

Drainage losses of N_2O and NO_3^- in Ferralsol is a major N-loss pathway

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Abstract

Increasing concentrations of atmospheric nitrous oxide (N_2O) are making a significant contribution to anthropogenic climate change and the depletion of stratospheric ozone. These increases are known to primarily result from the use of synthetic nitrogen fertilisers and manures. Our study aimed to answer some of the many remaining questions about the mechanisms of production and movement of N_2O in soil. In a field study we injected ^{15}N -labelled nitrate into repacked columns of Ferralsol, at a depth of either 75 mm or 200 mm. We sampled soil gas at 3 depths and surface emissions. In-soil concentrations of N_2O rose by approximately two orders of magnitude when water-filled pore space increased to >80 %. This coincided with periods of high hydraulic conductivity, potentially draining dissolved $^{15}\text{N}_2\text{O}$ from the 75 mm injected columns at $189 \mu\text{g } ^{15}\text{N-N}_2\text{O m}^{-2} \text{ h}^{-1}$ compared with a surface flux of $1.2 \mu\text{g } ^{15}\text{N-N}_2\text{O m}^{-2} \text{ h}^{-1}$ and from 200 mm injected columns at $30 \mu\text{g } ^{15}\text{N-N}_2\text{O m}^{-2} \text{ h}^{-1}$ compared with a surface flux of $0.24 \mu\text{g } ^{15}\text{N-N}_2\text{O m}^{-2} \text{ h}^{-1}$. Data suggests that indirect emissions of N_2O by leaching and surface runoff from some soils may be much greater than the default 0.225 % of N applied recognised by the IPCC. This may go some way towards reconciling the discrepancy between ‘top down’ (~4 %) and ‘bottom up’ (~1.3 %, IPCC default) estimates of direct N_2O emissions from applied N. We also show that deeper placement of nitrate fertiliser may decrease direct N_2O surface emissions, although the effect on indirect emissions remains unclear.

Key Words

Dissolved N_2O , hydraulic conductivity, indirect emissions

Introduction

Atmospheric nitrous oxide (N_2O) concentrations have increased 20 % since pre-industrial times (IPCC 2013). N_2O now accounts for 6 % of global radiative forcing, and is the dominant contributor to stratospheric ozone depletion (IPCC 2013). Soils are the major source of both natural and anthropogenic N_2O , largely by microbial production through nitrification and denitrification, and contribute approximately 70 % of global N_2O emissions (Butterbach-Bahl et al. 2013). Few studies have tried to relate subsurface N_2O concentrations to N leaching from soils (Weymann et al. 2008) or N_2O surface emissions. From 1961 to 2011 there was an over nine-fold global increase in the annual use of synthetic N fertilisers (International Fertilizer Industry Association 2011) and the consequential increase in food production, while helping world population to more than double (U.S. Census Bureau 2013), is allied to the increasing concentration of atmospheric N_2O . A ‘top down’ estimate (based on changes in atmospheric N_2O concentrations) by Smith et al. (2012) recently concluded that 3–5 % of N entering the agricultural cycle (including biologically fixed N) is converted to N_2O . The Intergovernmental Panel on Climate Change (IPCC) currently has a default ‘bottom up’ emission factor (EF) – based on the extrapolation of flux chamber measurements – of 1 % of N applied to managed soils being directly emitted as N_2O and a further 0.325 % indirectly emitted – 0.225 % being associated with leaching of NO_3^- (mainly) in groundwater and by surface runoff and a further 0.1 % by volatilisation (IPCC 2006). Thus there remains a clear discrepancy between the top down and bottom up estimates which demonstrates the need for a clearer understanding of the mechanisms of production and movement of N_2O in soil.

Emissions of N_2O are highest when soil water-filled pore space (WFPS) exceeds approximately 75–80 %, when denitrification is regarded as the dominant process of its production (Butterbach-Bahl et al. 2013).

However, the upward diffusion of N₂O through soil is increasingly retarded as soil becomes wetter (Moldrup et al. 2000) and the high solubility of N₂O in water ($2.88 \times 10^{-2} \text{ mol L}^{-1} \text{ atm}^{-1}$ at 20 °C in moist air) (Weiss and Price 1980) creates the potential for much of it to be drained from soil at times of its peak production. Ferralsol is a well-drained soil occupying some 750 million hectares worldwide, almost exclusively in the tropics (International Union of Soil Sciences Working Group 2006), and thus subject to periods of heavy rainfall. We used in-field columns of this soil type (Fig. 1), with injection of 62.8 atom % ¹⁵N-NO₃⁻ (¹⁵NO₃⁻) at two depths, to improve understanding of diffusion and leaching of N forms through soil. In-soil concentrations and surface flux of N₂O (and less frequently ¹⁵N₂O), soil moisture and temperature were measured throughout a 3-month period. Soil NO₃⁻ and ¹⁵NO₃⁻ were measured periodically.

Methods

A lysimeter field trial was established in PVC columns using a sieved Ferralsol ($\leq 2 \text{ mm}$) repacked with similar soil profile layers to give a uniform bulk density of 1.02 Mg m^{-3} , equivalent to that of the original field soil. Formerly a dairy pasture, the site had since been only mown for >10 years, with no fertiliser applied in that time. The soil had 4.9 % total C content, 0.47 % total N, NH₄⁺-N and NO₃⁻-N of 13 and 56 mg kg⁻¹ respectively and pH(CaCl₂ 1:5) of 4.2. Each column was fitted with a removable airtight cap, fitted with a butyl rubber septum to enable sampling of headspace gas and were arranged in an RCBD grid. The central column had soil moisture (standing wave) and temperature sensors (Fig. 1), with each parameter logged half-hourly. Silicone tubing (ST) was held in spiral form and, covering close to the full column diameter, inserted horizontally at depths of 110, 260 and 410 mm for sampling of soil gas by diffusion. Each was connected by Tygon® tubing to Luer-lock taps for gas sampling and the diffusion properties of the ST had been tested at soil temperatures of 10, 20 and 30 °C, with internal N₂O concentrations of 7 ppm found to reach >95 % equilibration with the atmosphere in ≤ 2 hours in each instance.

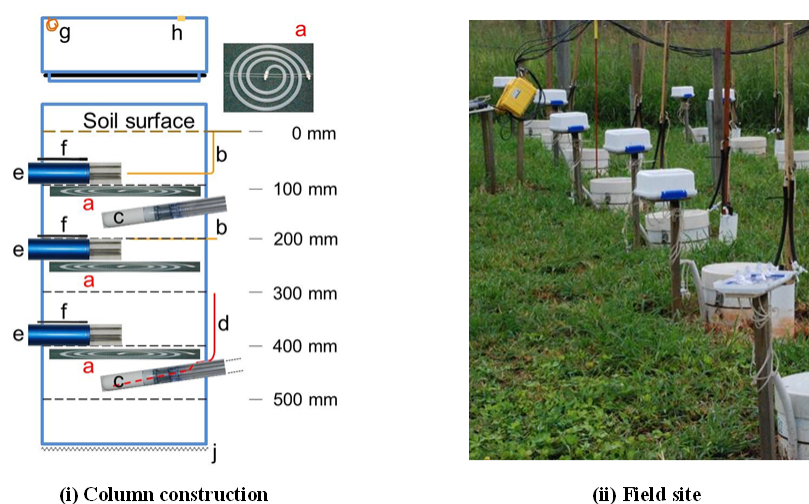


Figure 1 | (i) A 240 mm diameter PVC column with removable air-tight cap and components: a) silicone tubing for soil gas sampling – installed in a horizontal plane; b) tubing for NO₃⁻ injection; c) ceramic lysimeters for soil water sampling; d) water sample extraction tubing; e) soil moisture probes; f) soil temperature probes, at same depths as moisture probes; g) pressure equalisation vent; h) rubber septum for headspace gas extraction; j) fine mesh for exclusion of most soil mesofauna. (ii) A view of the field site with columns spaced at 1.3 m centres.

The columns were given 14 weeks to settle in the field before each column received one injection (on Day 0) of 1.68 g KNO₃ (53 kg N ha⁻¹, 62.8 atom % ¹⁵N) applied in 10 mL of Milli-Q water, followed by 3 mL of Milli-Q water to flush the tubing, at a depth of either 75 or 200 mm. There were 5 replicates of each and 5 columns that received no injection. Gas samples were taken from each depth and headspace, between 08:30 and 11:30, daily for the first week following NO₃⁻ injection, at least every 3rd day for the next 30 days and at a decreased frequency until the end of the trial on Day 89. Samples were analysed for N₂O and a sub-set of samples by isotope ratio mass spectrometer (IRMS) to determine the excess atom % ¹⁵N in N₂O and N₂. Water samples were withdrawn 9 days before, and 13, 23 and 40 days after NO₃⁻ injection. Saturated hydraulic conductivity in the columns of 71 mm h⁻¹, equivalent to 44.2 L m⁻² h⁻¹, was considered to be close to that of adjacent soil. At times of high soil moisture (>75 % WFPS) and low evaporation drainage rates were estimated from changes in soil moisture.

Results

Samples of soil water taken 9 days before NO_3^- injection (on Day 0) contained ammonium (NH_4^+) of $<0.05 \text{ mg L}^{-1}$. Concentrations of native NO_3^- ranged from 2.2 to 120 mg L^{-1} , so it was assumed that denitrification would effectively be the sole pathway of N_2O production through reduction of NO_3^- . Further water samples were taken on Days 13, 23 and 40. There was 305 mm of rain from Day 0 to Day 13 (Fig. 2), and in the 75 mm injected columns on Day 13 there was 7.0 atom % $^{15}\text{NO}_3^-$ at a depth of 160 mm and 32.7 atom % at 460 mm. Corresponding enrichments in 200 mm injected columns were 0.4 atom % and 22.4 atom % respectively. Enrichment of soil water declined by in all columns Day 23 and by Day 40 was highest at just over 2 atom % at 460 mm in 75 mm injected columns, and remained significantly higher ($p < 0.05$) in all columns at the greater depth. Combined with limited emissions of $^{15}\text{N}_2\text{O}$ after Day 23 (below), the decline in enrichment of soil water indicated that considerable leaching of NO_3^- had occurred.

In-soil N_2O concentrations increased markedly in all columns, particularly in middle layers where the increase was from $369 \mu\text{g N}_2\text{O-N m}^{-2}$ to $39,200 \mu\text{g N}_2\text{O-N m}^{-2}$ as soil moisture levels in all layers rose to $>80\%$ WFPS between Days 7 and 10 (Fig. 2). A similar trend was observed with $^{15}\text{N}_2\text{O}$, though to $4,090 \mu\text{g } ^{15}\text{N-N}_2\text{O m}^{-2}$ in the middle layers of 75 mm injected columns c.f. $119 \mu\text{g } ^{15}\text{N-N}_2\text{O m}^{-2}$ in those layers of 200 mm injected columns. Figure 2 shows how N_2O concentrations of middle layers had declined by Day 12 while increasing in adjacent, and most particularly bottom, layers and surface fluxes of N_2O reached a peak. Again, the same trends occurred with $^{15}\text{N}_2\text{O}$, being most apparent in 75 mm injected columns.

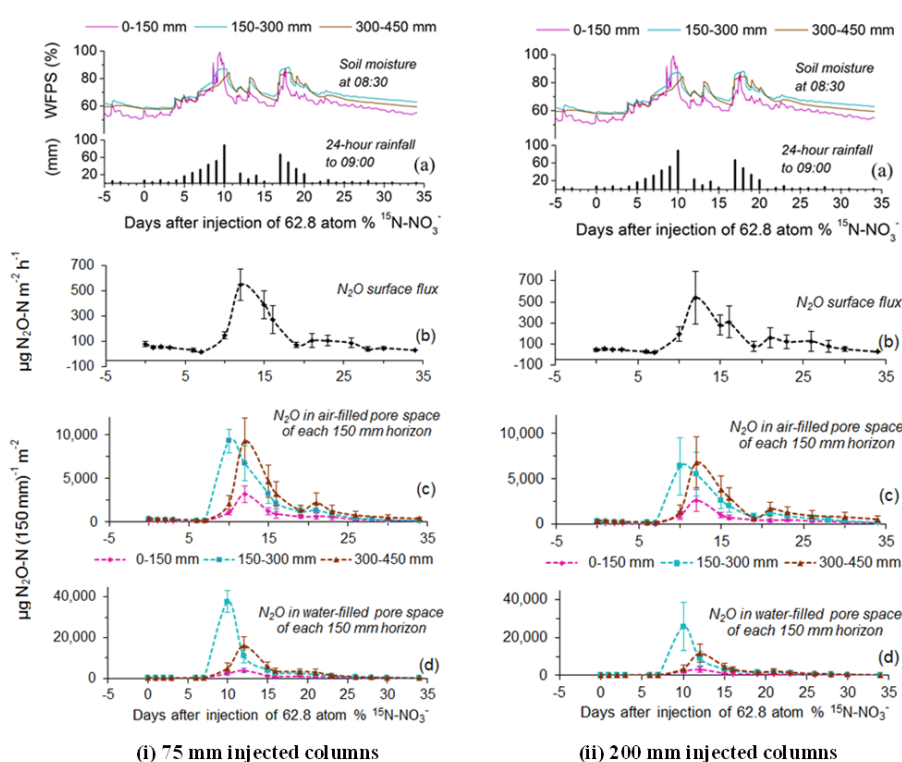


Figure 2 | For the columns where 62.8 atom % $^{15}\text{N-NO}_3^-$ was injected at a depth of (i) 75 mm and (ii) 200 mm: a) the daily rainfall and estimated water-filled pore space of each 150 mm layer of soil; b) the measured surface emissions of N_2O ; c) the estimated N_2O in the air-filled pore space of each 150 mm layer of soil; d) the estimated N_2O in the water-filled pore space of each 150 mm layer of soil (note different scale from air-filled pore space; all error bars represent $\pm \text{s.e.m.}$, $n = 5$).

When N_2O content of the middle layers were correlated (Pearson's r) with those of the top and bottom layers on each subsequent sampling day (i.e. Days 10–23 with Days 12–26) all values were ≥ 0.98 for 75 mm and 200 mm injected columns. These were much higher than 'same day' correlations and offered strong support for the middle layers being the regions of greatest N_2O production. It was calculated that there was 4.05 times as much N_2O dissolved in soil water of middle layers on Day 10 as there was in soil air (Fig. 2 (c) and (d)). Immediately prior to Day 10 gas sampling, the top layers drained in 30 minutes from 86 to 79 % WFPS at a rate of $13.0 \text{ L m}^{-2} \text{ h}^{-1}$ following cessation of rainfall. At the time of gas sampling on that day the 75 mm injected columns held an average of $4.38 \text{ mg N}_2\text{O-N L}^{-1} \text{ m}^{-2}$ of dissolved N_2O over all layers. Drained at the rate of $13.0 \text{ L m}^{-2} \text{ h}^{-1}$ its downward carriage would be 17.6 times the surface flux of N_2O on that day

and 4.7 times the Day 12 (peak) flux. For 200 mm injected columns the equivalent comparisons are 9.3 times the Day 10 surface flux and 3.3 times that of Day 12. If draining at the rate of K_s these ratios would increase by a factor of 3.4 although, in addition, the surface fluxes would almost certainly have decreased. At the time of gas sampling on Day 10 the 75 mm injected columns held an average of $17.1 \mu\text{g } ^{15}\text{N-N}_2\text{O L}^{-1} \text{ m}^{-2}$ of dissolved $^{15}\text{N}_2\text{O}$ in all layers. Drained at the rate of $13.0 \text{ L m}^{-2} \text{ h}^{-1}$ its downward carriage would be 189 times the surface flux of $^{15}\text{N}_2\text{O}$ on that day and 3.5 times the Day 12 (peak) flux. The 200 mm injected columns held $0.55 \mu\text{g } ^{15}\text{N-N}_2\text{O L}^{-1} \text{ m}^{-2}$ of dissolved $^{15}\text{N}_2\text{O}$ in all layers on Day 10. If drained at the rate of $13.0 \text{ L m}^{-2} \text{ h}^{-1}$ the downward carriage of dissolved $^{15}\text{N}_2\text{O}$ would be 30 times the Day 10 surface flux and 1.0 times that of the peak (Day 23) flux. Total emissions of $^{15}\text{N}_2\text{O}$ from 75 mm and 200 mm injected columns for Days 1–23 were $10.67 \text{ mg } ^{15}\text{N-N}_2\text{O m}^{-2}$ and $1.38 \text{ mg } ^{15}\text{N-N}_2\text{O m}^{-2}$ respectively, a substantial difference ($p = 0.084$) and corresponding to 0.50 % and 0.065 % of total NO_3^- injected. There was limited detection of excess $^{15}\text{N}_2$ within the soil (in both 75 mm and 200 mm injected columns) but not as surface flux, indicating that complete denitrification of injected NO_3^- had occurred, but it was unable to be quantified. Emissions of N_2O for Days 1–23 were 75 and 69 % of totals for Days 1–89 in 75 mm and 200 mm injected columns respectively and there was little further emission of $^{15}\text{N}_2\text{O}$ after Day 23, being measured three further times to Day 34. The decline in emissions of N_2O and $^{15}\text{N}_2\text{O}$ following the period of considerable drainage and decline in soil water content indicated that much that was dissolved was carried off-site in soil water. Without knowledge of the extent of complete denitrification (to N_2) the proportion of N_2O (or $^{15}\text{N}_2\text{O}$) indirectly emitted could not be determined.

Conclusion

The considerable downward drainage of dissolved N_2O suggests that the extent of indirect emissions of N_2O from freely draining soils such as Ferralsol may be greatly underestimated. As off-site carriage of dissolved N_2O is not included in the IPCC's estimate of 'indirect' emissions, this may contribute to explaining some of the discrepancy between 'top down' and 'bottom up' emission estimates. The substantially lower emissions of $^{15}\text{N}_2\text{O}$ from 200 mm injected columns than from those injected at 75 mm indicated that deeper NO_3^- placement may lower direct emissions of N_2O . The effect of downward drainage on indirect emissions of N_2O and the extent of full reduction to N_2 need to be more fully quantified across a wide range of soil environments.

References

- Butterbach-Bahl K et al. (2013). Nitrous oxide emissions from soils: how well do we understand the processes and their controls? *Philosophical Transactions of the Royal Society B: Biological Sciences* 368(1621).
- International Fertilizer Industry Association. (2011) World N Consumption. Accessed 11 August 2013 from www.fertilizer.org/ifa/ifadata/results.
- International Union of Soil Sciences Working Group (2006). World reference base for soil resources 2006. World Soil Resources Reports. Rome, FAO. No. 103: 145.
- IPCC (2006). N_2O emissions from managed soils, and CO_2 emissions from lime and urea application. 2006 IPCC Guidelines for National Greenhouse Gas Inventories - Volume 4: Agriculture, Forestry and Other Land Use. de Klein CAM, Novoa RSA, Ogle S et al. Hayama, Japan, IPCC - Prepared by the National Greenhouse Gas Inventories Programme. 4, Chapter 11: 54.
- IPCC (2013). Climate Change 2013: The Physical Science Basis. Contribution of Working Group I to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change. Stocker TF, Qin D, Plattner G-K et al. Cambridge, United Kingdom and New York, NY, USA, Intergovernmental Panel on Climate Change: 1535.
- Moldrup P et al. (2000). Predicting the gas diffusion coefficient in repacked soil: Water-induced linear reduction model. *Soil Science Society of America Journal* 64(5): 1588-1594.
- Smith KA, Mosier AR, Crutzen PJ and Winiwarer W (2012). The role of N_2O derived from crop-based biofuels, and from agriculture in general, in Earth's climate. *Philosophical Transactions of the Royal Society B-Biological Sciences* 367(1593): 1169-1174.
- U.S. Census Bureau. (December 19, 2013). World Population. International Programs. Accessed 3 January 2014, from www.census.gov/population/international/data/worldpop/table_population.php.
- Weiss RF and Price BA (1980). Nitrous-oxide solubility in water and seawater. *Marine Chemistry* 8(4): 347-359.
- Weymann D et al. (2008). Groundwater N_2O emission factors of nitrate-contaminated aquifers as derived from denitrification progress and N_2O accumulation. *Biogeosciences* 5(5): 1215-1226.