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Nitrate removal processes in a constructed wetland treating drainage from dairy pasture

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ABSTRACT

^{15}N-labelled NO_3^- was used in a surface-flow constructed wetland in spring to examine the relative importance of competing NO_3^- removal processes. *In situ* mesocosms (0.25 m^2) were dosed with 2 l of $^{15}NO_3^-$ ($NaNO_3$, 300 mg N l^{-1}, 99 atom% ^{15}N) and bromide (Br^-) solution (LiBr, 4.3 g l^{-1}, as a conservative tracer). Concentrations of NO_3^-, Br^-, dissolved oxygen and $^{15}N_2$ were monitored periodically and replicate mesocosms were destructively sampled prior to and 6 days after ^{15}N addition. Denitrification, immobilisation, plant uptake and dissimilatory NO_3^- reduction to NH_4^+ (DNRA) accounted for 77, 11, 9 and 2% of $^{15}NO_3^-$ transformed during the experiment. Only 6% of denitrification gases were directly measured as atmospheric or dissolved $^{15}N_2$; the remainder (71%) was determined via ^{15}N mass balance. This indicated that a large proportion of the denitrification gases were entrapped within the soil matrix and/or plant aerenchyma. The floating plant *Lemna minor* exhibited a significantly higher NO_3^- uptake rate (221 mg kg^{-1} d^{-1}) than *Typha orientalis* (10 mg kg^{-1} d^{-1}), but periodic harvest of plants would remove <3% of annual NO_3^- inputs. Our results suggest that this 6-year-old constructed wetland functions effectively as a sink for NO_3^- during the growing season with less than one-quarter of the NO_3^- processed sequestered into wetland plant, algal and microbial N pools and the balance permanently removed by denitrification.

1. Introduction

Constructed wetlands are frequently used to treat point-source urban, industrial and agricultural wastewaters (Knight et al., 2000; Vymazal, 2005), but they have been less commonly used as filters for diffuse pollution. However, agricultural watersheds with lower permeability soils and surface and/or subsurface drains may benefit from the use of constructed wetlands to intercept and treat pulses of diffuse runoff channelled through the drainage network. While surface drains often carry sediments and nutrients in particulate form, subsurface drainage waters are typically enriched with dissolved nutrient forms, particularly nitrate (NO_3^-) (Deal et al., 1986). Studies to date suggest that surface-flow constructed wetlands treating agricultural drainage waters may retain a moderate to large proportion of the NO_3^- and total N load, particularly during the initial years of operation (e.g. Tanner et al., 2005; Kovacic et al., 2006; Beutel et al., 2009).

Denitrification is generally considered to be the major NO_3^- removal process in constructed wetlands, particularly in those established for some time with an accumulated base of organic matter supplying carbon for this process (Cronk and Fennessy, 2001). Plant uptake is more important in newly established wetlands or those receiving low N loads (Cronk and Fennessy, 2001). However, other less well-studied biogeochemical processes can also transform and retain NO_3^- in wetlands including immobilisation into the organic N pools (via microbial uptake or algal uptake) and dissimilatory NO_3^- reduction to ammonium (NH_4^+) (Nijburg and Laanbroek, 1997; Matheson et al., 2002). In some natural wetlands, NO_3^- may also be lost by leaching. However, in constructed systems leaching losses are usually minimised with the installation of an impermeable base or liner (Kadlec, 1994).

The fate of NO_3^- in treatment systems is important to establish, as only denitrification represents a permanent loss mechanism. Other processes typically result in only transient storage, unless plant biomass is harvested or there is significant peat accumulation. Seasonal senescence, decomposition processes and fluctuating water levels are all natural processes that facilitate the remineralisation of nutrients sequestered into wetland plant and soil pools (Kroger et al., 2007; Niedermeier and Robinson, 2007).

The ^{15}N stable isotope may be used as a tracer to study the fate and transformation of N in soil–plant systems. A limited number of studies have applied this technique in wetland environments, most often using enclosed *in situ* plots (Moraghan, 1993; Xue et al., 1999) or reconstituting the wetland plant–soil system in lab-

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oratory microcosms (Lusby et al., 1998; Matheson et al., 2002). The present study aimed to identify the dominant NO_3^- removal pathways in a constructed wetland using ^{15}N-labelled NO_3^- added to *in situ* plots (mesocosms) during the growing season. Specifically, the study sought to determine the relative proportions of ^{15}N-labelled NO_3^- denitrified to N gases, assimilated into wetland plants, immobilised into the microbial/algal N pools and dissimilated to NH_4^+. Replicated, isolated sections of the wetland were dosed with ^{15}N–NO_3^- at a magnitude comparable to the natural NO_3^- inflows. A previous study of this wetland (Tanner et al., 2005) concluded that the majority of the NO_3^- removal in this wetland was probably due to denitrification on the basis of sufficient denitrification enzyme activity (DEA) and the timing and magnitude of outflow NH_4^+ pulses indicating negligible DNRA. This study sought to confirm this result using the ^{15}N tracer technique and examine in more detail the contribution of competing NO_3^- removal processes (denitrification, plant uptake, immobilisation and DNRA).

2. Materials and methods

2.1. Study site

The study site was a constructed wetland treating farm drainage waters at Toenepi, Waikato, New Zealand (37°44′S, 175°35′E). The 260 m^2 wetland (52 m length × 5 m width) was constructed in 2000 by excavating 1–1.5 m below the existing ground surface into low permeability clay subsoils. Excavated topsoil (50–200 mm depth) was placed in the base of the wetland as a growing medium and organic matter source. The soil is Rotokauri silt loam (NZ soil classification). This is an orthic gley soil, poorly drained and derived from Quaternary rhyolitic and andesitic tephra (Bruce, 1978). The wetland is a two-stage system with upper and lower sections of equal dimensions. Water accumulates to a depth of 0.6 m in the upper section of the wetland before overflowing to the lower section. The wetland soil in the upper section had the following properties 18 months after establishment (Tanner et al., 2005; values are mean ± SE, $n = 4$): pH 5.5 (±0.07), total C 6.1 (±0.11)%, total N 0.42 (±0.01)%, KCl-extractable NH_4^+ 18 (±1.11) mg N $kg\ soil^{-1}$, KCl-extractable NO_3^- 0.38 (±0.06) mg N $kg\ soil^{-1}$, denitrifying enzyme activity 7.2 (±0.25) mg N_2O–N $kg\ soil^{-1}\ h^{-1}$.

The wetland treats subsurface drainage from a 2.6 ha dairy catchment (2.9 cows ha^{-1}, fertilised with 150–175 kg urea–N $ha^{-1}\ y^{-1}$ and 9.2–18.4 kg superphosphate–P $ha^{-1}\ y^{-1}$) and which is vegetated with ryegrass (*Lolium perenne* L.) and white clover (*Trifolium repens* L.). Drainage water is rich in NO_3^-; the median concentration is 11.4 mg N l^{-1} (Tanner et al., 2005). The dominant vegetation of the wetland is a native species of cattail (*Typha orientalis* C. B. Presl.) and duckweed (*Lemna minor* L.). At the site a cellphone-telemetered automated weather station (NIWA Instrument Systems, Christchurch, NZ), incorporating a Campbell CR10X intelligent logger (Campbell Scientific Inc., Logan, UT, USA), records precipitation, wind speed and direction, and air temperature on an hourly basis.

2.2. Mesocosm installation

Six stainless steel mesocosms (0.5 m × 0.5 m × 1.0 m high) were installed in October (spring) 2006. Each mesocosm was placed to enclose wetland plants at their natural density and pushed firmly into the clay base of the wetland. Mesocosms were installed one week prior to the experiment to enable equilibration. A 5 cm diameter hole on each side of the mesocosms facilitated water exchange with the wetland but these were sealed with rubber bungs when the experiment began. All mesocosms were located within the upper half of the wetland. Water depths in the mesocosms were approximately 0.5 m at the beginning of the experiment.

2.3. ^{15}N experiment

Three mesocosms were sampled prior to application of ^{15}N–NO_3^- solution to provide background values. Overlying water samples (1 l) were collected the day prior to application for analysis of NO_3^-, NH_4^+ and TDN concentrations and atom percent (%) ^{15}N enrichment. The dissolved oxygen (DO) concentration at 5 and 30 cm below the water surface in the mesocosms and in the surrounding wetland was measured using a DO meter (Model 95, YSI Inc., OH, USA). The three mesocosms were sealed with transparent Perspex® (acrylic resin) covers fitted with rubber gas sampling septa. After 24 h, triplicate gas samples were collected from each mesocosm and stored in sterile 10 ml Vacutainers® (Becton Dickinson, NJ, USA). These mesocosms were then destructively sampled. All plant material (*Typha* and *Lemna*) was harvested, including *Typha* litter, and three cores (8.2 cm diameter × 10.0 cm depth) of the underlying soil were also collected.

The following day, the remaining three mesocosms were each dosed with 2 l of ^{15}N–NO_3^- and bromide solution ($NaNO_3$, 300 mg N l^{-1}, 99 atom% ^{15}N, LiBr 4.3 g l^{-1}). Bromide was added as a conservative tracer to detect any dilution as a result of precipitation inputs or leakage losses during the experiment. The added solution was thoroughly mixed with ambient overlying water, water samples (1 l) were taken for nutrient and isotope analysis as described above, and perspex covers placed on the mesocosms. Automatic vacuum samplers (Model 4907, Manning Environmental Inc., Georgetown, TX, USA) were used to periodically collect further 100 ml overlying water samples from each mesocosm for NO_3^- and Br^- analysis via a gas-tight tube line sealed through the mesocosm wall. Another gas-tight tube line attached to a syringe allowed periodic manual collection of 60 ml water samples for DO analysis. At 24 h intervals gas samples (10 ml) were collected from each mesocosm. After each sampling, perspex covers were removed for 1 h then replaced. While covers were removed water samples (10 ml) were collected and sealed in Vacutainers for dissolved gas (N_2) analysis. From day 3, covers were left on for a 72 h period, with gas samples collected and covers removed on day 6. Manual water and gas sampling took place 1, 2, 3 and 6 days after application of ^{15}N–NO_3^- solution. On day 6, the three mesocosms were destructively sampled with water, plant and soil samples collected as described above.

2.4. Sample analysis

Water samples were filtered through 0.45 μM Sartorius filters and analysed for NO_3^- and NH_4^+ by flow-injection analysis (Lachat Quik-Chem 8000 Series, methods 31-107-04-1-A, 31-107-06-1-1-B). Samples for TDN analysis were first digested (APHA, 1998; Method 4500N) then analysed using the NO_3^- method. DON was calculated as the difference between TDN and DIN (NO_3^- and NH_4^+). The atom% ^{15}N enrichment of NO_3^- and NH_4^+ in filtered water samples was determined following sequential diffusion onto acidified filter papers (Sorensen and Jensen, 1991; Stark and Hart, 1996) followed by analysis by Isotrace New Zealand Ltd on a Europa 20-20 update stable isotope ratio mass spectrometer (Europa Scientific, Crewe, UK) interfaced to a Carlo-Erba elemental analyser (NA1500, Carlo Erba, Milan, Italy). The atom% ^{15}N enrichment of TDN was determined by the same method but following persulphate digestion (APHA, 1998; Method 4500N) of water samples to convert all TDN to NO_3^-.

Soil cores were sectioned into 0–5 cm and 5–10 cm segments, weighed and homogenised. Soil subsamples (5 g) were extracted