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SHORT COMMUNICATION

Do increasingly depleted δ^{15}N values of atmospheric N_2O indicate a decline in soil N_2O reduction?

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Abstract Growing concentrations of N_2O within the atmosphere have been accompanied by decreasing δ^{15}N values, provoking the hypothesis of a global decline in the rate of N_2O reduction relative to its production in soil. We estimate that the ratio of N_2O produced to N_2O reduced within the soil profile has declined by about 10–25% relative to its pre-industrial value. To a smaller extent, a reduction in the uptake of atmospheric N_2O at the soil surface relative to its emission could also have contributed to the reported isotopic signal. This calls for a greater consideration of the process of N_2O reduction in soil and its role in the global turnover of N_2O.

Keywords Atmospheric isotope signal · N_2O reduction · Soil

Background and motivation

Increase in atmospheric N_2O concentrations since industrialisation have been accompanied by a decrease in heavy isotope content (Röckmann and Levin 2005; Bernard et al. 2006). Concentrations increased as a result of anthropogenic activities (Kroeze et al. 1999; IPCC 2001) and the anthropogenic source has been estimated to be depleted in δ^{15}N by about 6‰ against the pre-industrial source (Röckmann et al. 2003). This isotopic trend has been explained by the growing importance of agricultural soils as a source of N_2O and its relatively depleted isotopic signature (Perez et al. 2001). Globally, soils constitute about half of the total N_2O source with large uncertainties still remaining (Mosier et al. 1998; Olivier et al. 1998). Rates of industrial N fixation have reached those of terrestrial biological N-fixation (Galloway et al. 2004), accelerating global N cycling and stimulating the production of N_2O by the two main processes of nitrification and denitrification (Stein and Yung 2003). Both processes produce N_2O depleted in ^{15}N relative to the respective substrates NH_4^+ and NO_3^-, whereby nitrification leads to greater depletion (Robinson 2001). Conversely, reduction of N_2O to N_2 through further denitrification leads to an enrichment of the remaining N_2O between 1‰ and 24‰ (Wada and Ueda 1996).

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With this short paper we would like to bring forward the hypothesis of the observed isotopic trend in the atmosphere being an indication of a global decline in the rate of N_2O reduction relative to its production in soil. Hereby, we distinguish two types of N_2O reduction. First, a proportion of the N_2O produced within a soil is reduced on its way to the atmosphere (Neftel et al. 2000; Clough et al. 1999, 2005; Van Groenigen et al. 2005). Second, atmospheric N_2O diffuses back into the soil and part of it is reduced (Ryden 1981; Verchot et al. 1999; Donoso et al. 1993; Papen et al. 2001; Flechard et al. 2005). We will indicate possible reasons for the decline in soil N_2O sink activity in relation to its source activity, the impact this might have had on the anthropogenic N_2O signal and implications for further research.

Reduction of N_2O on its way to the atmosphere

Substantial fractions of N_2O produced at depth within the profile have been found to be consumed while diffusing to the soil surface. Clough et al. (1999) found 67% of N_2O to become reduced to N_2 while diffusing from 90 to 15 cm below surface. Neftel et al. (2000) determined uptake rates of N_2O within the profile of a fine textured soil in the order of 10^{-4} to 10^{-5} s^{-1}, resulting in scale lengths of only a few centimetres. Van Groenigen et al. (2005) observed a decrease in N_2O concentrations at 90 cm depth from 100.4 to 1.7 ppmv without significant fluxes at the soil surface but accompanied by an enrichment in $\delta^{15}N$ of about 50‰. Smaller proportions of N_2O reduced before emission, or in other words larger N_2O to N_2 ratios, were found to result in N_2O signals more depleted in $\delta^{15}N$ (Perez et al. 2000).

Why should reduction of N_2O within the soil profile have changed since pre-industrial times?

First, application of mineral fertiliser leads to high concentrations of NO_3^- at the soil surface (Jarvis and Barraclough 1991). This results in large N_2O to N_2 ratios in the emitted products of denitrification (Swerts et al. 1996; Stevens and Laughlin 1998; Bol et al. 2003). In other words, N_2O is to a lesser extent reduced to N_2 and therefore its $\delta^{15}N$ more depleted than under conditions of lower NO_3^- concentrations as found in undisturbed ecosystems (Perez et al. 2001).

Second, in natural and unfertilised systems, reactive N is produced by biological N-fixation and mineralisation. Both processes take place within the soil profile. Contrastingly, mineral fertiliser N is in general applied to the soil surface. This may shift the location of N_2O production closer to the soil surface, reducing its pathway to the atmosphere and with it the chance for complete reduction. This proposition is supported by the study of Liu et al. (2006), who found decreasing placement depth of reactive N from 10 to 5 cm below the soil surface to result in more than a doubling of N_2O emissions.

How much would N_2O consumption need to have declined to explain the observed signal of –6‰ in the anthropogenic source of $\delta^{15}N_2O$?

The decline necessary to explain the observed signal depends on the absolute value of the reduced fraction and the fractionation factor (ε) for the reduction of N_2O to N_2. For ε we may assume a mean value of –13‰ (Barford et al. 1999). If we further assume that today between 50% and 80% of N_2O produced within the soil profile is reduced before it would have reached the atmosphere, reduction rates must have declined between about 25% and 10% relative to their pre-industrial values (Table 1). In Table 1, values for the shift in $\delta^{15}N$ from pre-industrial to contemporary values (δ') were calculated as $\delta' = \varepsilon(\ln(1-f_c) - \varepsilon(\ln(1-f_p)$, where f_c is the contemporary fraction, and f_p is the pre-industrial fraction of N_2O reduced.

Reduction of atmospheric N_2O diffusing into the soil profile

Concentrations well below atmospheric background have been found within the soil profile over prolonged periods (Schmid et al. 2001). Net consumption of N_2O in dry conditions has been

Table 1 Calculated change in $\delta^{15}N$ (‰) in the soil N_2O source from pre-industrial to contemporary times (δ') resulting from a reduced fraction of N_2O consumed within the soil profile

Reduction in % of pre-industrial fraction	Contemporary fraction of N_2O consumed before potential emission (%)						
	50	55	60	65	70	75	80
10	–1.5	–1.9	–2.4	–3.0	–3.9	–5.3	–7.6
15	–2.5	–3.2	–4.0	–5.2	–6.9	–9.8	–15.9
20	–3.7	–4.7	–6.1	–8.1	–11.4	–18.0	
25	–5.3	–6.8	–9.0	–12.5	–19.6		

Assumed fractionation factor in the reduction of N_2O to N_2 is –13‰

reported (Donoso et al. 1993; Flechard et al. 2005). Consumption is by reduction to N_2. This has long been assumed to be limited to waterlogged soils. However, activity of N_2O reductase under aerobic conditions has been found in cultures of Thiosphaera pantotropha (Bell and Ferguson 1991). When concentrations of N_2O within the soil profile are similar to those in the atmosphere, N_2O diffuses from the atmosphere into the soil and is reduced the same way as discussed above. Current atmospheric N_2O concentration does not seem to be below a critical threshold for microbial reduction processes to be effective. Flux measurements at the soil surface determine net exchange rates, which are composed of gross emission and gross uptake rates. At times, gross uptake exceeds gross emission and net uptake of N_2O is observed. Studies reporting such activity are summarised in Table 2.

During these studies, uptake activity was observed on average over half the observation period. Mean uptake rates ranged from 0.02 to 0.11 nmol m^{-2} s^{-1}. Global annual N_2O emission from all soils is estimated between 8.5 and 10.2 Tg (Olivier et al. 1998; Kroeze et al. 1999). The global vegetated surface area is about 12×10^{13} m^2. Hence, mean emissions are equivalent to about 0.09 nmol m^{-2} s^{-1}. Most field studies so far were done on systems subject to agricultural N deposition or land use change, constituting major and growing sources of N_2O. Thus, it is not surprising that reports of net N_2O uptake by soil are rare. It is difficult to estimate the global importance of this phenomenon. As a starting point, we might speculate that half of the total vegetated area is half of the year taking up N_2O. Taking the range of values shown in Table 2, this would be equivalent to 6% to 30% of the total current soil N_2O source.

How could this have change since pre-industrial times?

Uptake of atmospheric N_2O in the soil profile is limited by diffusion. The increase in atmospheric

Table 2 Reported activities of N_2O sink in studies where at least part of the observed sink was statistically significant

Location (reference)	Ecosystem and management	Duration of study (years)	Duration of net sink activity (fraction of study)	Mean N_2O sink during sink period (nmol m^{-2} s^{-1})
Berkshire, UK (Ryden 1981)	Grassland, no fertiliser N	0.3	1.00	0.05
	Grassland, 250 kg N $year^{-1}$	0.7	0.46	0.11
Bolívar State, Venezuela (Donoso et al. 1993)	Undisturbed savannah, dry season	0.1		0.04
Eastern Amazonia, Brazil (Verchot et al. 1999)	Pasture, active	1.3	0.13	0.06
	Pasture, degraded	1.3	0.19	0.02
Black Forest, Germany (Papen et al. 2001)	Spruce forest, control	2.4	0.56	0.02
	Spruce forest, N-fertilised	2.4	0.33	0.02
Swiss Plateau (Flechard et al. 2005)	Extensive grassland, no fertiliser N	2.5	0.7	0.11

Table 3 Calculated changes in the depletion of the integrated soil N_2O signal (net surface exchange) resulting from the relatively smaller increase in uptake of atmospheric N_2O (1.17 times) compared to the increase in emission of N_2O (1.5 times)

Uptake/emission (contemporary ratio)	0.060	0.120	0.180	0.240	0.300
Uptake/emission (pre-industrial ratio)	0.073	0.146	0.220	0.293	0.366
Change in $\delta^{15}N$ (contemporary – pre-industrial) (‰)	–0.18	–0.40	–0.64	–0.94	–1.29

Assumed fractionation factor for N_2O reduction is –13‰

N_2O concentrations from around 270 to 317 ppbv today (extrapolated from IPCC 2001) will have reduced diffusion limitation by a factor of 1.17 since pre-industrial times. At the same time, global N_2O emissions from soil have increased by a factor of about 1.5 (Nevison et al. 1996). Thus, uptake will have decreased relative to emission by 22%, regardless of the absolute value of assumed global N_2O uptake. Suppose, a realistic value for the global uptake of atmospheric N_2O at the soil surface is between 6% and 30% of the current N_2O soil surface emission. Then, changes in $\delta^{15}N$ resulting from the decline of N_2O uptake at the soil surface relative to surface emission would be a depletion between –0.18‰ and –1.29‰ (Table 3).

Conclusion and outlook

A decrease between 10% and 25% since pre-industrial times in the proportion of N_2O reduced on its way to the atmosphere could explain the observed depletion of atmospheric N_2O in the heavy N isotope of the current anthropogenic source. Probably to a smaller extent, decreasing uptake to emission ratios at the soil–atmosphere interface could also have contributed to this phenomenon. There is undeniably large uncertainty in the presented estimates. Still, they indicate a possibly serious decline in N_2O consumption within the soil profile relative to N_2O production. Major questions regarding N_2O reduction in soil are still to be investigated in more detail before the global role of soil N_2O sink activity and its dynamics can be properly evaluated. Particular deficits in our understanding relate to the ecological significance of N_2O reduction, its kinetics, such as maximum rates, k_m values, temperature sensitivity and sensitivity to other parameters subject to global change. Further, there are still very few studies on microbial diversity in terms of N_2O reducers and how they might be affected by anthropogenic activity (Chèneby et al. 1998; Holtan-Hartwig et al. 2000; Cavigelli and Robertson 2001; Rich and Myrold 2004; Mei et al. 2004). From a purely N_2O accounting point of view, it is also necessary to search more certainty of the sink terms discussed. A recent discussion paper suggests the oceanic N_2O source has been under-estimated by a factor of 2 (Bange 2006). If this is confirmed, there will be a need to re-evaluate our current understanding of global N_2O sink terms. Thus, splitting net fluxes from soil surfaces into gross sink and gross source activity within the soil profile would help to better understand global N_2O turnover and, especially, interpret isotopic trends in atmospheric N_2O. It might also open new perspectives on the mitigation of N_2O emissions from soil.

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