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An assessment of N-cycling and sources of N_2O during a simulated rain event using natural abundance ^{15}N

Charlotte Decock*, Johan Six

Department of Plant Sciences, University of California, One Shields Ave., Davis, CA 95616, USA

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ABSTRACT

In order to accurately predict N_2O emissions from agricultural soils and to develop effective management strategies, it is important to understand mechanisms underlying N_2O emissions under field conditions. This involves identification of sources of N_2O, which is currently methodologically challenging, especially under field conditions. We assessed the suitability of ^{15}N tracers and natural abundance ^{15}N to study N cycling and sources of N_2O after a rainfall simulation in an annual cropping system in the Central Valley of California. Our natural abundance ^{15}N approach differed from other studies due to a combination of emphasizing a per-event (e.g. rainfall simulation in this study) assessment of N_2O emissions, applying high temporal sampling frequency during this event, determination of ^{15}N of NH_4^+ and NO_3^- in addition to N_2O, and data analysis using isotope models. In our study, the suitability of ^{15}N tracers to assess N cycling and sources of N_2O emissions was limited, likely due to a combination of a fine soil texture, the use of undisturbed soil cores, and a low ^{15}N application rate. Based on natural abundance ^{15}N, we were able to calculate gross NH_4^+ mineralization, NH_4^+ immobilization, nitrification and NO_3^- immobilization rates of 5.37 ± 1.72, 2.70 ± 1.72, 3.01 ± 1.13 and 0.15 ± 0.29 $\mu g\ N\ g^{-1}$ soil d^{-1}, respectively. Natural abundance ^{15}N was, however, a rather poor predictor of the contribution of nitrification versus denitrification to N_2O production. Nevertheless, important trends in N_2O reduction rates could be observed, showing a sharp increase from 48% to 78% in reduction of produced N_2O between 2 hours and 24 hours after rainfall simulation, followed by a gradual decrease to 46% of reduction by the fifth day after rainfall simulation. We conclude that the natural abundance ^{15}N approach is very promising to elucidate mechanisms driving N-cycling and N_2O emissions during agricultural management or weather events, especially if isotope dynamics are incorporated in site-specific biogeochemical process models.

1. Introduction

The agricultural sector has been identified as the largest emitter of the potent greenhouse gas N_2O, where most N_2O emissions are derived from soil (IPCC, 2007). Therefore, optimization of management practices to reduce N_2O emissions while maintaining yields is desirable when reducing GHG emissions from agriculture (CEC, 2005). However, one of the greatest challenges associated with predicting and mitigating N_2O emissions from soil is the large uncertainty around available data (Bouwman et al., 2002). This uncertainty can in part be attributed to the various microbial processes involved in the production and consumption of N_2O from soil, each of which can be affected differently by environmental changes and management practices (Firestone and Davidson, 1989; Wrage et al., 2001). Therefore, determination of the contribution of various microbial pathways involved in N_2O emissions is essential when developing effective mitigation strategies and improving biogeochemical models that predict N_2O emissions from soils (Mathieu et al., 2006a). Related to the multitude of processes contributing to N_2O emissions is the high temporal variability of N_2O fluxes observed in the field. In general, emissions of N_2O from agricultural soils are concentrated around particular management practices such as fertilization, tillage and irrigation as well as environmental factors such as rainfall (Smith and Dobbie, 2001; Flessa et al., 2002; Garland et al., 2011), further referred to as events. Since soil moisture content and available C and N – the major controls on N_2O emissions (Knowles, 1982; Firestone and Davidson, 1989) – can be affected differently from one event to the other, it is important to study mechanisms underlying N_2O emissions on a per-event basis. For a thorough assessment of mechanisms underlying N_2O emissions on a per-event basis, in situ measurements of sources of N_2O and N cycling are vital.

So far, source partitioning of N_2O has been limited by a lack of adequate methods, especially under field conditions (Baggs, 2008). Selective inhibition by C_2H_2 to distinguish between nitrification and denitrification derived N_2O emissions has proven to

* Corresponding author. Tel.: +1 530 752 3450; fax: +1 530 754 4361.
E-mail address: cldecock@ucdavis.edu (C. Decock).

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give inadequate results (Wrage et al., 2004), whereas the use of ^{15}N tracers is laborious and only effective for short time periods (Groffman et al., 2006). In addition, successful use of ^{15}N tracers requires homogeneous distribution of the ^{15}N label, which can be difficult to achieve under field conditions (Cliff et al., 2002). Natural abundance N and O isotopes could serve as non-invasive indicators for monitoring sources of N_2O (Tilsner et al., 2003), but greater validation of these indicators is required (Perez, 2005). Interpretation of natural abundance ^{18}O in N_2O is convoluted by the potential for oxygen exchange between oxygen-bearing N compounds and soil water during both nitrification and denitrification (Kool et al., 2007). Moreover, the number of studies reporting isotope fractionation factors for O during N_2O production and consumption is very small, increasing uncertainty and further complicating interpretation of ^{18}O in N_2O (Perez, 2005). The intramolecular distribution of ^{15}N in the N_2O molecule (expressed as site preference) has recently been studied for its suitability to source partition N_2O emitted from soil (Yoshida and Toyoda, 2000; Ostrom et al., 2010). A major advantage of site preference to source partition N_2O is its independence from isotope values of N_2O precursors (Sutka et al., 2006; Well et al., 2008). However, interpretations of site preference values have mostly been based on values for nitrification and denitrification derived N_2O emissions observed in a limited number of studies with pure microbial cultures (Sutka et al., 2006, 2008; Opdyke et al., 2009; Toyoda et al., 2011), while reproduction of these values in soil incubation studies has been unattainable (Well et al., 2006; Park et al., 2011). The natural abundance ^{15}N of N_2O has been studied longer than ^{18}O and site preference (e.g. Mariotti et al., 1981), which has yielded a larger database of fractionation factors for nitrification derived N_2O, denitrification derived N_2O and N_2O reduction to N_2, based on both pure bacterial cultures and soil incubation studies (Perez, 2005; Pörtl et al., 2007). Granted appropriate uncertainty deductions are in place and ^{15}N of NH_4^+ and NO_3^- is known, this should allow for reliable estimation of sources of N_2O using isotope mixing and fractionation models. Nevertheless, few studies that report natural abundance ^{15}N of N_2O present ^{15}N values for NH_4^+ and NO_3^- or apply isotope models that include mineral and gaseous N species, greatly limiting interpretation of existing literature data (Perez, 2005).

In this "proof-of-concept" study, we aimed to thoroughly assess the suitability of natural abundance ^{15}N to study N-cycling and N_2O emissions under field conditions, by determining ^{15}N of NH_4^+ and NO_3^- in addition to N_2O and by adopting isotope models and a high temporal sampling frequency. In order to assess this, we compared the use of natural abundance ^{15}N with the use of ^{15}N tracers at application rates appropriate for the environmental conditions under consideration. Our method evaluation situated around the characterization of mechanisms underlying N_2O emissions during a simulated rain event in an arable soil in the Central valley of California, an event that is expected to be associated with large N_2O fluxes.

2. Materials and methods

2.1. Study site

The experiment was conducted in a conventionally managed tomato field in Winters, CA (Lat. 38°35′12.10″ N; Long. 121°58′40.68″ W). The climate in the region is semi-arid Mediterranean and most precipitation falls as rain between October and April. The soil type is a Brentwood silty clay loam (fine, montmorillonitic, thermic Typic Xerochrept) with 28% sand, 38% silt, and 34% clay. Soil pH was 6.7 ± 0.2. Processing tomatoes (*Lycopersicon esculentum*, Var. AB 2) were cultivated as part of a tomato–winter wheat–summer fallow rotation. Management practices included sidedress fertilizer injection, furrow irrigation, and standard tillage.

2.2. Experimental setup

Nine 1 m^2 plots were established on 11 September 2010, 2 weeks after tomato harvest and 5 days after crop residue incorporation. We performed a rainfall simulation by applying 60 L of ground water in 10 L increments to each of the plots (equivalent to 60 mm rain) using a watering can. This amount of water is representative of a big Fall storm in the California Central Valley (http://www.ipm.ucdavis.edu/weather). After water application, three of the plots were allocated for natural abundance soil and gas sampling, while the other six received $NH_4NO_3 + KNO_3$ with ^{15}N enrichment of NO_3^- alone (i.e. $^{14}NH_4{}^{15}NO_3 + K^{15}NO_3$, further referred to as the $^{14}NH_4{}^{15}NO_3$ treatment) or in both NH_4^+ and NO_3^- (i.e. $^{15}NH_4{}^{15}NO_3 + K^{15}NO_3$, further referred to as the $^{15}NH_4{}^{15}NO_3$ treatment). Seven or eight metal soil cores (15 cm height, 5 cm diameter) were installed to a depth of 10 cm in the natural abundance and ^{15}N tracer plots, respectively. This left a 5 cm headspace that could be capped, air-tight, for gas measurements. The size of the soil cores is in agreement with Decock and Six (2012) and Davidson et al. (1991) and was purposely kept small to facilitate timely application of the ^{15}N label, sample handling and processing.

Tracer amounts of 99 atom% ^{15}N enriched mineral N were added at a rate of 2 μg g $soil^{-1}$ NH_4^+-N and 10 μg g $soil^{-1}$ NO_3^--N. These additions were approximately half of the NH_4^+ and NO_3^- concentrations present prior to the start of the experiment. We chose low N-addition rates to minimize disturbance of the system and avoid stimulation of N transformation rates, while care was taken that sufficient analytical measurement sensitivity could be achieved. Five injections of 2 mL ^{15}N tracer solution were applied over a depth of 10 cm in the metal cores using a syringe with a 10-cm needle. While this added a total water volume of 10 mL to each core in the ^{15}N tracer plots, soil moisture contents measured in the ^{15}N tracer plots were not significantly higher than those in the natural abundance plots (data not shown).

One of the metal cores in each plot was capped for a 1-hour period at 2 hours, and 1, 2, 3, 4 and 5 days after water application. Two headspace gas samples were collected from each core 1 hour after capping and transferred by syringe into 12 mL exetainers. Soil cores were sampled destructively for soil moisture content, bulk density and mineral N concentrations after each gas measurement. In addition, one core in each of the ^{15}N tracer plots was destructively sampled immediately after ^{15}N application to determine the ^{15}N content of mineral N at time 0. Finally, metal cores were installed in the zone between the nine plots prior to the start of the experiment. Gas measurements and destructive sampling of those cores provided data on N_2O emissions, soil moisture content and mineral N prior to the start of the experiment.

2.3. Gas and mineral N concentrations and isotope analyses

At each destructive sampling time in our field experiment, we took four subsamples of ~15 g from cores in natural abundance plots and two subsamples from cores in ^{15}N tracer plots. Those subsamples were added to pre-weighed specimen cups with 50 mL of 2 M KCl. The specimen cups were transported to the laboratory and placed on a shaker for 1 hour, after which we collected the extract by filtering the slurry (Whatman™ no. 42 ashless filter paper, 150 mm diameter).

The NH_4^+ and NO_3^- concentrations in the extracts were determined colorimetrically following the Berthelot reaction (Forster, 1995) and vanadium(III) chloride reduction (Doane and Horwath, 2003), respectively. The ^{15}N content of mineral N from the ^{15}N tracer plots and ^{15}N of NH_4^+ from the natural abundance plots