Nitrous oxide generation, denitrification, and nitrate removal in a seepage wetland intercepting surface and subsurface flows from a grazed dairy catchment

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Abstract. Little is known about seepage wetlands, located within agricultural landscapes, with respect to removing nitrate (NO\textsubscript{3}\textsuperscript{-}) from agricultural catchments, mainly through gaseous emissions of nitrous oxide (N\textsubscript{2}O) and dinitrogen (N\textsubscript{2}) via denitrification. These variables were quantified using a push–pull technique where we introduced a subsurface water plume spiked with\textsuperscript{15}N-enriched NO\textsubscript{3}\textsuperscript{-} and 2 conservative tracers [bromide (Br\textsuperscript{-}) and sulfur hexafluoride (SF\textsubscript{6})] into each of 4 piezometers and extracted the plume from the same piezometers throughout a 48-h period. To minimise advective and dispersive flux, we placed each of these push–pull piezometers within a confined lysimeter (0.5 m diameter) installed around undisturbed wetland soil and vegetation. Although minimal dilution of the subsurface water plumes occurred, NO\textsubscript{3}\textsuperscript{-}-N concentration dropped sharply in the first 4 h following dosing, such that NO\textsubscript{3}\textsuperscript{-}-limiting conditions (<2 mg/L of NO\textsubscript{3}-N) for denitrification prevailed over the final 44 h of the experiment. Mean subsurface water NO\textsubscript{3}\textsuperscript{-} removal rates during non-limiting conditions were 15.7 mg/L.day. Denitrification (based on the generation of isotopically enriched N\textsubscript{2}O plus N\textsubscript{2}) accounted for only 7% (1.1 mg/L.day) of the observed groundwater NO\textsubscript{3}\textsuperscript{-} removal, suggesting that other transformation processes, such as plant uptake, were responsible for most of the NO\textsubscript{3}\textsuperscript{-} removal. Although considerable increases in \textsuperscript{15}N-enriched N\textsubscript{2}O levels were initially observed following NO\textsubscript{3}\textsuperscript{-} dosing, no net emissions were generated over the 48-h study. Our results suggest that this wetland may be a source of N\textsubscript{2}O emissions when NO\textsubscript{3}\textsuperscript{-} concentrations are elevated (non-limited), but can readily remove N\textsubscript{2}O (function as a N\textsubscript{2}O sink) when NO\textsubscript{3}\textsuperscript{-} levels are low. These results argue for the use of engineered bypass flow designs to regulate NO\textsubscript{3}\textsuperscript{-} loading to wetland denitrification buffers during high flow events and thus enhance retention time and the potential for NO\textsubscript{3}\textsuperscript{-}-limiting conditions and N\textsubscript{2}O removal. Although this type of management may reduce the full potential for wetland NO\textsubscript{3}\textsuperscript{-} removal, it provides a balance between water quality goals and greenhouse gas emissions.

Additional keywords: bromide, denitrification, \textsuperscript{15}N, NO\textsubscript{3}\textsuperscript{-} removal, N\textsubscript{2}O, N\textsubscript{2}, wetland, SF\textsubscript{6}.

Introduction

Nitrogen (N) losses from applied chemical fertilisers, dairy effluent irrigation, and grazing animal excreta potentially cause eutrophication in receiving waters (Phipps and Crumpton 1994; Naiman \textit{et al}. 1995; Carpenter \textit{et al}. 1998). The export of N via surface and subsurface runoff to water bodies can either be minimised by best farm management practices: applying N fertiliser with N inhibitors (Zaman \textit{et al}. 2008a), and using riparian zones along river and stream banks (Cooper 1990; Ambus and Lowrance 1991; Haycock and Burt 1993; Carpenter \textit{et al}. 1998; Burt \textit{et al}. 1999), seepage wetlands (Blackwell \textit{et al}. 1999), or permanently wet swales located at gullies of agricultural hillslopes (Burns and Nguyen 2002; Rutherford and Nguyen 2004).

Nitrate moving through riparian and seepage areas is subject to denitrification, plant uptake, dissimilatory reduction of NO\textsubscript{3}\textsuperscript{-}

Abbreviations: BD, bulk density; DEA, denitrification enzyme activity; DNRA, dissimilatory reduction of nitrate to ammonium; I.D., internal diameter; LOI, loss on ignition; PVC, polyvinyl chloride.
Nitrous oxide has been found to be an important end product of denitrification in riparian soils receiving high NO$\text{}_3^-$ loadings (Hefting et al. 2003). Nitrous oxide in wetlands is produced not only by denitrification but also by nitrification and DNRA (Stevens and Laughlin 1998; Hefting et al. 2003; Smith et al. 2003). Nitrous oxide produced by various processes might form 1 pool before being reduced to N$_2$ by nitrous oxide reductase, the enzyme involved in reduction of N$_2$O to N$_2$ (Stevens and Laughlin 1998), which suggests that wetlands can act as a source or a sink of N$_2$O (Blicher-Mathiesen and Hoffmann 1999; Well et al. 2001). A wide range of N$_2$O:N$_2$ ratios has therefore been reported for wetlands, depending on factors (e.g. soil pH, carbon, anaerobicity, NO$_3^-$ concentrations) that govern the nitrification–denitrification–DNRA processes (Groffman et al. 2000, 2002; Smith et al. 2003). Thus, the use of wetlands in decreasing diffuse N pollution of streams and rivers may shift the potential environmental problem from water pollution to greenhouse gas emission (Well et al. 2001; Hefting et al. 2003).

Several techniques have been used to investigate NO$_3^-$ removal in wetlands. Many studies have focused on quantifying NO$_3^-$ removal by measuring the rates of processes such as denitrification in laboratory incubation and microcosm studies (Seitzinger 1994; Groffman and Hanson 1997; Zaman et al. 2008b). These studies suffer from the effects of soil disturbance on oxygen (O$_2$) status and hence N transformation processes, and from the difficulty of obtaining sediments from depths below the water table for microcosms (Jacinthe et al. 1998; Addy et al. 2002).

**In-situ** studies conducted by Burns and Nguyen (2002) have compared NO$_3^-$ movement in wetland groundwater to that of a more conservatively transported ion such as bromide (Br$^-$). Nitrate removal was then estimated from the changes in NO$_3^-$:Br$^-$ ratios and NO$_3^-$ and Br$^-$ mass with time, assuming that Br$^-$ is not taken up by plants or processed by soil microorganisms (Schnabel et al. 1996; Whitmer et al. 2000). Addy et al. (2002) successfully demonstrated the use of the push–pull method to determine in-situ subsurface water denitrification and NO$_3^-$ removal rates in riparian zones. In that study, collected wetland subsurface water was spiked with Br$^-$, sulfur hexafluoride (SF$_6$), and $^{15}$N-enriched NO$_3^-$ (potassium nitrate). The amended subsurface water was pushed (i.e. injected) into a mini-piezometer (diameter 18 mm with screen length 20 mm) and then pulled (i.e. extracted) from the same piezometer after an incubation period ranging from 6 to 48 h. Sulfur hexafluoride, an inert and slightly water-soluble gas with an extremely low atmospheric background concentration of 3 parts per trillion by volume, was found to behave as conservatively as Br$^-$, indicating negligible degassing, thus allowing the authors to confidently use the sum of $^{15}$N dissolved gas ($^{15}$N$_2$O and $^{15}$N$_2$) generation and changes in NO$_3^-$ concentration (NO$_3^-$ consumption) as estimates of the denitrification rate and NO$_3^-$ removal.
The objectives of this study were to (i) quantify in-situ $\text{NO}_3^-$ removal, $\text{N}_2\text{O}$ and $\text{N}_2$ emissions, and denitrification rates in a wetland swale in a dairy landscape using the push–pull technique; (ii) compare in situ denitrification rates as estimated by either the $^{15}$N tracer technique or the decrease in added $\text{NO}_3^-$ concentrations with time; and (iii) provide information on $\text{N}_2\text{O}$ : $\text{N}_2$ ratios in emitted gas from wetlands under non-limiting and limiting $\text{NO}_3^-$ conditions.

Materials and methods

Description of study site

The studied seepage wetland (6817 m$^2$) was located at a footslope of 3 pasture paddocks of a grazed dairy farm (3 cows/ha) in a dairy catchment at Kiwitahi, about 32 km from Hamilton (37°44′S, 175°35′E), New Zealand. The climate is humid–temperate with mean annual temperature of 15°C and annual rainfall of 1150 mm.

The wetland comprises a broad, low gradient (<1° slope) area that receives water from a spring (approximately 1 m from the wetland inlet), natural seepage, and discharges from shallow channels that intercept surface runoff and overland flow from the adjacent pasture paddocks. Grazing animals have been excluded from the wetland since 1999. An artificial swale that is now filled with sediment, organic floc, and wetland plants runs through the wetland and carries most of the flow. The entire wetland complex developed due to a flow constriction at the end of the permanently wet swale which creates partially flooded conditions within the area surrounding the swale (with a slope of <1° across the wetland).

There are 2 major soil types in the catchment, the Topehaehae silt loam and the Kiwitahi silt loam. The Topehaehae silt loam, which is derived from volcanic ash alluvium, is a gley recent soil (Aeric Haplaquent; USDA Soil Taxonomy) with silt loam topsoil and blocky clay loam at 0.3–0.75 m depth. It is a poorly drained soil with very slow subsoil permeability (<0.5 cm/h; Wilson 1980). The Kiwitahi silt loam is a yellow-brown loam (Typic Andept) with a brown silt loam soil texture and moderately permeable subsoil. Its parent material is volcanic ash over late Pleistocene terrace deposits. The soil is well drained and friable with well-developed fine crumbs. Our study focused on the wetland swale. The soil within the wetland swale is saturated to the surface and is composed of very loose organic material approximately 0.2 m deep. The top 0.1 m depth comprises mainly a thick root mat of wetland plants plus unconsolidated organic mucks. It is followed by a 0.1 m layer of unconsolidated organic flocs and decayed plant materials. Beyond the 0.2 m depth, sediment is more condensed with a mixture of organic matter, silt, and clay, probably originating from the eroded soil materials that have been washed in from the adjacent pasture paddocks plus organic matter decay from wetland vegetation. At a depth of 0.5 m, there is a transition to bluish grey silty clay that increases in its firmness and density with depth. A dense silty clay layer of low permeability particularly at 0.7–0.9 m depth acts as an aquiclude, restricting water movement to a deeper subsurface water. Beyond 0.9 m depth, sediments consisted of a sand and clay mixture. Using tracer tests in a similar seepage wetland, Rutherford and Nguyen (2004) found rapid dilution and pore water velocities of approximately 0.5 m/day within the upper layers of soil. Wetland vegetation consists mainly of soft brome ($\text{Bromus hordaceus}$ L.) with some floating glaucous sweet grasses ($\text{Glyceria declinata}$ Breb.) and soft rush ($\text{Juncus effusus}$ L.) and wiwi ($\text{Juncus edgariae}$ L.) in areas around the wetland channel and the remaining wetland area. The herbage in pasture paddocks was a mixture of ryegrass ($\text{Lolium perenne}$ L.) and white clover ($\text{Trifolium repens}$ L.).

Lysimeter installations

Push–pull studies are poorly suited to wetlands with high advection and dispersion that can carry the introduced plume away from the dosing piezometer. Because seepage wetlands have high advective and dispersive flux, we installed 4 large lysimeters made up of polyvinyl chloride (PVC) (0.5 m inner diameter and 1.2 m length with a sharpened bevel at the bottom end) to create a confined control volume for push–pull experiments in January 2003. This lysimeter set-up allowed us to investigate denitrification and to follow changes in $\text{N}_2\text{O}$ and $\text{NO}_3^-$ with time. To facilitate the installation of each lysimeter into the wetland, a serrated knife and 0.6-m machete were used to cut through the wetland plant roots and sediments around the lysimeter perimeter and to remove above ground wetland herbage within each lysimeter to 0.05 m height above the wetland surface. The lysimeter was then gently pushed through the wetland media to the underlying silt-clay layer and then slowly pounded into the aquiclude layer. Each lysimeter extended 0.25 m above the wetland surface and at least 0.25 m into the consolidated aquiclude layer of silty clay. Thus, in each lysimeter the depth of wetland sediment above the aquiclude material was approximately 0.7 m.

In the centre of each of the 4 lysimeters, a PVC piezometer (PVC pipe 0.03 m internal diameter and 1.25 m long screened with 0.25-mm slots at 6-mm intervals over the 0.15-m length between 0.20 and 0.35 m depth below the surface of the wetland subsurface water) was installed for the purpose of dosing tracers and water sampling. An impermeable barrier (PVC sleeve) was created within the piezometer at 0.35 m from the wetland ground surface. The estimated well volume of the piezometer over the top 0.35 m depth of the wetland was 247 mL (thereafter a well volume was designated as 250 mL). The piezometer was installed into a PVC sleeve, 0.08 m diameter and 0.40 m deep, hollowed out from the wetland sediment with an auger. The piezometer was inserted into this PVC sleeve and pounded into the clay aquiclude for stability. Each piezometer extended 0.35 m above the wetland ground surface and over 0.2 m deep into the aquiclude. After installation, the lower 0.2 m of space between the 0.08-m PVC sleeve and the piezometer was backfilled with quartz drilling sand (36% pore space), and the upper top 0.2 m was filled with bentonite before removal of the PVC sleeve. Added bentonite acted as a seal to minimise water flow along the side of each piezometer. Two additional piezometers, which were not confined within lysimeters, were also installed at the site to obtain ambient subsurface water to supply the amended dosing volumes used in the push–pull test. The screened depth, construction, and installation of these piezometers were identical to the piezometers in the lysimeters.
Pre-testing the modified push–pull technique in the wetland lysimeters

A preliminary study was conducted about 6 weeks before the initiation of the 15N-tracer push–pull study. The objective of this study was to provide background information on the physical behaviour of an introduced tracer plume and the approximate rate of NO3– removal within the studied lysimeters. We dosed 4 lysimeters through their piezometers with 10 L of wetland subsurface water at a rate of 0.2 L/min using a peristaltic pump. This subsurface water was amended with 200 mg/L of chloride (Cl–) and 8 mg/L of NO3–-N. Surface and subsurface water samples were then obtained 1, 2, 3, 4, 24, 48, 72, and 96 h after dosing and analysed for NH4+, NO3–, and Cl– concentrations. During and immediately following this study we extracted a total of 15 L from each lysimeter to remove most of the introduced plume.

Preparation of the dosing NO3– tracer solution for push–pull technique

To prepare a dosing solution for 4 lysimeters (10 L per lysimeter), about 42 L of clear wetland water was extracted from the 2 additional piezometers outside the lysimeters. To achieve clear wetland water, the dead volume (muddy water) was pumped until clear water was visible. The collected water was brought back to the laboratory in insulated boxes with ice cubes and stored at 4°C until used for preparation of the dosing solution. The dosing solution contained 30 mg/L of Br– (as LiBr) and 12 mg/L of 15N-labelled NO3– as KNO3 (99 atom% 15N). The level of Br– was higher than the background level (<1 mg/L) typically found in wetlands in the studied area while the NO3– level was comparable to subsurface water samples were collected from each lysimeter after 1, 2, 3, 4, 24, and 48 h of dosing and analysed for NH4+, NO3–, and Cl– concentrations. After storage overnight at 4°C the dosing solution was again sparged with SF6 to bring the DO to lower the dissolved oxygen (DO) to 3 mg/L. After SF6 sparging, the headspace was sparged with helium (He) gas to avoid exposure to air, and injected into 2 separate 120-mL pre-evacuated gas bottles. All samples were brought back to the laboratory in insulated boxes with ice cubes and stored at 4°C before analyses.

Wetland plant N status and sediment characteristics

Four samples of mixed ryegrass–white clover pasture herbage (standing pasture herbage of 0.1–0.15 m height) were randomly taken from adjacent paddocks by cutting to 20 mm height. Similarly, grab samples of vegetation in the wetland swale (mainly sweet grass) were also collected. Pasture herbage and wetland vegetation were dried at 60°C for 7 days, ground, sieved <2 mm, and analysed for total N. Four sediment samples per replicate (85 mm diameter) were taken from 0–0.1, 0.1–0.2, 0.2–0.4, and 0.4–0.7 m depths outside each lysimeter for bulk density (BD), porosity, and saturated hydraulic conductivity (Ks). Estimates of Ks for each horizon were obtained from undisturbed cores using a constant head laboratory method described in Rutherford and Nguyen (2004). Soils were then extruded and oven-dried at 105°C for 48 h to determine BD and porosity. The unconsolidated nature of the top 0–0.1 m sediment depth made it difficult to use the soil core technique for measuring Ks, and hence the pump test technique was used (Klute 1986). Four additional sediment samples (0.05 m diam.) were taken from the same depths and analysed for denitrification enzyme activity (DEA) (Tiedje et al. 1989), pH, organic matter, moisture, and NH4+ and NO3– contents.

Analytical methods and laboratory procedures

Water samples collected from the preliminary test were analysed for Cl– and Br– by ion chromatography (American Public Health Association 1998), and for total Kjeldahl-N, NO3–-N, and NH4+-N with a flow injection analyser (FIA). The DO and temperature of surface and subsurface waters were recorded at every sampling event using a WP-82Y Model DO/temperature meter (TPS). Water samples for ion analyses during the main experiment were filtered through GF/C filters (1 μm pore size) to remove suspended materials and subsequently analysed for Br– by inductively coupled plasma emission spectroscopy-mass spectrometry (American Public Health Association 1998), and for NH4+, NO3–, and NO2– by FIA.

Immediately after arrival at the laboratory, He gas was injected into the 120-mL gas bottle samples collected for dissolved gas analyses, to bring them to atmospheric pressure. After storage overnight at 4°C, the sample bottles were removed from each lysimeter after 1, 2, 3, 4, 24, and 48 h of dosing for analysis of dissolved gases (15N2O, 15N2, N2O, SF6) and ions (NH4+, NO3–, and Br–). Before subsurface water was taken from each piezometer for gas and ion analyses, 2 well volumes of water (500 mL) at the first sampling (i.e. 1 h after dosing) and 1 well volume at subsequent samplings (i.e. 2, 3, 4, 24, and 48 h after dosing) were pulled from each lysimeter using a peristaltic pump and discarded. Another 200 mL was then taken from each piezometer and stored in two 100-mL plastic bottles for ion analyses. For gas analyses, duplicate 20-mL subsurface water samples were collected from each piezometer using a 60-mL syringe through a closed system to avoid exposure to air, and injected into 2 separate 120-mL pre-evacuated gas bottles. All samples were brought back to the laboratory in insulated boxes with ice cubes and stored at 4°C before analyses.
were shaken for 30 s to equilibrate SF6, N2O, and N2 between the aqueous (subsurface water) and gaseous phases (headspace). Two gas samples of 12 mL each were then collected from each bottle headspace and stored in pre-evacuated 12-mL glass vials fitted with a screw cap and a rubber septum (Exetainers; Labco, High Wycombe, UK), one for 15N2O and 15N2 analyses and another for N2O and SF6 analyses. The 15N analyses of N2O and N2 were performed by automated continuous flow isotope ratio mass spectrometry (CF-IRMS) and N2O and SF6 concentrations were determined using a gas chromatograph (GC) (Shimadzu GC-17A, Japan) equipped with a 63Ni-electron capture detector operating at column, injector, and detector temperature of 55, 75, and 330°C, respectively. Correction for dissolved N2O and N2 in the water phase at 5°C was achieved by using the Bunsen solubility coefficients of 1.06 and 0.021 for N2O and N2, respectively (Weiss and Price 1980).

Sediment water content was determined gravimetrically by oven drying at 105°C for 48 h. Sediment NH4+ and NO3− contents were determined by shaking freshly collected sediment (10 g on oven-dried basis) with 20 mL of 2 M KCl solution for 1 h, followed by centrifugation at 4000g, filtration through Whatman no. 42 filters, and analysis by FIA. Sediment organic matter content was determined as the proportion of the weight of oven-dried soil based on loss on ignition (LOI) at 550°C for 4 h. Sediment pH was determined using a combination glass electrode after equilibrating freshly collected samples (10 g on oven-dried basis) with 10 mL of deionised water for 30 min. All sediment analyses were corrected for sediment water content.

Wetland sediment was bulked on a soil depth basis and 3 replicate samples from each depth were analysed for DEA using a Bunsen coefficient of 0.632 for 20°C (temperature of the laboratory) to account for N2O in aqueous solution (Tiedje et al. 1989). Sediment (5 g fresh weight) was amended with 5 mL solution containing NO3− (KNO3, 0.1 g/L) and glucose (0.2 g/L). The headspace was flushed with N2 gas and 10 mL acetylene (C2H2) to inhibit the reduction of N2O to N2. After 15 and 60 min of incubation at laboratory ambient temperature (20°C), duplicate headspace samples were transferred to 12-mL exetainers. The samples from exetainers were then analysed for N2O by the Shimadzu GC as described above.

Plant samples (0.1 g per sample) were digested with 5 mL of Kjeldahl mixture for 3 h at 350°C and N content was determined by automated analysis with a Technicon Auto Analyzer II (Technicon Instruments Corp., Tarrytown, NY). Total S and total P content in plant samples were determined using the technique of Quin and Woods (1976) in which plant samples were digested with nitric and perchloric acid mixture for 1 h at 200°C.

### Estimating denitrification rate and NO3− removal

Measured concentrations and 15N atom% in 15N14N16O (46N2O) and 14N15N16O (45N2O) in dissolved gases extracted from surface and subsurface water samples were used to determine denitrification rates after correcting for the 15N background (natural abundance) of 0.3663 atom%. The dissolved N2 concentration in water samples (obtained from CF-IRMS) was converted to the amount (µg/L) as described in Tiedje (1982) taking into account the volume of an exetainer, the volume of water samples collected from each lysimeter for N2 analyses, and the volume of a headspace in a 0.12-L bottle (i.e. 0.012, 0.020, and 0.10 L, respectively). The amount of N2 produced was then converted to a rate of N2 generation by multiplying it by the ratio of applied 15N (99% atom) present as 15N atom% in dissolved N2. The rate was expressed as µg/L/day after taking into account the time interval between each sampling event.

Similarly, the N2O concentration in water samples as measured by GC was converted to the amount of N2O produced (µg/L), which was then converted to the rate of N2O generation (i.e. the amount of N2O that was derived from the denitrification of labelled NO3−) by multiplying it by the ratio of applied 15N (99% atom) present as 15N atom% in dissolved N2O. The data on 15N atom% in 46N2O was used in this calculation since it was significantly correlated (r²=0.86; P<0.001) with the 15N atom% in 45N2O of the same samples.

Nitrification removal attributed to denitrification and other biological processes was calculated as the difference between measured and estimated 'conserved' NO3− concentrations in subsurface water at a sampling time (t). The 'conserved' NO3− estimate at t was based on concentration reductions associated with the introduced Br− tracer and represented an estimate for NO3− concentration reductions resulting from physical processes such as dilution and not denitrification or other biological processes. Based on this assumption, the estimated NO3− concentration was calculated by multiplying NO3− concentration at the time of dosing (t0) by the ratio of Br− concentration at t and t0 (Burns and Nguyen 2002).

### Statistical analyses

Standard deviation and standard error were calculated for different parameters using data collected from the 4 lysimeters. The first-order kinetic equation was used to fit the curve in the surface and subsurface data of NO3− concentration and ratio of NO3− over Br− concentrations.

### Results and discussion

**Wetland sediment physical and chemical characteristics and plant nutrient status**

The studied wetland sediment had low BD and high organic matter (LOI) content (Tables 1 and 2). Its high porosity and high hydraulic conductivity in the top 0.1 m depth (Table 1) made it difficult to use the push-pull technique of Addy et al. (2002) without the use of a confined lysimeter to investigate NO3− removal and gaseous emissions of N2O and N2 due to rapid dispersion of the introduced tracer plume. Using a confined

<table>
<thead>
<tr>
<th>Table 1. Sediment physical properties</th>
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<tr>
<td>Values are means ± standard deviations</td>
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<tr>
<td>--------------------------------------</td>
</tr>
<tr>
<td>Depth (m)</td>
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<tr>
<td>-----------</td>
</tr>
<tr>
<td>0–0.1</td>
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<tr>
<td>0–0.2</td>
</tr>
<tr>
<td>0.2–0.4</td>
</tr>
<tr>
<td>0.4–0.7</td>
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</table>
Lysimeter minimised advection–dispersion of the introduced Br\textsuperscript{−} tracer plume in the subsurface water. The major form of N in surface and subsurface depths of wetland sediments was NH\textsubscript{4}\textsuperscript{+}-N (Table 2) because anaerobicity inhibits nitrification (Zaman et al. 2007).

Both surface water and subsurface water had low DO levels (<1 mg O\textsubscript{2}/L; Table 3), suggesting that anaerobic conditions favourable for denitrification (Smith et al. 2003; Zaman et al. 2008b) were prevalent in this wetland. Various workers (Tiedje 1988; Patrick and Jugsujinda 1992; Achtchnich et al. 1995; Blicher-Mathiesen and Hoffmann 1999) have reported that NO\textsubscript{3}\textsuperscript{−} reduction occurs mainly when subsurface water DO falls below 0.5–1.6 mg O\textsubscript{2}/L.

The low level of NO\textsubscript{3}\textsuperscript{−} in wetland waters (Table 3) suggests that any NO\textsubscript{3}\textsuperscript{−} that enters the wetland via seepage springs and runoff is readily removed by denitrification (Zaman et al. 2008b) and other biological processes (Seitzinger 1994; Hill 1996; Fennessy and Cronk 1997; Matheson et al. 2002, 2003). Ammonium and organic N were the predominant N fractions in both surface and subsurface waters (Table 3), likely due to inputs from farmland runoff and/or the incomplete breakdown of organic matter originating from wetland organic sediments and/or plant vegetation under anaerobic conditions (Nguyen 2000).

Denitrification enzyme activity in the upper 0.4 m of wetland sediment ranged from 53 to 205 mg N\textsubscript{2}O-N/kg soil.day (Table 4). Highest DEA was measured in the top 0.1 m and decreased sharply with depth, probably due to a reduction in the level of organic matter and denitrifier populations with depth. Since NO\textsubscript{3} was unlikely to reach the lower depths because of active denitrification in the top sediment layer, DEA at the lower depths was also likely limited by low NO\textsubscript{3} concentrations (Xue et al. 1999; Hoffmann et al. 2000; Well et al. 2001).

At the time of the experiment, nutrient status of the sweet grass collected from the wetland channel was lower than that in pasture herbage of the adjacent paddocks (Table 5). These results were similar to those obtained in the following spring (6 months later in September) when wetland plants were at their most active growing stage. The lower N (and also P and S) status in wetland vegetation was likely to be due to the difference in plant species of wetland and pasture soils. Perennial ryegrass (Lolium perenne L.) is a highly nitrophilous species, selected for high production potential, whereas wetland plants do not require as much N as pastures; therefore, their root systems are less adventitious in accessing N. The high N concentrations (Table 5) of pasture herbage with a mixture of ryegrass and white clover (Trifolium repens L.) suggest a high level of soil fertility; the paddock results are consistent with those reported in New Zealand conditions (Machado et al. 2005; Blennerhassett et al. 2006; Zaman et al. 2008a).

**Table 2. Sediment chemical properties**

<table>
<thead>
<tr>
<th>Depth (m)</th>
<th>Loss on ignition (%)</th>
<th>pH</th>
<th>KCl-extractable (mg/kg soil): NH\textsubscript{4}\textsuperscript{+}-N</th>
<th>NO\textsubscript{3}\textsuperscript{−}-N</th>
</tr>
</thead>
<tbody>
<tr>
<td>0–0.1</td>
<td>48.5 ± 2.5</td>
<td>5.4 ± 0.1</td>
<td>50.3 ± 3.5</td>
<td>0.12 ± 0.013</td>
</tr>
<tr>
<td>0–0.2</td>
<td>26.6 ± 4.5</td>
<td>5.2 ± 0.2</td>
<td>31.2 ± 4.5</td>
<td>0.05 ± 0.013</td>
</tr>
<tr>
<td>0.2–0.4</td>
<td>12.2 ± 2.2</td>
<td>5.0 ± 0.3</td>
<td>13.5 ± 2.5</td>
<td>0.02 ± 0.010</td>
</tr>
<tr>
<td>0.4–0.7</td>
<td>4.5 ± 1.4</td>
<td>4.7 ± 0.2</td>
<td>5.7 ± 2.1</td>
<td>0.01 ± 0.006</td>
</tr>
</tbody>
</table>

**Table 3. Surface and subsurface water characteristics before the commencement of the study**

<table>
<thead>
<tr>
<th>Chemical properties</th>
<th>Surface water</th>
<th>Subsurface water</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dissolved oxygen (mg/L)</td>
<td>0.38 ± 0.02</td>
<td>0.41 ± 0.02</td>
</tr>
<tr>
<td>Total Kjeldahl N (mg/L)</td>
<td>3.6 ± 0.12</td>
<td>3.2 ± 0.015</td>
</tr>
<tr>
<td>NH\textsubscript{4}\textsuperscript{+}-N (mg/L)</td>
<td>0.67 ± 0.016</td>
<td>1.55 ± 0.018</td>
</tr>
<tr>
<td>NO\textsubscript{3}\textsuperscript{−}-N (mg/L)</td>
<td>0.010 ± 0.004</td>
<td>0.012 ± 0.002</td>
</tr>
<tr>
<td>NO\textsubscript{2}\textsuperscript{−}-N (mg/L)</td>
<td>0.0008 ± 0.001</td>
<td>0.007 ± 0.001</td>
</tr>
<tr>
<td>Cl\textsuperscript{−} (mg/L)</td>
<td>41.1 ± 0.03</td>
<td>18.5 ± 0.14</td>
</tr>
<tr>
<td>Br\textsuperscript{−} (mg/L)</td>
<td>0.09 ± 0.012</td>
<td>0.10 ± 0.065</td>
</tr>
<tr>
<td>pH</td>
<td>5.1 ± 0.03</td>
<td>4.9 ± 0.03</td>
</tr>
<tr>
<td>Water temperature (°C)</td>
<td>19.4 ± 0.02</td>
<td>17.5 ± 0.03</td>
</tr>
</tbody>
</table>

**Table 4. Denitrification enzyme activities at different depths in the studied wetland sediment**

<table>
<thead>
<tr>
<th>Depth (m)</th>
<th>mg N\textsubscript{2}O-N/kg soil.h</th>
<th>mg N\textsubscript{2}O-N/kg soil.day</th>
</tr>
</thead>
<tbody>
<tr>
<td>0–0.1</td>
<td>8.5 ± 1.01</td>
<td>205 ± 24.0</td>
</tr>
<tr>
<td>0–0.2</td>
<td>5.6 ± 0.20</td>
<td>134 ± 4.8</td>
</tr>
<tr>
<td>0.2–0.4</td>
<td>2.2 ± 0.17</td>
<td>53 ± 4.2</td>
</tr>
<tr>
<td>0.4–0.7</td>
<td>0.54 ± 0.111</td>
<td>13.0 ± 2.68</td>
</tr>
</tbody>
</table>

**Table 5. Nutrient status (g/100 g dry matter) of wetland sweet grass and pasture herbage in the adjacent paddocks**

<table>
<thead>
<tr>
<th>Nutrient status</th>
<th>Wetland plant</th>
<th>Mixed pasture herbage</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>February</td>
<td>September</td>
</tr>
<tr>
<td>N</td>
<td>2.6 ± 0.1</td>
<td>2.7 ± 0.02</td>
</tr>
<tr>
<td>P</td>
<td>0.27 ± 0.03</td>
<td>0.24 ± 0.02</td>
</tr>
<tr>
<td>S</td>
<td>0.19 ± 0.01</td>
<td>0.19 ± 0.02</td>
</tr>
</tbody>
</table>

Preliminary testing of the push–pull technique within a confined wetland lysimeters environment

The Cl\textsuperscript{−} concentration of the introduced plume changed <25% over a 72-h period (data not shown), suggesting that the introduced subsurface water plume in the in-situ wetland lysimeters was subject to minimal dilution. The low hydraulic conductivity of the wetland sediment at depths beyond the top 0.4 m (Table 1) may limit any water transfer out of, or into, this sediment zone. This was further confirmed by the slow drop in the level of the ponded water that occurred after injection of the dosing solution. No water was observed emerging around the piezometers or the bentonite seals, arguing against any dosing solution. No water was observed emerging around the piezometers or the bentonite seals, arguing against any significant short-circuiting of flow between surface and subsurface water in the piezometer–lysimeter system. Thus, the modification of the push–pull technique of Addy et al. (2002) with the use of 0.03-m internal diameter piezometers, instead of mini-piezometers in conjunction with in-situ lysimeters, was appropriate in our wetland environment.

Nitrate in both surface and subsurface water returned to background levels (<0.015 mg/L) within 24 h after dosing.
As a result of this rapid removal rate, we chose to use a higher initial concentration (12 vs. 8 mg N/L) during the denitrification study with $^{15}$N-enriched NO$_3$\textsuperscript{-}.

Nitrate dynamics in wetland waters after dosing with $^{15}$N-enriched NO$_3$\textsuperscript{-}

Following dosing with $^{15}$N-enriched NO$_3$\textsuperscript{-}, Br$^-$, and SF$_6$, NO$_3$\textsuperscript{-}/Br$^-$ concentrations (Fig. 2a, b; Table 6) and NO$_3$\textsuperscript{-}/Br$^-$ ratios (Fig. 3a, b) in both surface and subsurface waters significantly ($P<0.001$) decreased with time, indicating an active NO$_3$\textsuperscript{-} removal from surface water and particularly from subsurface water. Bromide is a conservative tracer and its fate over a short period of time (48 h) is probably governed by

![Fig. 2](image-url)  
Fig. 2. Nitrate concentration in (a) surface and (b) groundwater samples collected over a 48-h period after the dosing of nitrate-bromide and sulfur hexafluoride. Error bars represent standard error of the mean. The fitted line represents a least square regression of the first-order kinetics equation.

![Fig. 3](image-url)  
Fig. 3. Ratios of nitrate over bromide concentrations in (a) surface and (b) subsurface water samples collected over a 48-h period after the dosing of nitrate-bromide and sulfur hexafluoride. Error bars represent standard error of the mean. The fitted line represents a least square regression of the first-order kinetics equation.

<table>
<thead>
<tr>
<th>Time (h)</th>
<th>Measured</th>
<th>Expected</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Surface water</td>
<td>Subsurface water</td>
</tr>
<tr>
<td>1</td>
<td>1.75 ± 1.84</td>
<td>9.97 ± 0.30</td>
</tr>
<tr>
<td>2</td>
<td>1.37 ± 1.15</td>
<td>7.64 ± 1.33</td>
</tr>
<tr>
<td>3</td>
<td>1.20 ± 0.97</td>
<td>5.80 ± 1.64</td>
</tr>
<tr>
<td>4</td>
<td>0.96 ± 0.75</td>
<td>2.70 ± 2.29</td>
</tr>
<tr>
<td>24</td>
<td>0.19 ± 0.31</td>
<td>0.38 ± 0.47</td>
</tr>
<tr>
<td>48</td>
<td>0.01 ± 0.01</td>
<td>0.01 ± 0.01</td>
</tr>
</tbody>
</table>

Table 6. Measured and theoretical (based on the changes in bromide concentrations with time) concentrations of NO$_3$\textsuperscript{-}-N (g/cm$^3$) in wetland waters sampled over a 48-h study period

Values are means ± standard deviations.
hydrologic conditions and not by transformations from microbial processes or plant uptake (Xue et al. 1999; Addy et al. 2002; Burns and Nguyen 2002). If decreases in NO$_3^-$ concentrations were strictly due to physical processes, changes in NO$_3^-$ concentration with time would mirror the reduction in Br$^-$ concentration with time, yielding a constant NO$_3^-$/Br$^-$ ratio over the sampling period (Addy et al. 2002).

Changes in the ratio of Br$^-$ (C$_i$/C$_0$) concentration between t$_i$ and t$_0$ can be used to estimate the expected concentrations at time t$_i$ of ‘conserved’ NO$_3^-$ (the concentration resulting from physical processes such as dilution and dispersion). The conserved concentration estimates based on changes in the Br$^-$ (C$_i$/C$_0$) ratios were higher than measured NO$_3^-$-N concentrations within each lysimeter during virtually all (46 out of 48) of the sampling periods (Table 6). Measured NO$_3^-$-N concentrations remained $>$2 mg/L, the level at which NO$_3^-$-N availability begins to limit denitrification (Schipper and Vojodic-Vukovic 1998), for the first 3-4 h following dosing in all subsurface water samples and in the surface water of 2 of the 4 lysimeters. The surface water was a mixture of the dosing solution and displaced water and exhibited considerable dilution as it moved from the 0.2-0.35 m dosing depth to the surface, with relative Br$^-$ concentrations ranging from 0.1 to 0.3 (C$_i$/C$_0$) 1 h after dosing. All samples from all locations obtained after 24 and 48 h had low NO$_3^-$-N concentrations.

The average NO$_3^-$ removal rates during non-limiting conditions (i.e. NO$_3^-$-N $>$ 2.0 mg/L) were 3.96 and 15.7 mg/L/day for surface and subsurface water, respectively (Table 7). These rates were substantially higher than the average rates of $^{15}$N-enriched denitrification gas production (N$_2$O-N plus N$_2$) over the same period (0.25 and 1.1 mg/L-day in the surface and subsurface water, respectively; Table 7). Denitrification only accounted for 6-7% of NO$_3^-$ removal during non-limiting conditions, suggesting that other transformation processes were responsible for most of the NO$_3^-$ removal. Because many studies expressed the rates on a real basis, we transformed the rates by assuming that the observed cation gas production (N$_2$O-N and N$_2$) during non-limiting conditions does not change with time after its dosing; the transport of N$_2$O and N$_2$ to the atmosphere via stem and aerenchyma of wetland vegetation (Well et al. 2001; Hefting et al. 2003), or through the interface between the sediment and the edge of piezometers or channels in the sediment or around the dead roots (Blicher-Mathiesen et al. 1998), is assumed to be insignificant in our study.

Given that denitrification was a minor pathway for NO$_3^-$ transformation, the rapid NO$_3^-$ removal observed in the first several hours following dosing may be attributed to several processes that we did not measure; specifically DNRA (Silver et al. 2001; Matheson et al. 2002, 2003), abiotic immobilisation (Davidson et al. 2003), and microbial immobilisation and plant uptake (Hill 1996; Fennessy and Cronk 1997). Because the wetland soils likely included eroded materials from the adjacent Allophanic volcanic soils of the paddocks, there is potential for some portion of the dosed NO$_3^-$ to be subject to anionic sorption (Magesan et al. 1998). However, considerable NO$_3^-$ leaching has been observed in the paddock soils (Wilcock et al. 1999), suggesting that any sorption is likely to account for a limited proportion of the NO$_3^-$ removal. Uptake of NO$_3^-$ by wetland plants in our study appears to be plausible even over a short period of 48 h, particularly because the vegetation appeared to be N-deficient at the time of the experiment. Bowman et al. 1989a,

The observed groundwater denitrification rates are comparable to those (quoted below in mg N/m$^2$.day) reported for other wetland sediments (76.8–115.2, Christensen and Sorensen 1986; 33.6–336, Lindau et al. 1990, Lowrance et al. 1995; 48–283, Xue et al. 1999; 20–80, Hefting et al. 2003; 50–741, Pinay and Decamps 1988, Cooper 1990, Haycock and Burt 1993). The elevated rates we observed reflect environmental conditions conducive to denitrification, i.e. low DO (<1 mg O$_2$/L; Table 3) plus a highly enriched organic matter sediment (Table 2) and optimum sediment–water contact time within the confined lysimeter environment (Hill 1996; Fennessy and Cronk 1997; Hoffmann et al. 2000; Smith et al. 2003). The observed high denitrification rates could be attributed to the elevated DEA values (Table 4) in the wetland soils (Groffman et al. 1999).

The amount of N$_2$O and N$_2$ generation (and hence denitrification) did not account for most of the NO$_3^-$ removal; however, it is unlikely that we have underestimated the amount of N$_2$O and N$_2$ generation. The SF$_6$ concentration in wetland waters (data not shown) did not significantly change with time after its dosing; the transport of N$_2$O and N$_2$ to atmosphere via stem and aerenchyma of wetland vegetation (Well et al. 2001; Hefting et al. 2003), or through the interface between the sediment and the edge of piezometers or channels in the sediment or around the dead roots (Blicher-Mathiesen et al. 1998), is assumed to be insignificant in our study.

Given that denitrification was a minor pathway for NO$_3^-$ transformation, the rapid NO$_3^-$ removal observed in the first several hours following dosing may be attributed to several processes that we did not measure; specifically DNRA (Silver et al. 2001; Matheson et al. 2002, 2003), abiotic immobilisation (Davidson et al. 2003), and microbial immobilisation and plant uptake (Hill 1996; Fennessy and Cronk 1997). Because the wetland soils likely included eroded materials from the adjacent Allophanic volcanic soils of the paddocks, there is potential for some portion of the dosed NO$_3^-$ to be subject to anionic sorption (Magesan et al. 1998). However, considerable NO$_3^-$ leaching has been observed in the paddock soils (Wilcock et al. 1999), suggesting that any sorption is likely to account for a limited proportion of the NO$_3^-$ removal. Uptake of NO$_3^-$ by wetland plants in our study appears to be plausible even over a short period of 48 h, particularly because the vegetation appeared to be N-deficient at the time of the experiment. Bowman et al. 1989a,
1989b) found extremely high, short-term N uptake rates by moderately N-deficient turfgrass. In particular, they noted that N uptake rates by N-deficient ryegrass during the first 6 h of exposure to NO$_3^-$-enriched solution was >4-fold greater than the rates that occurred after 96 h of exposure.

The pasture growth rate in the studied Waikato region during February–March is at least 45–50 kg dry matter (DM)/ha.day and the standing biomass in our wetland site was estimated to be 3–4 times that of the adjacent pastoral land (data not shown). Assuming a daily wetland plant above-ground growth rate of 135–200 kg DM/ha.day (assuming that production rate is proportional to standing biomass), the amount of N that can potentially be taken up by wetland vegetation with N concentration of 2.6–2.7% (Table 5) is 3.5–5.4 kg N/ha.day (351–540 mg N/m$^2$.day). In our study approximately 680 mg NO$_3^-$-N/m$^2$ was depleted over a 4-h period, suggesting that short-term plant uptake by N-deficient plants could account for a substantial portion of the NO$_3^-$ removal.

Although considerable increases in $^{15}$N-enriched N$_2$O-N levels were initially observed following NO$_3^-$ dosing, no net emissions were generated over the 48-h study (Fig. 4a, b). The wetland served as a source of N$_2$O during the non-NO$_3^-$-limiting phase of the experiment, but functioned as a sink for

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**Fig. 4.** Dissolved isotopically enriched nitrous oxide concentration in (a) surface and (b) subsurface water samples collected over a 48-h period after the dosing of nitrate-bromide and sulfur hexafluoride. Error bars represent standard error of the mean.

**Fig. 5.** Dissolved isotopically enriched dinitrogen concentration in (a) surface and (b) subsurface water samples collected over a 48-h period after the dosing of nitrate-bromide and sulfur hexafluoride. Error bars represent standard error of the mean.
Table 8. Nitrous oxide (N$_2$O-N) fluxes, their $^{15}$N atom%, and ratios of N$_2$O-N : N$_2$ in wetland waters sampled over a 48-h study period.

<table>
<thead>
<tr>
<th>Time (h)</th>
<th>N$_2$O-N fluxes (μg/L.day)</th>
<th>15$^N$ atom %</th>
<th>N$_2$O-N : N$_2$ ratios</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Surface water</td>
<td>Subsurface water</td>
<td>Surface water</td>
</tr>
<tr>
<td>1</td>
<td>19.9 ± 14.2</td>
<td>404.2 ± 313.2</td>
<td>38.7 ± 18.2</td>
</tr>
<tr>
<td>2</td>
<td>259.4 ± 275.9</td>
<td>1162.0 ± 424.5</td>
<td>69.6 ± 17.5</td>
</tr>
<tr>
<td>3</td>
<td>143.1 ± 273.8</td>
<td>1561.9 ± 988.6</td>
<td>77.1 ± 15.1</td>
</tr>
<tr>
<td>4</td>
<td>-94.0 ± 317.7$^A$</td>
<td>-24.2 ± 1297.7$^A$</td>
<td>59.1 ± 19.6</td>
</tr>
<tr>
<td>24</td>
<td>-15.8 ± 8.9$^A$</td>
<td>-119.8 ± 118$^A$</td>
<td>39.4 ± 7.3</td>
</tr>
<tr>
<td>48</td>
<td>-0.5 ± 0.4$^A$</td>
<td>-29.2 ± 33.8$^A$</td>
<td>21.2 ± 5.1</td>
</tr>
</tbody>
</table>

$^A$All these values generated under NO$_3^-$-N limiting conditions with <1 mg N/L.

N$_2$O during the NO$_3^-$-limited phase of the study. Concentrations of N$_2$O rapidly increased with time, reaching a peak 4 h after dosing and declining to background by 24 h after dosing (Fig. 4a, b). This was observed for both surface and subsurface waters and was related to the decline in NO$_3^-$ concentration with time ($r = 0.41$–0.46; $P < 0.05$). Nitrous oxide generation was more predominant than isotopically enriched N$_2$ generation (Fig. 4a, b). This predomiance declined with time (after 3–4 h of tracer dosing; Table 8), suggesting that the generation of N$_2$O and N$_2$ is dependent on the level of NO$_3^-$ in sediments. With a decline in NO$_3^-$ concentration with time (Fig. 2a, b), the N$_2$O : N$_2$ ratio decreased, and more N$_2$ instead of N$_2$O was emitted (Fig. 5a, b), probably because of the reduction of N$_2$O to N$_2$. Our results are in agreement with several studies (Swerts et al. 1996; Cho et al. 1997; Dendooven et al. 1997; Blicher-Mathiesen and Hoffmann 1999; Well et al. 2001; Zaman et al. 2008b) which found that during the initial stages of denitrification and in the presence of significant NO$_3^-$ inputs, NO$_3^-$ may be denitrified to N$_2$O and not fully reduced to N$_2$. However, when NO$_3^-$ becomes limited, N$_2$O that is dissolved in wetland water is reduced to N$_2$ by microbes due to the demand for electron acceptors when NO$_3^-$ in wetland waters but also by the depth from which N$_2$O was produced. If N$_2$O is produced at sites just below the top sediment layer, it may readily diffuse into sediment–air water interface as N$_2$O, instead of being reduced to N$_2$. In contrast, N$_2$O produced in subsols may be entrapped in subsurface waters and subsequently be reduced to N$_2$ by sediment denitrifiers (Hefting et al. 2003; Smith et al. 2003). In addition to NO$_3^-$ concentration and depth, sediment pH, C, and O$_2$ content and temperature may also affect the generation rates of N$_2$O and N$_2$ (Del Grosso et al. 2000; Dobbie and Smith 2001; Smith et al. 2003; Zaman et al. 2004, 2007, 2008b). The influence of this variety of sediment and environmental factors as discussed above could explain why a range of N$_2$O : N$_2$ ratios (0–20) has been reported in the literature (Rolston et al. 1978; Weier et al. 1993; Maag and Vinther 1996; Cho et al. 1997; Well et al. 2001; Rochester 2003) and in our study (0.33–188; Table 8) and in other associated laboratory studies using pastoral and wetland sediments collected from areas within the same catchment (0.9–1.4) (Zaman et al. 2007).

Since the potential contribution of a wetland to greenhouse emissions is dependent on the amount and fraction of N emitted as N$_2$O, and these parameters are likely to vary depending on sediment and environmental factors as outlined above, the net annual production (net balance between source and sink) of N$_2$O from the studied wetland with temporal variation in NO$_3^-$ inputs is not known. This aspect needs to be evaluated in future studies. Various studies have shown that the extent and duration of contact time between wetland inflows and wetland sediment (Hill 1996; Cirmo and McDonnell 1997; Devito et al. 2000, 2007) can affect the extent of denitrification and hence the wetland capacity to remove NO$_3^-$-N. During high flow events, low removal is expected because high NO$_3^-$-containing water bypasses microbially active wetland sediments by flowing across the top of wetlands (Gold et al. 2001; Burns and Nguyen 2002; Rutherford and Nguyen 2004). The use of engineered bypass flow designs to regulate NO$_3^-$ loading may enhance sediment–water contact time, thus promoting NO$_3^-$ removal and the potential for NO$_3^-$-limiting conditions. Our results suggest that the studied wetland may be a source of N$_2$O emissions when NO$_3^-$ concentrations are elevated (non-limited), but can readily remove N$_2$O (function as a N$_2$O sink) when NO$_3^-$ levels are low. Although the proposed bypass flow design may short-circuit some of wetland NO$_3^-$ inflows and hence reduce the full potential for wetland NO$_3^-$ removal, it provides a balance between water quality goals and greenhouse gas emissions. Future research is therefore required to investigate this balance issue and assess temporal variations in NO$_3^-$ removal rates, denitrification, and N$_2$O generation in response to changes in NO$_3^-$ inputs and water-sediment contact time.

Conclusions

The studied seepage wetland can remove substantial amount of NO$_3^-$ under conditions where sediment water contact time is optimum (confined lysimeter) for denitrification. The amount of NO$_3^-$ removal was much higher than the amount of denitrification gases (N$_2$O and N$_2$) produced, suggesting that additional processes (e.g. plant uptake) were responsible for NO$_3^-$ removal. The push–pull method, in combination with confined lysimeters to minimise advection and dispersion of...
water, is a promising tool for quantifying NO$_3^-$ removal and N$_2$O and N$_2$ generation rates under a variety of conditions.

Acknowledgments

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