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Ammonia volatilisation is not the dominant factor in determining the soil nitrate isotopic composition of pasture systems

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ABSTRACT

Nitrate dual isotopes ($\delta^{15}N{-}NO_3^-$ and $\delta^{18}O{-}NO_3^-$) are increasingly used to assess the sources and sinks of nitrogen (N) pollution in freshwater systems. However, the application of this methodology to pasture agroecosystems is currently limited by the lack of information on how, or even if, the primary N inputs to the systems (livestock urine and urea fertiliser) are expressed in the isotopic signature of exported NO_3^-. To remedy this gap, direct measurements of fractionation during ammonia volatilisation were linked with changes in the concentration and isotopic composition of the residual soil inorganic N pool (NO_3^-, nitrite, and ammonium) following the addition of differing levels of bovine urine and urea fertiliser. Ammonia volatilisation, with a $\delta^{15}N$ enrichment factor of $+35 \pm 5$‰, removed from 5 to 40% of N inputs from the different treatments, which should have enriched the residual inorganic N pool to 25‰ and 3‰, respectively. However, this fractionation did not propagate into the soil NO_3^- pool due to a combination of urine-induced mineralisation (up to 120 μg N g soil^{-1} day^{-1} in the high urine treatment) and on-going nitrification. Consequently, NO_3^- measured within the treatments was not as enriched in ^{15}N as the values typically ascribed to excreta-N sources. Up-scaling these results, the whole-pasture NO_3^- isotopic composition primarily reflected time since fertilisation, regardless of urine inputs. These findings necessitate expanding the range of $\delta^{15}N{-}NO_3^-$ values ascribed to livestock sources to encompass values as low as −10‰, highlighting the need to account for post-deposition soil N cycling in order to accurately define NO_3^- isotopic source ranges.

1. Introduction

A century of agricultural intensification has dramatically accelerated global nitrogen (N) turnover, with excess N inputs to farm lands 'cascading' through the environment and jeopardising the ecosystem services of waterways and soils (Galloway et al., 2003). Pastoral livestock production is a particularly 'leaky' system: leaching nitrate (NO_3^-) into the surrounding waterways (Di and Cameron, 2002), releasing ammonia (NH_3) gas, and producing the greenhouse gas nitrous oxide (N_2O) (Smith et al., 2008). As a result, soil-N stocks are declining in pastoral systems (Stevenson et al., 2010). This situation is exacerbated by the fact that intensifying livestock production both increases N losses (Romera et al., 2012) and decreases N use efficiency, with the proportion of N fertiliser that goes into the food declining from ~60% to 8% as intensity increases (Powell et al., 2010). However, the multiple biological and chemical pathways that transform N between seven redox states, combined with the diffuse nature of NO_3^- pollution, makes assessing when and where N is 'leaked' from agroecosystems difficult (Groffman et al., 2009). Accurate and precise tracers of N movement from land to water are thus needed in order to sustainably manage pastoral systems, particularly in New Zealand, where grazed pastures account for 45% of land use (Stevenson et al., 2010) and declining water quality is linked to intensifying dairy production (McDowell et al., 2011).

Nitrate isotopes ($\delta^{15}N$ and $\delta^{18}O$) are a potential tool for identifying sources and quantifying losses of pasture N to waterways as they are modified by, and thus reflect, their environmental origin (Kendall, 1998; Rock et al., 2011 Xue et al., 2009). The use of NO_3^- isotopes as source indicators derives from the fact that the distribution of light versus heavy isotopes within the environment reflects kinetic (e.g., nitrification and denitrification) and equilibrium (e.g., ammonia (NH_3) volatilisation) fractionation processes, during which light isotopes typically react faster, creating differentially weighted product and reactant pools (Fig. 1). During kinetic reactions the changes in substrate concentration are related to

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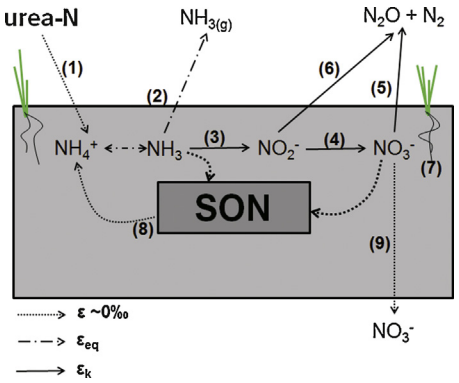

Fig. 1. Multiple, often co-occurring processes affect N turnover and isotopic composition in pasture systems: (1) Once urea (from fertiliser or urine) comes into contact with the soil, urea-N forms are immediately and completely hydrolysed to NH_4^+ with no apparent isotopic fractionation (ε ~0‰); (2) NH_4^+ exists in equilibrium with NH_3, which will further equilibrate into aqueous and gaseous forms (the latter of which can be volatilised out of the soil zone), wherein the balance between the three pools is determined by soil pH, equilibrium fractionation (ε_{eq}) of N pool causes 'light' N to be preferentially volatilised (Heaton, 1986; Heaton, 1986a); (3) under aerobic conditions residual soil NH_3 is nitrified to NO_2^-, which causes kinetic fractionation (ε_k) of N (Casciotti et al., 2003), while O is incorporated from soil H_2O and O_2 (Casciotti et al., 2010); (4) NO_2^- is further oxidised to NO_3^- in the second step of nitrification, causing inverse kinetic fractionation of N (i.e., residual pool gets lighter as the reaction progresses) (Casciotti, 2009) and O, in addition to incorporating another O from adjacent H_2O (Buchwald et al., 2012); (5) under anaerobic conditions, NO_3^- can be denitrified to N_2O and N_2, which causes parallel kinetic fractionation of both N and O (Granger et al., 2008); (6) new evidence suggests that NO_2^- can be directly reduced to N_2O and/or N_2 via co-denitrification (Spott et al., 2011) and nitrifier-denitrification (Kool et al., 2010), neither of which have known fractionation factors; (7) plant roots compete with these microbes to assimilate NO_3^- and NH_4^+ (Kaye and Hart, 1997), both with minimal isotope effects (Cernusak et al., 2009); (8) microbial immobilisation of inorganic N will reincorporate it into the large soil organic N (SON) pool; (9) SON can be mineralised back into the organic pool with minimal kinetic fractionation of N (and causing the O isotopes to be effectively 'reset') (Mengis et al., 2001; Mobius, 2013); (10) any NO_3^- that is not taken up by plants, immobilised or attenuated to N

changes in isotopic composition using the process-specific fractionation factor (α, $\varepsilon = (\alpha - 1) \times 1000$)) (Eq. (1)):

$$\frac{R}{R_0} = \left(\frac{C}{C_0}\right)^{\alpha-1} \quad (1)$$

where C and R represent the concentration and isotopic composition of the substrate at a given time point, and C_0 and R_0 represent the initial concentration and isotopic composition, respectively, of said substrate. If the reaction goes to completion, the isotopic composition of the product equals that of the original reactant. Equilibrium fractionation (ε_{eq}) is the product of differences in the zero-point energy between different species (R_A vs. R_B) (Eq. (2))

$$\varepsilon_{eq} = \{(R_A : R_B) - 1\} \times 1000 \quad (2)$$

where ε_{eq} is the result of the equilibrium between the two species (the stronger the fractionation effect, the further ε is from 0) (Hogberg, 1997; Kendall, 1998).

It is currently assumed that NO_3^- leached from pastures is primarily defined by equilibrium fractionation caused by NH_3 volatilisation (Frank et al., 2004; Heaton, 1986; Lee et al., 2011), based on the knowledge that livestock urine accounts for up to 95% of NO_3^- leached from grazed pastures (Decau et al., 2004). Once urea, in fertiliser or urine, is deposited onto soil it hydrolyses to ammonium (NH_4^+) and bicarbonate, increasing soil pH and pushing the chemical NH_4^+:NH_3 equilibrium towards NH_3 (Clay et al., 1990; Sherlock and Goh, 1985a)). This promotes the potential for physical NH_3 volatilisation, which occurs with a net enrichment factor (ε_{av}) of approximately −30‰ (Heaton, 1986) and can remove between 0–60% of applied urine-N (Cameron et al., 2013). As soil pH dynamics during NH_3 volatilisation prevent complete NH_x ($NH_x = NH_{3(gas)} + NH_{3(aqueous)} + NH_4^+$) removal (Sherlock and Goh, 1985a), livestock-derived NO_3^- is assumed to primarily reflect fractionation by NH_3 volatilisation, producing $\delta^{15}N{-}NO_3^- > +10‰$ (with subsequent nitrification contributing a $\delta^{18}O{-}NO_3^-$ range from −5‰ to +5‰) (Xue et al., 2009). Corroborating this assumption, two studies found ^{15}N enrichment of the soil N pool following application of urea-N sources (artificial urine (Frank et al., 2004) and cattle slurry (Kriszan et al., 2009)).

However, both kinetic and equilibrium fractionating processes occur within the pasture soil N cycle (Fig. 1): for ~20 days after urine deposition the residual soil NH_3 pool is oxidised to nitrite (NO_2^-) and then NO_3^- by nitrifying microbes (Clough et al., 2009). Soil acidification occurs during nitrification, counteracting the pH increase caused by urea hydrolysis. Nitrate in soil can then be taken up by plants, immobilised, leached, or biologically reduced to N_2O and dinitrogen (N_2). These biological processes could also influence the isotopic composition of pasture derived NO_3^- if the transformation of NH_3 to NO_3^-, or of NO_3^- to N_2 is incomplete when the NO_3^- is leached from the system (Fig. 1). Additionally, there is evidence that the NO_3^- isotopic composition of different source pools can be homogenised during transport through soils. Mengis et al. (2001) determined that the enriched $\delta^{18}O$ composition of NO_3^- fertilisers was only detectable in soil leachate at temperatures <10 °C; while both Schwarz et al. (2011) and Billy et al. (2010) found that the degree of denitrification, rather than the $\delta^{15}N$ of the inputs, determined the isotopic composition of NO_3^- leached from soils in a montane rainforest and a temperate agricultural field, respectively.

Process-level information is therefore required in order to accurately constrain how pasture N inputs influence the isotopic composition of the leached NO_3^-. To test the extent to which the $\delta^{15}N$ signature of pasture systems may reflect post-deposition biological N cycling rather than variations within the physical volatilisation process, we measured changes in the size and isotopic composition of the three main inorganic N pools (volatilised NH_3, soil NH_4^+, and soil NO_3^-) following bovine urine and urea application. This enabled a mass-balance approach to be used to, 1) assess the effects of NH_3 volatilisation, nitrification, denitrification, and mineralisation on the isotopic composition of soil NH_4^+ and NO_3^-, and, 2) up-scale this information to establish the appropriate $\delta^{15}N{-}NO_3^-$ vs. $\delta^{18}O{-}NO_3^-$ range for pastoral agriculture.

2. Materials and methods

2.1. Experimental set-up and design

The experiment was carried out in August 2012 (winter) at Lincoln University, Canterbury, New Zealand (E172°20.031′, S43°39.375′), where the mean annual precipitation is 650 mm and the mean annual air temperature is 12 °C. The soil was a Templeton silt loam (Typic Immature Pallic Soil, New Zealand classification, C = 34 mg g^{-1}, N = 3 mg g^{-1}; 18% clay, 49% silt, 33% sand) (see Orwin et al. (2010) for more details). The study area was planted with rye grass (*Lolium perene*), which was trimmed to 4 cm height 48 h before the start of the experiment.

In-situ chambers (diameter: 0.23 m) were set up in a randomised design (five replicates per treatment), with soils receiving either: 600 kg N ha^{-1} of bovine urine (high), 80 kg N ha^{-1} of bovine urine (low), or 80 kg N ha^{-1} of urea fertiliser (Sigma–Aldrich), or no N (controls). Chambers were installed two-weeks prior to treatment application to minimise disturbance effects. Treatments were made by diluting either urine or urea with deionised water to