Review of Nitrogen Attenuation in New Zealand Seepage Wetlands

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Contents

Tables

Figures

Executive summary

This report is part of a project assessing the effectiveness of the seepage wetland module in OVERSEER. It complements a recent review of wetland processes for water quality protection (McKergow et al. 2017), an analysis of the sensitivity of the OVERSEER seepage wetland module to input data and model coefficients (Rutherford 2017) and a summary for stakeholders (Rutherford et al. 2017). Existing studies of nitrogen removal by seepage wetlands in New Zealand are re-examined with two main objectives. First, to decide whether the conceptual model and coefficients used in OVERSEER are ‘fit for purpose’. Second, to identify major information gaps and suggest investigations that would improve the seepage wetland module.

Seepage wetlands are naturally occurring zones along stream banks, or at the heads of streams, characterised by water tolerant plants, together with saturated, organically enriched and anaerobic soils where detritus accumulates and denitrification rates are high. The seepage wetland module in OVERSEER comprises: a simplified, conceptual model; coefficients estimated from a small number of experimental studies and ‘expert opinion’; and ‘look up’ tables to help users specify input data. The module furnishes semi-quantitative estimates of nitrogen removal (also termed attenuation[1]), allows the user to assess the potential of seepage wetlands to reduce nitrogen losses from farms, and demonstrates the benefits of reducing stock damage and channelization, and managing vegetation. This is in keeping with the spirit of OVERSEER and hence the wetland module is considered to be ‘fit for purpose’.

Nitrate removal in wetlands occurs through denitrification (viz., conversion to nitrogen gases by bacteria in the organically enriched, waterlogged, anaerobic wetland soils) and biological uptake (viz., uptake by microbes and plants growing within the wetland). In the studies reviewed a proportion of the nitrate removed could have been converted to, and exported as, other bioavailable forms of nitrogen (e.g., ammonium or labile organic nitrogen). The decay of dead pasture and/or wetland vegetation is a likely source of ammonium, dissolved organic nitrogen and particulate nitrogen.

This report reviews existing literature on nutrient removal in New Zealand wetlands. All the studies reviewed found that seepage wetlands significantly reduced (by 51-98%) the concentration and mass flow of nitrate.

The OVERSEER seepage wetland model could be tested using results from four pasture wetland studies. The OVERSEER rates were found to be 36-67% of the measured rates of nitrate removal. The current wetland module in OVERSEER, therefore, appears to be conservative in its estimation of nitrate removal (viz., underestimates removal).

Of the studies reviewed, three found that at times wetlands were nett sources of ammonium, dissolved organic nitrogen and/or particulate nitrogen. High ammonium outflows may result from the decay of dead plant matter, the reduction of nitrate to ammonium, or be the result of low rates of oxidation of inflowing ammonium. However, one study found that the wetland did not generate and export ammonium or dissolved/particulate nitrogen. High flows sometimes caused the outflow of particulate and/or dissolved organic nitrogen to exceed the inflow, probably because fine particles of organic N, and/or dissolved organic nitrogen, originating from the death and decay of wetland plants contributed to the exports during high flows. During low flows, wetlands were usually found to be sinks of nitrogen. Two studies found that the wetlands were consistently a nett sink of total nitrogen even at high flows and despite intermittent disturbance by cattle.

[1] In this report ‘attenuation’ means the difference between nitrogen inflows and outflows.

The bioavailability of dissolved organic nitrogen and particulate nitrogen leaving seepage wetlands has not been quantified, although it is likely to be lower than for nitrate and ammonium. It is not clear, therefore, whether OVERSEER is conservative in its estimation of attenuation for all forms of bioavailable nitrogen.

Nitrate removal rates were found to vary with concentration and hence varied spatially, being highest where runoff first entered the wetland and nitrate concentrations were highest. OVERSEER assumes a spatially uniform removal rate which is clearly an over-simplification. Modelling showed that OVERSEER is likely to underestimate nitrogen attenuation in small wetlands (<2% of catchment area) as a result of assuming a spatially uniform removal rate, although further experimental and modelling investigations are desirable to confirm this conclusion.

Two studies found significant vertical mixing between high nitrate surface flow and microbially active wetland soils, typically to a depth of 5-10 cm. Were it not for this mixing, seepage wetlands would remove very little nitrate. Compaction and channelization of wetlands reduces mixing, reduces soil/water contact times, and hence reduces nitrogen attenuation.

One difficulty facing researchers and OVERSEER users is to determine the ‘effective’ area of the catchment (viz., the proportion of the total catchment area from which runoff enters the wetland). Currently ‘effective’ area is estimated from soils data or wetland area. However, if the user could determine the wetland outflow rate and the flow yield in adjacent streams then it would be possible to calculate the ‘effective’ area more accurately. Further work is required to refine this approach. Alternatively, it may be possible to establish an empirical relationship between wetland size, catchment slope, rainfall and ‘effective’ area if additional field investigations across a range of wetland sizes, types and locations were undertaken.

It is desirable to better understand the bioavailability of organic nitrogen exports from wetlands. However, the farm module in OVERSEER does not predict dissolved organic nitrogen losses, and probably underestimates particulate organic nitrogen losses, from farmland. Thus OVERSEER does not currently quantify the inflow to wetlands of all the bioavailable forms of nitrogen. Before contemplating modifying the wetland module to predict the removal of not only nitrate but also organic nitrogen, the farm module in OVERSEER would need to be modified.

This review found data from only a small number of studies under New Zealand conditions. However, those studies all demonstrated high nitrate removal rates and a strong case can be made to protect and enhance seepage wetlands as a way of managing nitrogen concentrations in streams. The studies indicate that OVERSEER is conservative in its estimates of nitrate attenuation (viz., underestimates nitrate removal) but there is insufficient data to assess whether it is conservative in its estimates of total nitrogen attenuation. Because only a small number of studies have been conducted, mostly in the Waikato-Bay of Plenty regions, it is desirable to expand the available dataset by conducting inflow/outflow studies on a range of sizes and types of seepage wetland in different parts of New Zealand. Nitrogen outflows can be measured using weirs and samplers, but it is very difficult to measure nitrogen inflows because they are diffuse (viz., dominated by shallow sub-surface flow). One approach would be to estimate nitrogen inflows using OVERSEER and fine-scale farm data for the catchment that drains to the study wetland.

1 Background

In early 2016 DairyNZ commissioned NIWA to review the wetland attenuation module in OVERSEER. Attenuation is the difference between the mass of nitrogen that flows into and out of a wetland, which may be the result of permanent removal (e.g., denitrification), temporary storage (e.g., uptake by plants) and/or transformation (e.g., dissolved inorganic nitrogen (DIN) to particulate nitrogen (PN) and/or dissolved organic nitrogen (DON)).

In 2008 a seepage wetland model for use in OVERSEER was developed by NIWA and delivered to AgResearch in the form of VBA code within EXCEL (Rutherford et al. 2008). Also provided was guidance to users on how to estimate the required input data for the model. AgResearch implemented the model within OVERSEER version 5 and joint testing was undertaken by NIWA and AgResearch to check that the EXCEL model was correctly implemented (Rutherford & Wheeler 2011). Several modifications to OVERSEER have been made since 2008.

Two types of wetland can be modelled in OVERSEER.

i. Constructed wetlands (also known as artificial wetlands) are wetlands specially created to collect and treat runoff from farmland.

ii. Seepage wetlands (also known as natural or riparian wetlands) are naturally occurring areas (usually in the headwaters of, and alongside, streams) characterised by saturated, organic, anaerobic soils and wetland vegetation (e.g., reeds and sedges).

Detailed measurements have been made of nutrient removal and processing in a number of constructed wetlands, their performance is well quantified, and this study does not review their effectiveness. NIWA has identified the potential of seepage wetlands to remove nitrogen from pasture runoff (see for example the review by McKergow and Hughes, 2016) but their effectiveness has not been quantified as accurately as for constructed wetlands, largely because of the difficulty of measuring their inputs (diffuse seepage). The seepage wetland module in OVERSEER considers nitrogen only and does not quantify the removal of phosphorus.

The number of stakeholders routinely applying the seepage wetland module within OVERSEER is not known, although DairyNZ assert that few stakeholders use it. DairyNZ confirmed that it is keen to assess the potential of seepage wetlands to attenuate nitrogen while acknowledging that there are only sparse data to quantitatively test the module. Three objectives were agreed between DairyNZ and NIWA.

1. Collate information from existing experimental wetland locations around New Zealand to guide future monitoring requirements and identify any case studies with sufficient information for a quantitative assessment of attenuation.

2. Run a sensitivity analysis of the OVERSEER seepage wetland module predictions to input variables.

3. Run a technical workshop to present our findings on the potential of the wetland module as a tool to quantify attenuation.

This report address Objective 1. It was agreed that the project would be a desk-top modelling exercise, making use of data and information about New Zealand seepage wetlands available from published reports, presentations and journal articles. No field work would be undertaken, although the study would help identify important information gaps that might lead to fieldwork in the future.

2 Available information

Information was collated for several NIWA-led studies of seepage wetlands, riparian buffer strips and sub-catchments conducted in the 1980s and 1990s. The original data was checked and re-analysed.

Attenuation is best quantified as the difference between measured inflow and outflow, expressed as mass flows. In many of the studies reviewed, mass outflows were measured by installing an outlet weir and sampling regularly for flow and concentration. Mass inflows to seepage wetlands are difficult to measure because they tend to be diffuse and sub-surface. Some studies measured sub-surface concentrations in piezometers and estimated water inflows, while other studies relied on OVERSEER to estimate mass inflows. Some studies estimated attenuation by comparing inflow and outflow concentrations although this takes no account of differences in flow rate and assumes that samples are collected along the same flow path. The estimates of nitrogen attenuation from the studies reviewed are inherently uncertain. Nevertheless this study enables an assessment to be made of the reliability of the OVERSEER wetland module, and highlights major information gaps.

In OVERSEER the user is required to define the Type and Condition of any seepage wetlands (see Table 2-1 and Table 2-2). The user is also required to specify either the area of the catchment that drains to the wetland (the 'effective' catchment area) or the area of the surface catchment together with certain soil and drainage parameters, which OVERSEER then uses to estimate the 'by-pass' flow (viz., the 'effective' catchment area).

Table 2-1: Wetland type. As defined in OVERSEER

	Flow	Vegetation	Stock
Type A	Always flows	Dominated by sedge & reed May contain flax & willow	Avoided by sheep. Easily damaged by cattle
Type B	Dry in droughts	Dominated by sedge & reed	Moderate pugging if cattle have access all year Avoided by sheep in winter & spring
Type C	Dry in summer	Abundant sedge & reed Some pasture grass	Pugging if cattle have access in winter Grazed by sheep in summer
Type D	Ephemeral	Dominated by pasture grass	Grazed by sheep except during wet periods in winter

Table 2-2: Wetland class or condition. As defined in OVERSEER.

	Fencing	Vegetation/ Stock	Surface flow	Channels	Condition factor
Class 1	Fenced	Well vegetated No stock access	Evenly distributed	None	90%
Class 2	Unfenced	Lightly grazed by sheep only	Evenly distributed	No pugging	75%
Class 3	Unfenced	Lightly grazed by sheep or set stocked[1] cattle	Minor pugging	No major channels	50%
Class 4	Unfenced	Accessible by cattle	Signs of pugging	Signs of channelization	20%
Class 5	Unfenced	Inflowing water by-passes vegetation	Highly channelized even if fenced	Deeply incised	10%

[1] permanently in the paddock but at a low stocking rate.

3 Results

This section reviews data from a number of published New Zealand studies. In some cases the authors reanalysed the original data. As a result, some of the original results have been modified and a number of minor errors corrected. Where the original data has been reanalysed, details are set out here as a record for any future analysis. To make it easier to compare studies, each is assigned a short code (e.g., RC, JS, BARK) based on the names of the study sites.

3.1 RC wetland

3.1.1 Description

During the 2000s two seepage wetlands were studied in the Tutaeuaua catchment that drains into the north-western end of Lake Taupo (Figure 3-2). RC wetland was a small, seepage wetland 160 m long with an average width of 13 m (Figure 3-1 and Table 3-1) and an average slope of 10^{o}. Over most of its length the wetland flowed continuously (even during a severe drought) and soils were waterlogged[2]. The catchment was steep (up to 25^{o}), lay at an elevation of 440-606 m ASL and was dominated by permeable pumice soils (Oruanui loamy sand) (McKergow et al. 2012). The catchment was pasture which, during the study, was extensively grazed by sheep and cattle that had access to the wetland[3]. RC wetland was classified Type A, Class 4.

Figure 3-1: Left: RC wetland looking upslope from the outlet weir. Right: upper part of the JS wetland
Photo: Left: Rob Collins, 2005. Right: James Sukias, 2004.

[2] At the top end the wetland dried out in summer with no visible surface flow.
[3] The wetland was subsequently fenced to exclude cattle.

Table 3-1: Summary of catchment, wetland and hydrology data for the RC wetland.

Parameter	Value	Comment	Reference	Value	Comment	Reference
Catchment area, ha	5	Coarse DEM	McKergow et al. 2012	2.7	Contour map	This study
Wetland area, m^2	1725	EDM survey		2198	EDM survey	Sukias & Collins unpub Collins et al. 2005
Wetland length, m	160			162		
Wetland width, m	13.6			10.8		
Volume water + soil, m^3				892		
Porosity				83%		
Annual rainfall, mmy^{-1}	1266	RC wetland	Rutherford et al. 2009			
Annual PET, mmy^{-1}	820	Taupo airport				
Mean air temperature, C	11.7					
Mean outflow, $mL\ s^{-1}$	415		McKergow et al. 2012	405		Rutherford et al. 2009
Mean outflow, $mm\ y^{-1}$	437	3 ha catchment		426	3 ha catchment	
Mean outflow, $mL\ s^{-1}$				469		This study
Mean outflow, $mm\ y^{-1}$				493	3 ha catchment	
Mean yield at LWR, $mm\ y^{-1}$				485		Rutherford et al. 2009

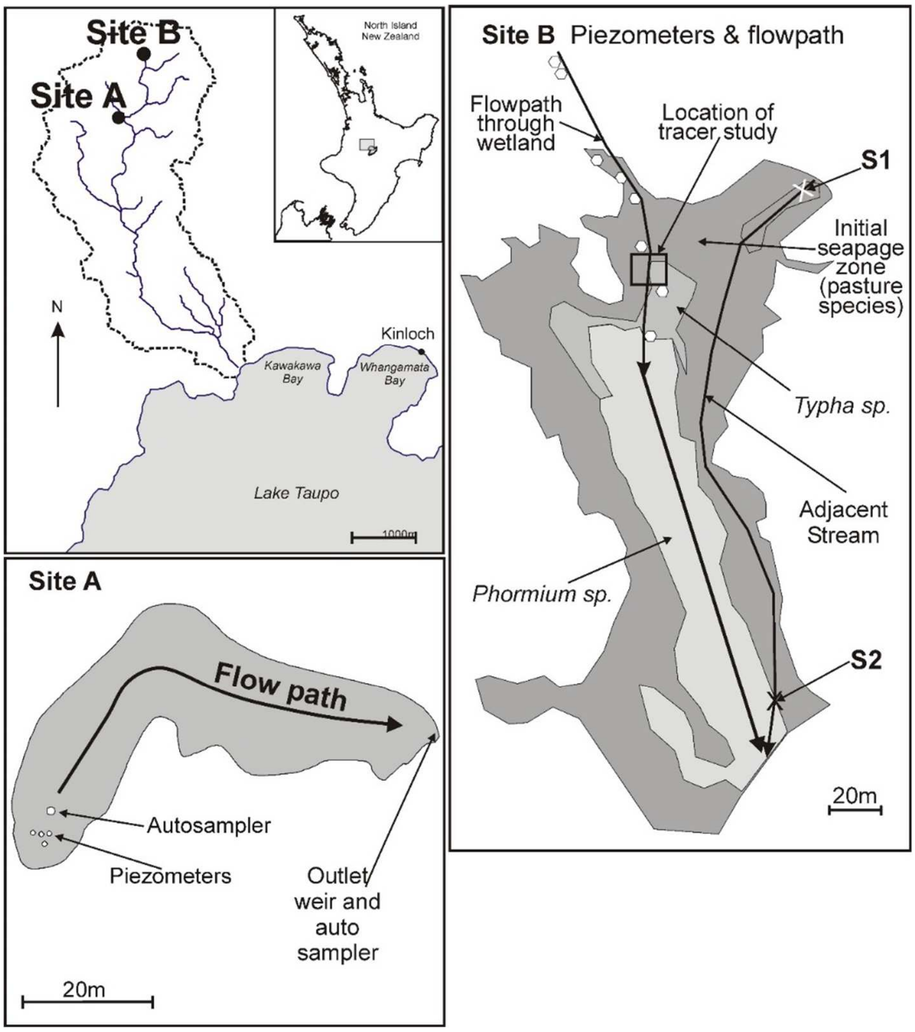

Figure 3-2: Location map and sketch maps of the RC wetland (Site A) and the JS wetland (Site B). Both wetlands lie in the Tutaeuaua Catchment and flow into the Tutaeuaua Stream, northwest Taupo.

3.1.2 Hydrology

Wetland soils were dark coloured, organically enriched and anaerobic. Soil depth varied from 20-120 cm (average 60 cm) and porosity averaged 83%. The total volumes of soil + water, and water were 890 and 740 m^3 respectively (Collins et al. 2005). Wetland area was measured twice using a laser EDM (Sukias & Collins unpublished, McKergow et al. 2012). The two measurements (1725 and 2198 m^2) differed by c. 20% which illustrates the difficulty of identifying the edges of seepage wetlands, especially when the headwaters dry out in summer (Types C and D in Table 2-1). Estimating the catchment area draining to wetlands was also difficult. Using a low resolution DEM Rutherford et al. (2009) estimated the catchment area of the RC wetland to be 5 ha. This study re-examined contour lines on the topographic map and concluded that the catchment area could be as low as 2.7 ha. Based on these figures the wetland occupied between 4-7% of the surface catchment which is similar to the average of 5% for the entire Tutaeuaua catchment (McKergow et al. 2007).

From 2004-2008 rainfall at a gauge adjacent to the wetland averaged 1266 mm y^{-1} while potential evapotranspiration (PET) at Taupo airport averaged 820 mm y^{-1} (Rutherford et al. 2009). By difference, the annual runoff is 446 mm y^{-1}. McKergow et al. (2012) and Rutherford et al. (2009) reported a mean outflow from the RC wetland of 415 and 405 mL s^{-1} respectively.

Re-examining the outflow time series from 30/6/2005 to 1/6/2007 (the period for which wetland exports were calculated) yielded a mean outflow of 469 mL s^{-1}. The mean water yield for the wetland based on the mean flow of 469 mL s^{-1} and catchment area of 2.7 ha was 493 mm y^{-1}. Two flow recorders on the Tutaeuaua Stream, into which the RC wetland drains, were found to have mean flow yields of 683 mm y^{-1} (BBR recorder) and 485 mm y^{-1} (LWR recorder) (Rutherford et al. 2009). Flow ratings at BBR were affected by channel instability and flows at LWR were considered more accurate.

Assuming a catchment area of 2.7 ha, the water yield at the RC wetland outlet (493 mm y^{-1}) was almost identical to the yield at the LWR recorder (485 mm y^{-1}), and both yields were similar to the difference between rainfall and PET (446 mm y^{-1}). If the catchment area of the RC wetland was 5 ha then its flow yield would have been 296 mm y^{-1} which is only 60% of the yield at the LWR recorder. It is not inconceivable that some runoff by-passed the RC wetland (e.g., as groundwater) and entered the stream downstream from the outlet. Gaining and losing reaches were identified along streams in the Tutaeuaua catchment (Rutherford et al. 2009). In the OVERSEER wetland module there is a coefficient ⍰ that quantifies the proportion of total runoff draining to deep groundwater and hence by-passing the wetland. The water balance indicated that if the area catchment of the RC wetland was 5 ha then the by-pass factor was ⍰ ~ 40%.

OVERSEER users need to specify the 'effective' catchment area that drains to the wetland. Assuming flow yields for the RC wetland and the LWR recorder were identical, then the 'effective' area of the wetland was 2.7 ha. The foregoing calculations indicate that the 'effective' area (2.7 ha) may not be the same as the topographic area (5 ha). It also indicates that the 'effective' area can be estimated provided the user knows the flow yield of the receiving stream and the outflow from the wetland.

3.1.3 Nitrogen outflows

McKergow et al. (2012) measured nitrogen outflows from the wetland from 2004-2008 when sheep and cattle had intermittent access. Flow and turbidity were measured continuously at the wetland outlet. Monthly grab samples were collected to quantify nutrient fluxes during baseflow while automatic samplers (triggered by flow) collected flow proportional samples during wet weather (termed 'rainfall events'). The automatic samplers were also triggered by turbidity to collect samples when sheep or cattle disturbance occurred (termed 'livestock events'). High turbidity triggered cameras to confirm the presence of stock in the wetland. Samples were analysed for NO_3, NH_4, DON and TN. There were some gaps in the records due to equipment failure.

Over a 328 day period in 2005-2007 the export of total nitrogen (TN) was 33.8 kg of which 80% was organic. Baseflow, rainfall and livestock events occurred 81%, 18% and 8% of the time, but each made similar contributions to TN export (viz., baseflow ~ rainfall events ~ livestock events ~ 33% of total export). Assuming that the unsampled days were either all baseflow, or equal proportions of baseflow, rainfall and livestock disturbance events, the annual export of TN were re-calculated as 35.6-37.6 kg y^{-1} respectively. These exports were used to make two separate estimates of attenuation.

3.1.4 Nitrogen inflows

Dr Keith Betteridge (AgResearch, pers. comm.) classified the paddock containing the RC wetland as 'unimproved' and using OVERSEER (version 4 or 5) estimated nitrogen losses of 11 kg ha^{-1} y^{-1}. Betteridge classified adjacent paddocks 'improved' for which nitrogen losses averaged 28 kg ha^{-1} y^{-1}. McKergow et al. (2012) state that at the time of their study (2004-2008) the catchment draining to the RC wetland was 'improved' pasture (which is at variance with classification of 'unimproved' by Betteridge) and that the catchment was receiving 400 kg ha^{-1} y^{-1} of 10% potassic serpentine sulphur superphosphate fertiliser with cobalt and selenium, plus 83 kg ha^{-1} of urea applied three times per year. Stocking rates on 'unimproved' and 'improved' pasture were 6 and 12 SU ha^{-1} respectively (1 ewe = 1 SU, 1 beef cow = 5.5 SU) comprising 50:50 sheep beef. As part of this study, OVERSEER version 6 was run using the input data from McKergow et al. (2012) giving predicted losses of 13 and 23 kgN ha^{-1} y^{-1} for 'unimproved' and 'improved' pasture respectively.

3.1.5 Attenuation based on loads

Assuming the catchment comprised 'unimproved' pasture (OVERSEER nitrogen yield 11-13 kg ha^{-1} y^{-1}) and an 'effective' catchment area of 3 ha, attenuation was negligibly small (Table 3-2). It is conceivable that high exports of organic nitrogen during livestock disturbance events negated any benefits arising from nitrogen uptake by wetland plants and soils. If so then it would be beneficial to exclude stock (especially cattle) from seepage wetlands as recommended by McKergow et al. (2012).

Assuming the catchment comprised 'improved' pasture (OVERSEER nitrogen yield 23-28 kgN ha^{-1} y^{-1}) and an effective area of 2.7 ha, attenuation was 46-58% (average 52%) with an areal removal rate of 50-77 (average 64%) mg m^{-2} d^{-1} at 11.7C (Table 3-2 and Table 3-3). Assuming an effective area of 5 ha, attenuation was 67-75% but the water balance suggests the 'effective' area was not as large as 5 ha and hence that attenuation was not as high as 67-75%.

In OVERSEER removal rates vary with temperature (monthly average air temperature is used).

$$U_T = U_{20} 1.1^{T-20} \qquad 1$$

where T = temperature (C) (OVERSEER uses air temperature) and U_T and U_{20} = uptake rates at temperatures T and 20C respectively[4]. Rates corrected to 20C using Eq 1 are 110-170 (average 140) mg m^{-2} d^{-1} for disturbed wetlands.

3.1.6 Effects of cattle exclusion

McKergow et al. (2012) document very high concentrations of organic nitrogen leaving the wetland during 'livestock events' which occurred infrequently but accounted for c. 30% of the annual nitrogen export. Despite these sporadically high exports, Table 3-2 and Table 3-3 indicate that if the catchment was 'improved' pasture then attenuation was c. 50% (46-58%) even when cattle had access to the wetland. An obvious question is: 'What would attenuation have been if cattle did not have access to the wetland?'

Table 3-4 shows that when 'livestock event' exports are replaced with 'baseflow' exports during periods when cattle were known to be present in the wetland, then attenuation increased to 61-68% for 2.7 ha 'effective' of 'improved' pasture with an areal removal rate of 66-90 mg m^{-2} d^{-1}. In this

[4] Note that in Rutherford et al. (2008) the reference temperature is stated to be 15C not 20C. However, in OVERSEER the reference temperature is 20C.

calculation, rainfall event loads remained unchanged even though cattle disturbance may damage the wetland, making it easier for high flows during rainfall to entrain particulates.

Table 3-5 shows that when 'livestock event' and 'rainfall event' exports are replaced with 'baseflow' exports, attenuation increases to 75-79% with an areal removal rate of 82-106 mg m^{-2} d^{-1}. This is a likely over-estimate because wetlands are unlikely to remove nitrogen at the same rate during rainfall and baseflow conditions even if cattle are excluded.

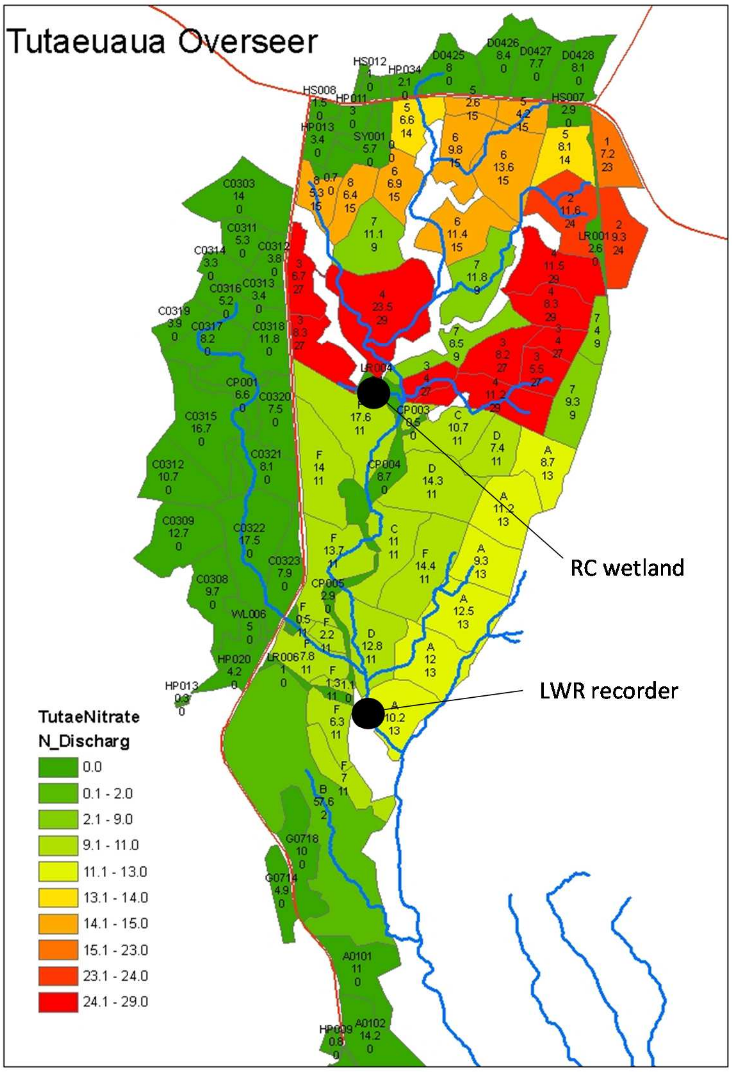

Figure 3-3: Map of the paddocks within the Tutaeuaua catchment. The three numbers are (e.g., in the red paddock north of the RC wetland) paddock code (4), area (23.5 ha) and nitrogen yield (29 kg ha^{-1} y^{-1}). The map was compiled from farm data relevant to the early 2000s. Yields were estimated using OVERSEER version 4 or 5. Source: Dr Keith Betteridge, AgResearch, Hamilton. The streams (blue line) seem to be misaligned and probably should run through the dark green and white areas.

Table 3-2: Estimated wetland attenuation –1: Unmonitored = monitored. Unmonitored load = monitored load scaled by unmonitored/monitored days.

	Unimproved		Improved		Unimproved		Improved	
	Betteridge	This study	Betteridge	This study	Betteridge	This study	Betteridge	This study
Loss kg/ha/y	11	13	23	28	11	13	23	28
Catchment area ha	5				3			
Inflow kg/y	55	65	115	140	33	39	69	84
Outflow kg/y	37.6							
Baseflow kg/y	12.7							
Rainfall kg/y	11.4							
Livestock kg/y	9.7							
Unmeasured kg/y	3.8 Monitored load scaled by unmonitored/monitored days							
Attenuation	32%	42%	67%	73%	-14%	4%	46%	55%
Removal kg/y	17	27	77	102	-5	1	31	46
Wetland area ha	0.1725							
Removal mg/m2/d	28	43	123	163	-7	2	50	74

Table 3-3: Estimated wetland attenuation –2: Unmonitored = baseflow. Unmonitored loads set to baseflow loads.

	Unimproved		Improved		Unimproved		Improved	
	Betteridge	This study	Betteridge	This study	Betteridge	This study	Betteridge	This study
Loss kg/ha/y	11	13	23	28	11	13	23	28
Catchment area ha	5				3			
Inflow kg/y	55	65	115	140	33	39	69	84
Outflow kg/y	35.6							
Baseflow kg/y	12.7							
Rainfall kg/y	11.4							
Livestock kg/y	9.7							
Unmeasured kg/y	1.8 Assumed baseflow							
Attenuation	35%	45%	69%	75%	-8%	9%	48%	58%
Removal kg/y	19	29	79	104	-3	3	33	48
Wetland area ha	0.1725							
Removal mg/m2/d	31	47	126	166	-4	5	53	77

Table 3-4: Estimated wetland attenuation –3: Livestock events assumed baseflow. Livestock event loads set to baseflow loads.

	Unimproved		Improved		Unimproved		Improved	
	Betteridge	This study	Betteridge	This study	Betteridge	This study	Betteridge	This study
Loss kg/ha/y	11	13	23	28	11	13	23	28
Catchment area ha	5				3			
Inflow kg/y	55	65	115	140	33	39	69	84
Outflow kg/y	27.2							
Baseflow kg/y	12.7							
Rainfall kg/y	11.4							
Livestock kg/y	1.3 Assumed baseflow							
Unmeasured kg/y	1.8 Assumed baseflow							
Attenuation	51%	58%	76%	81%	18%	30%	61%	68%
Removal kg/y	28	38	88	113	6	12	42	57
Wetland area ha	0.1725							
Removal mg/m2/d	44	60	139	179	9	19	66	90

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Table 3-5: Estimated wetland attenuation – 4: Livestock & rainfall events = baseflow.

	Unimproved		Improved		Unimproved		Improved	
	Betteridge	This study	Betteridge	This study	Betteridge	This study	Betteridge	This study
Loss kg/ha/y	11	13	23	28	11	13	23	28
Catchment area ha	5				3			
Inflow kg/y	55	65	115	140	33	39	69	84
Outflow kg/y	17.4							
Baseflow kg/y	12.7							
Rainfall kg/y	1.7 Assumed baseflow							
Livestock kg/y	1.3 Assumed baseflow							
Unmeasured kg/y	1.8 Assumed baseflow							
Attenuation	68%	73%	85%	88%	47%	55%	75%	79%
Removal kg/y	38	48	98	123	16	22	52	67
Wetland area ha	0.1725							
Removal mg/m2/s	60	76	155	195	25	34	82	106

3.1.7 Attenuation based on concentrations

Sukias & Collins (unpublished) installed piezometers at the head of the RC wetland and measured nitrogen concentrations in shallow sub-surface flow where it first entered the wetland. On 23 occasions from 2005-2007 measurements were made on the same day in the outflow and the piezometers, which enables a paired comparison to be made and the decrease in concentration calculated.

The rate of change of concentration with distance was calculated as

$$C(x) = C(o)e^{-kx} \qquad 2$$

where x = distance (m), $C(x)$ = concentration at location x (mg m^{-3}) and k = removal rate coefficient (m^{-1}). k quantifies the nett change in concentration and ignores any mixing (e.g., vertical or transverse mixing with adjacent groundwater) and inflows (e.g., upwelling groundwater or surface inflows).

Flow in the piezometers was not measured. However, total inflow into the wetland was estimated as the measured outflow plus evaporation from the wetland. Evaporation was assumed to be PET (mm y^{-1}) multiplied by wetland area (m^2) with a unit conversion to mL s^{-1}. Areal removal rate was calculated as the decrease in massflow divided by the wetland area (1725 m^2).

For 11 of the days when measurements were made, photographic and turbidity data were available which indicated 1 livestock and 1 rainfall event – either of which may have reduced nitrogen removal. For 12 of the measurements days there was no data to indicate whether or not cattle were present in the wetland.

In Figure 3-4 there are 3 occasions when there was little (<25%) reduction in TN concentration. For 1 of these, cattle were known to be present near the outlet but for the other 2 occasions event data are missing. For 20 of the 23 paired comparisons, reductions in TN concentration were >50% even during the single rain event. On 1 occasion piezometer concentrations were abnormally high at the upper location (notably ammonium (NH_4), suggesting local contamination) resulting in high TN removal. Omitting 4 sampling occasions when either disturbance was thought to have occurred near the outlet or the piezometer was thought to have been contaminated, the decrease in concentrations averaged 91% ± 4% and 72% ± 9% for DIN and TN respectively, while the removal rates averaged 0.017 ± 0.002 and 0.009 ± 0.002 m^{-1} (mean ± 95% confidence interval) (Table 3-7). Omitting the same 4 sampling occasions, the areal removal rates were 49 and 55 mg m^{-2} d^{-1} for DIN and TN respectively (Table 3-6). When corrected to 20C from the local temperature (sinusoidal pattern with an annual average of 11.7C) these rates averaged 113 and 123 mg m^{-2} d^{-1}.

These calculations make three assumptions. First, groundwater concentration is assumed to be spatially uniform. It seems likely, based on field observations, that seepage flow occurs not only where the piezometers were installed but also along the edges of, or within, the wetland. It is assumed that concentrations in these other locations were the same as those in the piezometers. Second, the wetland was assumed to be at steady state, and the differences between inflow and outflow concentrations were assumed to quantify removal. The median residence time of water in the wetland under baseflow conditions (calculated as water volume divided by mean outflow rate) was c. 20 days. Strictly outflow concentration on Day N should be compared with inflow concentration on Day N-20 to quantify removal but this was not possible using the available data. Instead concentrations were compared on the same day. Third, the inflow rate was not measured but was estimated based on the measured outflow plus estimated evaporation. Rain occurred on 9/10/2007, the day prior to the sampling identified as a 'rainfall event'. No correction was made on any day for rain falling directly onto the wetland surface.

3.1.8 Effects of flow

Sukias et al. (2006a) reported on the first year of the study and described one high nitrogen removal event (>98%) when flow was high. They reported a weak negative relationship between flow and outflow NO_3 concentration which they speculated was the result of dilution by rain falling directly onto the wetland. It could also have been the result of low NO_3 runoff entering the wetland. Sukias & Collins (unpub. data) estimated hydraulic residence times (pore volume/flow) of 21.5 and 5.7 d when outflow was 400 and 1500 mL s^{-1} (the range of outflow rates measured during the study) and concluded that even at the shortest retention, the wetland had sufficient contact time to remove almost all the inflowing DIN.

This study examined the full four years of data and also found that removal rate did not decrease at high flows (Figure 3-4). Similarly, Cooper (1990) found in a small seepage wetland at Scotsman's Valley that denitrification capacity exceeded inflowing NO_3 fluxes even at times of high inflow. In contrast, Rutherford & Nguyen (2004) suggested, based on limited sampling during rainfall events, that attenuation in Barkers Wetland was likely to decrease with increasing flow.

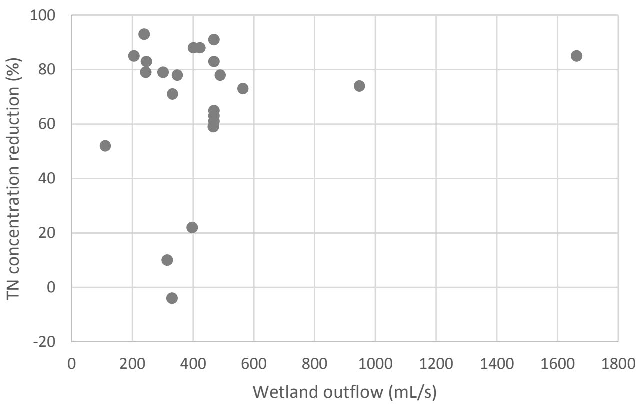

Figure 3-4: Percentage decrease in TN concentration between the piezometers at the head, and the weir at the outlet, of the RC wetland on 23 occasions when paired samples were collected. One of the three occasions when reductions were low (<25%) is known to be a livestock event, but there are no event data for the other two occasions. There is a single rainfall event (1650 mL s^{-1}) but reduction remained high (>80%).

Table 3-6: Areal removal rates in the RC wetland estimated from inflow and outflow concentrations. Missing outflows were assigned the average (469 mL s^{-1}). ND denotes no data. Data were omitted on four days (grey lines) when either cattle disturbance was thought to have affected the outflow or the inflow piezometer was thought to have been contaminated.

	Inflow g m^{-3}		Outflow g m^{-3}		Flow mL s^{-1}			Inflow gN d^{-1}		Outflow gN d^{-1}		Removal mg m^{-2} d^{-1}		Removal at 20C mg m^{-2} d^{-1}		
Day	DIN	TN	DIN	TN	Outflow	AET	Inflow	DIN	TN	DIN	TN	DIN	TN	DIN	TN	Events
30/08/2005	3.56	4.13	0.24	0.392		39	508	156	181	10	16	85	96	239	270	ND
29/09/2005	1.851	2.134	0.04	0.364		45	514	82	95	2	15	46	46	102	102	ND
21/10/2005	1.868	2.48	0.059	0.876		49	518	84	111	2	35	48	44	89	82	ND
9/11/2005	1.626	2.91	0.177	1.09		52	521	73	131	7	44	38	50	62	81	ND
12/01/2006	1.733	4.86	0.081	1.02	244	56	300	45	126	2	22	25	60	35	83	ND
9/02/2006	2.49	3.16	0.153	0.668	301	53	354	76	97	4	17	42	46	64	71	ND
16/03/2006	4.428	5.08	0.036	0.362	239	48	287	110	126	1	7	63	69	123	134	ND
12/04/2006	2.088	2.72	0.568	2.84	331	43	374	67	88	16	81	30	4	73	10	ND
9/05/2006	1.69	2.6	0.192	0.577	489	38	527	77	118	8	24	40	54	118	160	ND
13/06/2006	1.271	1.45	0.223	0.569		34	503	55	63	9	23	27	23	94	80	ND
17/07/2006	0.973	1.19	0.175	0.489	467	34	501	42	52	7	20	20	19	70	66	ND
14/08/2006	0.931	1.09	0.076	0.281	948	37	985	79	93	6	23	42	41	131	128	ND
4/09/2006	0.673	1.05	0.049	0.286	564	40	604	35	55	2	14	19	24	52	65	ND
11/10/2006	1.092	2.02	0.035	0.236	401	47	448	42	78	1	8	24	41	48	83	
14/11/2006	2.177	3.71	0.783	2.88	397	53	450	85	144	27	99	34	26	54	41	stock
11/12/2006	2.123	3.37	0.726	3.02	315	55	370	68	108	20	82	28	15	39	21	
9/01/2007	1.103	1.37	0.117	0.659	111	56	167	16	20	1	6	9	8	12	11	
14/02/2007	1.49	2.4	0.065	0.364	205	53	258	33	53	1	6	19	27	30	43	
15/03/2007	3.976	6.24	0.409	1.82	332	48	380	131	205	12	52	69	89	133	172	
24/07/2007	3.521	3.8	0.257	0.83	348	35	383	117	126	8	25	63	59	216	202	
14/08/2007	3.72	4.03	0.112	0.483	422	37	459	148	160	4	18	83	82	258	255	
13/09/2007	1.462	1.78	0.043	0.299	246	42	288	36	44	1	6	20	22	51	56	
10/10/2007	2.497	2.7	0.03	0.396	1663	47	1710	369	399	4	57	212	198	431	403	rain
Median												**40**	**46**	**89**	**83**	
IQR												**34**	**39**	**76**	**79**	
Count												**19**	**19**	**19**	**19**	
Mean												**49**	**55**	**113**	**123**	
95%CI												**45**	**42**	**100**	**95**	

Table 3-7: **Removal rate coefficients estimated from inflow and outflow concentrations using Eq 2.**

	Inflow g m^{-3}		Outlet g m^{-3}		Reduction %		Removal rate *k* m^{-1}	
Day	**DIN**	**TN**	**DIN**	**TN**	**DIN**	**TN**	**DIN**	**TN**
30/08/2005	3.56	4.13	0.24	0.392	93%	91%	0.017	0.015
29/09/2005	1.851	2.134	0.04	0.364	98%	83%	0.024	0.011
21/10/2005	1.868	2.48	0.059	0.876	97%	65%	0.021	0.006
9/11/2005	1.626	2.91	0.177	1.09	89%	63%	0.014	0.006
12/01/2006	1.733	4.86	0.081	1.02	95%	79%	0.019	0.010
9/02/2006	2.49	3.16	0.153	0.668	94%	79%	0.017	0.010
16/03/2006	4.428	5.08	0.036	0.362	99%	93%	0.030	0.016
12/04/2006	2.088	2.72						
9/05/2006	1.69	2.6	0.192	0.577	89%	78%	0.013	0.009
13/06/2006	1.271	1.45	0.223	0.569	82%	61%	0.011	0.006
17/07/2006	0.973	1.19	0.175	0.489	82%	59%	0.011	0.005
14/08/2006	0.931	1.09						
4/09/2006	0.673	1.05	0.049	0.286	93%	73%	0.016	0.008
11/10/2006	1.092	2.02	0.035	0.236	97%	88%	0.021	0.013
14/11/2006	2.177	3.71						
11/12/2006	2.123	3.37	0.726	3.02	66%	10%	0.007	0.001
9/01/2007	1.103	1.37	0.117	0.659	89%	52%	0.014	0.005
14/02/2007	1.49	2.4	0.065	0.364	96%	85%	0.019	0.012
15/03/2007	3.976	6.24	0.409	1.82	90%	71%	0.014	0.008
24/07/2007	3.521	3.8	0.257	0.83	93%	78%	0.016	0.009
14/08/2007	3.72	4.03	0.112	0.483	97%	88%	0.022	0.013
13/09/2007	1.462	1.78	0.043	0.299	97%	83%	0.022	0.011
10/10/2007	2.497	2.7						
Median	**1.851**	**2.700**	**0.117**	**0.569**	**93%**	**78%**	**0.017**	**0.009**
IQR	**1.127**	**1.855**	**0.154**	**0.489**	**8%**	**20%**	**0.008**	**0.005**
Count	**23**	**23**	**19**	**19**	**19**	**19**	**19**	**19**
Mean	**2.102**	**2.881**	**0.168**	**0.758**	**91%**	**72%**	**0.017**	**0.009**
95%CI	**1.851**	**2.700**	**0.117**	**0.569**	**4%**	**9%**	**0.002**	**0.002**

3.1.9 Discussion

Attenuation in the RC wetland was calculated in two different ways. First, as the difference between estimated mass inflows (OVERSEER catchment losses multiplied by 'effective' catchment area calculated from a water balance) and measured wetland TN outflow. The most likely scenario is considered to be that the RC catchment pasture was 'improved' and the 'effective' catchment area draining to the wetland was 2.7 ha. Making this assumption, attenuation was 46-58% (average 52%) with areal nitrogen removal rate 50-77 mg m^{-2} d^{-1} (average 64 mg m^{-2} d^{-1}) when cattle had access to the wetland. Attenuation is estimated to have been 61-79% (average 70%) and areal removal rate 66-106 mg m^{-2} d^{-1} (average 86 mg m^{-2} d^{-1}) if cattle had been excluded. These removal rates apply to the prevailing temperature (annual mean air temperature is 11.7C) and when corrected to the standard temperature (20C) using Eq 1 are 110-170 (average 140) and 145-235 (average 190) mg m^{-2} d^{-1} for disturbed and undisturbed wetlands respectively. However, the possibility cannot be excluded that pasture in the 'effective' (2.7 ha) catchment was 'unimproved' in which case attenuation would have been negligibly small when cattle had access to the wetland, and 19-55% had they been excluded. This implies areal nitrogen removal rates of 19-34 mg m^{-2} d^{-1} for undisturbed wetlands at 11.7C equivalent to 42-75 mg m^{-2} d^{-1} at 20C.

Second, by making a paired comparison of inflow (piezometer) and outflow concentrations multiplied by estimated inflow and outflow rates. This approach estimated attenuation in the range 91% and 72% with areal removal rates of 113 and 123 m^{-2} d^{-1} for DIN and TN respectively (at 20C). Collins estimated a lower removal rate for NO_3 of 21 ± 11 mg m^{-2} d^{-1} for 6 paired samples in 2005 (including one livestock event) but the piezometer concentrations were unusually high, possibly as a result of contamination, and the results are ignored.

OVERSEER assumes a maximum areal removal rate of 250 mg m^{-2} d^{-1} at 20C which is multiplied by the 'Condition Factor' for the appropriate wetland Class. The RC wetland was classified as Type A, Class 4 for which the removal rate in OVERSEER is 50 mg m^{-2} d^{-1} at 20C[5]. This is lower than either of the averages estimated by the field study (140 mg m^{-2} d^{-1} and 118 mg m^{-2} d^{-1} both including cattle disturbance). The OVERSEER wetland module, therefore, significantly underestimates the effectiveness of the RC wetland (the OVERSEER rate is 36-42% of the measured rates).

Estimating the 'effective' catchment area that drains to the wetland proved to be challenging. 'Effective' area can be estimated if the flow yields (mm y^{-1}) of both the wetland and the receiving stream can be estimated, but such information may not be readily available to OVERSEER users.

[5] Areal removal rate decreases with decreasing air temperature (calculated within OVERSEER using Eq. 1).

3.2 JS wetland

3.2.1 Description

JS wetland was a seepage wetland near the head of the Tutaeuaua catchment (Figure 3-1). Its catchment was rolling and lay at an elevation of 500-600 m ASL. The geology of the area comprised rhyolite pumice soils/rock, volcanic ashes and underlying ignimbrite. Soils were permeable pumice (Oruanui loamy sand) with high porosity (60-75%, Stenger et al. 2006). There was a paleosol soil layer at the Spydia experimental site (Stenger et al. 2006) close to the JS wetland. The JS wetland was 200 m long with an area of 1.85 ha. Vegetation in the first 50-80 m was exotic perennial pasture with occasional patches of rushes, from 100-150 m was predominantly native cattail (*Typha orientalis*) and from 150-200 m predominantly flax with occasional native scrub. Water appeared permanently at the surface amongst the flaxes and was at, or just below, the surface elsewhere in the wetland. The study area was unfenced but sheep tended to avoid the wetland. Cattle grazed the upper, grassy parts of the wetland but avoided areas of dense cattail and flax. Thus, the majority of the wetland was unaffected by livestock. The outflow from the wetland to the main stream was diffuse, and not suitable for flow measurement. JS wetland was classified Type A, Class 3.

3.2.2 Piezometer study

A series of piezometers was inserted longitudinally on a well-defined flow path 122 m in length in the JS wetland (Figure 3-5 and Figure 3-1). Where sediments were deep enough, two piezometers were installed: shallow (40-60 cm) and deep (75-100 cm). Samples were collected monthly from March to August 2004 from piezometers that contained water (some were dry during late summer) and analysed for NO_3, NH_4 and TN.

Figure 3-5: Close-up photograph of piezometers installed in the lower part of the JS wetland. Photo: James Sukias, 2004.

DIN and TN concentrations in deep and shallow wells were high at the upstream sites, but there was an overall decrease with distance along the wetland flow path (Figure 3-6 and Figure 3-7). High concentrations at T8, and the increase in concentration between the flax zone (T12) and the stream edge (T14) may be the result of additional high concentration inflows. Concentrations of DIN and TN at the stream edge (T13) were higher than in the flax (T11) possibly as a result of additional high concentration inflows.

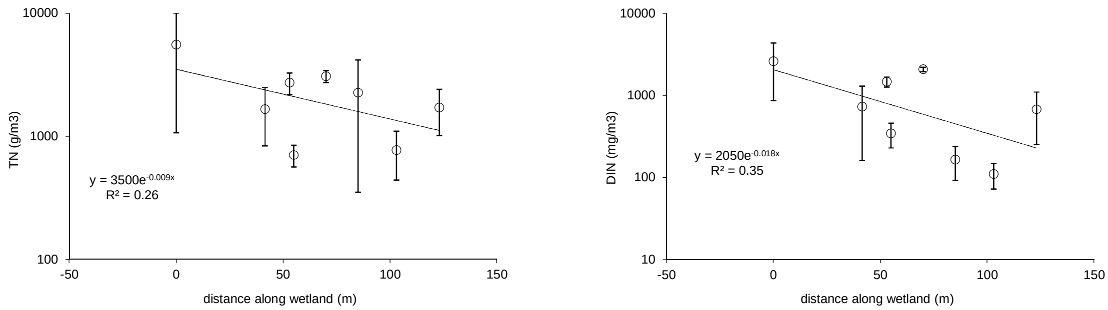

Figure 3-6: Deep wells: changes with distance along the flow path in the JS wetland of TN (left) and DIN (right) concentrations. Mean +/- 95% CI concentration.

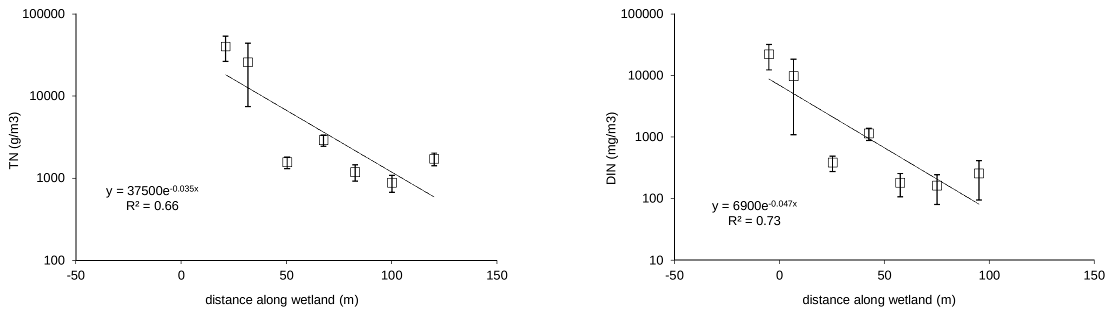

Figure 3-7: Shallow wells: decrease with distance along the flow path in the JS wetland of TN (left) and DIN (right) concentrations. Mean ± 95% CI concentration.

The first-order nett rate of change (removal) coefficients, k, were calculated using Eq. 2. Table 3-10 indicates nett rates of change for DIN and TN of k = 0.018 ± 0.010 and 0.0093 ± 0.0064 m^{-1} respectively in the deep wells (mean ± standard error). These estimates assume steady state and ignore inflows and vertical mixing. If there were high concentration inflows near T8 and T14 then these are likely lower bound estimates of nitrogen removal. Table 3-11 indicates nett rates of change for DIN and TN of k = 0.047 ± 0.013 and 0.035 ± 0.011 m^{-1} respectively in shallow wells.

Nett rates of change of concentration in shallow wells were on average 3 times (range 2.6-3.8) higher than in the deep wells. This suggests that shallow soils are more biologically active than deep soils. Possible reasons for higher removal rates in shallow soils include higher supply rates of organic carbon required for denitrification, greater root density leading to higher rates of uptake by plants, and higher nitrogen concentrations. However, in the shallow wells concentrations at T2 and T3 were well above, and strongly influenced the slope of, the regression lines. It is conceivable that the decrease in concentrations from T2/T3 to T5/T7 was the combined result of vertical mixing (which would have increased concentrations in the deep wells and decreased them in the shallow wells) and removal. If so then k = 0.047 and 0.035 m^{-1} may over-estimate removal rates.

Table 3-8: DIN (top) and TN (bottom) concentrations in deep wells along the flow path in the JS wetland.

Date	T1	T4	T6	T6a	T8	T10	T12	T14
	Top			Seep	Seep	Raupo	Flax	Stream
Depth, cm		80	90	100	100	75	100	85
Distance, m	-27	16.5	25.3	30	42.6	57.6	75.1	95.1
DIN, mg m^{-3}								
24/03/2004		87	545		2447	377	335	1851
30/04/2004		34	1113		2651	358	120	992
8/06/2004		241	1319		1985	130	183	202
2/07/2004		213	1839		1953	205	199	292
20/08/2004	1853	202	2229		2411	137	200	67
20/09/2004	3917	31	2297		2275	33	88	161
21/10/2004		3906	1859		2217	622	83	556
18/11/2004	6310	177	1325		2077	93	92	127
15/12/2004		3623	1192		1578	147	57	141
27/01/2005		1102	1104		1842	123	113	616
23/02/2005		726	1272		1813	97	73	326
22/03/2005		324	1623		1856	124	47	607
21/04/2005		901	1114		1864	80	86	3579
24/05/2005	665	232	1365	483	2036	87	57	1268
17/06/2005	720	317	1509	388	1774	71	48	384
18/07/2005	2142	80	1484	284	2123	47	49	166
30/08/2005		103	1666	216	2223	59	30	118
Average	**2601**	**723**	**1462**	**343**	**2066**	**164**	**109**	**674**
SD	**2170**	**1186**	**435**	**117**	**279**	**153**	**79**	**889**
count	**6**	**17**	**17**	**4**	**17**	**17**	**17**	**17**
95%CI	**1736**	**564**	**207**	**115**	**133**	**73**	**37**	**423**
TN, mg m^{-3}								
24/03/2004		833	971		5207		2804	4611
30/04/2004		202	1300				412	1304
8/06/2004			1690					2754
2/07/2004								
20/08/2004	3110	727	3100		3680	1280	1260	290
20/09/2004	4430	528	2700		3030	1270	1460	583
21/10/2004		4950	2330		3020	13900	493	1100
18/11/2004	16900	724	3270		2930	1310	650	690
15/12/2004		5690	2610		2730	915	341	659
27/01/2005		1280	4450		2740	1030	736	1370
23/02/2005		1700	3220		2480	1440	760	1110
22/03/2005		1140	5320		2980	1810	466	3300
21/04/2005		3090	2340		2750	920	409	4720
24/05/2005	3000	1080	2470	850	2790	1790	470	2330
17/06/2005	2340	987	2000	709	2710	1610	470	1290
18/07/2005	3520	1030	2270	746	2990	971	526	766
30/08/2005		920	3460	505	3000	1120	290	490
Average	**5550**	**1659**	**2719**	**703**	**3074**	**2259**	**770**	**1710**
SD	**5603**	**1628**	**1102**	**145**	**672**	**3511**	**652**	**1425**
count	**6**	**15**	**16**	**4**	**14**	**13**	**15**	**16**
95%CI	**4483**	**824**	**540**	**142**	**352**	**1909**	**330**	**698**

Table 3-9: DIN (top) and TN (bottom) concentrations in shallow wells along the flow path in the JS wetland.

	T2	T3	T5	T7	T9	T11	T13
	Top				Raupo	Flax	Stream
Depth, cm	90	40	45	60	60	50	50
Distance, m	21.05	31.7	50.3	67.6	82.6	100.1	120.1
DIN, mg m^{-3}							
24/03/2004		46	331	1167	443	235	1353
30/04/2004		7	321	1304	227	185	160
8/06/2004		3820	241	1028	140	96	61
2/07/2004	11040	2001	1047	504	550	239	187
20/08/2004	6163	1999	355		57	82	31
20/09/2004	10327	1406	266	702	85	111	38
21/10/2004	32804	4503	298	1158	63	246	85
18/11/2004	24002	7335	292	195	44	183	96
15/12/2004	27508	36208	505	516	139	105	342
27/01/2005	51607	46413	551	2200	425	760	158
23/02/2005	56827		394	811	119	184	687
22/03/2005	15865		527	1606	91	70	249
21/04/2005	45536		448	1353	286	64	109
24/05/2005	11501	10570	309	1805	79	16	536
17/06/2005	12125		127	1260	48	74	95
18/07/2005	1117	2066	104	1003	104	42	88
30/08/2005	721			1496	170	47	45
Average	21939	9698	382	1132	181	161	254
SD	18472	15229	218	517	155	171	336
Count	14	12	16	16	17	17	17
95% CI	9676	8617	107	253	74	81	160
TN, mg m^{-3}							
24/03/2004		2606	1306	4277	1505		2603
30/04/2004		501		1624	780		707
8/06/2004		26260		3790	1106		
2/07/2004							
20/08/2004	16100	5260	1750	3180	762	461	1930
20/09/2004	13000	2130	1300	2030	599	926	1040
21/10/2004	45600	9950	1040	2700	559	875	2100
18/11/2004	42400	16600	1380	2810	788	1750	1920
15/12/2004	48600	86900	1630	1460	620	491	2130
27/01/2005	70700	59600	1410	3620	1020	1340	1530
23/02/2005	53000		1450	1610	1640	955	2340
22/03/2005			2210	4110	1160	1120	1670
21/04/2005	72000	67100	2790	3740	1730	577	999
24/05/2005	20200		1770	2850	2250	998	2130
17/06/2005	22300		1660	2250	1570	802	1530
18/07/2005	5490	5240	953	3630	787	617	2220
30/08/2005	68400		1060	2390	2000	447	812
Average	39816	25650	1551	2879	1180	874	1711
SD	23835	30822	490	925	535	380	591
Count	12	11	14	16	16	13	15
95% CI	13486	18214	257	453	262	206	299

Table 3-10: Parameters of regression equations fitted to average TN and DIN concentrations in deep wells.

TN in deep wells						
R^2	0.263					
Obs	8					
	Coefficients	***SE***	***t Stat***	***P-value***	***Lower 95%***	***Upper 95%***
Intercept	8.16	0.479	17.0	2.62E-06	6.99	9.33
Distance	-0.00931	0.00636	-1.46	0.194	-0.0249	0.00626
DIN in deep wells						
R^2	0.348					
Obs	8					
	Coefficients	***SE***	***t Stat***	***P-value***	***Lower 95%***	***Upper 95%***
Intercept	7.62	0.753	10.1	5.4E-05	5.73	9.47
Distance	-0.0179	0.0099	-1.79	0.124	-0.0423	0.0066

Table 3-11: Parameters of regression equations fitted to average TN and DIN concentrations in shallow wells.

TN in shallow wells						
R^2	0.657					
Obs	7					
	Coefficients	***SE***	***t Stat***	***P-value***	***Lower 95%***	***Upper 95%***
Intercept	10.5	0.8	12.5	0.0000	8.4	12.7
Distance	-0.0346	0.0112	-3.10	0.0269	-0.0633	-0.0059
DIN in shallow wells						
R^2	0.722					
Obs	7					
	Coefficients	***SE***	***t Stat***	***P-value***	***Lower 95%***	***Upper 95%***
Intercept	10.0	1.0	10.2	0.0002	7.50	12.6
Distance	-0.0469	0.0130	-3.60	0.0154	-0.0804	-0.0134

The nett areal removal rate for the wetland is

$$U = HV\frac{dN}{dx} \qquad 3$$

where U = nett removal rate (mg m^2 d^{-1}), H = soil depth (m), V = pore water velocity (m d^{-1}), $\frac{dN}{dx}$ = rate of change of concentration with distance (mg m^{-3} m^{-1}), and $N(x)$ = concentrations at distance x (mg m^{-3}). Nitrogen concentrations decreased exponentially with distance, and so

$$\frac{dN}{dx} = kN(x) \qquad 4$$

where k = exponential removal rate (from Eq 2).

Nett removal rates in the shallow and deep wells were estimated from Eq 2-4 assuming soil depths of 50 cm (shallow) and 100 cm (deep) wells (see Table 3-12). Velocity was assumed to equal the velocity of the centroid of lithium bromide injected into a well near site T1 (as described in the next section). Removal rates were not adjusted to 20C because experiments were conducted in summer.

The nett removal rates were highest at the upstream sites T1 and T2 but then decreased with distance downstream in both shallow and deep wells (Figure 3-8 and Figure 3-9). The most likely explanation is that nitrogen concentrations were high in the shallow sub-surface flow at the bottom of the hillslope. When this water first encountered organically enriched and microbially active wetland soils nitrogen removal was rapid. As water moved further along the flow pathway within the wetland, nitrogen concentrations decreased which in turn decreased the rate of microbial activity and removal rate. Cooper (1990) measured very high rates of denitrification where shallow sub-surface flow first entered a riparian wetland in Scotsman's Valley, Hamilton. Denitrification rates decreased with distance along the flow path which Cooper attributed to the decrease in NO_3 concentration and microbial activity. It is also possible that vertical mixing occurred between high concentration shallow, and low concentration deep, sub-surface flow. This would have the effect of increasing apparent removal rates in shallow wells, and decreasing apparent rates in deep wells.

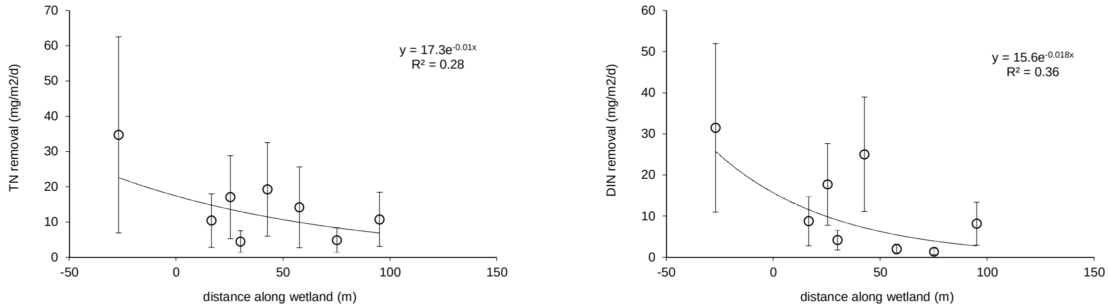

Figure 3-8: Deep wells: changes in nett removal rate with distance along the flow path in the JS wetland of TN (left) and DIN (right). Mean +/- SE.

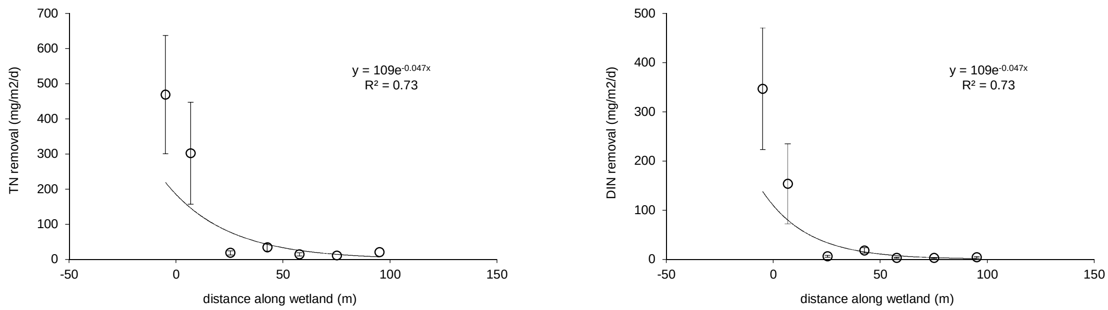

Figure 3-9: Shallow wells: changes in nett removal rate with distance along the flow path in the JS wetland of TN (left) and DIN (right). Mean +/- SE.

Table 3-12: Nett removal rates along a flow path in the JS wetland.

		Deep wells							
Site		**T1**	**T4**	**T6**	**T6a**	**T8**	**T10**	**T12**	**T14**
Distance	m	0	41.5	53	55	70	85	103	123
Well depth	cm		80	90	100	100	75	100	85
Soil depth	cm	100							
Velocity	m h^{-1}	0.028							
		DIN							
Removal rate	per m	0.018 ± 0.010							
Removal	mg m^{-2} d^{-1}	31	9	18	4	25	2	1	8
SE		21	6	10	2	14	1	1	5
		TN							
Removal rate	per m	0.0093 ± 0.0064							
Removal	mg m^{-2} d^{-1}	35	10	17	4	19	14	5	11
SE		28	8	12	3	13	11	3	8
		Shallow wells							
		T2	**T3**	**T5**	**T7**	**T9**	**T11**	**T13**	
Distance	m	21.05	31.7	50.3	67.6	82.6	100.1	120.1	
Well depth	cm	90	40	45	60	60	50	50	
Soil depth	cm	50							
Velocity	m h^{-1}	0.028							
		DIN							
Removal rate	per m	0.047 ± 0.013							
Removal	mg m^{-2} d^{-1}	346	153	6	18	3	3	4	
SE		124	81	2	5	1	1	2	
		TN							
Removal rate	per m	0.035 ± 0.011							
Removal	mg m^{-2} d^{-1}	468	302	18	34	14	10	20	
SE		168	145	6	11	5	3	7	

3.2.3 Tracer injection study

A small rectangular section (1 m wide and 2 m long) of the permanently wet pasture seepage zone was isolated from lateral inflows on two sides by embedding plastic sheets 60-70 cm into the soil down to the consolidated base layer. The upstream and downstream ends were left open to allow water to flow through the enclosed section. Four (input) piezometers were inserted equidistant across the upstream end of the enclosure to a depth of 30 cm and used to inject tracer solution. A large (100 mm) slotted well was inserted to a depth of 30 cm at the downstream end of the enclosure as the final sampling point. Paired (shallow and deep) piezometers were inserted at 0.5 m and 1.0 m from the tracer insertion point to act as additional sampling points. Insertion of piezometers and isolating sheets to the wetland was undertaken 4 weeks prior to the start of the experiment. Boardwalks were placed over the poorly consolidated wetland soils outside the isolated section of wetland to minimise disturbance, and the area upstream of the isolated section of wetland was avoided. An electric fence was placed around the wetland to exclude stock during the experiment and for the preceding four weeks.

During a 4 week period of dry weather (June 2004) 200 ml of tracer solution (433 g m^{-3} NO_3-N as KNO_3 with 33 g m^{-3} Br as LiBr as a conservative tracer) was injected into each of the four inflow piezometers. After 15 minutes, an additional 200 ml of deionised water was injected into the inflow piezometers to displace the added tracer solution. Samples were collected hourly from the downstream well (either by hand or using an automatic sampler) and stored on ice until delivered to the laboratory for analysis for NO_3, NH_4 and Br. During daylight hours, samples were also collected from the paired piezometers at 0.5 and 1.0 m.

Bromide took approximately 24 h to first appear at the downstream sampling well 1.5 m downstream. The tracer peak arrived after 36 h (pore water velocity, 0.042 m h^{-1}), and the centroid after 54 h (0.028 m h^{-1}). The Br profile was strongly skewed, with the tail taking around c. 7 days to pass the downstream sampling point (Figure 3-10).

At the downstream well NO_3 concentrations reached 10 mg m^{-3} shortly after injection. This indicates either rapid transfer of some of the added tracer (possibly by surface flow) and/or soil disturbance during the installation of the wells or during tracer injection. A second peak of 11 g m^{-3} occurred 24 hours later which preceded the Br peak by 8 hours. Ammonium concentrations were high (on average c. 100 times the NO_3 concentrations) notably at and immediately following tracer injection (Figure 3-10). The reasons for the high initial NO_3 and NH_4 concentrations, and the timing difference between peak NO_3 and Br in the outlet well, are unclear.

Nitrate concentrations in the outlet well were below detection at times on 12, 13 and 14 June before stabilising at 2-3 mg m^{-3} after the majority of Br had passed. The well was sampled again during July 2004 during which time NO_3 concentration was typically 2-3 g m^{-3} although occasionally concentrations were 4-13 g m^{-3}.

Sampling stopped on 14 June 2004 while Br concentration (0.47 g m^{-3}) was higher than background (0.05 g m^{-3}). Bromide concentrations were extrapolated using log-linear interpolation, and were estimated to return to background after a further 24 hours.

Sukias & Collins reported that 800 mL of stock solution containing 33 g m^{-3} Br was injected giving a Br mass of 26.4 g. Assuming Br to be conservative, flow was estimated to be 13.4 mL s^{-1} by dividing the injected mass by the integral over time of outlet Br concentration (corrected for background). However, Sukias & Collins reported the mean pore water velocity to be 100 cm d^{-1} based on the time of travel of the Br centroid. This study re-calculated the velocity of the centroid to be 60 cm d^{-1}. Both estimates are higher than the 30 cm d^{-1} reported by Burns & Nguyen (2002) in Barkers wetland, Whatawhata.

The enclosure in the JS wetland was 1 m wide and if soil depth was 50 cm, porosity 0.8 and pore-water velocity 100 cm d^{-1} then flow was 6.9 mL s^{-1}. This is c. 50% lower than the estimate made from the Br mass balance. Either Br was not conserved, Br was retained in the enclosure after 18 June and/or soil depth exceeded 50 cm.

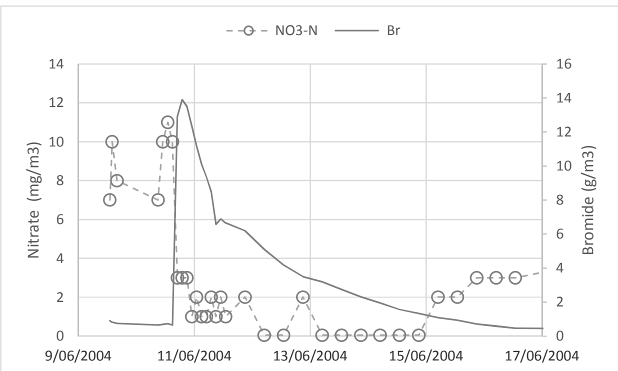

Figure 3-10: Nitrate and bromide concentrations in the downstream well following tracer injection on 9 June 2004. .

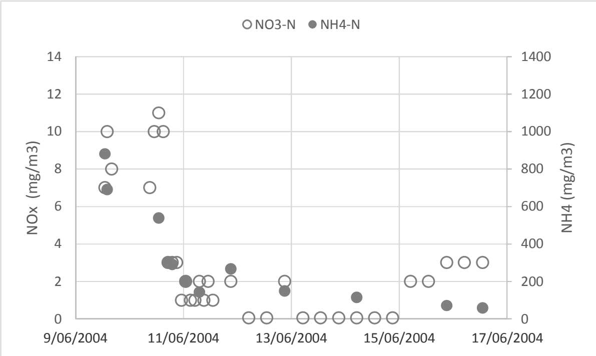

Figure 3-11: Nitrate (NO_3) and ammonium (NH_4) concentrations in the downstream well following tracer injection on 10 June 2004. .

Nitrate removal rates were estimated as the difference between the expected flux (Br flux multiplied by the NO_3/Br ratio in the stock solution) and the observed flux. Flow was assumed to be 13.4 mL s^{-1} and removal was expressed per unit area of wetland surface. In the Br and NO_3 time series reported by Sukias & Collins (Figure 3-12 left) the peak concentrations occurred c. 24 hours apart and the maximum removal rate was 135 mg m^{-2} d^{-1} at 7C (425 mg m^{-2} d^{-1} at 20C). When the NO_3 time series was lagged by 24 hours the Br and NO_3 concentration peaks coincided and the maximum removal rate dropped to 61 mg m^{-2} d^{-1} at 7C (190 mg m^{-2} d^{-1} at 20C).

3.2.4 Discussion

In the transect study, DIN and TN concentrations in wells decreased with distance along a longitudinal flow pathway through the wetland. Nett rates of change of concentration in deep wells averaged 0.009 ± 0.006 m^{-1} and 0.018 ± 0.010 m^{-1} for DIN and TN – rates similar to the RC wetland of 0.009 ± 0.002 and 0.017 ± 0.002 m^{-1}. Nett rates of change in shallow wells, however, were significantly higher – averaging 0.047 ± 0.013 m^{-1} and 0.035 ± 0.006 m^{-1} for DIN and TN. These nett rates of change of concentration do not account for vertical mixing (which would increase apparent removal rates in shallow wells and decrease them in deep wells) or high concentration inflows (which would decrease apparent removal rates).

Nett areal removal rates were highest where drainage first entered the wetland but decreased with distance downstream. Maximum removal rates (at the most upstream site) for TN in deep wells (35 ± 28 mg m^{-2} d^{-1}) were lower, and in shallow wells (468 ± 168 mg m^{-2} d^{-1}) were higher, than the average rates in the RC wetland (110-170 mg m^{-2} d^{-1})[6].

Betteridge estimated nitrogen losses of 14-15 kgN ha^{-1} y^{-1} from pasture at the JS study site (see Figure 3-3). Rutherford et al. (2009) measured stream runoff of 485 mm y^{-1} and dividing losses by runoff gives an expected nitrogen concentration in runoff of c. 3 g m^{-3}. Sukias & Collins measured DIN and TN concentrations of 2.1 ± 1.9 and 2.9 ± 2.7 g m^{-3} (mean ± 95% confidence interval) in wells at the top of the nearby RC wetland (see Table 3-6) which are similar to the estimate of c. 3 g m^{-3} for the JS wetland. Sukias and Collins measured DIN and TN concentrations in the deep upstream wells at the JS wetland of 2.6 ± 1.7 and 5.6 ± 4.5 g m^{-3} respectively (Table 3-8). However, in shallow wells they measured much higher concentrations of 22.0 ± 9.7 and 39.8 ± 13.5 g m^{-3} for DIN and TN respectively (Table 3-9). Concentrations were lower in wells further along the flow path. The reason for the very high concentrations at the upper well site is unclear but may have resulted from a point source of nitrogen. In the first three samples collected at the downstream well prior to tracer injection, NO_3 concentrations were high (7-10 g m^{-3}) (Figure 3-10). Again the reason for the high concentrations is

[6] Corrected to 20C

unclear but may have been the result of soil disturbance when installing the piezometers. The maximum observed and 'expected' outlet NO_3 concentrations during the injection experiment were 0.01 and 0.18 g m^{-3} respectively – significantly lower than typical inflow concentrations. Thus the areal NO_3 removal rates of 190-425 mg m^{-2} d^{-1} estimated from this tracer experiment occurred at lower NO_3 concentrations than typically flow into seepage wetlands draining pasture, and hence may underestimate typical wetland removal rates.

Sukias & Collins reported that, based on the ratio of Br to NO_3 in the original tracer solution, the peak NO_3 concentration without any biological transformations or removal was c. 180 mg m^{-3}. The decrease from 180 to 10 mg m^{-3} represents >98% removal over 1½ d. This study integrated the observed and expected NO_3 concentration time-series from 9-17 June (viz., including concentrations on 9 June (before any Br reached the downstream well) and on 15-17 June 2004 (when concentrations were higher than on previous days)). Background concentrations of 1-3 mg m^{-3} (NO_3) and 0.05 g m^{-3} (Br) were subtracted. There were 8 anomalously low observed outlet NO_3 concentrations on 12-14 June which were replaced by the background concentrations. Removal was estimated to be 96-98% of the added NO_3.

There are two unresolved questions arising from this study. First, 'background' NO_3 and NH_4 concentrations were high at the start of the injection but decreased over time. Second, the peak Br concentration lagged the peak NO_3 concentration. Both increase uncertainty in estimated removal rates. Nevertheless, 96-98% of the added NO_3 was removed from the sub-surface flow during the 6-8 days it took to travel past the downstream well. Ammonium concentrations measured at the outlet well were c. 0.8 g m^{-3} on the first day of the experiment and decreased to c. 0.07 mg m^{-3} over the next 7 days. The source of the NH_4 is not known but it may have been the end product of the dissimilatory reduction of NO_3 to NH_4 (DRNA).

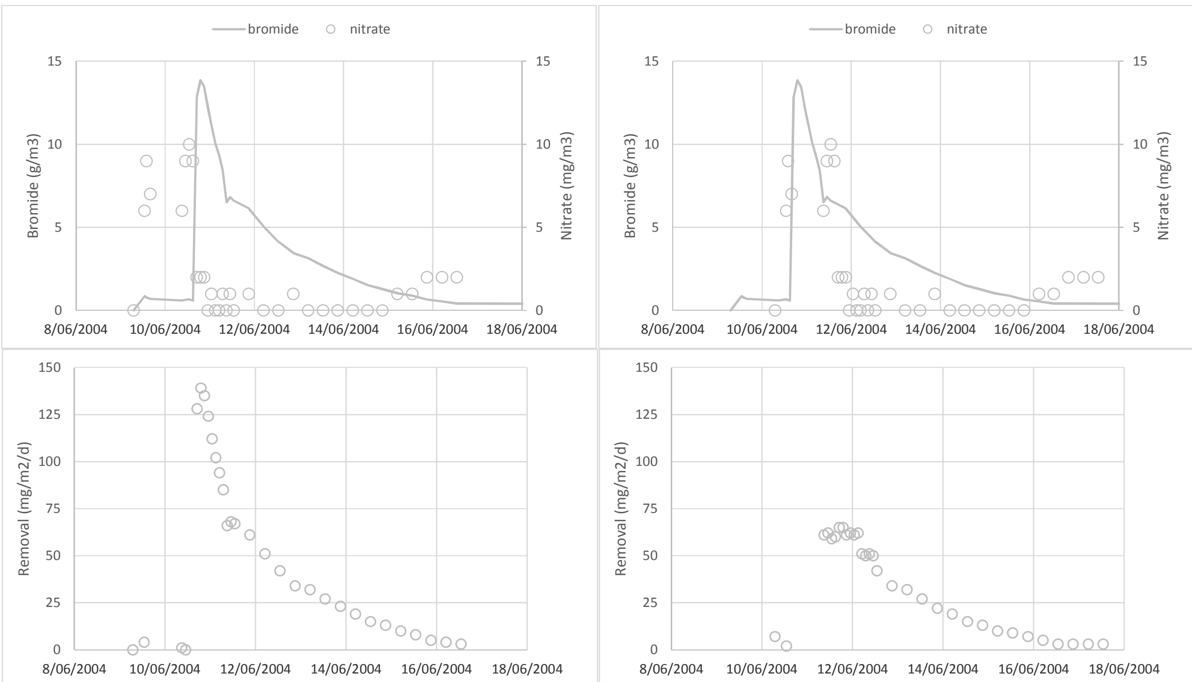

Figure 3-12: Top: observed (o) and expected (-) nitrate concentrations at the outlet well. Bottom: removal rates estimated as the difference between observed and expected nitrate fluxes. Left: time series as reported by Sukias & Collins. Right: nitrate time series lagged by 24 h.

3.3 TUT catchment

3.3.1 Water and nitrogen balance

In the previous section, we reviewed studies in two wetlands in the Tutaeuaua catchment near Taupo. In this section we review a study of the combined effect of wetlands at catchment scale in the same catchment.

Rutherford et al. (2009) measured flows leaving several wetlands in the Tutaeuaua catchment (including the RC wetland) and compared them with stream flows, in order to estimate the proportion of catchment runoff passing through seepage wetlands. They found that wetlands occupied 5% of the catchment (Figure 3-13) but that 11% of runoff passed through wetlands as baseflow and another 8% during rainfall events. Based on the observation that the RC and JS wetlands removed 95% or more of incoming NO_3, then they estimated that wetlands probably attenuate 10-18% of NO_3 runoff in this catchment.

Betteridge estimated the average nitrogen loss from the Tutaeuaua catchment to be 17 ± 5 kg ha^{-1} y^{-1} based on OVERSEER. Rutherford (unpublished) summarised results from several studies in the Tutaeuaua and estimated the average groundwater TN and DIN concentrations to be 3 ± 0.3 and 2 ± 0.5 g m^{-3} respectively. Multiplying these concentrations by average runoff of 585 ± 70 mm y^{-1} (Rutherford et al. 2009) gives nitrogen yields in the range 18 ± 3 kg ha^{-1} y^{-1} which are not significantly different from the OVERSEER estimates.

Nitrogen concentrations were measured monthly for 4 years at a stream site (LWR) with continuous a flow recorder (Rutherford unpublished data). The annual stream yield of TN was calculated (using a rating-curve approach) to be 5.3 ± 0.7 kg ha^{-1} y^{-1}. Assuming catchment losses were 17 ± 5 kg ha^{-1} y^{-1} and stream yields were 5 ± 1 kg ha^{-1} y^{-1} then catchment attenuation would be 70 ± 25 %. Catchment-scale attenuation of 50% was estimated in the Waikato catchment (Alexander et al. 2002) and a similar value has been estimated for catchments in the Manawatu. Thus the lower bound estimate for the Tutaeuaua is comparable with widely accepted catchment-scale attenuation values, but the average and upper bounds are unexpectedly high.

If wetlands attenuate 10-18% (14 ± 4%) (from above) and overall attenuation is 70 ± 25 % then a further 56 ± 29 % is unexplained. Rutherford et al. (2009) may have underestimated wetland outflows because some of their flow recorders needed to be located some distance upslope from the receiving streams (viz., part way up the wetlands). Thus wetland flow may have been higher than 11-19% of runoff and hence nitrogen removal higher than 10-18%. However, unmeasured wetland outflows are unlikely to explain all of the unaccounted attenuation.

Comparing catchment losses with stream yields assumes that a steady-state has been reached. Dr Mike Stewart (formerly GNS-Science) measured the mean residence time (MRT) of water in the Tutaeuaua to be c. 40 years using tritium and other gas tracers (Stewart, unpublished data). Thus groundwater concentrations are likely to reflect agriculture as practised in the 1970s when the catchment was in the process of being developed for farmland and nitrogen losses may have been lower than they are currently. There is insufficient information about historic farming practices to reliably estimate the changes in nitrogen losses over time and determine whether these explain the apparently high attenuation.

These calculations indicate that the wetland attenuation of 10-18% cannot be dismissed as unrealistically high. Indeed if there are no groundwater time lags in the Tutaeuaua, and no NO_3 attenuation in the deep groundwater, then wetland attenuation could be as high as 70 ± 25%. The Tutaeuaua is unusual in that approximately 5% of its area comprises seepage wetlands or fenced riparian buffer strips. These were established in the 1970s to combat high erosion of the fragile soils following conversion to pasture and appear to be having a significant beneficial effect in terms of reducing nitrogen runoff into Lake Taupo.

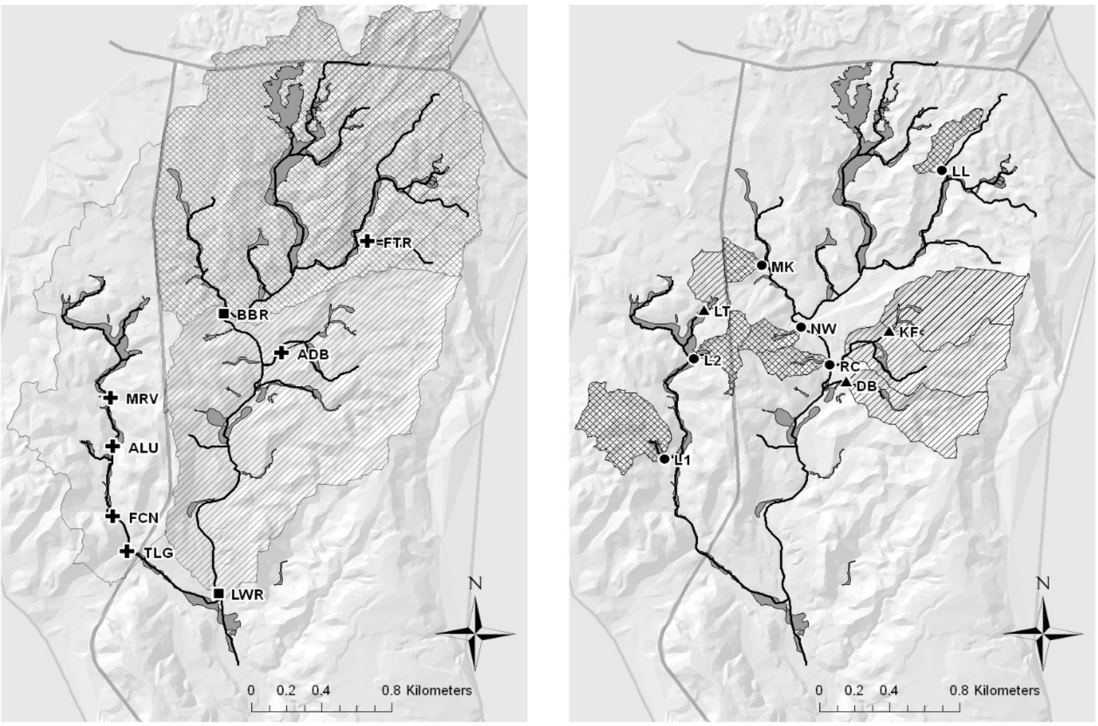

Figure 3-13: Left: Map showing the streams, flow recorders (squares), catchments draining to recorders (hatched) and spot gauging sites (crosses). Right: Map showing the catchments of the study wetlands with recorders (double hatch) and spot gaugings (single hatch). Both maps show roads, topography (20 m DEM) and wetlands (shaded).

3.3.2 Riparian zone surveys

Matheson et al. (2002) measured changes in nutrient concentration across fenced, riparian buffer zones at 13 sites in the Tutaeuaua catchment, Taupo. Piezometers were installed in pasture within 2m of the buffer fence line and in the riparian zone within 2m of the stream edge to a depth of 0.5 m below the groundwater table and were slotted from 0.25 m below the soil surface to enable groundwater entry. Soils were saturated at most of the stream edge piezometers (viz., the riparian buffers were seepage wetlands). Piezometers were re-sampled in spring (November 2005), summer (December 2006) and autumn (May 2007) (Matheson unpub. data). Five of the 13 sites were studied in more detail with 3 piezometers installed at the pasture edge, 3 in the middle of the riparian buffer and 3 at the stream edge. Sampling occurred in spring (October 2007), summer (February 2008) and autumn (May 2008) although some piezometers were dry in summer.

In 2005-2006 the average NO_3 concentration across all 13 sites decreased significantly between pasture (336 ± 128 mg m^{-3}) (mean SE, N=39) and riparian (82 ± 21 mg m^{-3}) piezometers which indicates an average attenuation of 75%. At 11 sites attenuation ranged from 36-99% but at 4 sites there was a gain of NO_3 (viz., stream edge concentrations were higher than pasture concentrations). There were no significant changes in average NH_4 concentrations between pasture and riparian piezometers. The average DON concentration across all 13 sites increased significantly between pasture (548 ± 40 mg m^{-3}) and riparian (967 ± 101 mg m^{-3}) piezometers which indicates an average gain of 75%. At 11 sites there were gains of 13-275% but at 4 sites there were loses of 6-52%. The 4 sites where NO_3 increased were not the same 4 sites where DON decreased.

In 2007-2008 there were significant reductions in spring and autumn NO_3 concentrations at 4 sites, with attenuation in the range 95-99%. At one site NO_3 attenuation was 91% in autumn but in spring, NO_3 concentrations increased between pasture and riparian piezometers. NH_4 was attenuated at one site but not at the other four. In autumn when DON concentrations in pasture piezometers were high, they were lower in the riparian piezometers at four sites (attenuation 20-75%) but higher at one site (gain 80%). In spring DON concentrations decreased at two sites (attenuation 18-30%) but increased at three sites (gain 31-143%).

The finding that NO_3 concentrations in shallow groundwater decreased significantly as it flowed through the seepage wetlands in riparian zones is consistent with other New Zealand studies and overseas literature. The reductions of 95-99% at some sites, and 75% on average, fall within the range of other New Zealand studies reviewed here. On a small number of sampling occasions NO_3 concentrations were higher in the riparian than pasture piezometers, but such events were the exception rather than the rule and may have arisen as a result of local contamination or the upstream and downstream piezometers lying on different flow pathways.

A key finding of this study was that the riparian buffer zone could be a source of DON. There were occasions when DON concentrations decreased between pasture and riparian piezometers, but on most occasions DON concentrations increased. The source of the DON has not been identified, but is likely to be decaying wetland vegetation. Riparian fencing occurred at Taupo 20-30 years ago to combat soil erosion, and vegetation within the riparian buffers is mature. This should serve as a warning that although riparian seepage wetlands may be effective in removing NO_3 from runoff through denitrification, they may be sources of other forms of nitrogen (e.g., NH_4, DON and PN). Ammonium can cause toxicity problems (notably to fish which are very sensitive) although in most New Zealand streams and river NH_4 is rapidly oxidised to non-toxic NO_3. Both NH_4 and NO_3 are readily taken up by aquatic plants and hence can contribute to eutrophication and problems with excessive periphyton biomass in cobble-bed streams and phytoplankton in lakes. Dissolved organic nitrogen includes a large group of compounds. Some are immediately available for uptake by aquatic plants, others are readily broken down by bacteria and fungi to NH_4 and others do not readily breakdown. There is very little information available concerning the bioavailability of dissolved and particulate organic matter leaving seepage wetlands in New Zealand.

This study found that on occasions the decrease in NO_3 concentration was similar to the increase in DON + NH_4 concentration (viz., overall the riparian zone <u>transformed</u> but did not <u>remove</u> nitrogen). This is in contrast with two other studies reviewed in this report (the RC and ARM wetland studies) measured the attenuation of NO_3, NH_4 and TN. While the authors of those studies noted that wetlands generally act as nitrogen transformers rather than removers, both studies reported significant attenuation of TN (viz., NO_3 losses exceeded gains in NH_4, DON and PN). One possible explanation is that the Tutaeuaua riparian zones contain a large reservoir of detritus (viz., decaying vegetation) which is a source of dissolved and particulate organic nitrogen. If so, then it suggests periodic 'harvesting' of vegetation from riparian zones may increase their capacity to attenuate nitrogen runoff from catchments.

3.4 BARK wetland

3.4.1 Description

Barkers (BARK) wetland is a fenced, seepage wetland draining pasture at the Whatawhata Hill country Research station near Hamilton. The catchment is steep (10–30^{o}) pasture sown with ryegrass–clover pasture (*Lolium perenne–Trifolium repens*) and grazed by sheep and cattle. The mean annual temperature is 13.7C and annual rainfall averages 1614 mm. The catchment is predominantly Waingaro steepland soil (a northern yellow-brown earth, USDA Soil Taxonomy: Umbric Dystrochrept) derived from sedimentary greywacke parent material. There is a shallow (50–75 cm depth) clay loam topsoil of fine and medium nut structure, underlain by a sub-soil of firm clay with weakly developed nut structure.

During the study in 1999-2001 the wetland was a permanently wet swale with a surface area of 350 m^2 and a slope of 8–9^{o}. It filled a small valley and appears to have been formed by the accumulation of sediment and organic matter washed in from the catchment that had been partially stabilized by vegetation. The wetland was well vegetated with floating sweet grass (*Glyceria declinata*), rush (*Juncus* spp.), sedge (*Carex* sp.), and lotus (*Lotus pedunculatis*) (Figure 3-14). Wetland measurements are summarised in Table 3-13.

3.4.2 Methods

A series of 20 auger holes indicated that the top 20–30 cm was dark brown-black, organically enriched fine clayey textured soil (much finer than the upland soils) containing plant roots, twigs and occasional tree branches. The surface soils were poorly consolidated and could not support the weight of a person, so board-walks were built to provide access and minimize soil disturbance during sampling. Shortly after the study the top 50 cm of wetland soil was scoured out during a storm down to the clay layer; behaviour that has been observed in several adjacent wetlands. At a depth of 50–60 cm there was a transition to bluish-grey clay that became increasingly consolidated with depth. There was clear evidence of springs near the head and centre of the wetland and their location was confirmed after the surface soils were washed out. The wetland surface was moderately even probably because of periodic stock grazing prior to the wetland being fenced. Water from the springs rose to the surface, spread out across the wetland, and moved down-slope either over the surface or in shallow, sub-surface seepage in the poorly consolidated topsoil.

The wetland was classified Type A, Class 2. In dry weather a small amount of surface flow was visible underneath the grass. Typically the water depth was 1–3 mm and occurred in poorly defined preferred flow paths (micro-channels) around root mounds that occupied 10–30% of the total surface area. When it rained, surface flow increased within a few minutes, spread rapidly across the entire wetland, increased to a depth of 5–10 mm, and persisted for about 12 h.

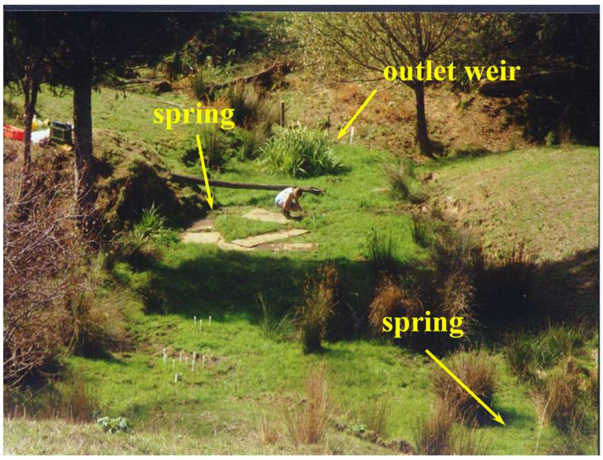

Figure 3-14: Barkers wetland looking downstream towards the receiving stream. Burns & Nguyen (2002) and Rutherford & Nguyen (2004) conducted nitrogen removal experiments in this wetland. Photo: Kit Rutherford, 2003.

3.4.3 Nitrate removal from surface flow

Rutherford & Nguyen (2004) measured NO_3 removal rates within an enclosure created by embedding sheets of plywood parallel with the flow. Weirs measured surface inflow and both surface and sub-surface (10 cm) outflow. Tracer (LiBr plus KNO_3) was injected at the wetland surface over a period of 30 minutes.

Table 3-13: Geometry of Barkers wetland and a summary of measurements following an injection of inert tracer and nitrate.

Variable	Units	Wetland mean	Enclosure SD	Comment
Area	m^2	350	1.59	Short cropped grass
Length	m	32	1.5	Grazed by sheep in summer
Width	m	11	1.06	Shallow surface flow
Slope	°	8-9		Even surface with little channelization
Soil depth	cm	20-30		Fragile, organic soils overlying a clay aquiclude
Flow	$mL\ s^{-1}$	4.0	0.7	Steady flow prior to rain
			Lithium	
Input	g	12.1	0.7	
Outflow	g	11.2	0.8	
Recovery	%	93	9	sampling stopped early because of rain
			Bromide	
Input	g	186	11	
Outflow	g	154	11	
Recovery	%	83	9	sampling stopped early because of rain
Travel time	h	7.4		centroid Br concentration
Arrival time	h	1.7		25% peak Br concentration
Departure time	h	8.3		25% peak Br concentration
			Nitrate	
Input	g	4.6	0.2	
Outflow	g	3.5	0.2	
Recovery	%	76	9	

The inert lithium bromide tracer injected at the surface over 30 minutes was detected at the outlet for >24 hours and was detected in piezometers at depths of 5 and 15 cm within the enclosure. This indicates vertical mixing between surface flow and the wetland soils to a depth of c. 10 cm (Rutherford et al. 2001). Soils were organically enriched, anaerobic and had high denitrification enzyme activity (DEA) values (viz., they had the potential to remove NO_3 by denitrification to N_2 gas)

(Burns & Nguyen 2002). It has also been shown that dissimilatory nitrate reduction to NH_4 (DRNA) occurs in similar wetland soils (Burns & Nguyen 2002) but NH_4 dynamics were not studied in Bakers wetland. NO_3 may also have been removed by plant uptake.

A total of 1.1 g of NO_3 was removed within the enclosure either. It is tempting to calculate the areal removal rate as the NO_3 mass lost (1.1 g) divided by the surface area of the enclosure (1.59 m^2) divided by the mean transit time (7.4 h) which gives 2243 mg m^{-2} d^{-1} at 13.7C equivalent to 4088 mg m^{-2} d^{-1} at 20C. However, this calculation assumes that all the added NO_3 took 7.4 h to pass through the enclosure (plug flow) whereas Br was detected at the outlet for >24 h indicating a much longer travel time for some of the added NO_3.

Figure 3-15 shows that the NO_3/Br ratio in water flowing out of the enclosure decreased with time. There was a lag of 3 hours immediately after injection. Dye indicated that early in the experiment tracer travelled across the surface of the wetland without encountering wetland soils which probably explains the initial low NO_3 removal. From 3 to 20 hours the N/Br ratio decreased linearly with time.

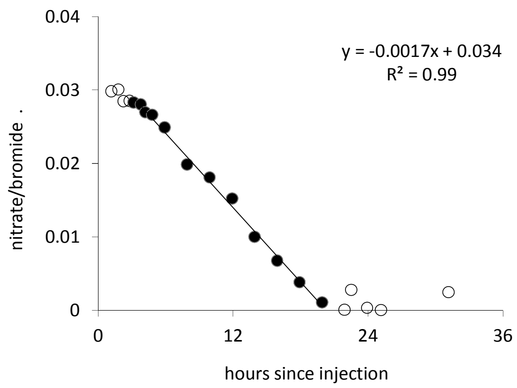

Figure 3-15: Variation of nitrate to bromide ratio over time. The regression line was fitted to the closed circles. Open circles were omitted from the analysis.

Figure 3-16 shows the NO_3 removal rate per unit area for water arriving at the outlet at different times. The removal rate was calculated

$$U(t) = H(N^* - N(t))/t \qquad 5$$

where t = time (d), $U(t)$ = removal rate experienced by water reaching the outlet at time t (mg m^{-2} d^{-1}), $N(t)$ = NO_3 concentration at the outlet at time t (mg m^{-3}), N^* = the 'expected' outlet NO_3 concentration at time t in the absence of any NO_3 removal.

$$N^* = B(t)N_o/B_o \qquad 6$$

where $B(t)$ = bromide (inert tracer) concentration at the outlet at time t (mg m^{-3}), N_o and B_o = NO_3 and Br concentrations in the injected stock solution (mg m^{-3}). H = 'effective' soil depth (m) (viz., depth of soils that interacted with the added tracer)

$$H = qT/WL \qquad 7$$

where q = flow rate (m^3 s^{-1}), T = time taken for the centroid of the tracer to reach the outlet (s), W = width of the enclosure (m) and L = length of the enclosure (m).

The 'effective' soil depth cannot be measured directly and was estimated as follows. For q = 4.2 mL s^{-1}, T = 7.4 h, W = 1.05 m and L = 1.50 m it can be calculated that H = 7.1 cm. Note that the total sediment depth was 20-30 cm. Thus the 'active' layer of the wetland (viz., the 'effective' depth) was the top c. 10 cm (viz., 25-30% of the total soil).

The removal rate decreased with time (viz., tracer arriving later at the outlet experienced a lower areal removal rate than tracer arriving earlier).

Figure 3-17 shows that removal rate varied with concentration (the average of the measured and 'expected' outlet concentrations). During the tracer experiment, NO_3 concentrations were significantly higher than typical inflow concentrations to seepage wetlands in pasture catchments. Nitrogen losses from sheep pasture are typically 15-25 kgN ha^{-1} y^{-1}. Rainfall and evapotranspiration at Barkers averaged 1600 and 800 mm y^{-1} respectively meaning runoff averaged 800 mm y^{-1}. Dividing loss rate by runoff gives nitrogen concentration in runoff of 2-3 gN m^{-3}. Figure 3-17 indicates that at NO_3 inflow concentrations of 2-3 g m^{-3} removal rates range from 235-305 (average 270) mg m^{-2} d^{-1} at 13.7C which is equivalent to 430-560 (average 495) mg m^{-2} d^{-1} at 20C.

Barkers is a Type A, Class 2 wetland for which OVERSEER specifies a removal rate of 188 mg m^{-2} d^{-1} at 20C Thus, based on results from the surface injection experiment, OVERSEER underestimates NO_3 removal in Barkers wetland on average by 160%.

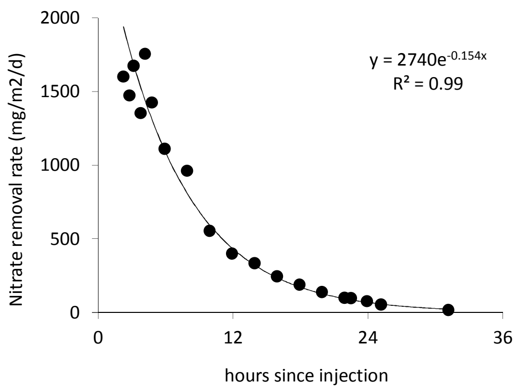

Figure 3-16: Variation of nitrate removal rate versus time.

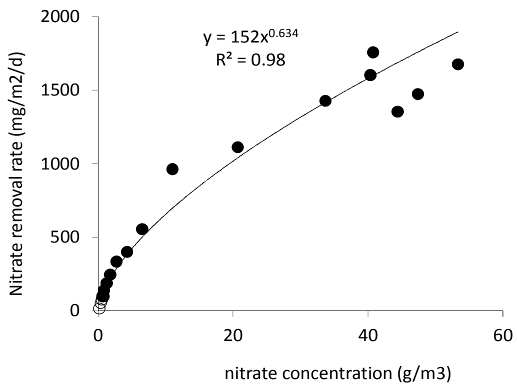

Figure 3-17: Variation of nitrate removal rate versus concentration.

3.4.4 Nitrate removal from sub-surface flow

Burns & Nguyen (2002) injected lithium Br and NO_3 into wells at a depth of 10-20 cm in two 1 m^2 enclosures in Barkers wetland, and sampled wells at similar depths 30, 60 and 100 cm downslope.

99% of samples collected after tracer injection had a lower NO_3/Br ratio than the injected tracer which indicates NO_3 removal. Nitrate fluxes were calculated in each piezometer and found to vary spatially and over time. However, by comparing the maximum fluxes in each piezometer, Burns & Nguyen estimated that >90% of the added NO_3 was removed along the 100 cm flow path, with the majority removed within the first 30 cm.

The time of travel of the Br peak concentrations ranged from 2 to 4 days across the piezometers, yielding an estimated groundwater flow velocity of 7.5-30 cm d^{-1}. Pump tests gave saturated hydraulic conductivity (K_s) at 12.5 and 30 cm depth of 300 and 80 cm d^{-1}, respectively. Soil porosity was 0.88 in the 0-30 cm depth range, and 0.77 in the 30-60 cm depth range. Multiplying K_s by the slope of the wetland (0.1) and dividing by soil porosity gave estimated pore water velocities at 12.5 and 30 cm of 34 and 9 cm d^{-1}, respectively, in good agreement with the range of groundwater flow velocities (7.5-30 cm d^{-1}) calculated from the Br tracer data.

Nett NO_3 removal rates were calculated by considering Br and NO_3 mass balances in a control volume of soil between the injection and sampling wells (Figure 5.4). The approach was similar to Eq. 5 to 7 but removal rates were expressed per unit soil mass (μg kg^{-1} d^{-1}). The highest removal rate 2300 μg kg^{-1} d^{-1} occurred in the control volume from 0-30 cm (viz., between the injection point and the first row of piezometers) and decreased to 390 and 130 μg kg^{-1} d^{-1} in the 0-60 cm and 0-100 cm control volumes (Figure 3-18). The maximum average NO_3 concentration 420 mg m^{-3} occurred in the 30 cm piezometers but decreased to 120 mg m^{-3} at 60 cm and c. 5 mg m^{-3} at 100cm (Figure 3-19). Nitrate concentration varied significantly between piezometers and removal rates in Figure 3-18 were calculated using average concentrations.

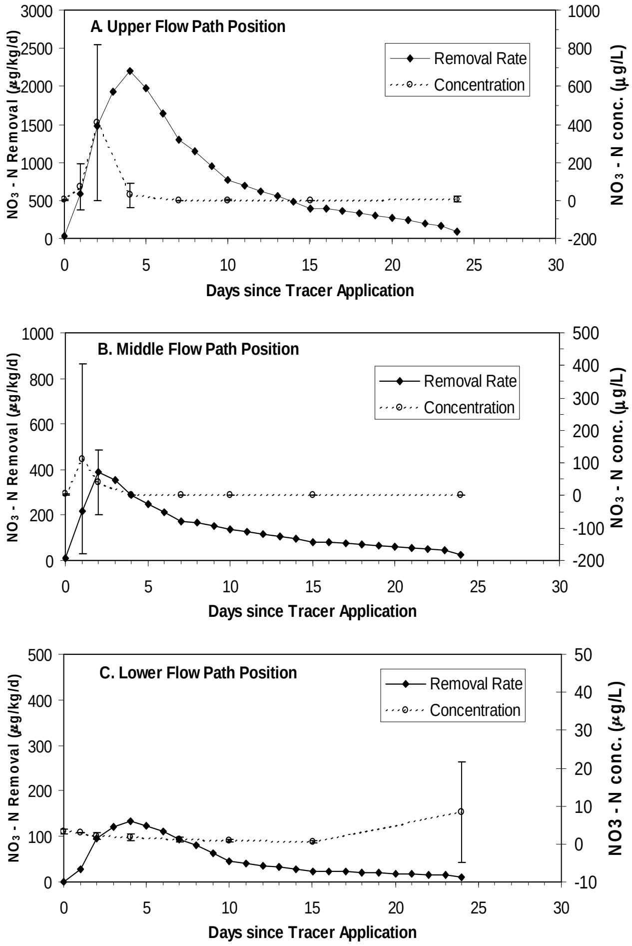

Figure 3-18: Average nitrate concentrations and removal rates in piezometers 30, 60 and 100 cm downslope from the injection point.

This study re-examined data in Figure 3-18. The maximum areal removals in the control volumes 0-30, 30-60 and 60-100 cm were calculated by multiplying the maximum removal rates from Figure 5.4 by the soil mass of the control volumes and dividing by the surface area of the control volume. This gave areal removal rates of 155, 26 and 9 mg m^{-2} d^{-1} at 11C (equivalent to 365, 61 and 21 mg m^{-2} d^{-1} at 20C) for the control volumes 0-30, 0-60 and 0-100 cm respectively.

Nitrate concentration in the tracer injected at 0 cm was 194 g m^{-3}. Injected tracer would have dispersed transversely soon after injection. Figure 3-19 indicates an initial concentration at 0 cm of 3.68 g m^{-3}. Figure 3-20 shows the variation of areal removal rate with the median of the initial (3.68 g m^{-3}) and average piezometer concentrations at 30, 60 and 100 cm.

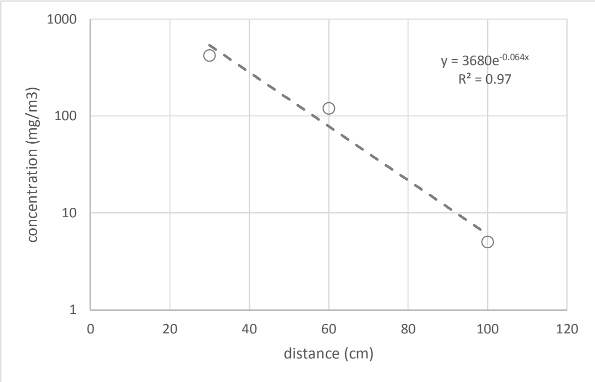

Figure 3-19: Decrease in average nitrate concentration with distance below the injection well.

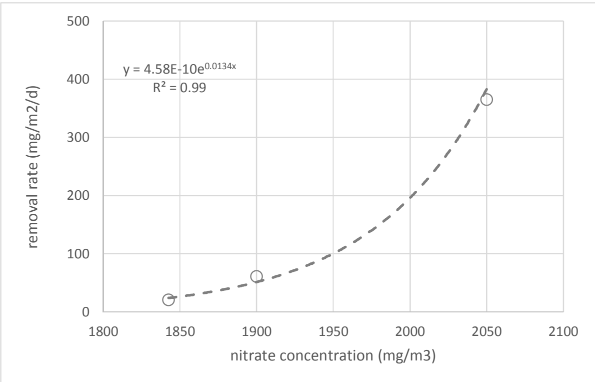

Figure 3-20: Relationship between areal removal rate and median nitrate concentration.

As discussed in the previous section, nitrogen concentrations in runoff at Barkers would be expected to lie in the range 2-3 g m^{-3}. Figure 3-20 indicates an areal removal of 200 mg m^{-2} d^{-1} (corrected to 20C) at 2 g m^{-3} which is close to the OVERSEER value for Barkers of 188 mg m^{-2} d^{-1}. The exponential relationship in Figure 3-20 predicts a very high, and unrealistic, removal rate at 3 mg m^{-3}. The maximum value in Figure 3-20 of 365 mg m^{-2} d^{-1} at a NO_3 concentration of 2.05 g m^{-3} is approximately twice the OVERSEER value for Barkers.

3.4.5 Discussion

Average areal removal rates in the Barkers wetland estimated by the surface and sub-surface injection experiments were 495 and 280 mg m^{-2} d^{-1} at 20C, compared with the OVERSEER value for a Type A, Class 2 wetland of 188 mg m^{-2} d^{-1}. Thus OVERSEER underestimates NO_3 removal rate in Barkers wetland on average by 50-160%. However, both experiments involved injecting NO_3 tracer at concentrations significantly higher than typical wetland inflow concentrations. There is clear evidence from the results of this, and other, experiments that uptake rate increases with increasing concentration. Although uptake rates from the Barkers experiments were extrapolated to ambient concentrations, the uncertainty in doing so is high. Injection experiments like those conducted at Barkers wetland need to balance the need to raise NO_3 concentration high enough above ambient to measure changes accurately against the desire not to significantly change the metabolic activity of the microbial communities that remove NO_3. An alternative methods is to add labelled NO_3 (e.g., using ^{15}N) at close to ambient concentrations, but this technique is expensive and requires specialist equipment.

3.5 WHAKA wetlands

3.5.1 Description

In 1991 the sewage system for Rotorua City was upgraded to include biological nutrient stripping at the treatment plant followed by spray irrigation in the Whakarewarewa pine forest with the aim of reducing phosphorus and nitrogen inputs to Lake Rotorua. The Rotorua Land Treatment Scheme (RLTS) was designed following field studies of nutrient uptake by pine trees, soils and natural wetlands in Whakarewarewa Forest. It was found that soils and pine trees could remove large amounts of phosphorus, but could not remove enough NO_3 to meet the load limit for the lake. Wetland soils were found to have high denitrification rates and were able to reduce NO_3 concentration substantially in sub-surface flow. Wetland denitrification was an important component of the final design of the RLTS.

A significant increase has been detected in NO_3 concentration in the Waipa Stream which drains the RLTS since 1991. Irrigation has increased not only the loading of nitrogen to the catchment but also the loading of water (equivalent to an increase in rainfall of 9 mm d^{-1}) and consequently there have been increases in flow rates from springs along the edges of the wetlands. It has been postulated that wetland NO_3 removal at Whakarewarewa is low because there is insufficient contact time between microbially active wetland soils and high NO_3 water draining from the irrigated hillslopes.

3.5.2 Methods

Rutherford et al. (2000) measured NO_3 removal in a seepage wetland draining the RLTS. Two channels (width 1.0 and 1.3 m, length 5.75 m) were built in a spring fed wetland by embedding plywood sheeting to a depth of 75 cm into the underlying clay layer. Weirs at the top and bottom of each channel were used to measure surface inflow and outflow, and were sampled for NO_3 and Br concentration. Sub-surface collectors at the outlet allowed concentrations in shallow sub-surface flow to be sampled. Piezometers at depths of 10-20, 15-25, 20-30 and 30-40 cm were sampled either daily using a syringe or hourly using automatic samplers. Conductivity was measured at 15 minute intervals in the piezometers using conductivity probes.

Four soil cores (PVC tube 7.5 cm diameter, 50 cm long) were randomly collected, taking care to minimise soil compaction. Cores were sealed in plastic bags to prevent moisture loss and transported to the laboratory. Three sub-samples (c. 10 cm long) from each core were extruded into another 7.5 cm tube and petroleum jelly was smeared around the top and bottom edges of the soil to minimise leakage. A constant head of water was maintained above the soil sample, the seepage flow monitored for 24-36 hours and the hydraulic conductivity estimated. Soils were oven dried to constant mass at 85C to estimate bulk density (dry mass/volume of sampling core) and porosity ([wet mass-dry mass]/wet mass). Soil samples were also randomly collected from eight sites and the denitrification rate (DEA) measured in the laboratory with and without added NO_3 and glucose. Pump tests were conducted on piezometers using a battery operated vacuum pump. The piezometer was pumped dry to waste and then pumped continuously to a collection bottle. Flow rate was measured 4-6 times over 1 hour and hydraulic conductivity estimated.

Figure 3-21: Enclosures in a seepage wetland at Whakarewarewa Forest. Photo: Kit Rutherford 1999 and 2000.

3.5.3 Surface injection experiment

On 24/5/1999 10.5 L of tracer containing 33 g L^{-1} Br and 4.27 g L^{-1} NO_3 was injected at the surface into Channel R for 40 minutes and samples collected for 5 days. Gauged flow averaged 22 ± 8 mL s^{-1} (mean ± SD, n = 35). The mass of Br injected divided by the time integral of the outlet Br time series gave a flow of 20 mL s^{-1} which was used in calculations. On the same day c. 15 L of tracer containing 58 g L^{-1} Br and 4.1 g L^{-1} NO_3 was injected into Channel L. The injection pump malfunctioned for 50 minutes resulting in two pulses. Gauged flow averaged 34 ± 12 mL s^{-1} (mean ± SD, N = 33). The mass of Br injected divided by the time integral of the outlet Br time series gave a flow of 27 mL s^{-1} and 30 mL s^{-1} was used in calculations.

In both channels tracer injected at the surface travelled quickly to the outlet. Bromide concentrations were high for c. 1 hour, decreased rapidly over the next 5-6 hours but took >24 hours to return to background concentrations (Figure 3-22). Ambient NO_3 concentrations were high as a result of wastewater irrigation. Upstream surface concentrations ranged from 8.4-9.1 g m^{-3} and returned to 8.4 g m^{-3} 72 hours after tracer injection.

'Expected' NO_3 concentrations at the surface outlet were estimated as the Br concentration (minus background) multiplied by the ratio of NO_3/Br in the injected stock solution. Observed NO_3 concentrations (minus background) were lower than 'expected' concentrations, indicating NO_3 removal. The difference between the integrals over time of observed and 'expected' NO_3 concentrations in the surface collector at the outlet indicated 17% (Channel R) and 23% (Channel L) removal from surface flow. Maximum removal rates averaged 30 g m^{-2} d^{-1} at a NO_3 concentration of 350 g m^{-3} (Channel R, Figure 3-22) and 25 g m^{-2} d^{-1} at 130 g m^{-3} (Channel L, Figure 3-24).

Ambient NO_3 concentrations in the sub-surface collector (4.6-5 g m^{-3}) and piezometers (0.1-6.6 g m^{-3}) were lower than in surface flow. This is consistent with water having mixed vertically and come into contact with organically rich soils where denitrification occurred.

The average denitrification enzyme activity (DEA) was high (4.6 $\pm$ 0.8 µg g^{-1} h^{-1}) but comparable with previous measurements made at Whakarewarewa (2.8-4.7 µg g^{-1} h^{-1}). Bulk density was 0.30 $\pm$ 0.09 g cm^{-3} and assuming an active soil depth of 10 cm, the measured DEA implies a NO_3 removal rate of 3.3 $\pm$ 0.6 g m^{-2} d^{-1}. This is an order of magnitude lower than the nett uptake rate of 25-30 g m^{-2} d^{-1} estimated from tracer experiment.

In the Channel R the difference between the integrals over time of observed and 'expected' NO_3 concentrations in the sub-surface collector at the outlet indicated 73% removal from sub-surface flow. Hydraulic conductivity measured in the laboratory decreased with depth from 12-2.8 cm d^{-1} (Figure 3-25). The average slope of the ground was s = 0.115 giving Darcy velocities of 42-0.80 cm d^{-1} and seepage flow rates of 0.5-0.01 mL s^{-1} at depths of 5-25 cm. Total seepage flow (0.57 mL s^{-1}) was 3% of surface flow (20 mL s^{-1}).

The weighted average of surface (17%) and sub-surface (73%) removal indicates 19% removal of NO_3 from the added tracer.

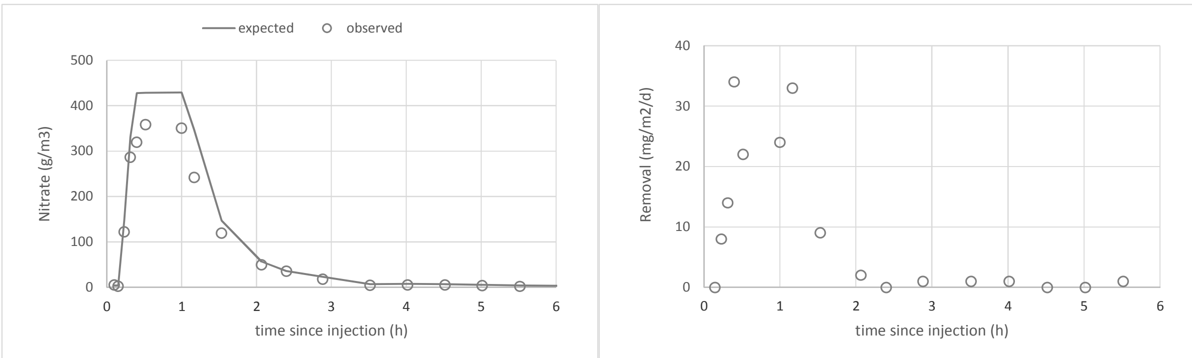

Figure 3-22: Channel R. Left: observed (o) and 'expected' (-) nitrate concentrations in surface flow at the channel outlet following a surface injection. Right: nitrate removal rates estimated for the difference between observed and 'expected' concentrations and measured flow.

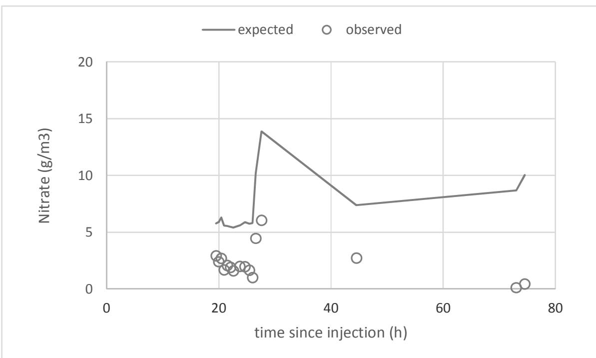

Figure 3-23: Channel R. Observed (o) and 'expected' (-) nitrate concentrations in sub-surface flow at the channel outlet following a surface injection.

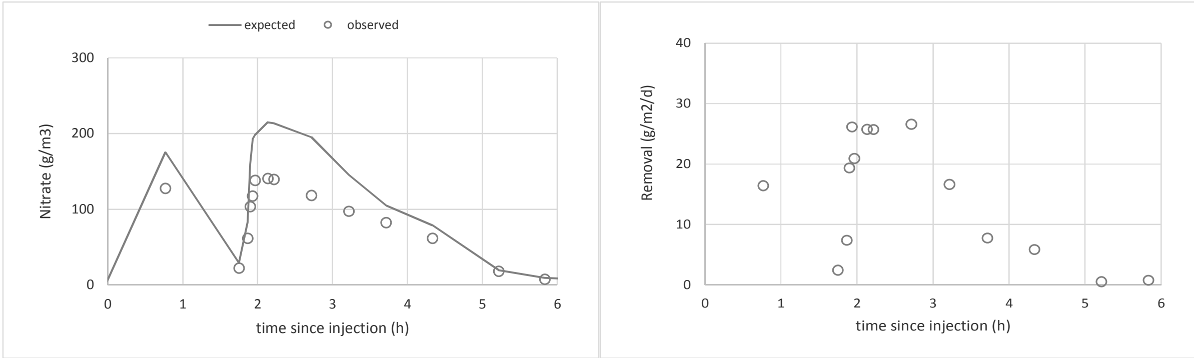

Figure 3-24: Channel L. Left: observed (o) and 'expected' (-) nitrate concentrations in surface flow at the channel outlet following a surface injection. Right: nitrate removal rates estimated for the difference between observed and 'expected' concentrations and measured flow.

3.5.4 Sub-surface injection experiment

On 3/5/2000 7.5 L of tracer containing 97 g L^{-1} Br and 85.6 g L^{-1} NO_3 was injected 20-30 cm below the surface into a 15 cm diameter PVC slotted pipe 75 cm in length in Channel R. Four rows of three piezometers were installed at c. 1 m intervals downslope (A-D) at depths of 20, 25-30 and 40 cm. Piezometers were sampled either daily using a syringe (individual wells) or hourly using automatic samplers (composite sample from 3 replicate wells). During the experiment flow averaged 9.7 ± 0.7 mL s^{-1} (mean ± 95% CI, n = 66).

Hydraulic conductivity decreased with depth, as had been observed at Barkers wetland (Figure 3-25). This implies higher horizontal seepage flows in the near-surface soils and the likelihood of higher rates of vertical mixing. Bromide was detected at high concentrations in the shallow (20 cm) piezometers closest to the injection point (row A) soon after injection (Figure 3-26). Bromide in shallow wells (20-25 cm) further downslope (rows B, C and D) did not increase as quickly and concentrations were lower. Bromide found its way into the intermediate depth wells (25-30 cm) in rows A, C and D but not at row B even though it was closer to the injection point than rows C and D. Bromide was detected in the deep wells (40 cm) at row A (closest to the injection point) but very little was detected at rows B, C and D.

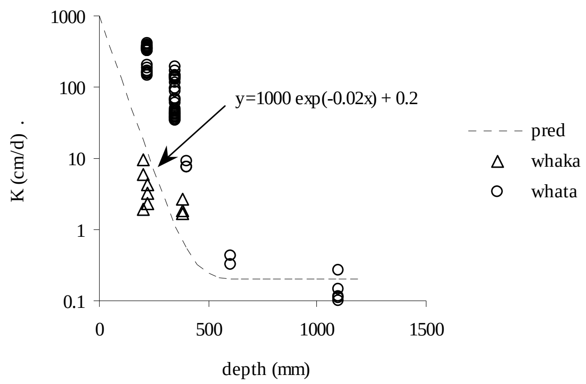

Figure 3-25: Hydraulic conductivity of soils in the Whakarewarewa (whaka) and Barkers (whata) wetlands.

Seepage velocities (calculated as slope multiplied by hydraulic conductivity) in the 0-10 and 10-20 cm layers were 42 and 5.7 cm d^{-1} respectively. If the tracer had moved down the wetland solely as a result of seepage in the 0-10 cm layer it would have taken 4 and 6 days to reach rows B and C respectively, and if it had moved in the 10-20 cm layer it would have taken 28 and 44 days. These calculations discount any time taken for tracer to diffuse upwards from where it was injected (20-30 cm).

In contrast to these calculations, the conductivity peaks took only c. 2-3 days to reach rows B and C and the peak concentrations occurred simultaneously at the two rows, instead of several days apart as expected (Figure 3-26).

'Expected' NO_3 concentrations in each piezometer were calculated as measured Br concentration (minus background) multiplied by the NO_3/Br ratio of the injected tracer. The time integrals of observed (minus background) and expected NO_3 concentration were calculated for each piezometer and compared to determine the percentage removal.

Removal was lowest (28-32%) in the shallow (20 cm) piezometers and highest (81-100%) in the deep (40 cm) piezometers. However, seepage flows almost certainly decreased with depth and the arithmetic average removal would over-estimate the effectiveness of the wetland. The weighted average removal was calculated based using seepage velocity as the weighting factor. Seepage velocities at the mid sampling depth of the piezometers (15, 20, 25 and 35 cm) were calculated as slope (0.115) multiplied by hydraulic conductivity (from Figure 3-25). The weighted average removal was 36%. Sampling stopped before Br and NO_3 concentrations returned to background and the wetland is likely to have removed more than 36% of the added tracer.

Assuming the wetland removed 36% (229 g) of the added tracer (642 g) over 9 days then the average areal removal rate was 3.9 g m^{-2} d^{-1}. Nitrate concentrations during the experiment ranged from 0-196 g m^{-3} (median 14 g m^{-3}) which is higher than typical NO_3 inflow concentrations to seepage wetlands in pasture catchments (2-3 g m^{-3}).

Table 3-14: Nitrate removal in piezometers following a sub-surface tracer injection. 'Observed' is the time integral of observed NO_3 concentrations in each piezometer. 'Expected' is the time integral of the 'expected' NO_3 concentration (measured Br concentration multiplied by the NO_3/Br ratio of the injected tracer). 'Conductivity' is the hydraulic conductivity of the wetland soils and 'Velocity' is the seepage velocity (slope multiplied by 'Conductivity').

Row	Distance m	Depth cm	Observed g m^{-3} d	Expected g m^{-3} d	Removal	Conductivity cm d^{-1}	Velocity cm d^{-1}
A	1	10-20	1224	1803	32%	50.0	5.75
A	1	20-30	274	430	36%	6.9	0.80
A	1	30-40	156	821	81%	1.1	0.13
B	2	10-20	174	253	31%	50.0	5.75
B	2	20-30	11	47	77%	6.9	0.80
B	2	30-40	1	5	86%	1.1	0.13
C	3	10-20	188	262	28%	50.0	5.75
C	3	20-30	147	254	42%	6.9	0.80
C	3	30-40	0	22	100%	1.1	0.13
D	4	15-25	136	254	47%	18.5	2.13
D	4	30-40	27	153	83%	1.1	0.13

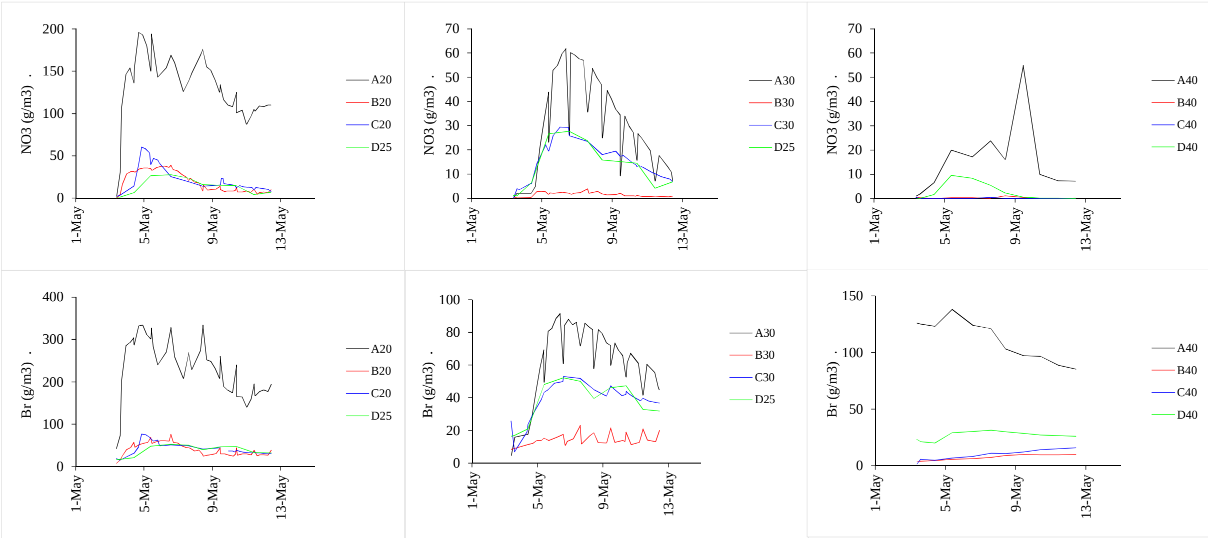

Figure 3-26: Nitrate and bromide concentrations measured in piezometers following a sub-surface injection of tracer.

3.5.5 Discussion

Following sub-surface injection >36% of the applied NO_3 was removed. By comparison, following surface injection, only 19% of the applied NO_3 was removed. This is consistent with longer residence times of tracer in the sub-surface injection enabling longer contact between high NO_3 water and microbially active wetland soils. Nitrate concentrations were consistently lower in the deep (40 cm) piezometers. This is the likely result of lower rates of vertical mixing between high concentration near-surface water together with long residence times. It is consistent with the ‘active’ layer of wetland soils being the top 10-20 cm.

Seepage flow through the wetland soils accounted for <5% of total flow and the majority of flow occurred across the surface. This suggests that there is little opportunity for contact between NO_3 in surface water and wetland soils where removal rates are high. However, there was evidence of significant vertical exchange between the surface water and the upper soil layers. Soils were porous and had low bulk density which facilitated water movement driven by the uneven surface topography, spatial variations in permeability and plants. Were it not for this vertical exchange, the wetland would remove very little of the inflowing NO_3. The sub-surface injection experiment provided further evidence of vertical mixing within wetland soils. Although tracer was injected at depth, it found its way into downslope piezometers faster than can be explained by Darcy seepage flow. The likely explanation is that tracer mixed vertically upwards from the injection well, travelled in surface flow, and mixed vertically downwards into downslope piezometers. Although care was taken not to disturb the wetland when installing piezometers, and to seal them against vertical flow (using bentonite) it is possible that vertical mixing was higher in this experiment than occurs naturally. On the other hand, the irregular surface topography and spatial variations in soil porosity and conductivity are likely to have induced vertical mixing (termed ‘pumping’).

The removal rates estimated in the surface (25-30 g m^{-2} d^{-1}) and sub-surface (3.9 g m^{-2} d^{-1}) injection experiments were significantly higher than the maximum rate in OVERSEER (0.25 g m^{-2} d^{-1}). However, the NO_3 concentrations in the surface (120-360 g m^{-3}) and sub-surface (median 14 g m^{-3}) were also significantly higher than is normally encountered in wetlands draining pasture (2-3 g m^{-3}). It appears that the Whakarewarewa forest wetlands have a greater ability to remove NO_3 than the pasture wetlands reviewed in this study. This is probably because they have been exposed to high nitrogen loadings since the RLTS was commissioned and microbial communities have built up in the soils.

The areal removal rate estimated from the DEA measurements (3.3 ± 0.6 g m^{-2} d^{-1} assuming an 'active' layer depth of 10 cm) was an order of magnitude higher than the maximum rate in OVERSEER. DEA is measured in the laboratory at higher than ambient temperature and with soils exposed to excess NO_3. Microbial NO_3 uptake, together with limited vertical mixing, restricts the availability of NO_3 to wetland soils. Hydraulic conductivity decreased significantly with depth and the rate of vertical mixing almost certainly reduced with depth. This helps explain why ambient NO_3 concentrations were lower in the deep piezometers than in shallow piezometers and surface flows, and why Br took a long time to appear in deep piezometers and remained at low concentrations. One would not expect NO_3 removal to have occurred at the measured DEA rate over the entire depth of wetland soil.

We conclude that the removal rates measured in the Whakarewarewa experiments are higher than would be expected in pasture wetlands.

3.6 ARMS wetland

3.6.1 Introduction

Hughes et al. (2013), Hughes et al. (2016) and Uuemaa et al. (in prep) are studying a seepage wetland draining pasture on the Armstrong property in the Toenepi catchment, near Hamilton (Figure 3-27). The Toenepi catchment is intensively farmed with approximately 75% of the area occupied by dairy farms with a stocking rate of ~3 cows ha^{-1}. Mean annual rainfall is 1377 mm and the catchment is comprised almost exclusively of Morrinsville clays (NZ Soil Classification: Typic Orthic Granular Soil). The upper Toenepi catchment is hilly with ~80% of the area classified as either rolling or steep (>10% gradient).

The wetland soil is deep (>1 m) and perennially saturated. The wetland vegetation is dominated by glaucous sweet grass (*Glyceria declinata*), jointed rush (*Juncus effusus*), sedge (*Carex sp.*) and lotus (*Lotus pedunculatis*). Flows are measured at two 45° v-notch weirs. One weir is located near the head of the wetland in an area thought to be a significant ground water seepage area. The catchment area above the upper weir is c. 2.9 ha. The second weir is located within a naturally constricted part of the lower wetland. The wetland above the lower weir has an area of c. 1500 m^2 with a catchment area of c. 5.2 ha.

3.6.2 Preliminary results

Baseflow samples have been collected every 4-6 weeks from the upper and lower weirs. Auto samplers have collected samples during high flow events at both weirs. A small number of groundwater samples have been collected from piezometers situated within or adjacent to the wetland.

Continuous flow records are available for the period 1 November 2011 to 8 July 2012. The total flow recorded over this period at the upper and lower weirs was 0.51 and 6.00 ML respectively. This indicates that <10% of the flow at the lower weir enters via the upper weir. This is surprising because c. 50% of the catchment area lies upstream of the upper weir and the upper weir is located in a gulley which is an obvious conduit for overland flow during rainfall events. Most of the flow at the lower weir must enter the wetland from sub-surface and groundwater flow.

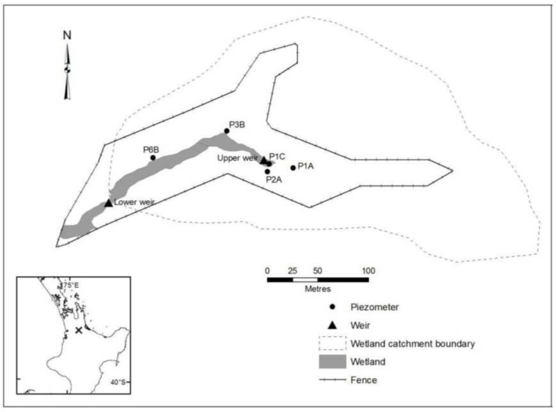

Figure 3-27: Sketch map of the Armstrong wetland, Toenepi.

Preliminary analysis shows that median NO_3 concentrations decrease significantly between the upper and lower weirs: by an order of magnitude in baseflow and during summer/autumn, and by a factor of 3 during winter/spring (Table 3-15). TN concentrations also decrease by a factor of 2-3. High concentrations at the upper weir indicate that the upper catchment is a significant source of poor quality water. However, it is difficult to determine the reason for the decrease in concentration between the two weirs because the upper wetland area contributes <10% of total wetland flow. The decrease may indicate significant attenuation within the wetland (50-66% for TN and 66-90% for NO_3) but only if inflows between the weirs have similar concentrations to inflows above the upper weir. However, concentrations in groundwater and shallow sub-surface flow (which contributes c. 90% of flow at the lower weir) are not well quantified – to date only 20 groundwater samples have been collected. Further information on the composition and flow of water entering the wetland between the two weirs is required before wetland attenuation can be quantified accurately.

The upper wetland appears to be very efficient at removing NO_3 entering via sub-surface flow. During baseflow the median NO_3 concentrations were 3155 and 186 mg m^{-3} in groundwater and at the weir respectively. This indicates c. 95% removal of NO_3 possibly through denitrification.

Table 3-15: Summary of nitrogen concentrations measured in the Armstrong wetland.

Site	Number	NO_3 mg m^{-3}	TN mg m^{-3}
Gully groundwater	8	3155 (1960-3930)	3610 (2660-4270)
Other groundwater	12	36 (1-885)	1305 (427-3850)
Overland flow	6	2460 (367-4860)	7180 (4830-7910)
Upper weir			
Baseflow	11	186 (4-923)	884 (640-2510)
Summer/Autumn	9	934 (346-1330)	3540 (2630-6083)
Winter/Spring	38	715 (447-1680)	3245 (2490-4360)
Lower weir			
Baseflow	12	13 (1-52)	463 (129-1600)
Summer/Autumn	36	28 (1-376)	859 (550-4830)
Winter/Spring	47	237 (1-1450)	1490 (283-2130)

Uuemaa et al. (in prep) calibrated a cells-in-series model for the wetland using the available flow and concentration data. They estimated that the wetland removed 75.5% of incoming NO_3. Since the TN loading was 60 mg m^{-2} d^{-1} this implies an areal removal rate of 45 mg m^{-2} d^{-1} at the prevailing temperature. The prevailing temperature and condition of the wetland are not stated so no comparison can be made with the maximum OVERSEER areal uptake rate of 250 mg m^{-2} d^{-1} at 20C. In contrast with NO_3, total organic nitrogen (TON = DON + PN) passed through the wetland with very little removal. The main load of TON entered the wetland in surface flow during storms and it appears that little DON was generated within the wetland through the conversion of NO_3 and NH_4 via plant uptake and decay. The NH_4 load entering the wetland was low (c. 9% of TN load) and removal was high (73%).

3.6.3 Discussion

This study illustrates two serious challenges to quantifying nitrogen attenuation in seepage wetlands, namely to identify the area of land that drains to the wetland and where on the hillslope that land is situated. Based on the fact that c. 50% of the topographic catchment lies above the upper weir at Armstrong's wetland, one might expect c. 50% of runoff to pass through it, whereas <10% does. Clearly ongoing research needs to measure the composition and flow of shallow sub-surface and deep groundwater flows that make up >90% of catchment runoff. The OVERSEER user also needs to estimate the area of land and its location (viz., nitrogen losses) if they are to use the seepage wetland module, and this study illustrates how difficult that can be. The Armstrong's study indicates that the upper wetland removes c. 95% of NO_3 from upwelling sub-surface flow under baseflow conditions – a figure that is consistent with other New Zealand wetland studies reported here. Overall the wetland removes >70% of the incoming NO_3 and NH_4. However, it removes very little of the DON and PN entering the wetland in surface flow during rainfall. There is no evidence that significant amounts of NO_3 and NH_4 are converted to DON and PN and exported from the wetland. Thus, the Armstrong wetland, which receives a relatively low nitrogen loading, appears to be a significant nett sink for nitrogen.

3.7 SCOT riparian zone

3.7.1 Summary

Cooper (1990) measured rates of NO_3 depletion in the riparian zone of a small stream draining pasture in Scotsman's Valley, near Hamilton. Mass balance calculations indicated that 56-100% of NO_3 removal occurred in organic riparian soils even though these occupied only 12% of the stream bank. The active soils were located at the base of hollows and 37-81% of groundwater flow passed through them to the stream (viz., by-pass flow averaged ⍰ = 40%). The soils were anoxic, and high in both denitrifying enzyme activity and available carbon.

In soils near the upslope edge of the seepage wetland denitrification rate was 338 mg m^{-2} h^{-1} (8100 mg m^{-2} d^{-1}) and NO_3 concentration 640 mg m^{-3}. Close to the stream denitrification rate averaged 0.3-2.1 mg m^{-2} h^{-1} (7-50 mg m^{-2} d^{-1}) and NO_3 concentration 13 mg m^{-3}. At an intermediate site denitrification rate averaged 250 mg m^{-2} h^{-1} (6100 mg m^{-2} d^{-1}) and NO_3 concentration 218 mg m^{-3}. Cooper concluded that in many parts of the wetland denitrification rates were limited by the supply of NO_3.

3.7.2 Discussion

Denitrification rates of 7-50 mg m^{-2} d^{-1} in the lower part of the wetland (15-100 mg N m^{-2} d^{-1} when adjusted to 20C) are lower than the maximum rate in OVERSEER (250 mg N m^{-2} d^{-1} at 20C) but match OVERSEER if the wetlands were Class 3 or 4. The rates of 6100-8100 mg m^{-2} d^{-1} are significantly higher than the rate in OVERSEER.

The fact that NO_3 removal rate varies with NO_3 concentration is consistent with results from other studies reported here. The implication is that NO_3 removal rate varies spatially within wetlands – being highest where groundwater or sub-surface flow, with high NO_3 concentrations, first enters the wetland, and lowest after water has been in contact with the wetland soils for some time.

3.8 CAM wetland

3.8.1 Summary of findings

Nguyen et al. (2002) studied a wetland (6817 m^2) that drained paddocks on a dairy farm at the Cameron property in the Toenepi catchment near Hamilton. The wetland was fenced to exclude grazing animals two years prior to the study and two of the three paddocks draining to the wetland were irrigated with farm dairy effluent (October-March). Wetland vegetation consists mainly of soft brome (*Bromus hordaceous*) with some floating sweet grasses (*Glyceria declinata*) and rush (*Juncus effuses* and *Juncus gregiflorus*) around the wetland channels.

Wetland inflows and outflows were measured automatically at 15 min. intervals using V-notch weir boxes and depth recorders linked to data loggers. Water samples were taken automatically during storms, or otherwise at 2-day intervals, using portable vacuum samplers. Samples were analysed for NH_4, NO_3 and total Kjeldahl nitrogen (TKN).

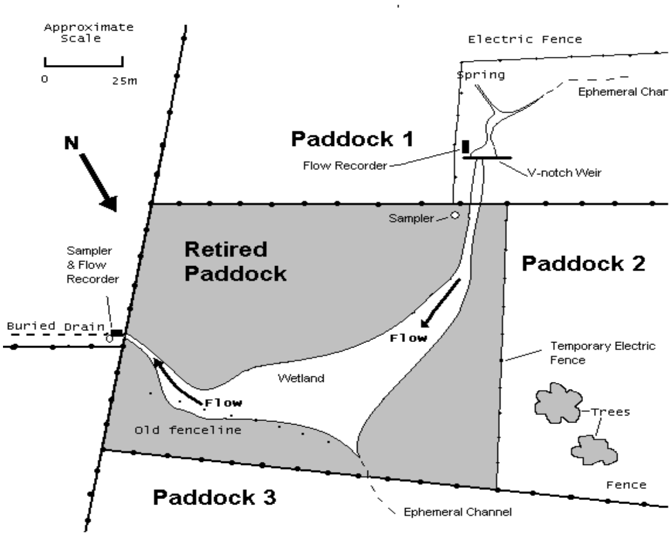

Figure 3-28: Cameron wetland study site.

During July-September outflows of 5-10 L s^{-1} exceeded inflows by 1-2 L s^{-1} suggesting that there were unmonitored sub-surface seepage inflows and/or surface runoff from the catchment. Inflow concentrations varied throughout the study and were highest in January-March when paddocks were sprayed with dairy shed effluent (Figure 3-29). A high proportion of nitrogen inflow was TKN predominantly in the form of DON and PN. This contrasts with most pasture seepage wetlands where inflows are dominated by NO_3.

Mean monthly NO_3 concentrations in the outflow were consistently lower than those in the inflows (Figure 3-29). Mass balance calculations of monthly load indicated that the wetland reduced NO_3 by 70-95% except during occasional high flow events (Figure 3-30). In contrast to NO_3, both NH_4 and TKN concentrations in the wetland outflow were frequently higher than in the inflows and mass balance calculations indicate that the wetland was, at times, a source of NH_4, DON and PN.

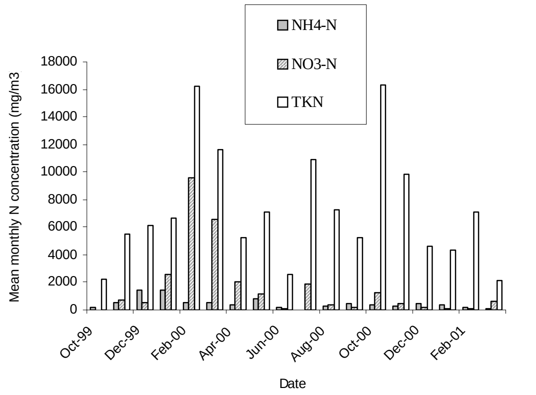

Figure 3-29: Summary of outflow concentrations.

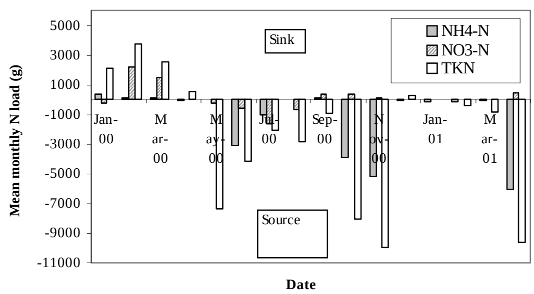

Figure 3-30: Monthly gains (source) and losses (sink) in the Cameron wetland.

3.8.2 Summary

In common with other studies, a proportion of the inflow was unmonitored which prevents an accurate assessment of nitrogen removal. Nevertheless NO_3 removal was estimated to be 70-95% under baseflow conditions – a finding consistent with results from other studies reviewed in this report.

This study considered not only NO_3 but also other nitrogen species. Whereas at an annual scale the wetland was a sink for NO_3, it was a source of NH_4 and TKN. The paddocks draining into the wetland were used for dairy shed effluent disposal meaning that the loadings of NH_4, DON and PN were high. Notwithstanding, it appears that NH_4, DON and PN were generated within the wetland. NH_4 may have originated from the decay of wetland plants and/or the dissimilatory reduction of nitrate to NH_4 (DRNA). NH_4 is readily absorbed by aquatic plants in receiving waters (viz., is readily bioavailable) while even low concentrations are toxic to fish at high pH. DON and PN are likely to have originated from the decay of wetland plants. The bioavailability of DON and PN is poorly understood under New Zealand conditions.

3.9 KIWI wetland

3.9.1 Summary of results

Zaman et al. (2008) conducted an injection-resampling experiment in a wetland which drains paddocks on a dairy farm near Hamilton. Four lysimeters (0.5 m diameter) were installed to confine control volumes of soil during the experiments and prevent advection and dispersion. In the pore water there were low concentrations of dissolved oxygen (DO) and NO_3, but high concentrations of NH_4. Low DO favours denitrification (viz., conversion of NO_3 to N_2O and N_2). Surface inflows and outflows from the wetland also had high concentrations of NH_4 and DON.

Tracer was injected 20-35 cm below the surface and re-sampled 1, 2, 3, 4, 24 and 48 h after injection. The tracer contained inert LiBr and ^{15}N-labelled KNO_3. The NO_3/Br ratio decreased exponentially with time. For NO_3 concentrations >2 g m^{-3} (the concentration at which the rate of denitrification becomes nitrate-limited) the rates of removal of NO_3 ranged from 3.96-15.7 g m^{-3} d^{-1}. Denitrification accounted for only 6-7% of the observed NO_3 removal – the balance being attributed to other transformation processes including plant and microbial uptake, anionic sorption and DNRA. It was estimated that plants growing in the wetland could remove 350-540 mg m^{-2} d^{-1} compared with the measured depletion of 680 mg m^{-2} over 4 hours. Thus plant uptake could have explained a significant proportion of the measured NO_3 removal.

Taking soil porosity to be 0.65 and the active soil depth to be 40 cm, the areal NO_3 removal rate was calculated to be 4094 mg m^{-2} d^{-1} and the denitrification rate 289 mg m^{-2} d^{-1}.

3.9.2 Discussion

OVERSEER assumes a maximum nitrogen removal rate of 250 mg m^{-2} d^{-1} at 20C which is an order of magnitude lower than the 4094 mg m^{-2} d^{-1} NO_3 removal rate measured in the Kiwitahi study. The removal rate was measured when NO_3 concentrations >2 g m^{-3} which are typical of inflowing concentrations to seepage wetlands in pasture catchments. Notwithstanding, NO_3 concentrations decrease with distance along flow pathways in seepage wetlands and, as a result, removal rates decrease (e.g., Cooper 1990). Thus the removal rate of 4094 mg m^{-2} d^{-1} is a likely maximum removal rate that might be expected to occur where high nitrate water first enters the wetland. In contrast, the OVERSEER value of 250 mg m^{-2} d^{-1} is an average value for the wetland which would be expected to be lower than the maximum. It is not clear from the Kiwitahi study how the *in situ* removal rate varies with NO_3 concentration or spatially within the wetland.

6-7% of the observed removal in the Kiwitahi study was attributable to denitrification (viz., permanent removal). The areal rate of denitrification was 289 mg m^{-2} d^{-1} which is comparable with the rate in OVERSEER. For reasons discussed in the preceding paragraph, 289 mg m^{-2} d^{-1} is a likely maximum denitrification rate that might be expected to occur where high nitrate water first enters the wetland. It is, however, significantly lower than the 8100 mg m^{-2} d^{-1} reported by Cooper (1990) where high nitrate water first entered the wetland at Scotsman's Valley (see Section 3.7).

The Kiwitahi study estimated the rate of uptake of nitrogen by wetland plants, and showed that it was a significant proportion of the observed NO_3 depletion. Uptake by plants may temporarily remove nitrogen from inflowing water and storage it in plant biomass. However, when those wetland plants die they decompose and release nitrogen in the form of NH_4, DON and/or PN. The Kiwitahi study showed that denitrification (viz., the permanent loss of NO3 through conversion to gaseous forms N2O and/or N2) only explained a 6-7% of NO_3 removal. This reinforces the conclusion that NO_3 removal may be largely through plant uptake and hence may only represent temporary removal, followed by transformation to other forms.

3.10 PUKE wetland

Nguyen et al. (1999) summarised results from a 6 month study (August 1997 to March 1998) of nitrogen, phosphorus and suspended sediment retention by a small (62 m^2), narrow wetland in the Pukemanga sub-catchment situated in sheep-grazed hill country at Whatawhata, near Hamilton. Samples were collected weekly at the wetland outlet (outflow) and occasionally in the seepage zone at the bottom of the hillslope (inflow).

During dry periods, water in the wetland was predominantly (72-100%) 'old' groundwater. Following a summer drought (March 1998), a rainfall event displaced 'old' groundwater which comprised 90% of outflow. However, a rainfall event in autumn (April 1997) resulted in surface inflow and a lower proportion (46-66%) of 'old' groundwater. Nitrogen inflows in 'old' groundwater were predominately NO_3-N but surface flow contained a higher proportion of PN.

Inflow and outflow loads were calculated on 10 sampling occasions as the product of instantaneous measurements of flow and concentration. The wetland was consistently a sink for NO_3-N – the only exception was 1 sampling occasion when flow was high. Overall 51% of NO_3-N was removed which was attributed to high denitrification enzyme activity (DEA) in the wetland soils (Nguyen and Downes 1997a, b). The wetland was a nett sink of TN on 7 sampling occasions and a source on 1 occasion when flow was high, while on 2 occasions outflow matched inflow. Over the 6 month sampling period, approximately 54% and 56% of the TN and PN inflows were retained within the wetland. During low flows, the wetland was a sink for suspended solids (SS) but during high flows material was scoured from the wetland and it was a nett source of SS. The authors suggested that fine particles of organic N originating from the death and decay of wetland plants contributed to the high TN and PN exports during high flows. The wetland was a nett source of NH_4-N on 6 occasions, while on 4 occasions the NH_4-N outflow matched the inflow. High NH_4-N exports were attributed to low rates of nitrification (oxidation of NH_4-N to NO_3-N) and/or DRNA (reduction of NO_3-N to NH_4-N).

3.11 Spatial variation in wetlands

The question arises whether the use in OVERSEER of a constant, average removal rate leads to significant errors when assessing their potential to remove NO_3. A simplified wetland model was developed which assumes either a constant removal rate (250 mg m^{-2} d^{-1}) or a rate that varies with concentration. A seepage zone extending 1 m along the stream bank and 10 m up the hillslope (area 10 m^2) was modelled. The length of hillslope contributing runoff (and nitrogen) to the wetland varied from 100 to 1000 m (viz., wetland/catchment area varied from 1% to 10%). Nitrogen loss from the hillslope was 50 kg ha^{-1} y^{-1} and runoff was 800 mm y^{-1}. These values are typical of seepage wetlands in the Toenepi, Scotsman's Valley and Whatawhata studies.

Figure 3-31 shows the relationships between NO_3 removal rate and concentration inferred from the Barkers (Rutherford & Nguyen 2004) and Scotsman's Valley (Cooper 1990) studies. Removal rates were an order of magnitude higher in the Scotsman's Valley study. Figure 3-32 shows predicted cumulative NO_3 removal moving down a 10 m wide wetland using the Barkers removal/concentration relationship. When the wetland/catchment area is 10% all the incoming NO_3 is removed within c. 5 m and there is little difference between the two models. When the wetland/catchment area is 1%, less than the half the incoming NO_3 is removed and the constant uptake model predicts slightly lower removal than the variable uptake model. This simulation suggests that assuming a constant removal rate is unlikely to lead to significant errors when using OVERSEER to assess the potential of wetlands to remove NO_3. However, using the Scotsman's Valley removal/concentration relationship (Figure 3-33) a different picture emerges. The variable model predicts rapid removal (100% removal within 1 m). Both models predict 100% removal when wetland/catchment area is 10%. However, for a small wetland (wetland/catchment area ratio 2%) the variable uptake model predicts 100% removal but the constant uptake model predicts only 40% removal.

This simulation indicates that if maximum NO_3 removal rates are as high as those inferred from the Scotsman's Valley study then assuming a constant removal rate may lead to OVERSEER under-estimating NO_3 removal by small wetlands.

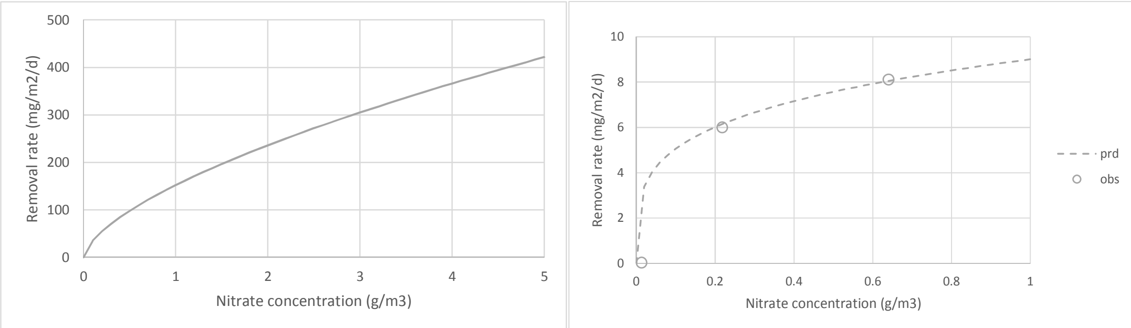

Figure 3-31: Relationship between nitrate removal rate and concentration inferred from wetlands studies at Barkers (left) and Scotsman's Valley (right) wetlands.

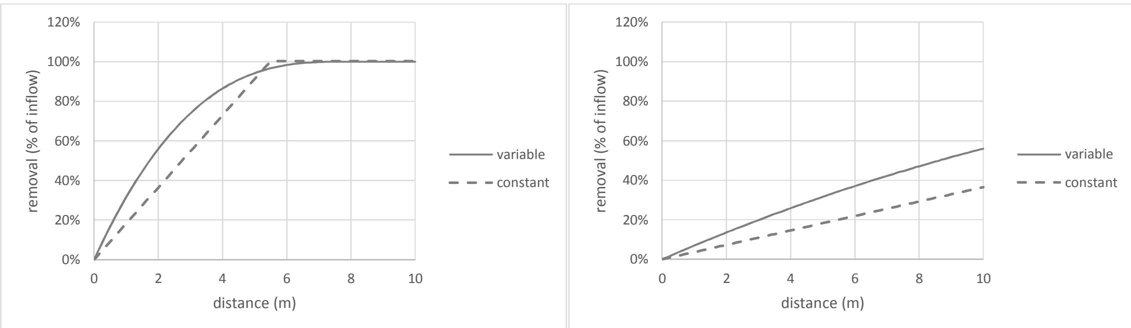

Figure 3-32: Variation with distance of cumulative nitrate removal predicted assuming a constant uptake rate (dashed) and assuming uptake rates that vary with concentration (solid). Results assume wetland/catchment areas of 10% (left) and 2% (right). The relationship between uptake rate and concentration is that inferred from studies in Barkers wetland.

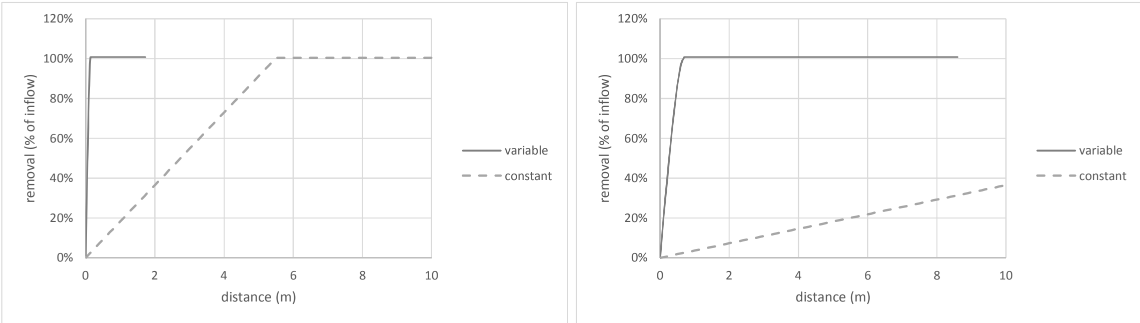

Figure 3-33: Variation with distance of cumulative nitrate removal predicted assuming a constant uptake rate (dashed) and assuming uptake rates that vary with concentration (solid). Results assume wetland/catchment areas of 10% (left) and 2% (right). The relationship between uptake rate and concentration is that inferred from studies in Scotsman's Valley.

4 Discussion and conclusions

Table 4-1 summarises results from the studies reviewed. All of the studies found that seepage wetlands significantly (75-98%) reduced the concentrations NO_3. This was true regardless of whether the studies measured changes in 'natural' inflows or introduced a mixture of NO_3 and inert tracer, and whether they compared concentrations or loads.

The disappearance of NO_3 could have been the result of denitrification to gaseous N_2 or N_2O and escape to the atmosphere (permanent loss), dissimilatory reduction to NH_4 (transformation), or uptake by plants (temporary storage). However, while NO_3 concentrations decreased by 75-98%, it is not clear whether this accurately quantifies the permanent removal of 'bioavailable' nitrogen. Zaman et al. (2008) found that denitrification only accounted for 6-7% of observed NO_3 removal and suggested that plant uptake was the principal removal mechanism. Five studies examined changes in concentration of different forms of nitrogen. Matheson et al. (2002) found that, at times, NH_4 and DON concentrations increased between pasture and stream edge across the riparian zone. Although NO_3 concentrations decreased, in some situations TN concentrations remained unchanged. They postulated that the decay of pasture and/or wetland vegetation was a source of NH_4, DON and PN. The riparian zones studied were 30-40 years old with mature vegetation and some 'recycling' of stored nitrogen is plausible. Nguyen et al. (2002) also found that the Cameron wetland was a source of NH_4, DON and PN at certain times. In contrast, Collins et al. (2005) found that the RC wetland was consistently a nett sink for nitrogen despite intermittent disturbance by cattle. Uuemaa et al. (in prep) found that the Armstrong wetland did not retain any of the DON and PN entering in surface flow during rain events but neither did it generate and export DON and PN through transformations of NO_3 and NH_4. Overall it was a nett sink for TN. Thus some wetlands can act as 'transformers' that, at times, release nitrogen as NH_4, DON and/or PN. Ammonium is readily utilised by aquatic plants, but the bioavailability of dissolved and particulate organic nitrogen is not well quantified for seepage wetland outflows in New Zealand. It is conceivable that a proportion of the organic nitrogen exported from seepage wetlands is bioavailable in which case it would contribute to eutrophication in downstream water bodies.

Denitrification results in the permanent removal of NO_3 from water (although it releases the greenhouse gas nitrous oxide). Several studies have measured high denitrification enzyme activities (DEA) in the anaerobic, organically enriched wetland soils. This shows that the soils have the potential for denitrification if high NO_3 water reaches them and they contain reserves of organic carbon. Only two studies (Cooper 1990, Zaman et al. 2008) measured *in situ* denitrification rates and these studies confirms that seepage wetlands can permanently remove NO_3 although denitrification does not explain 100% of NO_3 removal – implying that some NO_3 is transformed (e.g., by plant uptake and/or DRNA) to NH_4, DON and/or PN.

Cooper (1990) found that denitrification rates were high where sub-surface flow first entered the wetland and NO_3 concentration were high, but that denitrification rate decreased with distance downslope as a result of decreasing NO_3 concentration. Reworking results from the tracer injection study by Rutherford & Nguyen (2004) shows that the NO_3 removal rates decreased with decreasing NO_3 concentration (Figure 3-17) which is in agreement with the findings of Cooper (1990). Thus accurate quantification of NO_3 removal requires an understanding of the spatial variation of concentration and soil uptake rate.

Tracer studies inject a mixture (typically KNO_3 and inert LiBr) and infer NO_3 removal rates from the rate of change of NO_3/inert tracer (NO_3/Br) ratio. This method requires NO_3 concentrations to be higher than 'ambient' and consequently removal rates need to be 'adjusted' to typical runoff concentrations. In the studies reviewed NO_3 concentrations were significantly higher than typical of runoff from pasture and the ‘adjustment’ process introduces uncertainty into estimated removal rates.

DEA measures the denitrification rate of wetland soils exposed to excess NO_3 concentration in the laboratory. An estimate of the <u>maximum</u> areal removal rate can be made knowing DEA, bulk density measurements and the depth of the ‘active’ layer. The ‘active’ layer is the soil depth in which wetland soils are exposed to high NO_3 water (viz., the depth to which inflowing NO_3 mixes readily). In the Barkers and Whakarewarewa wetlands the ‘active’ layer depth was estimated to lie in the range 5-20 cm (average 7 cm). DEA measurements were found to be similar across several different wetlands (typically 3-5 $\mu g\ g^{-1}\ h^{-1}$) and bulk density was typically 0.30 gDM cm^{-3}. This implies removal rates of 2-3 $g\ m^{-2}\ d^{-1}$. Cooper (1990) measured higher rates (6-8 $g\ m^{-2}\ d^{-1}$) where high NO_3 groundwater first entered the wetland. Tracer injection studies measured NO_3 removal rates of 3-5 g $m^{-2}\ d^{-1}$ in the Whakarewarewa forest wetlands which received high NO_3 loadings from sprayed urban wastewater and where wetland soils were deep and highly porous. Removal rates at Whakarewarewa were higher than in pasture wetlands.

In the Whakarewarewa and Barkers wetlands NO_3 concentrations were found to be lower in deep piezometers (30-40 cm) than in surface waters and shallow piezometers (10-20 cm). Porosity, hydraulic conductivity, horizontal seepage flow and the rate of vertical mixing decreased with depth. Thus although deep soils had a similar DEA to shallow soils and NO_3 did reach them as readily, they depleted the available NO_3 and the removal rate decreased.

The horizontal seepage flow decreased with depth and the integral of flow over depth was small compared with measured inflow and outflow. Thus the conceptual model of seepage wetlands is of high flow surface (pathway 1) and low flow sub-surface seepage flow (pathways 3 and 4, Figure 4-1). Although NO_3 concentrations decrease rapidly with distance along pathways 3 and 4 (Burns & Nguyen 2002, Collins et al. 2005), seepage flow alone is not enough to explain the observed nitrogen attenuation (Rutherford et al. 1999, 2000). Following surface and sub-surface injections, inert Br tracer was found in piezometers at depths of 10-20, 20-30 and (at low concentrations) 30-40 cm which indicates significant vertical mixing (pathway 2). Were it not for this vertical mixing, seepage wetlands would remove very little NO_3 (Rutherford & Nguyen 2004).

Areal removal rates calculated from DEA measurements only apply where NO_3 concentrations are high. Thus they may apply at the upstream edge of the wetland (where sub-surface flows first encounter microbially active wetland soils) but are expected to decrease with distance downslope as NO_3 concentration decreases. Applying the maximum rate to the entire wetland would significantly over-estimate NO_3 removal. A model which accounts for vertical and longitudinal mixing and relates NO_3 removal rate to concentration has been developed (Rutherford et al. 1999, 2000) but requires further development and testing.

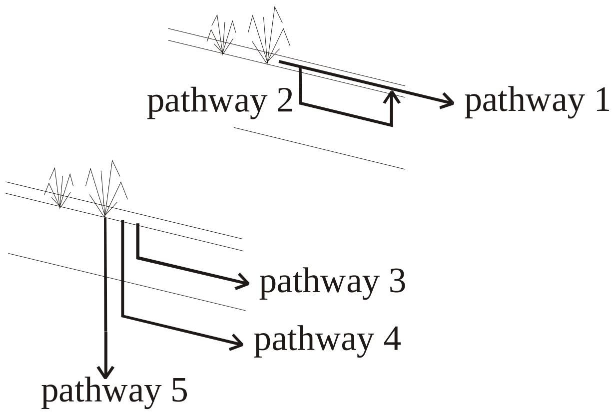

Figure 4-1: Schematic showing likely flow pathways in seepage wetlands. Vertical mixing (pathway 2) is important in nitrate removal.

OVERSEER assumes an average attenuation rate of 250 mg m^{-2} d^{-1} (at 20C) which is adjusted by wetland Class (condition, Table 2-2) and temperature. This value was recommended for use in OVERSEER because it closely matches the value of 253 ± 79 mg m^{-2} day^{-1} reported by Sukias et al. (2006b) for constructed wetlands at Toenepi. One aim of this study was to assess the reliability of the figure.

Collins et al. (2005) reported nitrogen loads and estimated areal removal rates for TN in the RC pasture wetland at the spatial scale of the wetland. We recalculated an average removal rate of 140 mg m^{-2} d^{-1} despite cattle disturbance. RC is a Class 4 wetland for which OVERSEER assigns an attenuation rate of 50 mg m^{-2} d^{-1}. Thus OVERSEER would significantly underestimate nitrogen attenuation – the OVERSEER rate is 36% of the average measured rate.

Collins et al. (2005) also reported results of studies in the JS wetland. We recalculated median TN removal rates of 35 and 468 mg m^{-2} d^{-1} in deep wells and shallow wells respectively from a longitudinal survey, and 310 mg m^{-2} d^{-1} from a tracer injection experiment. JS is a Class 3 wetland which OVERSEER assigns a removal rate of 100 mg m^{-2} d^{-1}. Thus OVERSEER would again underestimate nitrogen removal – the OVERSEER rate is 37% of the average of the rates measured in well transects the (35 and 468 mg m^{-2} d^{-1}) and tracer injection (310 mg m^{-2} d^{-1}) studies.

Burns & Nguyen (2002) and Rutherford & Nguyen (2004) measured loads and estimated areal removal rates in a pasture wetland (Barkers) at small spatial scales. The removal rates (corrected to 20C) averaged 280 mg m^{-2} d^{-1} (range 200-365 mg m^{-2} d^{-1}, Burns & Nguyen 2002) and 495 mg m^{-2} d^{-1} (range 430-560 mg m^{-2} d^{-1}, Rutherford & Nguyen 2004). Barkers was Class 2 for which OVERSEER assigns an attenuation rate of 188 mg m^{-2} d^{-1}. Thus OVERSEER would underestimate nitrogen attenuation – the OVERSEER rate is 38% and 67% of the rates measured by sub-surface and surface injection respectively.

Cooper (1990) and Rutherford & Nguyen (2004) found that NO_3 removal rate varies with concentration. However, the two studies furnished significantly different maximum removal rates. Simplified models were used to simulate wetlands assuming a spatially uniform removal rate (as in OVERSEER) and a removal rate that varied with concentration. It was found that if the maximum removal rate was very high then OVERSEER would underestimate nitrogen removal for small wetlands (<2% of catchment area). For larger wetlands the two models gave similar predictions because both predicted ~100% removal.

One of the major difficulties facing researchers is to determine the 'effective' area of the catchment. This is the proportion of the topographic catchment whose runoff enters the wetland. In seepage wetlands the majority of inflow is shallow groundwater flow. Because of its diffuse nature shallow groundwater flow is very difficult to quantify accurately. The RC wetland study installed three piezometers at the head of the wetland to measure sub-surface inflow concentrations but were unable to quantify inflow rates and neglected lateral inflows. An array of piezometers has been installed in the Armstrong wetland in an attempt to quantify sub-surface inflows, but few results are yet available.

The OVERSEER user is required to specify the area of the catchment that drains to the wetland. This is the 'effective' area which is used to determine the proportion of total runoff that enters the wetland (the balance by-passes the wetland to deep groundwater). Many users may be unable to do this accurately. If the user does not specify the 'effective' area, OVERSEER estimates it based on soil properties and aquitard depth, but relies on the user to specify the aquitard depth. Again many users may not be able to estimate aquitard depth accurately. Thus, estimating 'effective' area is a significant information gap.

Reworking of the RC wetland data shows that if the wetland outflow can be measured (L s^{-1}), the flow yield in the receiving stream is known (L s^{-1} km^{-2}), and the flow yields of stream and wetland are identical, then the 'effective' area can be calculated. It may be possible to use this approach within OVERSEER although further testing is required and a method developed to estimate stream yields across the country. It would require the user to measure or estimate wetland outflows but this may be easier than estimating 'effective' area and more accurate than relying on the aquitard depth/soil type method.

Currently the seepage wetland module relies on measurements from a small number of field studies, and it is desirable to expand the available dataset by conducting inflow/outflow studies on a range of sizes and types of seepage wetland. Outflows can be measured using weirs and samplers, but it is very difficult to measure inflows because these are diffuse (viz., dominated by shallow sub-surface flow). Rather than attempting to measure nitrogen inflows, it may be possible to estimate them using OVERSEER based on fine-scale farm data for the catchment that drains to the study wetland. This approach still requires knowledge of the 'effective' area but it may be possible to establish an empirical relationship between wetland size, catchment slope, rainfall and 'effective' area if additional field investigations were undertaken.

The seepage wetland module in OVERSEER consists of a simplified, conceptual model of seepage wetlands which was calibrated and tested using data from a small number of experimental studies. The user is required to specify input data based on 'expert opinion' with the help of 'look up' tables. Consequently, the wetland module furnishes semi-quantitative estimates of nitrogen removal. In keeping with the spirit of the farmland module in OVERSEER, the wetland module allows users to assess the potential of seepage wetlands to reduce NO_3 loss from farms, and to see how removal varies with characteristics such as wetland/catchment area ratio and condition factors such as channelization, vegetation and stock damage.

Table 4-1: Summary of nitrogen attenuation estimates.

Wetland	Catchment ha	Effective ha	By pass	Wetland ha	Type	Class	Form	Removal %	Removal coefficient m^{-1}	Areal removal $mg\ m^{-2}\ d^{-1}$	Removal at 20C $mg\ m^{-2}\ d^{-1}$	Method	Inflow	Outflow	Notes
RC	5	2.7	40%	.17-.22	A	4	TN	52%		64	140	Load	OVERSEER	Weir	Pasture, occasional cattle disturbance.
							DIN	91%	0.017	49	113	Conc	Wells	Weir	No decrease with increasing flow
							TN	72%	0.009	55	123				
						1	TN	61-79%		66-106	145-235	Estimated			Without cattle disturbance
JS				1.85	A	3	DIN		0.018	31	31	Conc	Deep wells		Ignores mixing. Possible underestimates
							TN		0.009	35	35				
							DIN		0.047	346	346		Shallow wells		Ignores mixing. Possible over-estimates
							TN		0.035	468	468				
							NO_3	97%		135	425	Tracer	Wells		As reported
										61	190				Timing adjusted
BARK				0.035	A	2	NO_3	24% [a]		270	495 [b]	Tracer	Weir	Weir	Surface injection. Active layer depth 7 cm
								>90% [a]			280	Tracer	Wells	Wells	Sub-surface injection
WHAKA					A	1	NO_3	19% [a]		4500 [c]	4500	Tracer	Weir	Weir	Surface injection
											3300	DEA			Active layer depth 10 cm
								>36% [a]		3900	3900	Tracer	Weir	Weir	Sub-surface injection
ARMS	5.2			0.15	A		NO_3	78%				Conc	Weir	Weir	90% inflow unmonitored
							TN	58%							
							NO_3	95%				Conc	Wells	Weir	Upper wetland
ARMS	1.9			0.15	A		NO_3	75%				Conc	Weir	Weir	From fitted model
							NH_4	73%							
							TON	negligible							
CAM				0.7	A	2	NO_3	70-95%				Conc	Weir	Weir	
							NH_4	negative							NH_4 increased on average
							TKN	negative							TKN increased on average

Wetland	Catchment ha	Effective ha	By pass	Wetland ha	Type	Class	Form	Removal %	Removal coefficient m^{-1}	Areal removal $mg\ m^{-2}\ d^{-1}$	Removal at 20C $mg\ m^{-2}\ d^{-1}$	Method	Inflow	Outflow	Notes
TUT	660			33 (5%)			TN	70%				Load	OVERSEER	Stream	14% by wetlands, 56% unexplained
RS#1							NO_3	75%				Conc	Wells		
							NH_4	0%							
							DON	-75%							DON increased
RS#2							NO_3	>90%				Conc	Wells		NO_3 increased at one site in spring
							NH_4	~0%							NH_4 decreased at only one site
							DON	variable							Decreased on 6 but increased on 4 surveys
SCOT			40%				NO_3	98%		8100		Denit	Wells	Wells	NO_3 conc = 640 mg m^{-3}
										6100					NO_3 conc = 218 mg m^{-3}
										30	<100				NO_3 conc = 13 mg m^{-3}
KIWI				6.817			$^{15}N\text{-}NO_3$			289		Denit			6-7% denitrification
							NO_3			4094		Conc			Significant plant uptake
PUKE				.0062			NO_3	51%				Load	Seepage		
							NH_4	source							
							TN	54%							

Notes:
By pass = proportion of catchment runoff that does not enter the wetland. Effective = proportion of catchment from which all runoff enters the wetland.
Type and Class – see Table 2-1 and Table 2-2
Removal = (Inflow-Outflow)/Inflow (either Load or Conc).
Removal coefficient = first-order decay rate with distance (see Eq 2).
Areal removal = removal rate per unit surface area at the prevailing temperature. Areal removal rates converted to 20C using Eq 1.
Method denotes data used to estimate attenuation. Load = flow x conc or OVERSEER. Conc = inflow & outflow concentrations. Tracer = injected tracer (usually KNO_3 + LiBr). Denit = *in situ* denitrification. DEA = laboratory denitrification enzyme activity.

[a] of the injected tracer
[b] scaled to the prevailing input NO_3 concentration

[c] scaled to the prevailing input NO_3 concentration using data from Barkers

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