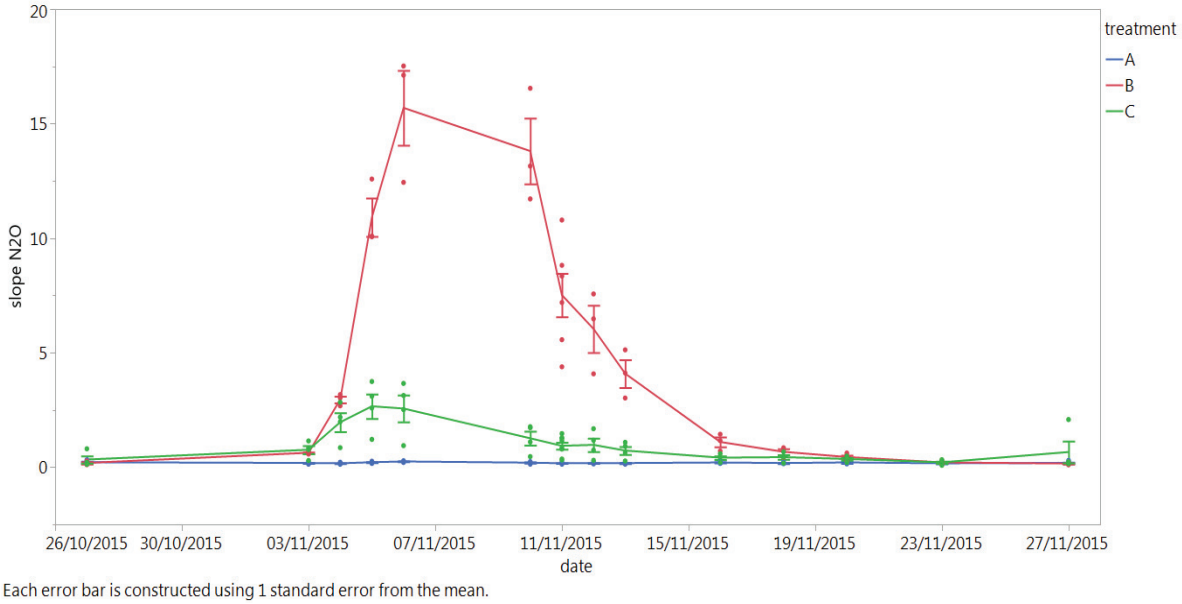
Quantifying sources of nitrous oxide (N_2O) (soil-N and applied N) is essential to improve our understanding of the global N cycle and to develop climate-smart agriculture, as N_2O has a global warming potential that is 300 times higher than that of CO_2. The isotopic signature and the intramolecular distribution (site preference) of ^{15}N are powerful tools to identify N_2O sources.

We have developed a protocol for continuous (closed-loop), real time measurement of the N_2O flux, the isotopic signature and the intramolecular distribution of ^{15}N by using off-axis integrated cavity output spectroscopy (ICOS, Los Gatos Research). The method was applied in a fertilizer inhibitor experiment, in which N_2O emissions were measured on undisturbed soil cores for three weeks. The treatments consisted of enriched ^{15}N labelled urea (5 atom %) applied at a rate equivalent to 100 kg N/ha), ^{15}N labelled urea with the nitrification inhibitor (NI) nitrapyrin (375 g/100 kg urea), and controls (no fertilizer or NI).

Measuring the isotopic signature of ^{15}N helps to distinguish N_2O emissions from soil and applied fertilizer. Characterization of site preference could additionally provide a tool to identify different microbial processes leading to N_2O emissions. Furthermore, the closed-loop approach enables direct measurement on-site and does not require removal of CO_2 and H_2O.

Results showed that cores with urea alone resulted in a total emission of 11 345 µg N_2O N/m^2, of which 75% originated from the fertilizer and 25% from the soil. Urea with nitrapyrin treatment yielded a total emission of 2 450 µg N_2O N/m^2, with 55% originating from urea. In the controls, the average emission amounted to 529 µg N_2O N/m^2 – corresponding to only 40% of the size of the corresponding pool from the fertilized cores. This difference shows the importance of using the isotopic signature, rather than relying non-treated cores to estimate soil emission rates. The latter method would have introduced bias in our dataset, as it would have resulted in an underestimation of the soil emission in fertilized soils.

The site preference of ^{15}N in N_2O (defined as the numeric difference between $\delta^{15}N\alpha$ and $\delta^{15}N\beta$) increased linearly over time for urea alone and urea with nitrapyrin. During the first 10 days, urea alone showed a more negative site preference than urea with nitrapyrin. This trend changed during the last 10 days of the measurements, when urea alone treatment showed a more positive site preference than urea with nitrapyrin. Our results suggest that site preference of ^{15}N may provide insights on the contribution of N_2O from different microbial processes. Low enrichment levels (5% atomic excess in this study) sufficed in order to separate N_2O emissions from soil and applied urea, making the proposed closed-loop approach a cost-effective and practical tool to obtain a continuous, in situ characterization of N_2O sources.



Each error bar is constructed using 1 standard error from the mean.

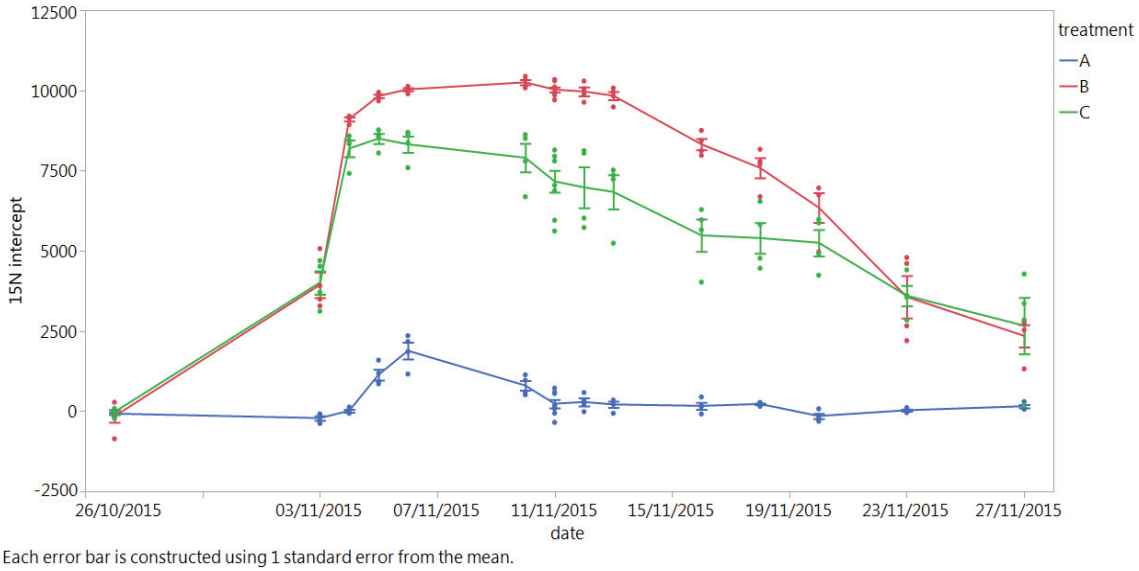


FIGURE 1. (top) Total N_2O emissions (ppm) and (bottom) ^{15}N-N_2O signature (‰) over time from undisturbed soil cores as influenced by ^{15}N labelled urea applied with or without nitrification inhibitor (nitrapyrin).

Treatment legends-A: Control, B: urea alone, C: urea with nitrapyrin

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Can we screen phosphorus movement in the landscape through the analysis of $\delta^{18}O$ isotopic abundance in phosphate?

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The SWMCNL explored the possibility of using $\delta^{18}O$ isotopic signature in phosphate for screening phosphorus (P) movement in the landscape. Phosphorus is essential for crop production, but extensive use of P fertilizer and animal manure can lead to eutrophication of rivers and lakes. To study these effects, numerous studies on P movement in the soil plant system and P transformation processes have been performed in the past decades. Assessing losses of P through erosion processes, however, is challenging – particularly at the landscape level and on a longer timescale. Using the isotopic signature of stable oxygen isotope (^{18}O) in the phosphate ion as a tracer could be a cost-effective way to study P movements. This approach is already applied as a paleo-temperature proxy (the fractionation between phosphate and water is temperature dependent) and can be used for quantifying P losses through leaching into surface and groundwater, as oxygen exchange between phosphate and water is slow in the absence of biological activity.

The aim of this study was to test if $\delta^{18}O$ signatures in phosphate could be used as tracers to screen P movements from uplands to lowlands. As several biochemical reactions lead to a shift of $\delta^{18}O$ in phosphate, this could lead to a limitation of the applicability of oxygen isotopes as tracers. Supposedly microorganisms preferentially take up lighter isotopologues of phosphate, leading to an enrichment of heavier isotopologues in the residual phosphate. Several enzymatic processes, which are necessary for living organisms to avoid phosphate toxication, lead to oxygen exchange from the surrounding water.

The silver phosphate method was applied in Petzenkirchen in the foothills of the Alps in Lower Austria and in Rauris, located in the national park Hohe Tauern in the Alps. Manure and soil samples of different altitudes were collected and processed for silver phosphate analyses.

The $\delta^{18}O$ in phosphate values had very similar signature in Petzenkirchen (14.69-15.09‰ $\delta^{18}O$ in soil and 13.77-15.23‰ $\delta^{18}O$ in manure samples), with no significant difference between different locations within Petzenkirchen. While the number of replicates was too small to show significant differences between the different soils at the Rauris site, at this location a depletion of ^{18}O of 2‰ $\delta^{18}O$ was observed with increasing altitude (Figure. 2). This decrease could be due to different isotopic oxygen composition of snow compared to that of rain water or because of different