Soil Biology & Biochemistry 65 (2013) 114–127

Contents lists available at SciVerse ScienceDirect

Soil Biology & Biochemistry

journal homepage: www.elsevier.com/locate/soilbio

Review paper

How reliable is the intramolecular distribution of ^{15}N in N_2O to source partition N_2O emitted from soil?

Charlotte Decock*, Johan Six

Department of Environmental System Science, ETH-Zurich, Tannenstrasse 1, 8092 Zurich, Switzerland

ARTICLE INFO

Article history:
Received 10 May 2012
Received in revised form
9 April 2013
Accepted 12 May 2013
Available online 6 June 2013

Keywords:
Stable isotopes
Site preference
Source-partitioning N_2O
Nitrification
Denitrification
Nitrifier denitrification
Fungal denitrification
N_2O reduction
Global N_2O budget

ABSTRACT

N_2O is a potent greenhouse gas and plays an important role in the depletion of stratospheric ozone. Hence, many efforts are now geared toward quantifying and mitigating N_2O emissions from soil in various ecosystems. This requires an in-depth understanding of the mechanisms and processes underlying N_2O emissions, which has been methodologically challenging. Recently, it has been suggested that the intramolecular distribution of ^{15}N in the N_2O molecule (known as site preference or SP) can indicate which processes contribute to N_2O fluxes. Here, we assess, through guidance by a framework of recommended validation steps, the suitability of SP to source partition N_2O emitted from soils. In individual studies, significant effects of soil moisture content and soil type on SP values from soil-emitted N_2O have been observed, supporting that SP could be a useful tool to source-partition N_2O emitted from soil. While process-specific SP values based on pure culture studies have been used in isotope mixing and fractionation models to source partition N_2O in environmental samples, effects of confounding factors such as unaccounted pathways, microbial community composition, process rate, and soil heterogeneity remain poorly quantified. This urges continued research to determine SP values for distinct N_2O producing and consuming processes under controlled laboratory conditions for soils from a variety of ecosystems and environments. As mechanisms underlying N_2O production and consumption are plentiful and complex, creation of large isotope databases should be complemented with the development of more advanced models that take into account $\delta^{15}N$ and $\delta^{18}O$ of precursors, variability of overall isotope effects, and bulk $\delta^{15}N$, $\delta^{18}O$, and SP of N_2O, as well as traditional proxies such as soil moisture content and C and N availability.

1. Introduction

As greenhouse gas concentrations in the atmosphere continue to increase, much research is now directed toward strategies to mitigate global climate change. This includes attempts to reduce emissions of N_2O, a potent greenhouse gas and major player in the depletion of stratospheric ozone (Crutzen, 1981; IPCC, 2007). Soils under agricultural management as well as under natural vegetation constitute the major global source of N_2O (Denman et al., 2007). N_2O emissions from soil are characterized by high temporal and spatial variability and underlain by a multitude of microbial and abiotic pathways (Wrage et al., 2001; Hayatsu et al., 2008; Hénault et al., 2012). A better understanding of pathways causing N_2O fluxes at any given time or place could greatly advance the development of more targeted mitigation strategies and narrow the uncertainty around N_2O emission predictions (Wrage et al., 2001).

Hydroxylamine (NH_2OH) oxidation, nitrifier-denitrification, denitrification and N_2O reduction to N_2 are considered the major processes controlling N_2O emissions (Firestone and Davidson, 1989; Wrage et al., 2001). NH_2OH-oxidation-derived N_2O is N_2O that is created as a byproduct during NH_4^+ oxidation to NO_2^- by autotrophic ammonium-oxidizers (Hooper and Terry, 1979; Chalk and Smith, 1983). The same organisms are capable of reducing NO_2^- to N_2O and/or N_2 under high NO_2^- partial pressure or low oxygen conditions, a process known as nitrifier-denitrification (Wrage et al., 2001). N_2O is also produced as an intermediate during the reduction of NO_3^- to N_2 by heterotrophic denitrifying bacteria under anaerobic conditions, i.e. denitrification-derived N_2O (Knowles, 1982). Moreover, alternative pathways such as

List of abbreviations: SP, site preference; AOA, ammonia-oxidizing archaea; AOB, ammonia-oxidizing bacteria; N_2O_N, N_2O produced by processes for which SP is around 32.8‰, including hydroxylamine oxidation by ammonia-oxidizing bacteria, fungal denitrification, abiotic N_2O production and N_2O production by ammonia-oxidizing archaea; N_2O_D, N_2O produced by processes for which SP is around −1.6‰, including denitrification and nitrifier-denitrification.

* Corresponding author.
E-mail address: charlotte.decock@usys.ethz.ch (C. Decock).

0038-0717/$ – see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.soilbio.2013.05.012

fungal denitrification, abiotic N_2O production, archaeal N_2O production, heterotrophic nitrification and co-denitrification could contribute to the N_2O flux from soils (Laughlin and Stevens, 2002; Venterea, 2007; Hayatsu et al., 2008; Schleper, 2010; Spott et al., 2011).

Given the highly variable emission patterns and the complexity of N_2O production and consumption pathways, source-partitioning N_2O is methodologically challenging at both the ecosystem and global scale (Groffman et al., 2006; Baggs, 2008). Previous efforts to identify N_2O production and consumption pathways have mostly relied on C_2H_2 inhibition and isotope labeling techniques (Baggs, 2008). These methods have some important limitations, including difficulties with homogeneous diffusion of the label or inhibitor, disturbance of the system during label or inhibitor application, and a narrow time frame during which N_2O production and consumption can be monitored before the label or inhibitor turns over (Groffman et al., 2006; Ostrom and Ostrom, 2011). Variation in the natural abundance ^{15}N and ^{18}O of N_2O has been explored as a non-invasive method to assess N_2O production and reduction mechanisms, but interpretation of bulk $\delta^{15}N$ and $\delta^{18}O$ of N_2O is challenging because of the dependency on $\delta^{15}N$ and $\delta^{18}O$ of the precursors and the uncertainty around isotope fractionation factors for various processes (Perez, 2005).

It has been suggested that the intramolecular distribution of ^{15}N in the N_2O molecule could serve as a tool to discern various N_2O producing and consuming processes and to help constrain the global N_2O budget (Yoshida and Toyoda, 2000; Perez et al., 2001). Molecules with differing distribution of ^{15}N in N_2O are sometimes referred to as 'isotopomers', i.e. molecules of the same mass in which trace isotopes are arranged differently (Ostrom and Ostrom, 2011). The term 'isotopologue' more generally refers to molecules that differ in their isotopic composition (Ostrom and Ostrom, 2011). Since N_2O is an asymmetric molecule, a central and terminal N atom can be distinguished (Toyoda and Yoshida, 1999). The central and terminal N atoms have been referred to as α and β (Toyoda and Yoshida, 1999) or 2 and 1 (Brenninkmeijer and Röckmann, 1999), respectively. In addition, the terminology 456 and 546 has been used to refer to the isotopomers $^{14}N^{15}N^{16}O$ and $^{15}N^{14}N^{16}O$, respectively (Stein and Yung, 2003). In this review, we will use the terminology α and β because this terminology is most prevalent in studies focused on source partitioning N_2O emitted from soil. The site-specific distribution of ^{15}N in N_2O has been expressed as site-preference (SP), and is calculated as the difference in $\delta^{15}N$ in the central compared to the terminal N atom ($SP = \delta^{15}N_\alpha - \delta^{15}N_\beta$) (Toyoda and Yoshida, 1999). A major advantage of the use of SP is the minimal disturbance associated with sampling, facilitating experimentation under field conditions (Ostrom and Ostrom, 2011). Determining SP could complement $\delta^{15}N_{bulk}$ (average ^{15}N content) and $\delta^{18}O$ data of N_2O, with the additional advantage that SP is presumed to be independent of $\delta^{15}N$ of the precursors (Toyoda et al., 2002). The ^{15}N content in the α and β positions can be determined based on mass analyses of the molecular (N_2O^+) and fragment (NO^+) ions of N_2O on an isotope ratio mass spectrometer (Toyoda and Yoshida, 1999). In addition, quantum cascade laser based absorption spectroscopy to determine the intramolecular distribution of ^{15}N within the N_2O molecule is under development (Waechter et al., 2008; Mohn et al., 2010). An extensive overview of analytical methods and challenges associated with measuring SP can be found in Ostrom and Ostrom (2011).

During N_2O production, two NO^- ions bind to form the intermediate hyponitrite ($^-O{-}N{=}N{-}O^-$), followed by cleavage of one N–O bond (Stein and Yung, 2003). An N–O bond is also broken during N_2O reduction to N_2 (Zumft, 1992). Ultimately, preferential cleavage of bonds between lighter atoms determines the degree of SP and can vary between microbial groups and/or enzymes involved (Stein and Yung, 2003; Schmidt et al., 2004). This variation across microbial groups or enzymes forms the basis for the use of SP to source partition N_2O emitted from soil. Values of SP have been determined for N_2O production and consumption pathways in pure microbial cultures and soil incubation experiments (Sutka et al., 2006; Well et al., 2006). Partial compilations of observed SP values are provided in Park et al. (2011), Toyoda et al. (2011) and Well et al. (2012). Values of SP observed in pure cultures have been used in a number of studies to interpret SP values observed in environmental samples (Opdyke et al., 2009; Toyoda et al., 2011). In a recent review, Ostrom and Ostrom (2011) promoted the use of SP values from pure cultures and a graphical analysis based on $\delta^{18}O$ and $\delta^{15}N$ of N_2O to estimate the contribution of different N_2O producing and consuming pathways to N_2O emissions from environmental samples. However, before SP can be used with confidence for source partitioning N_2O at ecosystem and global scales, a sequence of validation steps is warranted (Fig. 1). These include validation of the robustness of SP values presumed to be characteristic for various N_2O consuming and producing processes, identification of confounding factors and quantification of their effect, development and evaluation of models and strategies to interpret SP data, and assessment of the uncertainty in sources of N_2O estimated using SP. We synthesize here the progress that has been made in each of those validation steps, leading up to recommendations for future research.

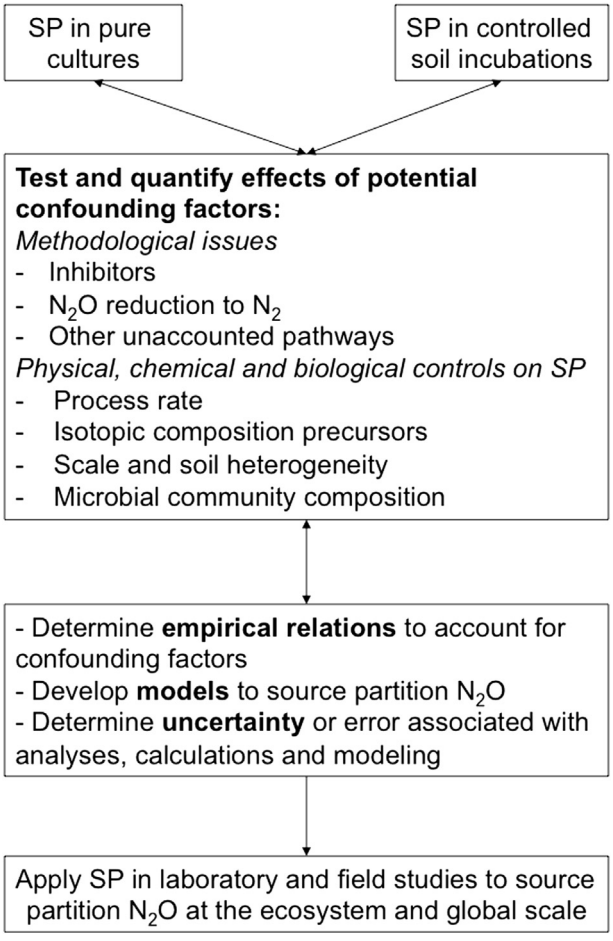

Fig. 1. Flowchart for SP method validation.