

# Significance of wetlands in the agricultural landscape as sources of nitrous oxide emissions

A review and synthesis of hypotheses

Diffuse Sources Ltd and NIWA

# The Significance of Wetlands in the Agricultural Landscape as Sources of Nitrous Oxide Emissions

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## Executive Summary

Agriculture contributes half of New Zealand's greenhouse gas emissions and is the major source of methane (88%) and nitrous oxide (96%). While the sources of methane are well known and understood, there is much less certainty about nitrous oxide. As is the case internationally, indirect emissions (of which leaching and runoff make up about 75%) account for a disproportionate share of the uncertainty in the estimates. If we are to manage nitrous oxide emissions, it is important that we gain a better understanding of the emission sources. Riparian wetlands within agricultural catchments are a likely source of nitrous oxide since they are natural conduits for nitrate-rich leachate and are known to have a high capacity for denitrification. Since retention and creation of wetlands within agricultural landscapes are promoted as a means of reducing the nitrate load to surface waters, it is important that we have an increased understanding of the role of wetlands in nitrous oxide emissions relative to that of the pasture catchment.

Because there have been no New Zealand studies that have explicitly measured nitrous oxide emissions from riparian wetlands, we abstracted information from international literature in order to obtain a range of emission rates from wetland systems, and to glean the principal processes and environmental conditions leading to nitrous oxide production. We used the understanding gained from this review to develop conceptual and empirical models. We used an empirical models to put some bounds on the likely flux arising from riparian wetlands in New Zealand pasture catchments, and as a basis for planning field measurements/experiments to fill knowledge gaps.

Nitrous oxide emission rates in wetland and riparian wetland studies overseas range from 0 (or net sink) to  $\sim 100 \text{ kg N ha}^{-1} \text{ y}^{-1}$ . In wetlands receiving runoff from agricultural fields, rates are commonly in the range  $0 - 45 \text{ kg N ha}^{-1} \text{ y}^{-1}$  with the high end of the range associated with high nitrate input and removal rates. Zero or low emission rates are associated with permanent inundation and low nitrate inputs. The range of emission rates in wetlands is within the range of rates obtained in terrestrial ecosystems, and high nitrogen input is a common factor in high emission rates measured in both systems. Far fewer studies have been carried out on wetlands than pasture and cropping systems. In addition there is evidence of distinct spatial trends of nitrous oxide emissions in riparian wetlands compared with a more random pattern regulated by water filled pore spaces in terrestrial systems. Riparian wetland studies that do not take account of this spatial pattern may calculate a low average nitrous oxide emission overall, but mask very high rates occurring within small areas. The identification of these small areas of riparian wetland may be key to minimising emissions from this source.

There are a number of microbially-mediated biochemical pathways (nitrification, denitrification, anammox, dissimilatory nitrate reduction to ammonia) that can produce nitrous oxide as intermediate products. Nitrification is frequently invoked as a significant (or even the main) pathway in aerobic soils, but in wetlands, where the supply of oxygen is limited, the evidence suggests that denitrification is mostly responsible. Contemporary

microbiological research, however, cautions against ascribing nitrous oxide flux to a single process or pathway because the microorganisms are physiologically defined, and are widespread amongst various taxa that vary in their responses to environmental conditions. Therefore, from a management viewpoint it is more important to understand the environmental factors leading to high rates of nitrous oxide emissions rather than the microbial processes *per se*.

Isolating individual factors influencing nitrous oxide emissions in a riparian wetland environment is difficult although insights have come from multivariate analysis. Further knowledge has been derived from detailed measurements at points along transects through riparian zones; in conjunction with laboratory studies where single environmental variables can be isolated. From a comparison of the 'state of the knowledge' with our understanding of New Zealand riparian wetlands we concluded that the main variables affecting nitrous oxide production are nitrate and oxygen concentration. Whilst pH and available carbon have been shown to be important in certain circumstances, our view is that they are of lesser importance in the New Zealand context. Maximum nitrous oxide (as a proportion of other products) occurs at oxygen concentrations that are sub-optimal for both nitrification and denitrification and some studies have shown this also corresponds to maximum nitrous oxide production. Because oxygen measurement at low levels in field situations is notoriously difficult, surrogates such as redox potential or water filled pore space are commonly used. In riparian wetlands, redox potential is a more appropriate measure and peak nitrous oxide production has been shown to occur over a very narrow range of +120-250 mV. This range of redox potential has also been shown to correspond to the zone where nitrate is predicted to be reduced under equilibrium conditions. Field studies have also shown that wetlands receiving high external loads of nitrate from the surrounding catchment have much higher nitrous oxide fluxes than those dependent on autochthonous (nitrification-induced) nitrate supply from water table fluctuations. The further reduction of nitrous oxide to dinitrogen appears to be regulated by nitrate supply.

Nitrous oxide emissions from riparian wetlands depend not only on the environmental conditions influencing nitrous oxide production but also the physical factors affecting the escape of nitrous oxide molecules to the atmosphere. Overlying water decreases the diffusion of nitrous oxide by ~ 4 orders of magnitude, which partly explains why permanently flooded wetlands (such as constructed wetlands receiving wastewater) have relatively low nitrous oxide emissions. Riparian wetland plants can provide the gaseous diffusion pathway that circumvents the barrier induced by overlying water, but this appears to be quite plant-specific. In general some aerobic interface appears to be necessary for significant nitrous oxide emission; whether it is through wetting and drying processes (as occurs seasonally in many New Zealand pastoral riparian wetlands) or at the upland/wetland interface (where pasture-derived nitrate leachate first contacts the saturated organic riparian soil). There is evidence that higher fluxes of nitrous oxide are associated with such breaks in the landscape and New Zealand studies have shown that this interface is associated with extremely high *in situ* denitrification rates (although nitrous oxide itself was not measured).

A number of authors have stated that predicting the ratio of nitrous oxide:dinitrogen gas is key to understanding nitrous oxide emissions from riparian wetlands. Recent Dutch studies have disputed that simple relationships exist between this ratio and environmental variables (pH, Eh, oxygen, available carbon etc). Nevertheless, faced with few other quantifiable predictors of nitrous oxide flux we envisaged that this ratio would be a pragmatic way of putting some upper bounds upon emissions from New Zealand riparian wetlands. We used a 'hole in the pipe' model to conceptualise the losses of nitrous oxide from a 'stream' of nitrate entering one end of a pipe, and dinitrogen gas (indicative of complete nitrate reduction) exiting the other end. However, we conclude that although the 'hole in the pipe' model is a useful conceptual model, it is currently of limited value for calculating nitrous oxide fluxes in New Zealand wetlands, because; (a) there are few simultaneous measurements of nitrous oxide emission and denitrification in wetlands with high denitrification rates and (b) it ignores the findings of spatial pattern of denitrification and nitrous oxide emission rates.

Complex models such as the DNDC model (even the wetland-DNDC model) are not suitable (in the first instance) for estimating nitrous oxide flux from wetlands in New Zealand agricultural landscapes because of a lack of input data. We have therefore constructed a simpler empirical model incorporating nitrate flux and known denitrification rates from pasture, wetland, and headwater stream environments. The model showed that increasing the area of riparian wetlands is likely to increase nitrous oxide emissions from the catchment if (i) the denitrification rate of headwater streams is low compared with the flux of N from the catchment, and (ii) if the N yield from the catchment exceeds the denitrification rate of the wetlands. Under scenarios where the denitrification potential of downstream rivers, floodplains and estuaries is comparable with the cumulative flux of N exported from upstream catchments then total emissions will remain constant; all that changes is the location where they occur.

There is no suitable inventory of wetlands in pasture catchments we can use to estimate the significance of nitrous oxide emissions from this source, however one study in the Lake Taupo catchment showed that wetlands comprised > 5% of the total farmed area.

Whilst our empirical model enables us to put some approximate bounds on nitrous oxide emissions from wetlands in New Zealand agricultural landscapes, we have no way of validating the model. There is, we believe, good justification for obtaining systematic measurements of nitrous oxide emissions coupled with environmental variables (such as nitrate flux, Eh, available carbon) across pasture-wetland transects. This will enable us to not only confirm or deny the predictions made in our model, but also make a significant international contribution to the understanding of nitrous oxide emissions and how to manage them.

Completing the additional objectives proposed under this programme will allow improved understanding of the spatial variability of nitrous oxide emissions across riparian wetlands, and, together with estimates of their area, allow a robust estimate to be made of the total nitrous oxide emissions wetlands within pasture catchments.

# 1 Introduction

## 1.1 The goal of this research - Why is it important to understand N<sub>2</sub>O emissions from wetlands?

In pastoral agricultural landscapes, wetlands commonly occupy a unique position adjacent to streams that drain the catchment of which they are a part. In this position they are often referred to as riparian wetlands, or even simply riparian zones. However 'wet' lands can also occur separated from any stream, at positions in the landscape where ephemeral flows converge, or where ephemeral springs emerge at a discontinuity in the soil profile. They are often grazed, but are characterised by gleying and/or growth of wetland species (e.g. *Juncus* spp.) amongst the pasture. Whether or not they are truly riparian, wetlands within agricultural landscapes intercept and process nitrate (NO<sub>3</sub><sup>-</sup>) from subsurface flow leached from pasture and transported towards streams. There have been numerous studies that have demonstrated that riparian wetlands can remove large amounts (> 100 kg N ha<sup>-1</sup> y<sup>-1</sup>) of leached NO<sub>3</sub><sup>-</sup>-N and denitrification is frequently invoked as the mechanism responsible (Hill 1996).

The denitrification reaction pathway has gaseous N<sub>2</sub> as its endpoint (NO<sub>3</sub><sup>-</sup> → NO<sub>2</sub><sup>-</sup> → NO → N<sub>2</sub>O → N<sub>2</sub>). As the focus of riparian wetland studies has been on removing nitrogen from stream water, there have been, until recently, relatively few studies that have shown the importance of the 'intermediate' products along the reduction pathway. Advances in methodology as well as increasing realisation of the importance of nitrous oxide (N<sub>2</sub>O) to global warming has resulted in a more critical appraisal of the denitrification sequence, and alternative biochemical pathways that result in either NO<sub>3</sub><sup>-</sup> reduction, or N<sub>2</sub>O production.

It is important to understand the influence that environmental conditions have on both the removal of NO<sub>3</sub><sup>-</sup> from receiving waters (a water quality perspective) and the emission of N<sub>2</sub>O to the atmosphere (a climate change perspective). Because of their unique place in the landscape and because the same process (denitrification) is potentially involved, there is a potential conundrum in terms of how riparian wetlands are managed. If riparian wetlands denitrify a large proportion of the nitrate-enriched leachate entering them, then it is a reasonable hypothesis that they could be 'hotspots' of N<sub>2</sub>O production in the landscape (Groffman et al., 1998). If this were the case then the environmental benefits of using riparian wetlands to mitigate agricultural impacts on water quality may be offset through the detrimental effects on climate change; so called 'pollution swapping' (Dhondt et al., 2004). This is an important issue because wetland restoration or creation is being promoted as a means of 'controlling' the effects of agriculture on water quality. For example in the Rotorua Lakes catchments, there have been major initiatives to reduce nutrient loads, including constructing wetlands to 'treat' runoff from pastoral catchments (see <http://www.niwa.co.nz/ncwr/wru/ma/2006-16/hope>). Internationally there is growing interest in subsidizing the restoration of wetlands by marketing carbon credits to power generators and other facilities releasing CO<sub>2</sub> from fossil fuel consumption (Ullah et al., 2005). Where restored or created wetlands also enhance denitrification, there is the



possibility that they will also increase the atmospheric burden of  $\text{N}_2\text{O}$ . This possibility remains a principal uncertainty in establishing their carbon credit value. Whether such restoration will significantly affect the atmospheric burden of  $\text{N}_2\text{O}$  depends on the extent of land restored, and any changes in both the rate of denitrification, and the  $\text{N}_2\text{O}:\text{N}_2$  emission ratio.

For 'pollution swapping' to be a significant issue, the rate of  $\text{N}_2\text{O}$  emission needs to significantly exceed that of the surrounding catchment. This is plausible if the environmental conditions within riparian wetlands are more conducive to denitrification, and if there is a disruption in the denitrification biochemical pathway leading to a higher rate of  $\text{N}_2\text{O}$  production relative to the rate of further reduction to  $\text{N}_2$  (Groffman et al., 2000).

The focus of this report is  $\text{N}_2\text{O}$  emissions from riparian wetlands as a contributor to climate change. Current Intergovernmental Program on Climate Change (IPCC) methodologies for calculating national  $\text{N}_2\text{O}$  emission inventories do not explicitly account for riparian  $\text{N}_2\text{O}$  production. We know that although riparian wetlands represent only a small fraction of the area within an agricultural catchment, their known impacts on export of nutrients can be large (Bowden et al., 1992). If this also applies to  $\text{N}_2\text{O}$  emissions, then their influence on regional budgets may also be large enough to justify being accounted for explicitly in the national inventory. This is particularly relevant to New Zealand because of our unique profile of greenhouse gas emissions (MfE, 2008) dominated by high agricultural contributions of methane ( $\text{CH}_4$ ) and  $\text{N}_2\text{O}$ . There is considerable uncertainty in New Zealand's annual  $\text{N}_2\text{O}$  emissions ranging from an overestimation of 74% to an underestimation of 42% (Saggar et al., 2007)), which also reflects the uncertainty in accounting for  $\text{N}_2\text{O}$  emissions internationally (Nevison, 2000). The IPCC guidelines divide the agricultural  $\text{N}_2\text{O}$  sources into 3 categories: direct emissions from agricultural land, emissions from animal waste management systems, and indirect emissions associated with N that is volatilized, leached, removed in biomass, or otherwise exported from agricultural land. Each of these 3 categories is estimated to contribute an equal 1/3 of the total estimated agricultural source, however, indirect emissions, account for a disproportionate share (approximately 2/3) of the uncertainty in the estimates (Nevison, 2000). Leaching and runoff make up about 75% of indirect sources and thus contribute markedly to the uncertainty in the estimates of indirect sources. Most indirect agricultural  $\text{N}_2\text{O}$  emissions occur in aquatic environments, since much of the nitrogen lost from agricultural land through leaching, runoff, crop harvest and human consumption ultimately ends up in groundwater, rivers, lakes and estuaries (Seitzinger et al., 2000). It is therefore likely that quantifying  $\text{N}_2\text{O}$  emissions from riparian wetlands, which are a key ecotone between terrestrial and aquatic environments, will reduce the uncertainty associated with indirect agricultural sources markedly.

This view is reinforced by Nevison (2000) who commented that the IPCC methodology might consider defining emission factors that distinguish between leached agricultural N which flows directly into rivers versus that which drains through groundwater and riparian zones.

## 1.2 The structure of this report

This report fulfills Objectives 1 and 2 of the proposal submitted for this programme.

We review contemporary international literature to distill information on the processes leading to  $\text{N}_2\text{O}$  emissions in wetland and adjacent environments. This includes quantifying  $\text{N}_2\text{O}$  flux as a function of position in the landscape and abstracting the key environmental drivers of, and constraints to,  $\text{N}_2\text{O}$  emissions in riparian wetland environments.

We use the concepts derived from the above review to synthesise hypotheses on  $\text{N}_2\text{O}$  emissions from riparian wetlands within a New Zealand pastoral landscape. The formulation of these hypotheses also draws upon our knowledge and experience of nutrient dynamics in New Zealand riparian wetland systems, and  $\text{N}_2\text{O}$  emissions in lowland streams.

The hypotheses generated above are used to construct a simple empirical model of a hypothetical New Zealand riparian wetland receiving nitrate-rich leachate from its pasture catchment. We use this model to put some theoretical limits on the amount of  $\text{N}_2\text{O}$  that could be emitted from riparian wetlands in a New Zealand pastoral landscape.

Finally, we summarise the conclusions that can be made with respect to  $\text{N}_2\text{O}$  emissions from riparian wetlands in agricultural landscapes. We also identify the major uncertainties in our conclusions and outline further research (as outlined in Objectives 3 and 4 of our proposal) that will reduce those uncertainties and fill knowledge gaps.

## 2 Synthesis of information on N<sub>2</sub>O emissions from wetlands

### 2.1 N<sub>2</sub>O flux in wetland environments

Systematic measurements of N<sub>2</sub>O emissions in wetland environments (dominantly riparian wetlands but also constructed wetlands) are presented in Table 1.<sup>1</sup>

**Table 1. N<sub>2</sub>O emissions measured in riparian and constructed wetland studies (denitrification rates are used in Section 3)**

<i>Reference</i>	<i>N<sub>2</sub>O emission (kg N<sub>2</sub>O-N ha<sup>-1</sup>y<sup>-1</sup>)</i>	<i>Denitrification rate (kg N ha<sup>-1</sup>y<sup>-1</sup>)</i>	<i>Comments</i>
Blicher-Mathiesen et al., 1999	0 (net)	66 (from NO <sub>3</sub> <sup>-</sup> reduction)	Permanently water covered – all reduced to N <sub>2</sub>
Boeck & Van Cleemput 2006	4.5 ± 4.0	Not given	Belgium riparian zone receiving high NO <sub>3</sub> -N in groundwater
Dhondt et al. 2004	4.5 ± 4.4	Only DEA measured	Riparian borders agricultural land, highest fluxes in forested riparian, especially at upslope border
Franken et al. 1992	8.2 ± 5.8	Not given	Both surface waters and wetlands – review of Dutch studies
Groffman et al, 2000 (citing Weller et al. 1994)	0.1-5.3	Averaged 0.00163 kg N <sub>2</sub> O-N per kg of N input	Riparian forests receiving agricultural runoff
Hefting et al. 2003	3.0 ± 1.0 grass buffers 20 ± 6 forested buffers	94 ± 29 (no significant difference between grass and forested buffers)	Buffers bordering agricultural fields
Hefting et al. 2006	36 ± 14 summer	278 ± 76	Holland – fluctuating

<sup>1</sup> Converted to common units of kg N<sub>2</sub>O-N ha<sup>-1</sup> y<sup>-1</sup>

	31 ± 11	127 ± 47	water table- highest along flowpath with high NO <sub>3</sub> removal.
Hernandez & Mitsch 2006	2.0 ± 1.4	408-474 (from NO <sub>3</sub> removal)	Created riverine wetlands. Highest in high marsh subject to fluctuating water table. Highest with vegetation than without.
Johansson et al., 2003	84 ± 73	Not given	Constructed wetland receiving wastewater.
Merbach et al 2001	26	Not given	Drained alder swamp
Paludan & Blicher-Mathiesen, 1996	0.5 ± 0.5	Not given	Permanently water covered -higher in NO <sub>3</sub> reduction zone than not
Picek et al., 2007	~0	Not given	Constructed wetland receiving sewage . N <sub>2</sub> the only denitrification product.
Schipper et al., 1993	266-306	3467-4088	NZ riparian organic soil irrigated with treated sewage effluent
Ullah et al., 2005	19 ± 5	146 ± 40	Forest wetland
	22 ± 5	60 ± 22	Forested wetland below cultivated site
Ullah & Zinati 2006	1.3 ± 0.2	30 ± 3	Forested wetland below nursery runoff
Verhoeven et al 1996	1.7± 0.5	3 ± 1	Higher N <sub>2</sub> O emissions at Dutch site than Polish sites - hypothesised due to greater N deposition at Dutch site- despite Polish sites have fluctuating water

			tables
Walker et al, 2002	24		More wet soil than true wetland
Weller et al. 1994	$2.7 \pm 2.6$	Not given	Riparian forest below agricultural area
Yu et al 2007	$0.5 \pm 0.1$	Not given	China - natural wetland not subject to anthropogenic inputs

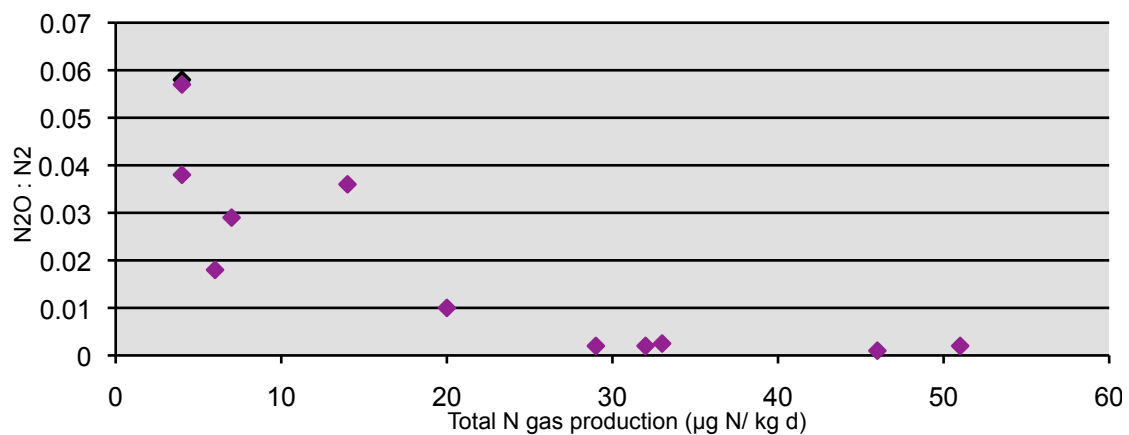
Further analysis of the studies presented in Table 1 showed:

1. Wetlands that had low inputs of  $\text{NO}_3\text{-N}$  had low  $\text{N}_2\text{O}$  emissions (Blicher-Mathieson et al., 1999; Yu et al., 2007)
2. Permanently flooded wetlands emitted lower  $\text{N}_2\text{O}$  than wetlands subject to a fluctuating water table, provided there was no difference in  $\text{NO}_3\text{-N}$  inputs (Verhoeven et al 1996, Hernandez & Mitsch, 2006). Even constructed wetlands receiving wastewater could have negligible  $\text{N}_2\text{O}$  emissions (Picek et al. ,2007) although such systems could also emit  $\text{N}_2\text{O}$  at the larger end of the spectrum (Johansson et al., 2003). Blicher-Mathieson et al. (1999) provide convincing evidence that although  $\text{N}_2\text{O}$  was produced in a permanently flooded wetland, it was further reduced to  $\text{N}_2$  at the same rate, resulting in no net  $\text{N}_2\text{O}$  emission. Similar inferences are made by the other authors.
3. Emissions from wetlands with fluctuating water tables, but low anthropogenic N inputs are attributed to coupled nitrification-denitrification (Yu et al., 2007; Verhoeven et al., 1996, Hefting et al., 2006).
4. Emissions of  $\text{N}_2\text{O}$  from wetlands processing high anthropogenic inputs of  $\text{NO}_3\text{-N}$  from adjacent agricultural systems were significantly higher than those in adjacent systems with lower or no  $\text{NO}_3\text{-N}$  input (Groffman et al., 2000; Hefting et al., 2003; Hefting et al., 2006; Boeck & Van Cleemput, 2006). In addition studies that measured removal of  $\text{NO}_3\text{-N}$  from groundwater along a transect from its upland source through the riparian wetland have found distinct spatial patterns in  $\text{N}_2\text{O}$  emissions with highest rates coincident with the zone of greatest  $\text{NO}_3\text{-N}$  removal. Where  $\text{NO}_3\text{-N}$  was present in surplus, high rates of  $\text{N}_2\text{O}$  emissions occurred even under winter conditions (suboptimal for denitrification) whereas where no groundwater  $\text{NO}_3\text{-N}$  was present, rates were higher in summer (Hefting et al., 2006).

Even in situations with low net  $\text{N}_2\text{O}$  emissions significantly higher rates of  $\text{N}_2\text{O}$  production have been recorded within the  $\text{NO}_3\text{-N}$  zone than outside it (Paludan & Blicher-Mathieson, 1996). Studies in which no areal emission rates were recorded provide additional evidence that high rates of  $\text{N}_2\text{O}$  production are associated with high N inputs. For example Hunt et al., 2007 showed that  $\text{N}_2\text{O}$  comprised ~25% of total denitrification products in a riparian wetland adjacent to a field irrigated with high amounts of piggy effluent, whilst Boustany et al., (1996) found higher

amounts of  $\text{N}_2\text{O}$  dissolved in the water column of a wetland receiving sewage effluent within the zone of greatest  $\text{NO}_3\text{-N}$  reduction. Verhoeven et al. (1996) found higher  $\text{N}_2\text{O}$  emissions in Dutch wetlands than those in Poland, despite the latter being subject to fluctuating water tables. This they attributed to significantly higher rates of atmospheric N deposition at the Dutch sites, compared with those in Poland.

5. Notwithstanding the above Groffman et al. (2000) reported that as total N gas production increases the proportion that is  $\text{N}_2\text{O}$  (as opposed to  $\text{N}_2$ ) decreases (Fig. 1).
6. In general higher  $\text{N}_2\text{O}$  emissions have been found in forested wetlands than those with grass vegetation (Hefting et al., 2003; Dhondt et al., 2004) although this has been attributed to higher  $\text{NO}_3\text{-N}$  inputs in groundwater from adjacent agricultural fields. Higher  $\text{N}_2\text{O}$  emissions were recorded in planted areas of a riverine wetland than in areas where there were no plants (Hernandez and Mitsch, 2006) although this may have been coincident with water level fluctuations.



**Fig. 1.**  $\text{N}_2\text{O}:\text{N}_2$  ratio versus total N gas production in groundwater mesocosms from two riparian sites with poorly drained soils (from Groffman et al., 2000)

Important points
<ul style="list-style-type: none"> <li>There is a large range in the reported annual <math>\text{N}_2\text{O}</math> emission rates from riparian wetlands from 0 to &gt; 100 kilograms <math>\text{ha}^{-1}</math>.</li> </ul>
<ul style="list-style-type: none"> <li>Riparian wetlands with low anthropogenic N inputs have low <math>\text{N}_2\text{O}</math> emissions.</li> </ul>
<ul style="list-style-type: none"> <li>Permanently flooded wetlands have lower <math>\text{N}_2\text{O}</math> emissions than those subject to fluctuating water tables.</li> </ul>
<ul style="list-style-type: none"> <li>Riparian wetlands 'processing' high anthropogenic inputs of <math>\text{NO}_3^-</math> have significantly higher <math>\text{N}_2\text{O}</math> emissions than adjacent wetlands with low inputs.</li> </ul>
<ul style="list-style-type: none"> <li>Even in wetlands with low <math>\text{N}_2\text{O}</math> emissions, <math>\text{N}_2\text{O}</math> production is significantly higher with zones of high <math>\text{NO}_3^-</math> reduction than outside that zone.</li> </ul>

## 2.2 N<sub>2</sub>O flux in other environments

Because wetlands are at the interface between terrestrial and aquatic environments many studies have measured N<sub>2</sub>O emissions in adjacent truly terrestrial or truly aquatic environments. In addition, wetlands have many characteristics of adjacent ecosystems that have been the subject of studies by terrestrial or aquatic scientists. In this section we review a selection of those studies with respect to N<sub>2</sub>O emissions in order to transfer knowledge gleaned from those ecosystems to the riparian wetland situation.

Data of N<sub>2</sub>O emissions in terrestrial and aquatic environments that share characteristics of wetlands is given in Table 2.

**Table 2. N<sub>2</sub>O emissions measured in terrestrial and aquatic environments**

<i>Reference</i>	<i>Environment</i>	<i>N<sub>2</sub>O emission (kg N<sub>2</sub>O-N ha<sup>-1</sup>y<sup>-1</sup>)</i>	<i>Comments</i>
Ambus and Christensen 1995	Drained arable soil	4.67	High % (values) water filled porespace
Barton et al. 1999	NZ pasture	0-11 <sup>2</sup> 5-24	N-fertilised, not irrigated N fertilised, irrigated
Carran et al. 1995	NZ grazed pasture soil	3.5	Emissions when soil at or near field capacity, soil water content and NH <sub>4</sub> <sup>+</sup> significant variables
Choudhary et al. 2002	NZ cropped soil & permanent pasture	1.7 (pasture) 9.2 (crop, conventional tillage) 12 (no tillage)	Strong positive correlations with soil water content
Cole & Caraco, 2001	Hudson River, USA	0.056	
De Klein et al. 2001 (Studies cited	NZ grass/clover pasture	<1-19	Added synthetic or cow urine at rates from 300-1000 kg N ha <sup>-1</sup> y <sup>-1</sup> Highest emissions at highest N

<sup>2</sup> Calculated from denitrification rate assuming N<sub>2</sub>O:denitrification ~ 10%

in)			input rate.
De Klein et al. 2004	NZ pasture	20-50	Annual average calculated from urine application trials
Hadi et al., 2000	Tropical peatland	0.8 – 10 (uncultivated) 7-91 (cultivated)	Flooding induced significantly higher emissions than at 60% water filled pore space
Jacinthe et al. 1998	Groundwater	Areal flux estimate not possible	Rates of production two orders of magnitude higher in groundwater at wetland end of riparian zone than upland end
Liikanen et al., 2003	Lake littoral sediments	1.3 (natural) 140 (with excess of NO <sub>3</sub> -N)	Emission not affected by addition of NH <sub>4</sub> <sup>+</sup> but addition of NO <sub>3</sub> <sup>-</sup> stimulated N <sub>2</sub> O production 10-100 times Fluctuating water table prolonged high emissions
Kasimir-Klemedtsson et al., 1997	Farmed organic soils Undrained peat	2-38 0.03-0.14	Drainage for agricultural purposes increases N <sub>2</sub> O emissions 1-2 orders of magnitude
Saggar et al. 2004	NZ grazed pastures	12 (poorly drained dairy, 190 kg N ha <sup>-1</sup> y <sup>-1</sup> fertiliser) 10 (well drained dairy, 130 kg N ha <sup>-1</sup> y <sup>-1</sup> fertiliser) 4 (poorly drained sheep, 80 kg N ha <sup>-1</sup> y <sup>-1</sup> fertiliser)	Emissions <20% of these when pastures were ungrazed, so animals provide N and C that drives N <sub>2</sub> O emission. Highest fluxes associated with WFPS >0.60
Smith 1997	Temperate grasslands Tropical rainforests	0.08-0.1 0.1-5.4	
Stehfest & Bouwman 2006	Agricultural and natural vegetation	Agricultural soils (0.08-4.13 means, 0-32 entire range)	Emissions >10 kg N ha <sup>-1</sup> y <sup>-1</sup> considered high from a global perspective. Emissions higher



	soils (Global synthesis)	Natural vegetation soils (0.03-1.18 means, 0-7.5 entire range)	with higher N application rates. Rates based on various measurement periods often <300 days, therefore estimates may be slightly conservative.
Velthof & Oenema 1997	Dutch dairy farms	15 (average) 5 (with model nutrient management)	Calculated using literature N <sub>2</sub> O emission factors
Walker et al., 2002	Grazed and 'recovering' riparian zone	24	N <sub>2</sub> O flux positively correlated with soil nitrate concentrations
Wilcock & Sorrell 2008	Lowland streams	0.11-0.17	Small on a catchment scale but significant flux in relation to low intensity pasture
Zaman et al. 2007	NZ pasture	18 158 195	Control Urine treated 90 day trial Urine treated 90 day trial

Aspects of the above studies that are relevant to predicting N<sub>2</sub>O flux from riparian wetlands include:

1. Percent water-filled pore space appears to be a good indicator of N<sub>2</sub>O flux in soil systems generally (Ambus & Christensen, 1995; Hadi et al., 2000; Smith, 1997). Smith (1997) presented a conceptual model showing the relationship between WFPS and N<sub>2</sub>O and N<sub>2</sub> production (Fig. 2). However the difference between this model and other reported results (e.g. Hadi et al., 2000) mean that it is just an indicator, and that other more mechanistic relationships need to be established to predict N<sub>2</sub>O flux.
2. In the studies reviewed, ammonium did not stimulate N<sub>2</sub>O production (Hadi et al., 2000; Liikanen et al., 2003) indicating that nitrification was probably suppressed by high water content.
3. Fluctuating water table on the other hand stimulated N<sub>2</sub>O emission (Hadi et al., 2000; Kasimir-Klemedtsson et al., 1997), although in the case of lake littoral sediments (Liikanen et al., 2003) it was only in the presence of excess NO<sub>3</sub>-N indicating it was the changing oxygen status rather than stimulating nitrification which was responsible. The biochemical processes resulting in N<sub>2</sub>O emissions are reviewed in the next section.
4. High organic matter in combination with an excess of NO<sub>3</sub>-N stimulated N<sub>2</sub>O production (Jacinthe et al., 1998; Schipper et al., 1993; Walker et al., 2002). Schipper

et al. (1993) noted that 77% of in-situ denitrification activity could be explained by soil  $\text{NO}_3\text{-N}$  concentration.

These findings as well as those from ‘true’ wetland studies indicate that the presence of an excess of  $\text{NO}_3\text{-N}$  is a prerequisite for high fluxes of  $\text{N}_2\text{O}$  and that oxygen status and carbon supply control whether the reduction of  $\text{NO}_3\text{-N}$  will be manifest as  $\text{N}_2\text{O}$ ,  $\text{N}_2$ , or other nitrogenous compounds. We explore the environment as controller of  $\text{N}_2\text{O}$  production in section 2.4.

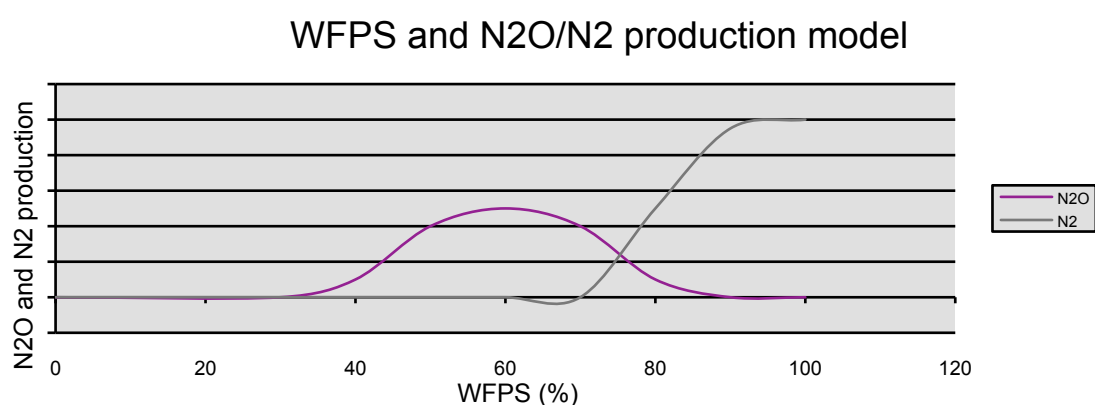


Figure 2. Schematic model showing the relationship between Water filled pore space (WFPS),  $\text{N}_2\text{O}$ , and  $\text{N}_2$  showing a predominance of  $\text{N}_2\text{O}$  until 60% WFPS, and then a rapid increase and dominance by  $\text{N}_2$  at and above 80% WFPS (from Smith, 1997)

Important points	
	• The range of $\text{N}_2\text{O}$ emission rates in other wet environments (irrigated organic soils, tropical peat, lake sediments) is similar to that reported for wetlands.
	• High $\text{N}_2\text{O}$ emissions under a fluctuating water level regime appears to be due to oxygen becoming suboptimal for denitrification, rather than stimulating nitrification.
	• Non-limiting carbon and $\text{NO}_3^-$ under the fluctuating water level regime above results in very high $\text{N}_2\text{O}$ production.

### 2.3 $\text{N}_2\text{O}$ flux as a function of biochemical process

The focus of this part of the report is on understanding the biochemical pathways that lead to the production of  $\text{N}_2\text{O}$  in wetlands. The amount of nitrogen being processed and in particular, the supply of  $\text{NO}_3^-$  determine the overall potential for production of  $\text{NO}$ ,  $\text{N}_2\text{O}$

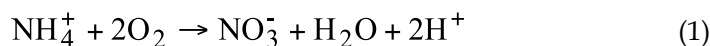
and  $N_2$ , whereas local conditions that affect key chemical and biochemical pathways determine (i) the degree to which reduction of nitrate occurs, and (ii) the relative amount of  $N_2O$  that is produced; viz. the  $N_2O:N_2$  ratio. In this section we firstly examine the key pathways that are frequently invoked as pathways leading to  $N_2O$  production in wetlands. We then review literature on the fundamental biochemistry and microbiology in relation to those pathways, and finally we review evidence from field studies on the dominant process occurring in different environments and comment on their significance.

### Concepts and processes

The key reactions for  $N_2O$  production are as follows:

#### Nitrification

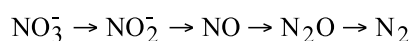
Nitrification is the oxidation of ammonium ( $NH_4^+$ ) to nitrate ( $NO_3^-$ ) (Eq. 1) and is a key part of the nitrogen cycle in pastoral agriculture. Urea excreted in urine and dung by stock is rapidly converted via the mineralisation process to ammonium, a relatively immobile form of nitrogen that binds to soil particles. When oxygen is available, nitrification follows and the nitrate ( $NO_3^-$ ) produced is negatively charged, does not readily bind to soil and is mobile. A gradual build up of  $NO_3^-$  in pasture during dry summer conditions is released in autumn and winter as soils become wetter and eventually saturated, resulting in characteristic nitrate concentration peaks during July-September in pastoral streams (Wilcock et al. 1999).



Nitrification can be autotrophic or heterotrophic. Both may produce  $N_2O$ . There are three mechanisms by which  $N_2O$  can be produced during nitrification: (1) certain nitrifying bacteria produce  $N_2O$  as a byproduct during the oxidation of  $NH_4^+$  (Anderson et al. 1993); (2) some bacteria produce  $N_2O$  as an intermediate during reduction of  $NO_2^-$  to  $N_2$ . This is referred to as nitrifier denitrification (Ma et al., 2008); and (3)  $N_2O$  is produced via various interactions between the intermediates formed during  $NH_4^+$  oxidation (Stevens and Lauglin 1998). Under low  $O_2$  conditions, chemical decomposition of  $NH_2OH$  and  $NO_2$  can produce  $N_2O$  (Firestone and Davidson 1989).

#### Denitrification

Denitrification is the reduction of nitrate to nitrite, nitrogen monoxide (nitric oxide), dinitrogen oxide (nitrous oxide) and ultimately dinitrogen catalyzed by microorganisms under anaerobic conditions in the sequence outlined below.



The hole-in-the-pipe conceptual model (Davidson et al. 2000) likens losses of the gaseous intermediates  $NO$  and  $N_2O$  in the denitrification pathway, to leakage from a pipe where

their rate of evasion is dependent on (i) the total N flowing through the pipe (i.e. the amount of nitrification and denitrification occurring), and (ii) soil water content and other factors influencing the  $\text{N}_2\text{O}:\text{N}_2$  ratio (Fig. 3). The electron donors or reducing agents (in Eqs. 2-4) are typically forms of “available carbon” that can be utilised by soil microbes for reduction of nitrate.

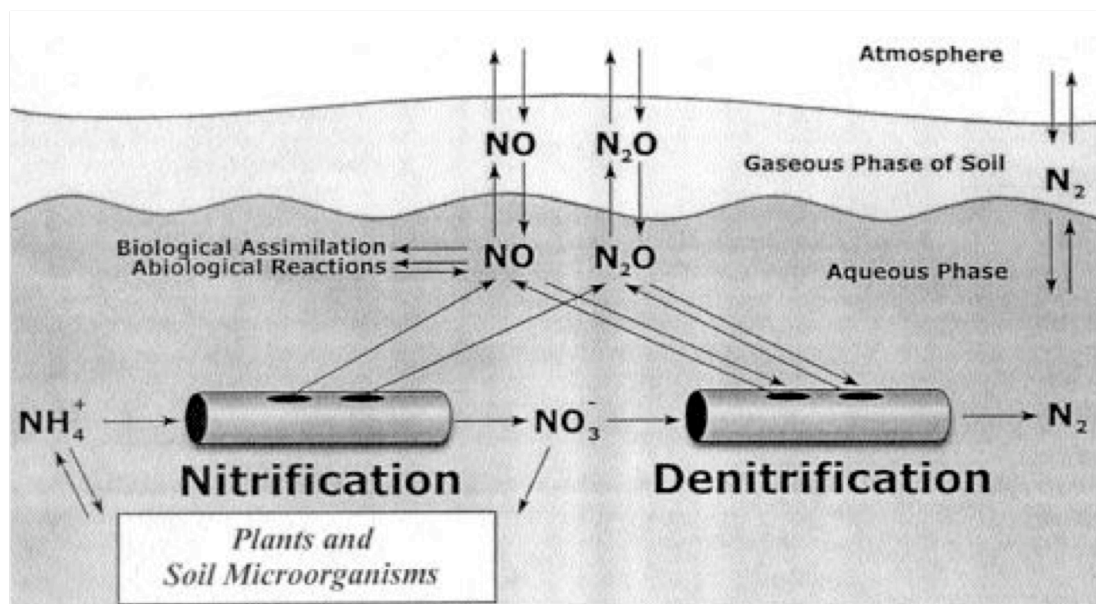
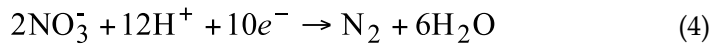
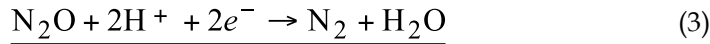
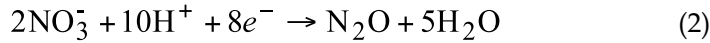


Fig. 3 The hole-in-the-pipe conceptual model (from Davidson et al. 2000). Soil emissions of NO and  $\text{N}_2\text{O}$  are regulated at two levels: (i) the rate of N cycling through the ecosystem (pipes), and (ii) the factors that influence NO and  $\text{N}_2\text{O}$  emissions, such as pH and soil water content, as depicted by the size of the holes in each pipe through which the gases “leak”.

Denitrification (coupled with ‘upland’ nitrification) is considered to be the dominant process for  $\text{N}_2\text{O}$  production in agricultural wetlands because nitrate formed from nitrification of animal wastes and nitrogenous fertiliser is the major form of soluble N in leaching and runoff (Groffman et al. 2002). Thus, the rate of production of  $\text{N}_2$  and its gaseous intermediates, NO and  $\text{N}_2\text{O}$ , in wetlands is dependent upon the rate of supply of  $\text{NO}_3^-$  as well as ambient conditions. Nitric oxide (NO) is a relatively unstable intermediate in aerobic environments and is rapidly oxidised within minutes in the atmosphere to produce nitrogen dioxide ( $\text{NO}_2$ ).

### Anammox

Anaerobic ammonium oxidation (anammox), i.e. the microbiological conversion of ammonium and nitrite to dinitrogen gas, is a comparatively recently discovered component of the biological nitrogen cycle. Discovered in 1986, it the least understood part of the nitrogen cycle. In marine ecosystems, anammox bacteria actively contribute to biological nitrogen cycling, being responsible for at least 50% of total nitrogen production in the oceans.



NO and hydrazine,  $\text{N}_2\text{H}_4$ , are intermediates of anammox. Anammox bacteria could be mediating dissimilatory nitrate reduction to ammonium in natural ecosystems and thereby produce small amounts of  $\text{N}_2\text{O}$  (Karta et al. 2007). Anammox may be the key mechanism for  $\text{N}_2$  and  $\text{N}_2\text{O}$  production in wetlands receiving high inputs of ammonium, such as anaerobic lagoons for treating animal wastes and require some oxygen for the formation of nitrite (Jones et al. 2000).

#### Dissimilatory $\text{NO}_3^-$ reduction to $\text{NH}_4^+$ (DNRA)



DNRA is performed by facultatively or obligately anaerobic bacteria using organic carbon,  $\text{H}_2$ , formate or a number of sulphur-reduced compounds as an electron donor to reduce  $\text{NO}_3^-$  (Tiedje 1988, Burgin and Hamilton 2007). Fermentative DNRA bacteria, using organic compounds (such as C) as electron donors, can reduce  $\text{NO}_2^-$  to  $\text{N}_2\text{O}$  as well as to  $\text{NH}_4^+$  but may not be able to reduce  $\text{N}_2\text{O}$  further to  $\text{N}_2$  (Stevens and Lauglin 1998). DNRA is carried out by *E.coli* and *Campylobacter sputorum* as well as species of *Citrobacter*, *Clostridia*, *Klebsiella*, *Desulfovibrio* and *Vibrio*. Microorganisms with the capability of DNRA are thought to be widespread in soil (Tiedje et al. 1982). DNRA results in transfer of eight electrons per mole of nitrate reduced compared to only five used by denitrification. It is hypothesised that this gives DNRA bacteria a competitive advantage over denitrifiers in electron donor-rich, nitrate limited environments. However, the oxidation state and pH of sediments might also be important factors determining whether  $\text{NO}_3^-$  is reduced via denitrification or DNRA. Denitrifying bacteria are typically facultative anaerobes while DNRA bacteria are generally obligately anaerobic so more highly anoxic sediments may favour DNRA while aerobic microsites around wetland plant roots may favour denitrification (Matheson et al. 2002, Burgin and Hamilton 2007). Nommik (1956) found that DNRA was favoured by strictly anaerobic conditions, high pH and large amounts of readily oxidisable organic matter.

#### Chemodenitrification

Chemodenitrification is the reduction of  $\text{NO}_2^-$  to  $\text{N}_2$  and  $\text{N}_2\text{O}$  as a result of reactions with organic compounds such as amine groups. This process is thought to be a significant source of  $\text{N}_2\text{O}$  and  $\text{N}_2$  where the bulk soil or microsite pH is  $<5$  (Stevens and Laughlin 1998).

### Summary

Nitrification can produce  $\text{N}_2\text{O}$  either as a byproduct of  $\text{NH}_4^+$  oxidation, as an intermediate of nitrifier denitrification reducing  $\text{NO}_2^-$  to  $\text{N}_2$ , or by chemical reaction between other intermediate compounds. All occur under oxygen-limited conditions. A number of bacterial groups can reduce  $\text{NO}_3^-$  to products that include  $\text{N}_2\text{O}$ .  $\text{NO}_x$  reduction represents the sum of denitrification, dissimilative reduction of  $\text{NO}_3^-$  to  $\text{NH}_4^+$ ,  $\text{NO}_x$  assimilation, and anammox. Of the  $\text{NO}_3^-$  reduction processes, only denitrification is known to produce a significant amount of  $\text{N}_2\text{O}$  (Allen et al., 2007).

### What does contemporary microbiology and biochemistry tell us?

There have been major advances in understanding the fundamental microbiology and biochemistry associated with  $\text{N}_2\text{O}$  production in recent years. As more is discovered, the more microbiologists caution about apportioning  $\text{N}_2\text{O}$  emissions to any one process or group of bacteria. For example, denitrifiers, nitrate respirers, and DNRA bacteria cannot be differentiated in situ, and autotrophic and heterotrophic nitrifiers cannot always be differentiated either (Conrad, 1996). Therefore the exact microbial basis of  $\text{N}_2\text{O}$  production and consumption is still not clear. The problem is compounded by the fact that the groups (denitrifiers, nitrifiers, nitrate respirers etc) are physiologically-defined, but are widespread amongst various taxa.

In addition, the enzymatic basis of the  $\text{N}_2\text{O}$ -producing and  $\text{N}_2\text{O}$ -consuming reactions is not well understood. The level of understanding is best for denitrification, however the biochemical pathways for enzymes involved in NO and  $\text{N}_2\text{O}$  production by other physiological groups are poorly understood.  $\text{N}_2\text{O}$  flux between the soil and the atmosphere results from complex and little understood interactions of different processes in soil that occur simultaneously. Even one process, e.g., denitrification, can be mediated by a composite of different bacterial species that may be phylogenetically distant from each other and express different types of enzymes. For example, the NO-producing nitrite reductase can be either a copper-type or a cytochrome cd-type enzyme.

Richardson and Watmough (1999) discuss the biochemical role of metal elements Mo, Fe and Cu with enzymes for each step of the denitrification pathway (Fig. 4). A heme-Fe complex assists NO reductase transform NO to  $\text{N}_2\text{O}$ . Cu complexes are catalytically involved with  $\text{N}_2\text{O}$  reductase reducing  $\text{N}_2\text{O}$  to  $\text{N}_2$ . Potentially,  $\text{N}_2\text{O}$  reduction to  $\text{N}_2$  may be limited by the availability of Cu, but this is highly speculative. In New Zealand, copper deficiency is most frequently seen on peats, podzols (for example, the Northland gumland soils), yellow-brown pumice soils derived from rhyolite ash, coastal sands, some yellow-

grey earths derived from greywacke loess, and limestone soils with high pH<sup>3</sup>. Similarly, available iron (Fe) is unlikely to be limiting for denitrification in acidic, anaerobic wetland soils in New Zealand (e.g. Eser & Rosen 1999). This is an area of current research and will be important to monitor progress in case trace metal limitation does affect denitrification and N<sub>2</sub>O evasion from New Zealand agricultural wetlands.

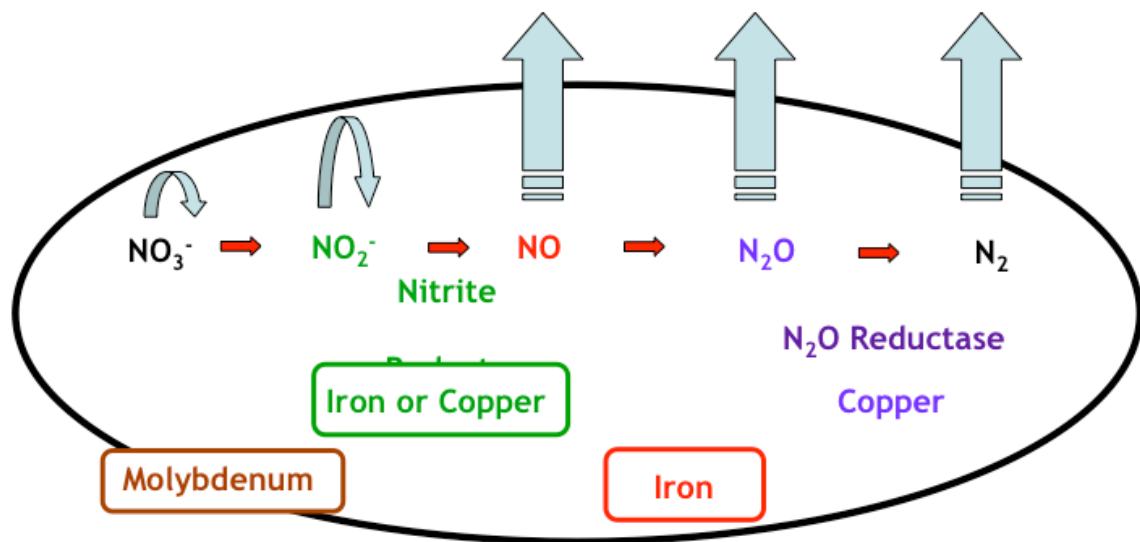


Fig. 4 Schematic showing key trace metals influence on denitrification pathways (Watmough & Thomson 2008).

<sup>3</sup> Balance Agri-Nutrients Ltd. Trace elements in the soil

Both NO and N<sub>2</sub>O production in denitrifiers are a function of the relative activity of the producing and the consuming enzymes, i.e., nitrite reductase and NO reductase for NO production and NO reductase and N<sub>2</sub>O reductase for N<sub>2</sub>O production (Conrad, 1996).

The available information on the regulation of enzyme synthesis suggests that partial pressure of O<sub>2</sub> and concentrations of nitrogen substrates are major regulators. More importantly, however, the patterns of regulation seem to be different in different species of denitrifiers. The expression of denitrifying enzymes shows different O<sub>2</sub> sensitivities for the different bacterial strains. The different effects of O<sub>2</sub> on the expression of the various bacterial nitrite reductases, NO reductases, and N<sub>2</sub>O reductases will affect whether NO or N<sub>2</sub>O is the dominant product when the O<sub>2</sub> availability in soil changes.

### Evidence from field studies

The cautionary tales of the microbiologists and biochemists notwithstanding, there appears to be good evidence that either nitrification or denitrification are the principal physiological groups of organisms leading to N<sub>2</sub>O production in soils, wetlands, and aquatic environments, with relatively logical switching points defining which of the two processes is dominant. There is of course a 'grey' area in which the environmental conditions mean that both processes can occur simultaneously and it is in riparian wetlands where such conditions are more likely than either mineral soils or aquatic sediments. We summarise the evidence on the dominant process from a number studies in Table 3.

**Table 3. Evidence for dominant biochemical pathway leading to N<sub>2</sub>O flux in field studies**

Reference	Environment	Dominant process <i>and evidence</i>
Allen et al., 2006	Mangrove sediments	Denitrification – <i>negative sediment Eh and a significant relationship between sediment nitrate levels and N<sub>2</sub>O emission; further, micro- sensor measurements revealed 2- to 3-fold higher NO<sub>x</sub> reduction rates compared to nitrification rates which suggests that denitrification was the main process controlling N<sub>2</sub>O flux</i>
Ambus, 1998	Temperate forest, grassland and agricultural soils	Nitrification or denitrification <i>depending on degree of saturation – with and without inhibitors</i>
Bedard-Haughn et al., 2006	Ephemeral wetlands	Nitrification or denitrification – <i>Stable <sup>15</sup>N isotope dilution</i>
Dhondt et al. 2004	Riparian wetlands	Denitrification – <i>high NO<sub>3</sub><sup>-</sup>-N and low NH<sub>4</sub><sup>+</sup>-N inputs via the shallow groundwater and the permanently high</i>



		<i>groundwater table suggested that nitrification did not significantly contribute to N<sub>2</sub>O emission</i>
Fey et al., 1999	Constructed wetlands treating farm dairy wastewater	Nitrification – <i>no real evidence except lower NO<sub>3</sub>-N than NH<sub>4</sub>-N in influent</i>
Freeman et al., 1997	Wetlands	Denitrification – <i>draining and flooding experiments demonstrated disruption to N<sub>2</sub>O emission and NO<sub>3</sub>-N on draining and resumption of both on flooding. The fall in nitrate release coincided exactly with the return of high nitrous oxide fluxes.</i>
Hefting et al. 2003 Hefting et al., 2006	Riparian wetlands	Denitrification- <i>Predominantly wet conditions , high nitrate and low ammonium inputs suggest nitrification would contribute little to N<sub>2</sub>O emissions from riparian buffer zones. Nitrification was almost exclusively restricted to the field border, while rates were negligible in the intermediate and stream border strips</i>
Ma et al., 2008	Ephemeral wetland soils	Nitrification dominant but also some denitrification – <i><sup>15</sup>N isotope experiments</i>
McSwiney et al., 2001	Tropical rainforest catena	Nitrification or denitrification – <i>techniques did not allow separation but a sequence of aerobic and anaerobic sites</i>
Stepanauskas et al., 1996	Saturated wetland soils	Denitrification – <i><sup>15</sup>N isotope pairing and dilution. DNRA shown to be negligible.</i>
Verhoeven et al., 1996	Mires (wetlands)	Nitrification – <i>evidence only that nitrification and N<sub>2</sub>O emission showed a strong positive correlation with soil redox status which indicates that “nitrification rather than denitrification is the process limiting N<sub>2</sub>O evolution”</i>

### Important points

- A number of microbially-mediated biochemical pathways (nitrification, denitrification, Anammox, DNRA) and chemodenitrification can produce N<sub>2</sub>O as intermediate products.

- The microbial ecology is complex and the exact basis of N<sub>2</sub>O production and consumption is still not clear at either a microbial or enzymatic level. Microbiologists caution about apportioning N<sub>2</sub>O emissions to any one process or group of bacteria.
- Partial pressure of oxygen and concentrations of nitrogen substrates are the major regulators of enzyme synthesis leading to N<sub>2</sub>O accumulation.
- Most riparian wetland field studies that have provided reasonable evidence for the pathway leading to N<sub>2</sub>O accumulation have concluded that denitrification is mostly responsible. However there have also been some studies using <sup>15</sup>N isotopes that have found evidence for significant nitrification.
- From a management viewpoint, the microbial process responsible for N<sub>2</sub>O production is less important than understanding the environmental conditions that result in high rates of N<sub>2</sub>O emission.

## 2.4 N<sub>2</sub>O flux as a function of environment

### Introduction

Studies done by microbiologists and biochemists show that N<sub>2</sub>O production is relatively higher under conditions that are suboptimal for either nitrification or denitrification (section 2.3). However, under field conditions, the simultaneous and interactive influence of different factors results in great variability. It is therefore difficult to predict which circumstances are enhancing or limiting the microbial processes on the one hand, and the fraction of N<sub>2</sub>O (compared with other products) produced on the other (Hefting et al., 2003; Conrad, 1996).

The principal environmental variables identified as being correlated with N<sub>2</sub>O production in riparian wetland systems are: nitrate availability, Eh (oxygen status), carbon availability, water filled pore space (relates to Eh), presence of plants (relates to Eh and carbon availability), temperature, and pH. Despite the complexity alluded to above and the interaction between these variables, some authors have attempted to isolate single factor relationships between the the environmental variable and N<sub>2</sub>O production. Such relationships, together with those describing physical constraints on N<sub>2</sub>O emission to the atmosphere are useful for formulating a conceptual model of N<sub>2</sub>O emissions from wetlands in the New Zealand pastoral landscape.

### pH

The ratio of  $\text{N}_2\text{O}:\text{N}_2$  increases with decreasing pH in poorly drained soils (Groffman et al., 2000, Fig 5). Along with soil  $\text{O}_2$ , Groffman et al. (2000) hypothesised that low pH can denature the  $\text{N}_2\text{O}$  reductase enzyme. This would imply that  $\text{N}_2\text{O}$  reductase is more sensitive to low pH than the enzymes regulating nitrate, nitrite, and nitric oxide reduction, respectively.

The above study is the only one we have found that plots a definitive relationship between  $\text{N}_2\text{O}:\text{N}_2$  and pH. This does not necessarily imply that absolute  $\text{N}_2\text{O}$  emissions increase with decreasing pH as it is well established that denitrification activity decreases at low pH (Freeman et al., 1997; Hefting et al., 2006). In addition, Ullah et al. (2005) reported significantly higher  $\text{N}_2\text{O}$  emission from a cultivated soil of pH 6.1 than an adjacent forest soil of pH 5.4, even though both had similar denitrification activity; a result that they attributed to the forest soil having higher available organic carbon reserves.

In a situation where denitrification itself is 'stressed' and/or the supply of electron acceptors ( $\text{NO}_3^-$ ) is low, the little that is produced is less likely to be further reduced. Studies on a vigorously denitrifying constructed wetland (Picek et al., 2007) support this premise as denitrification activity was markedly reduced when pH was artificially lowered to ~5, but only then was  $\text{N}_2\text{O}$  detected.

In a study of 20 grassland soils with diverse physical and chemical characteristics, Malone (1997) found that soil pH was the variable having the most influence on the mole fraction of  $\text{N}_2\text{O}$  while %WFPS was the main factor affecting the total  $\text{N}_2 + \text{N}_2\text{O}$  flux. An increase of one pH unit lowered the  $\text{N}_2\text{O}$  mole fraction by 0.2 (Cited in Stevens and Laughlin 1998).

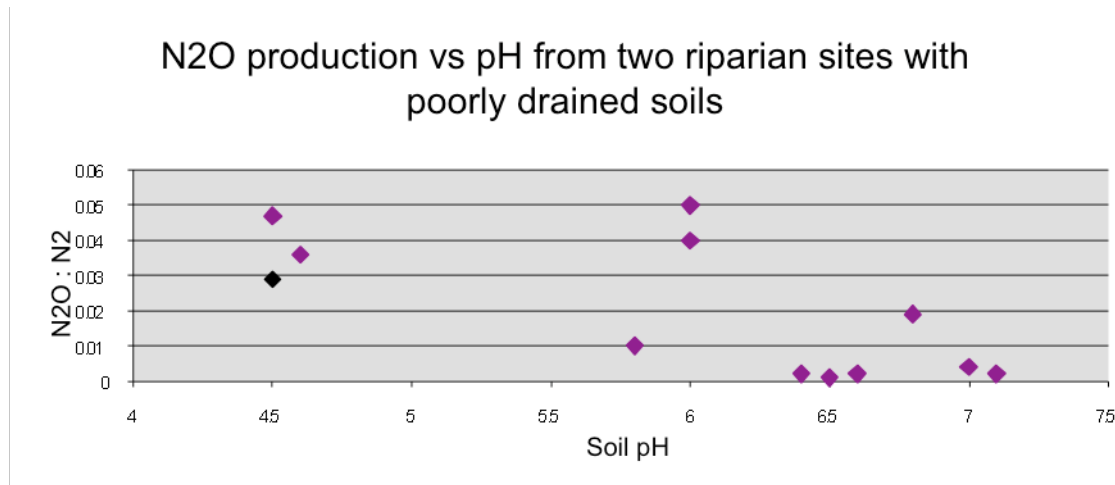


Fig. 5  $\text{N}_2\text{O}:\text{N}_2$  ratio versus pH in mesocosms from two riparian sites with poorly drained soils (from Groffman et al., 2000)

Important points	
	<ul style="list-style-type: none"> <li>The ratio <math>\text{N}_2\text{O}:\text{N}_2</math> increases with decreasing pH, but so does the overall rate of denitrification.</li> </ul>
	<ul style="list-style-type: none"> <li>pH does not seem to be an important driver of <math>\text{N}_2\text{O}</math> flux within the range of pH (4-7) common in New Zealand wetlands (Tank &amp; Winterbourne, 1995).</li> </ul>

## Oxygen

As with pH, there are few definitive single factor studies linking  $O_2$  concentrations with  $N_2O$  concentrations in riparian wetlands. Oxygen controls the proportion of  $N_2O$  produced by nitrification and denitrification but is not consumed or produced by the processes, so should be a good predictor of  $N_2O$  production. However, McSwinney et al., (2001) present one of the few studies to make this link directly. Using soil-air probes deployed over a transect from true upland to true wetland they showed a pronounced peak in  $N_2O$  at 11%  $O_2$  (Fig. 6). Oxygen concentrations were lower and changed more with depth in the slope-riparian break, riparian zone, and streambank topographic positions.

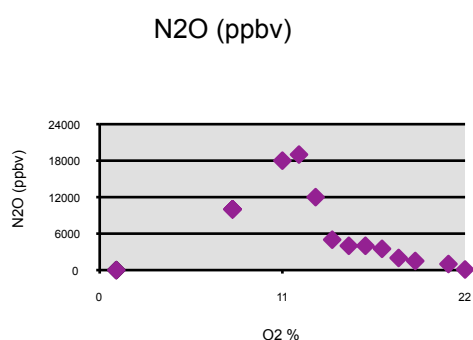


Fig. 6. Relationship between  $O_2$  and  $N_2O$  in soil-air probes across a tropical rainforest catena (abstracted from McSwinney et al., 2001).

A very similar relationship was obtained by Stepanauskas et al. (1996) who used  $^{15}N$  isotope pairing and dilution to study  $N_2O$  efflux in wetland soil cores in response to 4 different infiltration rates of nitrate-enriched water. They reported that the greatest  $N_2O$  efflux corresponded to 8% dissolved oxygen (DO) in the infiltrated water and that at 0% and 38% DO,  $N_2O$  efflux was 10 and 5 times less, respectively.

The relationships between  $N_2O$  and  $O_2$  in both soil and groundwater were consistent with laboratory studies on nitrification and denitrification, which show that  $N_2O$  is produced when  $O_2$  concentrations are not optimal for each process (Hynes & Knowles, 1984; Tiedje, 1988).

### Important points

- Oxygen concentration controls the proportion of  $N_2O$  produced by both nitrification and denitrification.
- Greatest  $N_2O$  efflux appears (from 2 studies) to correspond to oxygen concentrations in the range 8-11%.

### Water filled pore space (WFPS)

Both the concentration of oxygen in soil air and the dissolved oxygen concentration in wetland water are difficult to measure accurately and hence there are few studies on the relationship between oxygen concentration and  $\text{N}_2\text{O}$ . There are, however considerably more that have used the more readily measured “water filled pore space”, which simply gives a measure of the percentage of soil pores filled with water. This is not strictly analogous to soil oxygen in that the dissolved oxygen concentration within the water filled pores is not known, but where pores are not filled, atmospheric oxygen can be dispersed directly to the exterior of soil peds where it can promote nitrification. The diffusion rate of oxygen through aqueous media is considerably slower than through porous media.

Many wetlands undergo alternate wetting and drying cycles and due to this, changing oxygen status. Since  $\text{N}_2\text{O}$  production from both nitrification and denitrification processes is sensitive to oxygen concentration, there are reasons to suspect that flooding and draining of a soil will influence the  $\text{N}_2\text{O}$  emissions (Davidson et al., 1997).

There are a number of wetland studies that have shown that when  $\text{WFPS} < 60 - 70\%$ ,  $\text{N}_2\text{O}$  emissions are low (Ambus & Christensen, 1995; McKenny & Drury, 1997; Ullah et al., 2005; Bernard-Haughn et al., 2006; Hefting et al., 2006) and that conversely increasing saturation (above 70%) is a necessary but not sufficient condition for appreciable  $\text{N}_2\text{O}$  flux (Regina et al., 1999; Dowrick et al., 1999; Davidsson et al., 2002; Ullah et al., 2005). In all cases a source of  $\text{NO}_3^-$  was a necessary precursor consistent with denitrification being the mechanism responsible for  $\text{N}_2\text{O}$  flux. Thus there is no robust relationship describing  $\text{N}_2\text{O}$  production as a function of WFPS; only a boundary condition that crudely describes whether significant  $\text{N}_2\text{O}$  emission is likely.

In terms of water table management Regina et al. (1999) showed that lowering the water table on peat monoliths even by 25 cm was sufficient to get an increase in  $\text{N}_2\text{O}$  production. Conversely raising the watertable again reduced  $\text{N}_2\text{O}$  emission, possibly because nitrification was cut off, or the elevated water table facilitated the conversion of  $\text{N}_2\text{O}$  through to  $\text{N}_2$ . Davidsson et al. (2002) also noted that no spontaneous production of  $\text{N}_2\text{O}$  occurred in flooded soils, whereas at a drained site, an increase in spontaneous  $\text{N}_2\text{O}$  concentration was measured. The higher denitrification in the drained area seems paradoxical compared to the general idea that flooding promotes denitrification, however in  $\text{NO}_3^-$  limited systems draining allows oxidation in the topsoil layers promoting production of  $\text{NO}_3^-$  by nitrification. This  $\text{NO}_3^-$  can then diffuse to anaerobic microsites, where it is denitrified.

#### Important points

- There is no simple relationship between WFPS and  $\text{N}_2\text{O}$  emissions, but a threshold of  $>60-70\%$  WFPS appears necessary before significant  $\text{N}_2\text{O}$  emission occurs.
- Where  $\text{NO}_3^-$  supply from external sources is limited, lowering the water table is necessary to get a spontaneous increase in  $\text{N}_2\text{O}$  emissions.

**Eh**

Yu et al. (2001, 2006) have shown that  $\text{N}_2\text{O}$  accumulates only within a very small range in soil redox potential between +120 and +250mV. Very little  $\text{N}_2\text{O}$  emission occurred at redox potentials outside of this range (Fig. 7). Cooke & White (1987) found a very similar narrow range of redox corresponding to a zone of maximum denitrification activity in sediment microcosms in which the overlying water was nitrate-enriched.

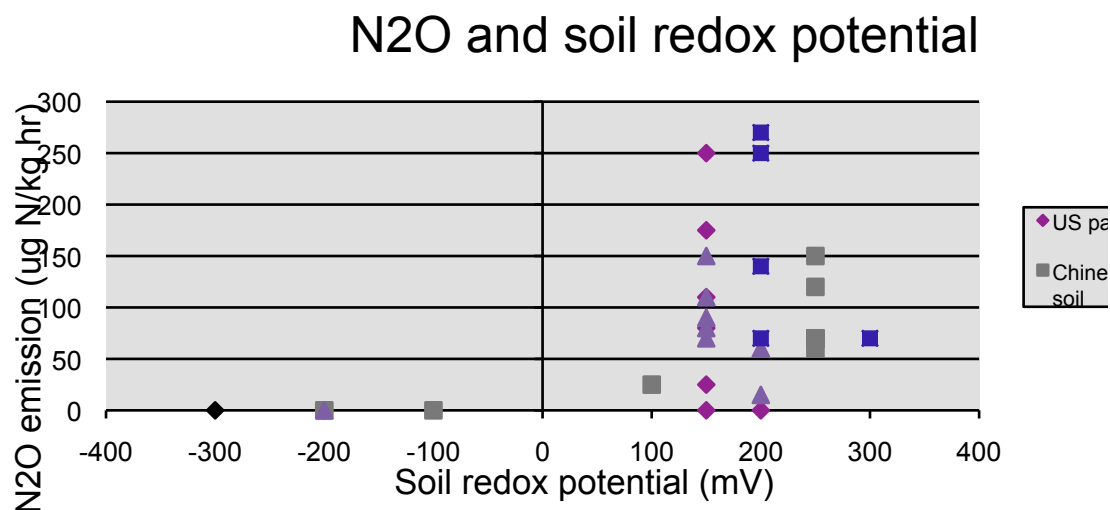


Fig. 7.  $\text{N}_2\text{O}$  emissions in paddy soils at different redox potentials (abstracted from Yu et al., 2001, 2006)

Yu et al. (2006) noted that the microenvironment in structured soil aggregates consists of an outer aerobic layer (characterized by high Eh), and an inner anaerobic, reducing core (characterized by low Eh). Nitrous oxide can be produced at the outer oxidizing (for nitrification) and moderately reducing (for denitrification) layers of the soil aggregates where the soil Eh levels are close to what can be conventionally measured using a Pt-electrode. However,  $\text{N}_2\text{O}$  produced at the outer layers probably can move through the oxidizing soil pore space and emit to the atmosphere without significant loss, because  $\text{N}_2\text{O}$  can only be consumed by reduction to  $\text{N}_2$  under more reducing conditions. Such an Eh stratification in the soil microenvironment likely disappears in continuously flooded soils or wetlands when the entire soils become reducing with low Eh measured. When the reducing conditions in the soils are intense enough, complete denitrification is likely to occur with  $\text{N}_2$ , instead of the intermediate product of  $\text{N}_2\text{O}$ , as the end product. Within a typical riparian wetland found in a New Zealand pastoral environment this complete range of redox conditions are likely.

Hedin et al. (1998) formulated a thermodynamic equilibrium-based model (Fig. 8) that predicted  $\text{N}_2\text{O}$  accumulation would occur within a narrow range of redox state. They proposed that the effectiveness of denitrification as a mechanism for N retention depends critically on whether microbial denitrification reactions are thermodynamically favored in

riparian environments with rapid throughput of terrestrially-derived water. It should be noted, however, that in a natural environment such as a riparian wetland nonequilibrium conditions are more typical.

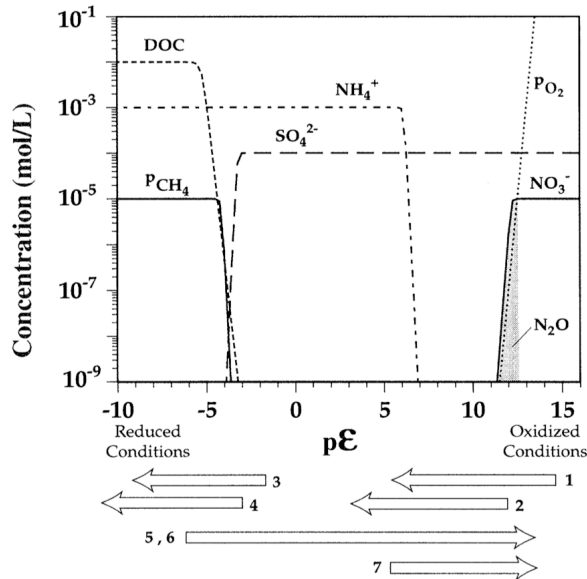


Fig. 8. Predicted thermodynamic equilibrium concentrations of selected electron donors and acceptors as a function of the redox state  $pE$  of the environment at pH 7 (from Hedin et al., 1998). Note the narrow shade area where  $N_2O$  is predicted.

#### Important points

- Nitrous oxide accumulates only within a very small range in redox potential between +120 and +250mV.

#### Temperature

While temperature is positively correlated with denitrification activity (Yu et al., 2007) there is no robust relationship between temperature and  $N_2O$  emissions from wetlands (Davidsson et al., 1997). Analysis of variance has found a positive relationship between  $N_2O$  emission and wetland soil temperature but only in combination with  $NO_3^-$  concentration (Fey et al., 1999). The lack of relationship with temperature alone may be due to the confounding physical effects of temperature on gas diffusion and the solubility of  $N_2O$  in water. These physical effects are covered in more depth in section 2.5. Significant seasonal variation in  $N_2O$  emissions has been reported in temperate wetlands (Liikanen et al., 2006, Allen et al., 2007) some of which may be due to changes in temperature per se, but some may be also due to seasonal variation in other factors (e.g. WFPS and nitrate supply).

#### Important points

- Although temperature is positively correlated with denitrification, there is no

robust relationship between temperature and N<sub>2</sub>O emissions from wetlands**Nitrate concentration**

As we have established that N<sub>2</sub>O production is primarily the result of denitrification in wetland systems and denitrification requires NO<sub>3</sub><sup>-</sup> as an electron acceptor, it is perhaps not surprising that many studies have found a positive relationship between NO<sub>3</sub><sup>-</sup> concentration and N<sub>2</sub>O flux (Franken et al., 1992; Ambus & Christensen, 1995; Davidsson et al., 1997; Kang et al., 1998; Fey et al., 1999; Groffman et al., 2000; Hernandez and Mitsch, 2006). While all these studies have reported that N<sub>2</sub>O flux increases with increasing NO<sub>3</sub><sup>-</sup> (usually in combination with temperature or some other environmental controller), only Kang et al. 1998 present a single factor quantitative relationship (Fig. 9) and this from controlled laboratory conditions.

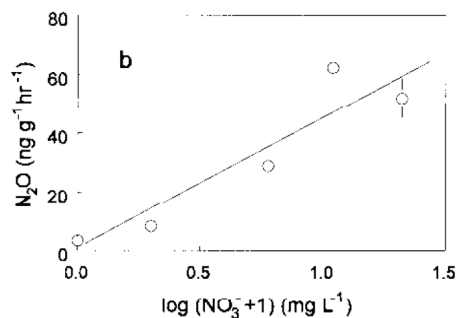


Fig. 9 Relationship between NO<sub>3</sub><sup>-</sup> and N<sub>2</sub>O flux in Welsh fen soils (Kang et al., 1998)

While the complexity of both the processes involved and natural variability in the field explains why there is not a more definitive field-based relationship, there is compelling evidence that in riparian wetland situations, NO<sub>3</sub><sup>-</sup> is the main driver of N<sub>2</sub>O flux. While the further reduction of N<sub>2</sub>O to N<sub>2</sub> is influenced by low pH and high soil O<sub>2</sub> levels that can denature the N<sub>2</sub>O reductase enzyme (Groffman et al., 2000) the reduction can also be affected by the demand for electron acceptors, i.e., if NO<sub>3</sub><sup>-</sup> levels are low and denitrification rates are high, N<sub>2</sub>O is more likely to be reduced but if NO<sub>3</sub><sup>-</sup> levels are high and denitrification rates are also high, then a greater proportion will not be reduced. Other studies (Cho *et al.*, 1997; Swerts *et al.*, 1997; Dendooven *et al.*, 1997; Blicher-Mathiesen and Hoffman, 1999; Well *et al.*, 2001) have shown that during the initial stages of denitrification and in the presence of significant nitrate inputs, NO<sub>x</sub>-N may be denitrified to N<sub>2</sub>O and not fully reduced to N<sub>2</sub>. However when NO<sub>x</sub>-N becomes limited (< 2 mg L<sup>-1</sup>), N<sub>2</sub>O that is dissolved in wetland water is reduced to N<sub>2</sub> by microbes due the demand for electron acceptors (Weier et al. 1993; Schipper & Vojvodić-Vuković, 1998). Cooper (1990) reported NO<sub>3</sub><sup>-</sup> removal rates in excess of 90% within the first five metres of a riparian wetland in a New Zealand hill pasture catchment, coincident with an extremely large in situ denitrification rate (equivalent to ~26 tonnes N ha<sup>-1</sup> y<sup>-1</sup>). While Cooper (1990) did not measure N<sub>2</sub>O (without acetylene block) it would seem reasonable in view of the above



discussion, that a significant proportion of his reported denitrification activity was produced as  $N_2O$  and not reduced further to  $N_2$ .

In New Zealand pastoral situations there is a pronounced seasonal variability in the concentration and flux of  $NO_3^-$  entering riparian wetlands (Cooke and Cooper, 1988). Recent stream studies (Wilcock & Sorrell 2008) show that  $N_2O$  concentrations covary with  $NO_3^-$  concentration (Fig. 10). The seasonality of  $NO_3^-$  concentration in pasture soil solution and in rivers receiving drainage from pasture (e.g. Wilcock et al. 1999) therefore has an important bearing on  $N_2O$  fluxes from wetlands in pastoral catchments

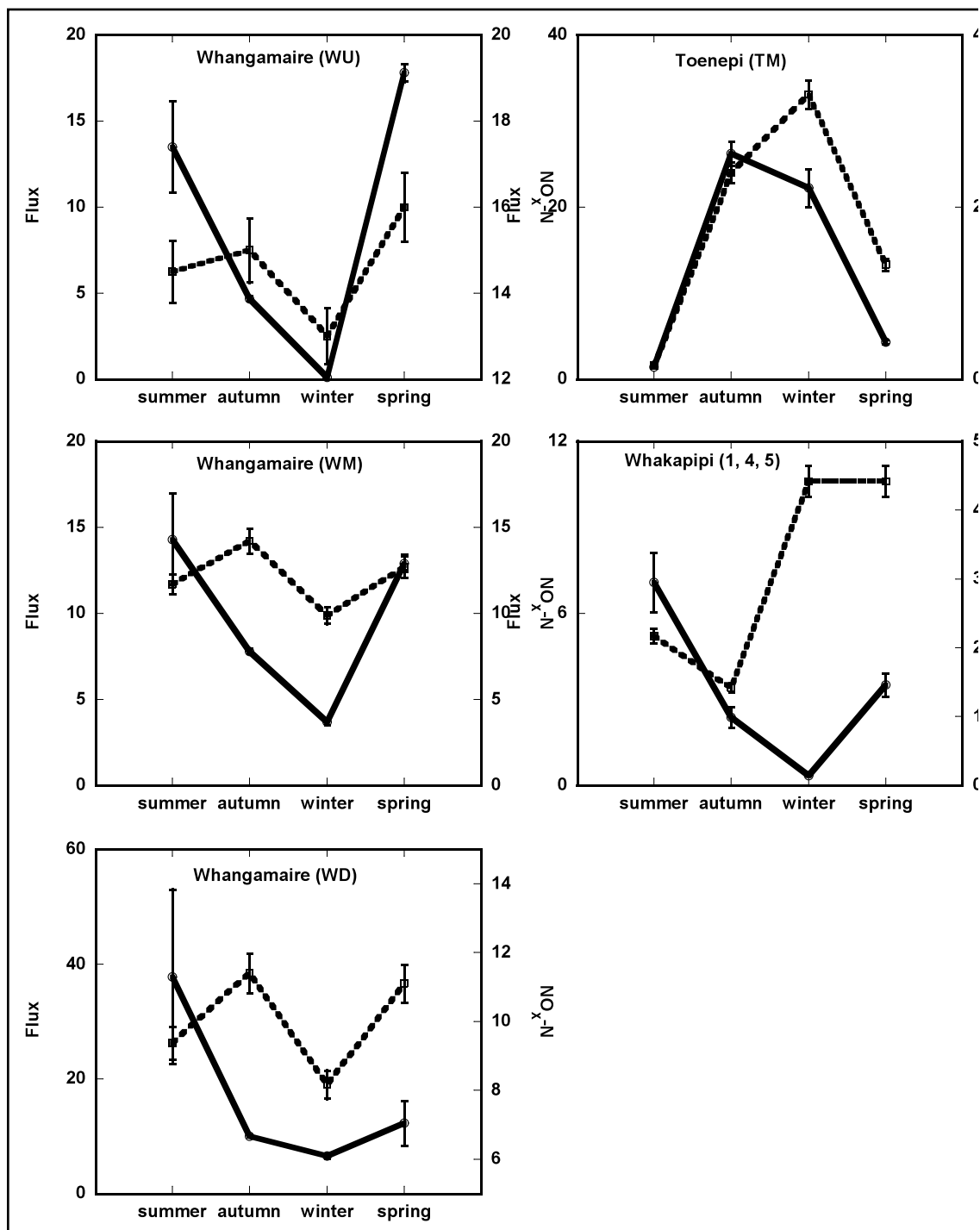


Fig. 10 Seasonal average  $\text{N}_2\text{O}$  fluxes (—) ( $\mu\text{mol m}^{-2} \text{hr}^{-1}$ ) and  $\text{NO}_x\text{-N}$  concentrations (•••) ( $\text{g m}^{-3}$ ) for three lowland streams in agricultural catchments. (Wilcock & Sorrell 2008).

Important points	
	<ul style="list-style-type: none"> <li>In riparian wetlands, there is compelling evidence that <math>\text{NO}_3^-</math> is the main driver of <math>\text{N}_2\text{O}</math> flux.</li> </ul>
	<ul style="list-style-type: none"> <li>Further reduction of <math>\text{N}_2\text{O}</math> to <math>\text{N}_2</math> appears regulated by the supply of electron acceptors. Where <math>\text{NO}_x^-</math> levels are low and denitrification rates are high, <math>\text{N}_2\text{O}</math> is likely to be reduced to <math>\text{N}_2</math>. However where electron acceptors (<math>\text{NO}_x^-</math>) are plentiful, then a greater proportion of <math>\text{N}_2\text{O}</math> will not be reduced further.</li> </ul>

### Available carbon and the C:N ratio

Whilst  $\text{N}_2\text{O}$  is a product of denitrification, it is carbon and more particularly, available carbon, which provides the energy for growth of denitrifying microorganisms (Tiedje, 1988). A direct linkage between available carbon levels in soils/wetlands and  $\text{N}_2\text{O}$  emissions is far from clear. Several studies have used the soil (wetland) C/N ratio as an indicator of  $\text{N}_2\text{O}$  and have concluded that when this ratio is  $> 25$ , essentially zero  $\text{N}_2\text{O}$  accumulates (Hefting et al., 2003; Klemmedtsson et al., 2005; Ullah et al., 2005; Ullah & Zinati, 2006; Hunt et al., 2007). In other words a C/N ratio of  $< 25$  is a threshold for  $\text{N}_2\text{O}$  production. This suggests in effect that  $\text{N}_2\text{O}$  accumulation only occurs in soils enriched with N. With the exception of Ullah et al. (2005), all the studies above took place in N enriched systems, whether by runoff, leaf amendment or N fertiliser. It is likely that the C/N ratio in the soils of the Whangamata forest receiving high rates of irrigated sewage effluent and with very high  $\text{N}_2\text{O}$  emissions rates (Schipper et al., 1993) also have a C/N ratio  $< 25$ . This similarity between the results indicates that soil C/N ratio may be a robust threshold indicator of  $\text{N}_2\text{O}$  production.

However the C/N ratio in itself does not tell us what is the underlying mechanism leading to  $\text{N}_2\text{O}$  accumulation at  $\text{C/N} < 25$ . Is it high N or low C? Ullah & Zinati (2006) reported that while microbial biomass C and total soil C are good predictors of denitrification they were not so for  $\text{N}_2\text{O}$  production whereas microbial biomass N and total soil N were much better. This would indicate that higher soil N pools, greater potential nitrification rates leading to higher localised  $\text{NO}_3^-$  concentrations may have reduced soil  $\text{N}_2\text{O}$  reductase activity, which has led to higher  $\text{N}_2\text{O}$  emissions. Alternatively a high C/N ratio (and low  $\text{N}_2\text{O}$  emissions) may simply be indicative of high available C leading to more complete oxygen reduction in the riparian soil, thus promoting more reduction of any  $\text{N}_2\text{O}$  produced through to  $\text{N}_2$  (Freeman et al., 1997; Ullah et al., 2005).

Particularly in the case of a riparian wetland, which is a transition zone between terrestrial and aquatic ecosystems, the C/N ratio may not be relevant because of the variability that is likely to exist. For example Jacinthe et al. (1998) demonstrated hotspots in denitrification activity in riparian wetland soil due to patchiness of particulate organic matter. (Clough et al. 2007) also found high variability between replicates in a riparian zone indicating 'hot

spots' for denitrification. They also demonstrated areas where  $\text{N}_2\text{O}$  was conserved despite a high denitrification rate. These conditions could represent a situation of patches where  $\text{N}_2\text{O}$  emissions could be relatively high (not going through to  $\text{N}_2$ ) or alternatively it may indicate a lag for  $\text{N}_2\text{O}$  reductase to be produced.

Blicher-Mathiesen & Hoffmann, (1999) provide evidence for the latter mechanism in a study that looked at  $\text{NO}_3^-$ ,  $\text{O}_2$ ,  $\text{N}_2$ , and  $\text{N}_2\text{O}$  following a transect from a hillside with high  $\text{NO}_3^-$  into a fen (permanently saturated wetland). They found that  $\text{NO}_3^-$  decreased to near zero within 8m of the fen boundary,  $\text{O}_2$  decreased to zero along same transect,  $\text{N}_2\text{O}$  fell to zero from 8m -15m into the fen and dissolved  $\text{N}_2$  increased. This indicates that although  $\text{N}_2\text{O}$  was produced it was further reduced to  $\text{N}_2$  in this water-saturated environment.

We conclude therefore, that although C/N ratio of 25 provides a useful threshold indicator of  $\text{N}_2\text{O}$  accumulation, it is of little use in a deterministic sense.

Important points
<ul style="list-style-type: none"> <li>The C:N ratio in wetland soil is a useful indicator of when significant <math>\text{N}_2\text{O}</math> production will occur. If C:N &gt; 25, essentially zero <math>\text{N}_2\text{O}</math> accumulates.</li> </ul>
<ul style="list-style-type: none"> <li>High soil C is a good predictor of total denitrification but not so for <math>\text{N}_2\text{O}</math> production where total soil N is much better.</li> </ul>
<ul style="list-style-type: none"> <li>It is unclear as to whether the relationship with C:N ratio is due to high localised soil N (<math>\text{NO}_3^-</math>) concentrations causing less <math>\text{N}_2\text{O}</math> reductase and hence higher <math>\text{N}_2\text{O}</math> production, or whether high C results in more complete <math>\text{O}_2</math> removal and hence optimal conditions for complete reduction to <math>\text{N}_2</math>.</li> </ul>

### Sulphide

$\text{H}_2\text{S}$  has been shown to play a key role in the regulation of  $\text{N}_2\text{O}$  accumulation in eutrophic lagoon sediments. Senga et al (2006) showed that  $\text{H}_2\text{S}$  had marked inhibiting and retarding effects on  $\text{N}_2\text{O}$  reduction in lagoon sediments. In anaerobic freshwater sediment slurries, Brunet and Garcia-Gil (1996) found that at very low free sulphide concentrations, nitrate reduction occurred via denitrification but with higher sulphide, there was dissimilatory reduction to ammonium and incomplete denitrification yielding  $\text{N}_2\text{O}$ . Free sulphide is considered to inhibit the final two steps in the denitrification sequence (Burgin and Hamilton 2007).

Important points
<ul style="list-style-type: none"> <li>High concentrations of free sulphide cause incomplete denitrification yielding <math>\text{N}_2\text{O}</math>.</li> </ul>

### The $\text{N}_2\text{O}:\text{N}_2$ ratio as a predictor of $\text{N}_2\text{O}$ emission

Pioneering studies on  $\text{N}_2\text{O}$  emission from riparian wetlands by Groffman et al., (2000) demonstrated a large variation in the ratio of  $\text{N}_2\text{O}:\text{N}_2$  and suggested that this ratio is a critical controller of riparian  $\text{N}_2\text{O}$  emission. While many subsequent studies have used this ratio as an indicator of conditions conducive to  $\text{N}_2\text{O}$  evolution, none have been able to successfully relate it to environmental conditions. In fact recent studies by Hefting et al., (2006) cast doubt on the whole premise that the ratio of  $\text{N}_2\text{O}:\text{N}_2$  can be a 'controller' of  $\text{N}_2\text{O}$  emission because of its high variability and the weak relationship with environmental variables including WFPS and pH. They concluded that the  $\text{N}_2\text{O}:\text{N}_2$  ratio is not an important indicator of  $\text{N}_2\text{O}$  emissions from riparian buffers and that when the focus was placed on the absolute  $\text{N}_2\text{O}$  emission rates, absolute denitrification rates and nitrate removal from the shallow groundwater seemed to be more useful factors.

#### Important points

- Recent studies have cast doubt on the hypothesis that the ratio of  $\text{N}_2\text{O}:\text{N}_2$  can be a controller of  $\text{N}_2\text{O}$  emission because of its high variability and the weak relationship with environmental variables.

## 2.5 The importance of physical processes governing net $\text{N}_2\text{O}$ emissions to the atmosphere

Thus far we have considered the environmental factors leading to  $\text{N}_2\text{O}$  production in riparian wetlands. However  $\text{N}_2\text{O}$  production does not necessarily lead to  $\text{N}_2\text{O}$  emissions. If an  $\text{N}_2\text{O}$  molecule can readily diffuse from the site of production into an oxygenated pore it has a good chance of being emitted to the atmosphere rather than being reduced to  $\text{N}_2$ . On the other hand, if the gaseous transfer of the  $\text{N}_2\text{O}$  molecule is impeded by soil water for example, then  $\text{N}_2\text{O}$  diffusion will decrease by approximately four orders of magnitude thereby increasing the time for microbial reduction of  $\text{N}_2\text{O}$  to  $\text{N}_2$  gas before its emission into the air (Smith et al., 2003; Clough et al. 2005).

As discussed in Section 2.3, both nitrification and denitrification can produce  $\text{N}_2\text{O}$  in riparian wetlands under conditions where oxygen status for either process is not optimal. With nitrification, the rate of  $\text{N}_2\text{O}$  production, and the ratio of  $\text{N}_2\text{O}$  to nitrate produced during nitrification all increase as the soil WFPS increases provided  $\text{O}_2$  is also present. With denitrification, the optimum WFPS for  $\text{N}_2\text{O}$  production appears to be around 70% when respiratory consumption of  $\text{O}_2$  in the soil exceeds the rate of replenishment by diffusion from the atmosphere; and  $\text{NO}_3^-$  is also present. Thus the efflux of  $\text{N}_2\text{O}$  to the atmosphere from both processes depends on a complex interaction of biochemical and physical process,

and in particular the proximity of a gaseous diffusion pathway from the point of  $\text{N}_2\text{O}$  production (Ambus, 1998).

In riparian wetlands, plants may provide the gaseous diffusion pathway that circumvents the diffusion-induced barrier caused by overlying water. Wetland soils containing plants appear to emit more  $\text{N}_2\text{O}$  than those without plants (Henandez & Mitsch, 2006; Cheng et al., 2007; Picek et al., 2007; Ström et al., 2007). Henandez & Mitsch (2006) found that  $\text{N}_2\text{O}$  fluxes were higher in plots with plants than in plots without plants when they were inundated, but plants did not have any effect on  $\text{N}_2\text{O}$  fluxes when they were exposed to air. They attributed this to the aerenchymal system being more active in transporting oxygen from the shoots to the roots and probably transporting gases from the soil to the atmosphere under flooded conditions than under exposed conditions. Wetland plant species vary in their capacity to transport gases and Ström et al. (2007) reported that plots containing *Phragmites* emitted twice the amount of  $\text{N}_2\text{O}$  than plots containing *Juncus* ( $0.078$  vs  $0.039 \text{ kg N}_2\text{O ha}^{-1}\text{d}^{-1}$ ).

The distribution of  $\text{N}_2\text{O}$  source regions in a riparian wetland is therefore a complex three-dimensional mosaic of anaerobic microsites producing  $\text{N}_2\text{O}$  within an otherwise aerobic matrix (eg. in overlying water and the sediment-water interface), and aerobic passages (plant culms) within an otherwise anaerobic matrix (eg. deeper within the sediments). Wetting and drying processes result in a dynamic reorganisation of these microsites, which can significantly change the amount of  $\text{N}_2\text{O}$  emitted through increasing or decreasing gaseous diffusion pathways. The principal physical processes affecting these pathways are temperature and water saturation (WFPS).

Many research studies have reported non-linear (exponential) increases in  $\text{N}_2\text{O}$  emission rate with increasing temperature. The temperature dependence is commonly and conveniently expressed in terms of the  $Q_{10}$  value, but observed values for the  $Q_{10}$  for  $\text{N}_2\text{O}$  emission range up to 10 or more, compared with the general range of 2–3 for most biochemical processes. An explanation for this marked response is provided by the theory of anaerobic zone development in soils. An increase in temperature leads to an increase in the size of the zones, because of increased respiration causing larger gradients in  $\text{O}_2$  and thus rendering more of the soil volume devoid of oxygen (Figure 11). An increase in temperature also decreases the solubility of  $\text{N}_2\text{O}$  in a nonlinear way and increases  $\text{N}_2\text{O}$  diffusion to air, and thus restricts the microbial reduction of  $\text{N}_2\text{O}$  to  $\text{N}_2$ . Therefore, the  $\text{N}_2\text{O}$  emission resulting from increasing temperature is not only the function of temperature-produced  $\text{N}_2\text{O}$  by microbial processes, but also temperature-induced  $\text{N}_2\text{O}$  solubility (Yu et al., 2007).

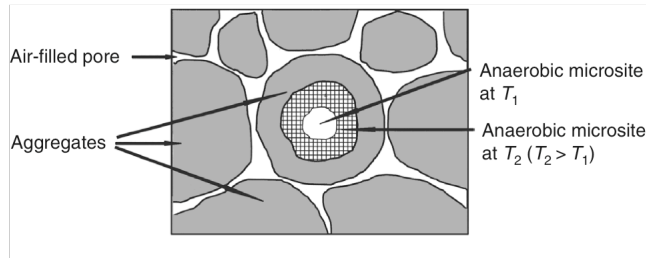


Fig 11. Conceptual relation between the size of an anaerobic microsite and the soil temperature (Smith et al., 2003).

An increase in soil WFPS, and the consequent decrease in  $O_2$  diffusion rate within the soil, has a similar effect on the system to that induced by a rise in temperature. Where the only supply of  $NO_3^-$  is from nitrification, raising the watertable will decrease  $N_2O$  emissions by cutting off the supply of  $NO_3^-$  and slowing the diffusion of  $N_2O$  (Regina et al., 1999). If, however, the water causing the rise in water table contains high  $NO_3^-$  then there may be an increase in  $N_2O$  production (Freeman et al., 1997). Where the rise in water table has been caused by a flux of upslope groundwater, then, depending of the path length, the  $N_2O$  in solution may be 'flushed' into stream channels (McSwinney et al., 2001; Wilcock & Sorrell, 2008) before it is further reduced to  $N_2$ .

Whether  $N_2O$  in solution is further reduced to  $N_2$  will depend upon the length of the hydrological pathway (Blicher-Mathiesen & Hoffman, 1999; Jacinthe et al., 2000) and the  $NO_3^-$  concentration of the throughflowing water. Due to the microbial preference for the reduction of nitrate above  $N_2O$ , further reduction of  $N_2O$  would be more likely in soil solutions that are relatively low in nitrate (Hefting et al., 2003).

Other than plant-mediated gas release, the primary mechanism for air-water exchange of gases in wetlands is wind shear at the air-water interface (Wilcock & Sorrell, 2008).

Gaseous evasion from wetlands, or flux ( $F$ ) (Eq. 7), is the product of  $k_{gas}$  the gas exchange velocity across the air-water interface and  $\Delta C$ , the difference between the aqueous dissolved gas concentration and its value in equilibrium with the atmosphere (Liss and Slater, 1974).

$$F = k_{gas} \Delta C \quad (7)$$

For wetlands, gaseous exchange is mainly from passive diffusion across the air-water interface and  $k_{gas}$  has a much lower value than for rivers, where turbulent mixing increases the rate of exchange.

Therefore under permanently flooded conditions,  $N_2O$  emissions directly from riparian wetlands are likely to be relatively low, but when the riparian zone is subject to frequent oscillations in water table and/or WFPS and its supply of  $NO_3^-$  comes from upslope, then the sum of gaseous emissions of  $N_2O$  and export of  $N_2O(s)$  to streamwater may be high.

Important points
<ul style="list-style-type: none"> <li>• N<sub>2</sub>O emissions from riparian wetlands depend not only on the environmental conditions influencing N<sub>2</sub>O production but also the physical factors affecting the escape of N<sub>2</sub>O molecules to the atmosphere.</li> </ul>
<ul style="list-style-type: none"> <li>• Water will decrease the diffusion of N<sub>2</sub>O by ~ 4 orders of magnitude.</li> </ul>
<ul style="list-style-type: none"> <li>• There is some evidence that in riparian wetlands plants may provide the gaseous diffusion pathway that circumvents the barrier induced by overlying water. This appears to be plant-specific.</li> </ul>
<ul style="list-style-type: none"> <li>• Wetting and drying processes result in a dynamic reorganisation of microsites, which can significantly change the amount of N<sub>2</sub>O emitted through increasing or decreasing gaseous diffusion pathways.</li> </ul>
<ul style="list-style-type: none"> <li>• Increasing temperature leads to an increase in the size of anaerobic microsites because of increased respiration causing greater anoxia.</li> </ul>
<ul style="list-style-type: none"> <li>• Increased temperature also decreases the solubility of N<sub>2</sub>O in a nonlinear way and increases N<sub>2</sub>O diffusion to air, and thus restricts further reduction of N<sub>2</sub>O to N<sub>2</sub>.</li> </ul>
<ul style="list-style-type: none"> <li>• Where the only supply of NO<sub>3</sub><sup>-</sup> is nitrification within the wetland, raising the watertable will decrease N<sub>2</sub>O emission by cutting off the supply of NO<sub>3</sub><sup>-</sup>. If, however, the water causing the rise in water table contains high NO<sub>3</sub><sup>-</sup> then there may be an increase in N<sub>2</sub>O production, though not necessarily emission.</li> </ul>
<ul style="list-style-type: none"> <li>• Where the rise in water table has been caused by a flux of upslope groundwater, then, depending of the path length, the N<sub>2</sub>O in solution may be 'flushed' into stream channels.</li> </ul>
<ul style="list-style-type: none"> <li>• For wetlands, gaseous exchange is mainly from passive diffusion across the air-water interface and <math>k_{\text{gas}}</math> has a much lower value than for rivers, where turbulent mixing increases the rate of exchange.</li> </ul>

## 2.6 Landscape influences on N<sub>2</sub>O flux

In New Zealand pastoral catchments, large amounts of NH<sub>4</sub><sup>+</sup> or NO<sub>3</sub><sup>-</sup> are imported into the riparian zone which has led to the hypothesis that N<sub>2</sub>O production rates within these zones may be higher than the catchment which provided the N; i.e. sites of mineral N production and reduction may be separated in space and time. In riparian zones, the factors regulating N<sub>2</sub>O production are typically spatially distributed, with gradients from the hill slope down toward the stream. In large portions of the riparian zones, soils are wet and rich in organic matter, thus providing optimal conditions for denitrification. As a consequence, the distribution of denitrification and N<sub>2</sub>O emission in riparian zones that have high rates of nitrate removal is expected to show a clear spatial pattern in contrast to the almost random

variation found for denitrification and N<sub>2</sub>O emissions in drained fertilized soils (Hefting et al., 2006)

Such spatial patterns have been found in other studies that have included riparian wetlands. Bowden et al. (1992) reported high N<sub>2</sub>O emission rates at topographic (and redox) breaks in the hillslope of a rainforest catchment, particularly where the change in slope was contiguous to a riparian wetland (Fig. 12). In this same catchment McSwinney et al. (2001) showed how these N<sub>2</sub>O emissions could be related to variations in NO<sub>3</sub><sup>-</sup>, NH<sub>4</sub><sup>+</sup>, DOC, and O<sub>2</sub>. Nitrate and DOC disappeared from soil solution at the slope-riparian interface, where soil N<sub>2</sub>O concentrations increased dramatically. Yu et al., (2006) showed that maximum N<sub>2</sub>O concentration in the soils, found at about Eh +250 mV, coincided in a break between a hillslope and a permanent swamp. Dhondt et al (2004) emphasised the importance of carbon-enriched soil layers within a river valley for controlling denitrification activity and N<sub>2</sub>O flux. Hefting et al. (2006) showed that the spatial variability of denitrification and N<sub>2</sub>O emission was lower and less random along flowpaths that show high nitrate removal compared to flowpaths with low nitrate removal, and Allen et al. (2007) demonstrated significantly higher N<sub>2</sub>O emission at the inland fringe of mangroves wetlands compared to interior positions. The very high denitrification (N<sub>2</sub>O alone not measured) rates measured at the upslope edge of a New Zealand riparian wetland receiving inputs of NO<sub>3</sub><sup>-</sup>-enriched groundwater (Cooper, 1990) is also consistent with this landscape effect.

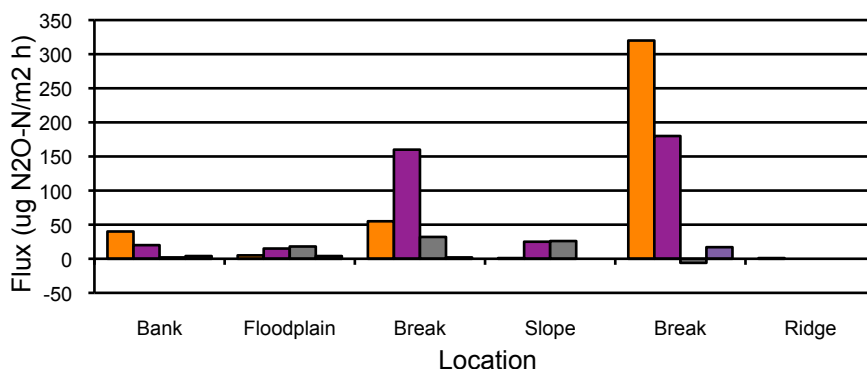


Fig. 12 N<sub>2</sub>O flux in relation to landscape position along a riparian catena (from Bowden et al., 1992). Colours represent different sites but categorized according to topographic position)

The study by Bowden et al., (1992) also pointed out that exports of N<sub>2</sub>O in stream water may not be inconsequential. Even their lowest estimate of N<sub>2</sub>O loss (0.9-26 kg N<sub>2</sub>O-N ha<sup>-1</sup> y<sup>-1</sup>) was comparable with inorganic N exports (NO<sub>3</sub>-N 0.9-2.8 kg ha<sup>-1</sup> y<sup>-1</sup>, NH<sub>4</sub>-N 0.2-0.8 kg ha<sup>-1</sup> y<sup>-1</sup>) and was similar to particulate N or dissolved organic N export. Similar load estimates for New Zealand lowland streams (Wilcock, pers. comm.) are that N<sub>2</sub>O load is very similar to that of NH<sub>4</sub>-N (0.1 -0.2 kg ha<sup>-1</sup> y<sup>-1</sup>) but very much less than that of NO<sub>3</sub>-N (7-20 kg ha<sup>-1</sup> y<sup>-1</sup>). If N<sub>2</sub>O is produced in riparian wetlands and is 'leached' in solution to



stream waters before it can be reduced further, then the streams themselves may be significant sites of N<sub>2</sub>O emission to the atmosphere (Wilcock & Sorrell, 2008) because turbulence induced by bed shear will induce much higher rates of gaseous diffusion than is possible in a wetland situation, where diffusion is limited by wind shear.

Important points	
	<ul style="list-style-type: none"> <li>The factors regulating N<sub>2</sub>O production in riparian wetlands are typically spatially distributed with gradients from the hill slope towards the stream.</li> </ul>
	<ul style="list-style-type: none"> <li>High N<sub>2</sub>O emission rates typically occur at topographic breaks (e.g. at the interface between a hillslope and the wetland) and may be recognised through changes in Eh.</li> </ul>
	<ul style="list-style-type: none"> <li>Spatial variability in N<sub>2</sub>O emission is lower along flow paths that show high nitrate removal compared with flow paths with low nitrate removal.</li> </ul>
	<ul style="list-style-type: none"> <li>Exports of dissolved N<sub>2</sub>O in stream water may not be inconsequential and in some circumstances can be comparable with inorganic N exports.</li> </ul>
	<ul style="list-style-type: none"> <li>In such circumstances (4 above) streams may be significant sites of N<sub>2</sub>O emissions to the atmosphere</li> </ul>

## 2.7 Modeling N<sub>2</sub>O emissions from wetlands - important variables

Several models of N<sub>2</sub>O emissions from both agricultural soils and natural ecosystems have been published. The most widely used and accepted model is the DNDC (denitrification and decomposition) model (Li et al., 1992) and its derivatives (Li et al., 2002). Versions of the DNDC model have been adapted for wetlands (Li et al., 2004) and for New Zealand pastoral conditions (Saggar et al., 2007).

A unique feature of the DNDC model is its use of coupled Nernst and Michaelis-Menten equations to predict Eh and subsequent gaseous emissions from various substrates. A simplified (assuming constant pH and temperature) Nernst equation is used to predict Eh. Based on the predicted Eh value, the soil is divided into proportions of relatively aerobic and relatively anaerobic microsites. 'Substrates' such as NO<sub>3</sub><sup>-</sup>, DOC, NH<sub>4</sub><sup>+</sup> are set to 'react' only in oxidative (e.g. nitrification) or reductive (e.g. denitrification) conditions depending on the soil volume to which they are assigned. The Michaelis-Menten equation is used to determine the rates of the reactions occurring within and outside of the anaerobic volumetric fraction (coined the 'anaerobic balloon'), which swells or shrinks as driven by the reduction-oxidation reactions. When a soil is irrigated or flooded, its oxygen content will decrease and that will drive the anaerobic balloon to swell. As soon as the oxygen is depleted, the anaerobic balloon will reach its maximum and burst. At this moment, a new

oxidant (i.e.,  $\text{NO}_3^-$ ) will become the dominant species in the soil, and a new anaerobic balloon will be created and swell as driven by the  $\text{NO}_3^-$  depletion. By tracking the formation and deflation of a series of anaerobic balloons driven by depletions of  $\text{O}_2$ ,  $\text{NO}_3^-$ ,  $\text{Mn}^{4+}$ ,  $\text{Fe}^{3+}$ , and  $\text{SO}_4^{2-}$ , wetland-DNDC estimates soil Eh dynamics as well as production and consumption of the products from the reductive-oxidative reactions, including  $\text{N}_2\text{O}$ .

The calculation of Eh (and hence the size of the anaerobic balloon) is dependent on calculation of partial pressure of soil  $\text{O}_2$ . This is modelled using explicit finite difference equations using Fick's first law. Partial pressure of soil  $\text{O}_2$  is in turn affected by soil structure and texture. A fine-textured soil has smaller pores, and thus anaerobic microsites are created at lower moisture contents than in a coarse-textured soil. DNDC uses soil field capacity as a surrogate measure of effective soil porosity and linear correlation to estimate the size of subsequent anaerobic balloon. For all its sophistication, the model predictions are ultimately dependent on these empirical relationships. Lamers et al. (2007) were not happy with the predictions made by DNDC and the fact that it is not open-source, so that the algorithms and parameters cannot be changed.

Saggar et al. (2007) modified DNDC to suit New Zealand pastoral conditions (in collaboration with the model developers). Significant changes to NZ-DNDC included changing the WFPS threshold for denitrification from 35% to field capacity and allowing N inputs from grazing animals. New Zealand-DNDC showed net  $\text{N}_2\text{O}$  emissions decreased with a 20% increase in rainfall, despite the increase in denitrification with WFPS. Saggar et al. (2007) rationalised this result by arguing that increased rainfall resulted in increased nitrate leaching, which reduces the amount of N in the soil available for denitrification. In other words the rate of  $\text{NO}_3^-$  loss (other than by reduction processes) exceeded the rate of  $\text{NO}_3^-$  supply (through nitrification or direct fertiliser inputs). If this was the case then there is a high probability that the leached nitrate would pass through riparian wetlands.

Empirical models that are based on correlation analysis involving easily measureable soil variables (e.g., temperature, moisture, texture, and organic carbon) often predict  $\text{N}_2\text{O}$  flux quite well (Conrad, 1996; Conen et al., 2000). The latter authors used boundary lines of mineral N and WFPS to define conditions for upper and lower limits of  $\text{N}_2\text{O}$  flux ranges. Whilst not giving discrete values, the model did provide a range within which a flux would be expected given relatively simple input values.

A similar empirical approach was used by Kang et al. (1998) to predict  $\text{N}_2\text{O}$  emissions from a fen (wetland) in North Wales as a function of hydrochemistry. They explained 80% of the variance in  $\text{N}_2\text{O}$  emissions measured in a field study from  $\text{NO}_3^-$ , water table depth and glucosidase activity. A possible weakness in the model is that water table depth and  $\text{NO}_3^-$  may be autocorrelated. Also unlike DNDC or the model used by Conen et al., 2000, the degree of water saturation (or water table depth) is not considered an important predictor of  $\text{N}_2\text{O}$  flux. While  $\text{N}_2\text{O}$  emissions in wetlands with fluctuating water tables are often significantly higher than those that are permanently submerged (Hendandez & Mitsch, 2006, Lamers et al., 2007), this is almost certainly a function of  $\text{NO}_3^-$  limitation with alternating wetting and drying being necessary for coupled nitrification-denitrification. However in wetland systems where  $\text{NO}_3^-$  is not limited because it is supplied from the catchment, there is no reason to think that wetting and drying periods are a necessary

prerequisite for high  $\text{N}_2\text{O}$  emissions. Such a result was noted by Hefting et al., (2006) who used principal component analysis to identify the main variables affecting  $\text{N}_2\text{O}$  emissions in a transect exhibiting very high rates of  $\text{NO}_3^-$  removal. They showed that the variance in  $\text{N}_2\text{O}$  emission rates could not be explained by any combination of WFPS, pH, or organic matter, but could be partly explained by temperature and nitrate in soil pore water. As discussed in section 2.4, this relationship also has some basis in terms of microbial ecology as when  $\text{NO}_3^-$  is limiting, there is more demand for electron acceptors and hence  $\text{N}_2\text{O}$  is more likely to be reduced to  $\text{N}_2$ . Therefore when  $\text{NO}_3^-$  is not limiting, there will be more  $\text{N}_2\text{O}$  production (provided other conditions are conducive to denitrification). We would therefore expect that there would be a relationship between  $\text{NO}_3^-$  at the upland/wetland boundary and  $\text{N}_2\text{O}$  emissions from riparian wetlands in New Zealand pastoral catchments.

Important points
<ul style="list-style-type: none"> <li>The DNDC model (denitrification and decomposition) and its derivatives is the most widely used deterministic model of <math>\text{N}_2\text{O}</math> emissions from terrestrial and wetland ecosystems.</li> </ul>
<ul style="list-style-type: none"> <li>DNDC uses coupled Nernst and Michaelis-Menten equations to predict Eh and subsequent gaseous emissions from various substrates.</li> </ul>
<ul style="list-style-type: none"> <li>DNDC is not truly deterministic in that it uses empirical relationships between field capacity and soil porosity to estimate the size of the anaerobic zone.</li> </ul>
<ul style="list-style-type: none"> <li>Empirical models based on correlation analysis can predict <math>\text{N}_2\text{O}</math> emissions from a particular site quite well.</li> </ul>
<ul style="list-style-type: none"> <li>Such models are particularly useful in identifying environmental variables that are important in regulating <math>\text{N}_2\text{O}</math> emissions.</li> </ul>

## 2.8 Hypotheses for conceptual modeling

From the review in Sections 2.1-2.7 and our own knowledge of wetland dynamics we hypothesise the following with respect to  $\text{N}_2\text{O}$  emissions from riparian wetlands in New Zealand pastoral landscapes:

1. Few wetlands will be dependent on in situ nitrification for  $\text{NO}_3^-$  supply. Most will have significant external inputs of  $\text{NO}_3^-$  generated within the pasture catchment. Intensively farmed catchments typically receive loadings in excess of 300 kg N/ha/yr from animal excreta. Much of this is converted to nitrate via mineralisation and nitrification, so that paddocks may export more than 50 kg N/ha yr. By the time the nitrate has passed through riparian wetlands and down a stream network this may be reduced to 10-30 kg  $\text{ha}^{-1} \text{yr}^{-1}$ : the typical yield for a stream draining an intensively grazed catchment. The majority of riparian wetlands will therefore have sufficient 'substrate' to support  $\text{N}_2\text{O}$  emissions at the upper end of the range given in Table 1.

2. The majority of riparian wetlands will have sufficient available carbon to drive denitrification. None would be expected to be carbon limited though there is likely to be a wide variation in redox potential ranging from highly negative (anaerobic) in lowland dairying catchments with high levels of organic input to moderately aerobic in perched peat wetlands. Therefore we predict a range of responses in terms of  $\text{NO}_3^-$  reduction pathways but for the majority with high  $\text{NO}_3^-$  inputs, conditions will be suitable for  $\text{N}_2\text{O}$  accumulation.
3. There will be a range in the degree of wetting and drying with some wetlands submerged perennially and others subject to major drawdown and re-flooding. This will affect the distribution of aerobic channels and hence the quantum of  $\text{N}_2\text{O}$  emitted directly to the atmosphere.
4. There have been a number of studies in New Zealand pastoral catchments that have demonstrated distinct gradients in  $\text{NO}_3^-$  removal along transects to wetlands and streams. Thus we would expect to find parallel examples of gradients in  $\text{N}_2\text{O}$  production to those found in studies overseas (e.g. Hefting et al., 2006).
5. Seasonal production of nitrate in pasture draining to wetlands will regulate the extent to which  $\text{N}_2\text{O}$  emissions occur. There are numerous examples of very high seasonal  $\text{NO}_3^-$  concentrations and loads from New Zealand pasture catchments. This is related to partial area hydrology (Cooke & Dons, 1988) and thus the extent to which groundwater-fed  $\text{NO}_3^-$  extends into riparian wetlands. Thus we would predict a similar seasonal trend in  $\text{N}_2\text{O}$  production with the highest fluxes generally expected in late autumn-early winter and the lowest in summer. This may be masked somewhat by the relationship between  $\text{N}_2\text{O}$  solubility and temperature as the highest solubilities would be coincident with the greatest  $\text{NO}_3^-$  flux.
6. Forested riparian wetlands within New Zealand pastoral landscapes are relatively rare which may mitigate against some of the highest  $\text{N}_2\text{O}$  emission rates reported internationally (although they have generally been associated with the highest  $\text{NO}_3^-$  inputs). However riparian wetlands in New Zealand pasture catchments commonly revert to wetland species (*Juncus*, *Typha* etc) which have been shown to enhance  $\text{N}_2\text{O}$  emissions compared to grassed wetlands (e.g. *Glyceria* spp).
7. Studies done on  $\text{N}_2\text{O}$  emissions from New Zealand grazed pastures have reported the highest rates are associated with high N inputs from grazing animals and WFPS >60%. Because riparian wetlands integrate and 'process'  $\text{NO}_3^-$ -rich leachate under more consistently optimal conditions for denitrification, we would expect higher  $\text{N}_2\text{O}$  production per unit area than the surrounding pasture.
8. With the exception of wetlands receiving dairy shed effluent, we would expect the redox conditions of the majority of riparian wetlands to favour denitrification, rather than DNRA or anammox.
9. In ephemeral wetlands (subject to significant fluctuations in watertable) we would expect the  $\text{NO}_3^-$  produced by nitrification to be a significant source of  $\text{NO}_3^-$  - However we hypothesise that quantitatively, this source will be small compared with the denitrification-mediated  $\text{NO}_3^-$  produced from  $\text{NO}_3^-$ -rich shallow groundwater.

10. From the studies on  $\text{N}_2\text{O}$  emissions as a function of Eh or oxygen status and New Zealand studies on  $\text{NO}_3^-$  loss and denitrification in riparian wetlands, we would expect very high  $\text{N}_2\text{O}$  flux at the leading edge of wetlands (where  $\text{NO}_3^-$ -rich shallow groundwater first makes contact with organic rich and saturated wetland soils) but to rapidly diminish within the interior of the wetland due to more reducing conditions, diminished  $\text{NO}_3^-$  and diffusion limitations. The hydrologic and hydraulic conditions of groundwater introduction to the wetland will control the spatial extent to which redox conditions are suitable for  $\text{N}_2\text{O}$  accumulation.
11. As the majority of riparian wetlands in New Zealand pastoral landscapes are adjacent to 1<sup>st</sup> order streams, we would expect that a high proportion of  $\text{N}_2\text{O}$  produced in the wetland will be 'flushed' into stream channels. A high proportion of  $\text{N}_2\text{O}_{(\text{s})}$  in streams will be emitted to the atmosphere through turbulent diffusion, particularly under elevated flow conditions.

### 3 Conceptual modeling

#### 3.1 Hypotheses for conceptual modeling

The issue addressed in this section is whether the encouragement of wetlands in pasture catchments increases the amount of nitrous oxide reaching the atmosphere. This issue needs to be considered at different spatial scales. First, consider a sub-catchment containing wetlands. If the areal emission rate of nitrous oxide from wetlands is significantly higher than the emission rates from other parts of the sub-catchment (viz., pasture and headwater streams) then increasing the area of wetlands will increase the total emission from the sub-catchment. Second, consider the catchment as a whole including the any rivers, floodplains, lakes and estuaries downstream from the wetlands. Encouraging wetlands will reduce the nitrate flux to these downstream waterways and floodplains where denitrification and the associated 'leakage' of nitrous oxide are known to occur (Seitzinger et al. 2006). The question arises whether reducing nitrate flux to these downstream locations reduces their nitrous oxide emissions and compensates for the increased wetland emissions. Third, consider the riparian wetland as an entity connected to the pasture upslope, and the stream downslope, and the possibility of a distinct spatial gradient in nitrous oxide emissions (as discussed in Section 2.6) with very high emissions at the upslope boundary but very low emissions (relative to pasture) at the downslope boundary. The question then arises as to whether very high emissions within a relatively small area of wetland exceed the average emissions (on an areal basis) from the pasture and if so, can we manage this zone in some way to reduce emissions?

To address this issue, the following questions need to be answered:

1. do the areal rates of nitrous oxide emission differ significantly between pasture, wetlands and headwater streams?
2. taking into account their relative proportions, are nitrous oxide emissions from wetlands large or small compared with the emissions from pasture and headwater streams?
3. do areal rates of nitrous oxide emission differ significantly between wetlands, rivers, lakes and estuaries?
4. what happens to the nitrous oxide emission rate in rivers, lakes and estuaries when the nitrate flux entering them decreases as a result of having more wetlands?
5. does nitrate removal by wetlands reduce denitrification and nitrous oxide emissions from rivers, lakes and estuaries which compensates for any increased nitrous oxide emissions from wetlands?

It was beyond the scope of this study to consider nitrous oxide emissions from large rivers, floodplains, lakes and estuaries in New Zealand, although a future study could do so. The following section explores questions (1) and (2) with the help of collated data on denitrification and nitrous oxide emission rates in pasture, wetlands and headwater streams making use of the 'hole in the pipe' model (Davidson et al. 2000).

### 3.2 The ‘hole in the pipe’ model

We focus on nitrate removal, denitrification and the associated emission of nitrous oxide and dinitrogen in wetlands. We have ignored nitrification because nitrate is considered to dominate the N loading to agricultural wetlands and in general the low redox and anoxia do not favour nitrification in wetlands except where there is significant wetting and drying, and localised aerobic zones around certain wetland plant roots.

Nitrate removal is the sum of nitrate uptake (e.g., by plants and microbes) dissimilatory reduction to ammonium (DNRA) and denitrification. Denitrification is the reduction of  $\text{NO}_3^-$  by microbial processes which results in the accumulation of nitrite  $\text{NO}_2^-$ , nitric oxide  $\text{NO}$ , nitrous oxide  $\text{N}_2\text{O}$ , and/or dinitrogen  $\text{N}_2$ . Accumulation is the generation rate (i.e., reduction of the precursor) minus the loss rate (either reduction to the successor or emission as gas), and includes both gas emission and increases in concentration. In wetlands  $\text{NO}_2^-$  and  $\text{NO}$  accumulation are negligible and denitrification rate is the rate of accumulation of  $\text{N}_2\text{O}$  and  $\text{N}_2$ . Commonly accumulation is reported as the ratio  $\text{N}_2\text{O}:\text{N}_2$  or the ratio  $\text{N}_2\text{O}:\text{N}_2\text{O}+\text{N}_2$  (viz.,  $\text{N}_2\text{O}:\text{total denitrification}$ ). Sometimes accumulation is reported as the ratio  $\text{N}_2\text{O}:\text{NO}_3^-$  removal but this can be misleading because  $\text{NO}_3^-$  removal is affected by uptake. We focus upon published estimates of denitrification rate based on measurements made using the acetylene block technique.

The ‘hole in the pipe’ model is shown in Fig. 13. For simplicity we assume that nitrate removal has been ‘corrected’ for plant/microbial uptake and DNRA so that nitrate removal equals the sum of the accumulations of  $\text{NO}_2^-$ ,  $\text{NO}$ ,  $\text{N}_2\text{O}$  and  $\text{N}_2$ . The ‘hole in the pipe’ model asserts that

$$N_2 = \alpha DNT$$

$$N_2O = \beta DNT$$

$$NO = \chi DNT$$

$$NO_2 = \delta DNT$$

where  $\alpha, \beta, \chi, \delta$  = empirical ‘leakage’ coefficients (dimensionless);  $DNT$  = total denitrification rate ( $\text{kg ha}^{-1} \text{y}^{-1}$ ); and  $N_2, N_2O, NO$  and  $NO_2$  = the rates of accumulation of  $\text{N}_2, \text{N}_2\text{O}, \text{NO}$  and  $\text{NO}_2$  respectively ( $\text{kg ha}^{-1} \text{y}^{-1}$ ). If nitrate removal has been ‘corrected’ for plant/microbial uptake then

$$\alpha + \beta + \chi + \delta = 1$$

$$DNT = N_2 + N_2O + NO + NO_2$$

The ‘hole in the pipe’ model asserts that  $DNT, \alpha, \beta, \chi$  and  $\delta$  vary depending on environmental conditions. Under optimal conditions  $\text{NO}_3^-$  removal rate is high (viz., the flow in the pipe is large) while the emission or accumulation of  $\text{NO}_2^-$ ,  $\text{NO}$  and  $\text{N}_2\text{O}$  are low (viz., the holes in the pipe are small). Thus  $\alpha \sim 1$  while  $\beta \chi \delta \sim 0$ .

Under sub-optimal conditions, the model predicts two things happen. Firstly,  $DNT$  decreases (viz., the rate at which nitrate is removed decreases). Secondly, a smaller

proportion of the nitrate removed is reduced to  $N_2$  and a larger proportion is accumulated as  $N_2O$ ,  $NO$  or  $NO_2$ . Thus under sub-optimal conditions the flow in the pipe decreases and the size of the holes increase –  $\alpha$  decreases while  $\beta$  and possibly  $\chi$  and  $\delta$  increase. Just because the ‘holes in the pipe’ are bigger when conditions are sub-optimal does not mean that the  $N_2O$  emission is necessarily higher. This depends on how much  $DNT$  decreases relative to the decrease in  $\alpha$  and the increases in  $\beta$ ,  $\chi$  and  $\delta$ . Conversely, just because the ‘holes in the pipe’ are smaller when conditions are optimal does not mean that the  $N_2O$  emission is necessarily negligible.

It is commonly reported that emissions and accumulation of  $NO$  and  $NO_2$  are low. Hereafter we assume that  $\chi$  and  $\delta \sim 0$ .

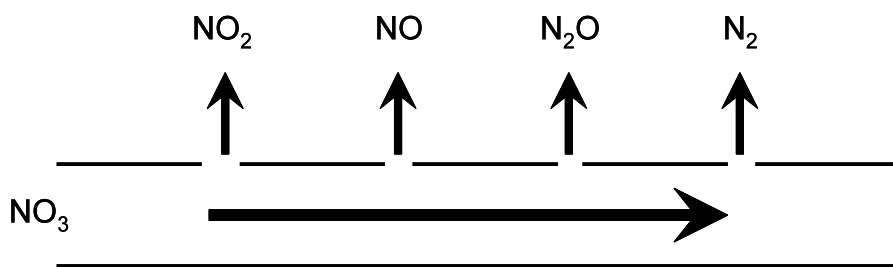


Fig. 13. Schematic diagram of the ‘hole in the pipe’ conceptual model.

Before the ‘hole in the pipe’ model can be used, reliable estimates are required of  $DNT$ ,  $\alpha$  and  $\beta$  under the range of conditions.

There are measurements of denitrification rate in New Zealand wetlands but we could only locate one measurement of denitrification rate and nitrous oxide emission (Schipper et al. 1993). This makes it difficult to estimate  $\alpha$  and  $\beta$  under the range of conditions found in New Zealand wetlands, and we are forced to rely on published data from overseas where denitrification and nitrous oxide emission have been measured simultaneously.

One striking feature of published denitrification rates for New Zealand wetlands is that some are much higher than published rates from overseas studies. Cooper (1990)<sup>4</sup>

<sup>4</sup> Both Cooper (1990) and Schipper et al (1993) used methodology for *in situ* denitrification rate that involved shaking soil cores. This is not usual practice for *in situ* determinations and may account for the much higher rates measured in these studies compared with studies carried out overseas. Cooper (1990) argued that the high water content of the structureless organic ooze required that they be shaken to ensure acetylene reached the sites of nitrous oxide reductase and then, after incubation, to ensure that any  $N_2O$  produced equilibrated between the liquid and gas phases. It is not part of this study to critique measurement techniques, and while it could be argued that Cooper’s (1990) technique will overestimate *in situ* rate because of shaking, it could equally well be argued that *in situ* denitrification rate measurements in saturated organic soils that fail to ensure acetylene reaches the sites of nitrous oxide reductase run the risk of underestimating the rate.



measured denitrification rates ranging from 6100-8100 mgN m<sup>-2</sup> d<sup>-1</sup> (mean 26 tN ha<sup>-1</sup> y<sup>-1</sup>) at the head of a pasture wetland while Schipper et al. (1993) measured 950-1120 mgN m<sup>-2</sup> d<sup>-1</sup> (mean 3.8 tN ha<sup>-1</sup> y<sup>-1</sup>) in a forest wetland irrigated with treated sewage. For New Zealand wetlands published nett removal rates (inflow minus outflow) lie in the range 5-250 mgN<sub>03</sub>N m<sup>-2</sup> d<sup>-1</sup> (20-1000 tN ha<sup>-1</sup> y<sup>-1</sup>) and 180-650 mgTN m<sup>-2</sup> d<sup>-1</sup> (650-2400 tN ha<sup>-1</sup> y<sup>-1</sup>). These include denitrification, storage and plant/microbial uptake and only place an upper bound on denitrification rate. By comparison measured denitrification rates from overseas studies lie in the range 0-150 mgN m<sup>-2</sup> d<sup>-1</sup> (mean 27, median 15 mgN m<sup>-2</sup> d<sup>-1</sup>) which is equivalent to 0-550 tN ha<sup>-1</sup> y<sup>-1</sup> (mean 98, median 55 tN ha<sup>-1</sup> y<sup>-1</sup>).

Groffman et al. (2000) reported an inverse relationship between the N<sub>2</sub>O:N<sub>2</sub> ratio and total gas production (N<sub>2</sub>O+N<sub>2</sub>) (see Fig. 1). Groffman's measurements are reported per unit mass of soil and consequently Fig. 1 cannot be used to determine the relationship between  $\beta$ ,  $\alpha$  and *DNT*. Fig. 14 shows the N<sub>2</sub>O:N<sub>2</sub>O+N<sub>2</sub> ratios recalculated from references in Table 1. Note that only studies using the acetylene block technique to measure denitrification are included. Fig. 14 indicates that proportionally less N<sub>2</sub>O is emitted as the denitrification rate increases. This is consistent with the idea that high denitrification rates occur when conditions are optimal for complete denitrification, and when conditions are near optimal a smaller proportion of N<sub>2</sub>O is emitted and a higher proportion is reduced to N<sub>2</sub>.

The dashed line in Fig. 14 bounds the individual measurements

$$\frac{N_2O}{N_2O + N_2} = 1 - 0.925 \frac{N_2O + N_2}{75 + N_2O + N_2} \quad (8)$$

while the solid line is fitted to the mean values for each study.

$$\frac{N_2O}{N_2O + N_2} = 0.7 - 0.625 \frac{N_2O + N_2}{75 + N_2O + N_2} \quad (9)$$

Both lines asymptote to a N<sub>2</sub>O/N<sub>2</sub>O+N<sub>2</sub> ratio of 7.5% at high denitrification rates. This is strongly influenced by the values measured by Schipper et al. (1993) in forest wetlands receiving runoff from sewage irrigated pine forest. There are individual measurements suggesting lower ratios. At low denitrification rates the mean values asymptote to 70% although individual measurements vary from 0-100%.

There is clearly a large uncertainty involved in estimating the N<sub>2</sub>O/N<sub>2</sub>O+N<sub>2</sub> ratio. Nevertheless it would appear that the ratio is <50% when N<sub>2</sub>O+N<sub>2</sub> production exceeds 100 kgN ha<sup>-1</sup> y<sup>-1</sup> and may drop below 10% at very high N<sub>2</sub>O+N<sub>2</sub> production rates. Conversely it would appear that the N<sub>2</sub>O/N<sub>2</sub>O+N<sub>2</sub> ratio >50% when N<sub>2</sub>O+N<sub>2</sub> production drops below 10 kgN ha<sup>-1</sup> y<sup>-1</sup> and may increase to 70% at very low N<sub>2</sub>O+N<sub>2</sub> production rates. This conclusion may be predicated by the possibility of systematic spatial variability in both N<sub>2</sub>O and N<sub>2</sub> production, and hence the N<sub>2</sub>O/N<sub>2</sub>O+N<sub>2</sub> ratio.

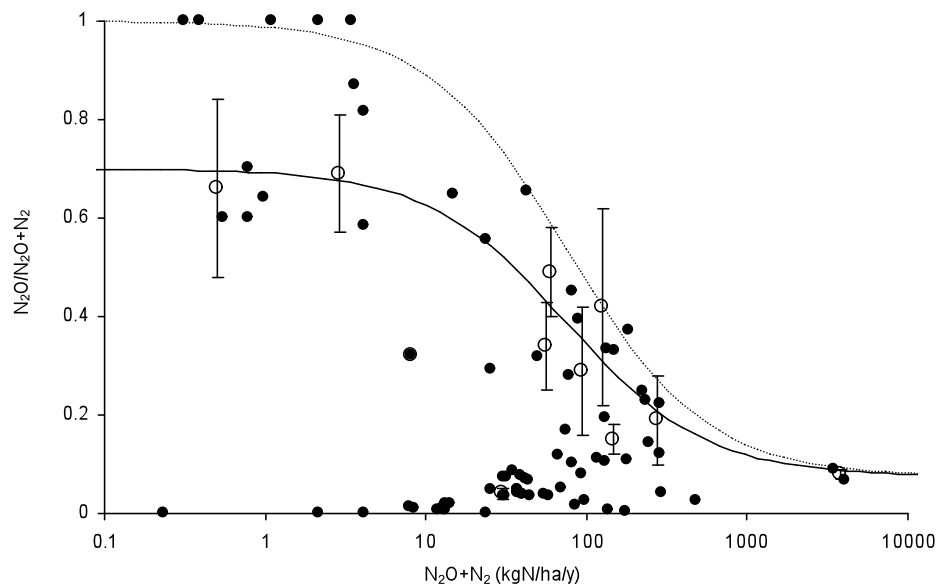


Fig. 14. Nitrous oxide emissions ( $\text{N}_2\text{O}$ ) and denitrification rates ( $\text{N}_2\text{O}+\text{N}_2$ ) measured in the field. The  $\text{N}_2\text{O}:\text{N}_2\text{O}+\text{N}_2$  ratio decreases with increasing  $\text{N}_2\text{O}+\text{N}_2$  in a similar manner to Fig. 1. The fitted lines are described in the text.

While the ‘hole in the pipe’ model is a potentially valuable conceptual model, it is currently of limited value for calculating nitrous oxide fluxes in New Zealand wetlands.

First, there are few simultaneous measurements of nitrous oxide emission and denitrification in wetlands with high denitrification rates ( $>100 \text{ mgN m}^{-2} \text{ d}^{-1}$ ). Although we might expect a low  $\text{N}_2\text{O}:\text{N}_2\text{O}+\text{N}_2$  ratio in such circumstances (see Fig. 14) even a small ‘leakage’ would generate a large nitrous oxide flux. Current estimates of the  $\text{N}_2\text{O}:\text{N}_2\text{O}+\text{N}_2$  ratio at high denitrification rates lie in the range 0-10%.

Second, the environmental conditions which determine denitrification rate and the  $\text{N}_2\text{O}:\text{N}_2\text{O}+\text{N}_2$  ratio are not well quantified. This situation is not unique to New Zealand as discussed by Hefting et al. (2006). It is clear from the work of Cooper (1990) that there are ‘hot spots’ of denitrification in wetlands. There may also be ‘hot spots’ of nitrous oxide emission. Further field investigations are required before the spatial variability of denitrification and nitrous oxide emission in wetlands can be understood, quantified and included in models.

### 3.3 Empirical model

In this section we present calculations made using a simple catchment model. The following input variables are specified:

- nitrogen yield from the catchment ( $Y_{\text{cat}}$ ,  $\text{kgN ha}^{-1} \text{ y}^{-1}$ )
- catchment area ( $A_{\text{cat}}$ , ha)
- wetland area ( $A_{\text{wet}}$ , ha)

- percentage of runoff entering wetlands ( $P_{\text{wet}}$ )
- percentage of runoff entering headwater streams but by-passing wetlands ( $P_{\text{stm}}$ )
- maximum wetland denitrification ( $D_{\text{wet}}$  kgN ha<sup>-1</sup> y<sup>-1</sup>)
- headwater stream surface area ( $A_{\text{stm}}$ , ha)
- maximum stream denitrification ( $D_{\text{stm}}$  kgN ha<sup>-1</sup> y<sup>-1</sup>)

Nitrogen that does not enter wetlands or headwater streams is assumed to enter groundwater. Maximum wetland ( $D_{\text{wet}}$ ) and stream denitrification ( $D_{\text{stm}}$ ) are assumed constant (viz, independent of nitrate input). Nitrogen removal by wetlands (kgN y<sup>-1</sup>) is the smaller of the maximum wetland denitrification ( $A_{\text{wet}}D_{\text{wet}}$ ) and the input from the catchment ( $A_{\text{cat}}Y_{\text{cat}}P_{\text{wet}}$ ). Input to headwater streams is input direct from the catchment ( $A_{\text{cat}}Y_{\text{cat}}P_{\text{stm}}$ ) plus wetland outflow (the difference between wetland inflow and removal). Stream removal is the smaller of the maximum stream denitrification and the stream input. Denitrification rates and nitrogen yields chosen for these simulations are based on published values.

Scenario 1. Catchment yield is 50 kgN ha<sup>-1</sup> y<sup>-1</sup> – a typical value for dairy pasture. 10% of runoff enters headwater streams. All runoff enters via wetlands whose area increases from 0-5% of catchment area. The area of headwater streams is fixed at 1% of the catchment area. Maximum denitrification rates in wetlands and streams are 50 and 25 kgN ha<sup>-1</sup> y<sup>-1</sup> respectively. Model coefficients are shown in Table 4.

Fig. 15A shows predicted nitrous oxide emissions from wetlands and headwater streams. Nitrogen delivery to wetlands always exceeds the maximum wetland denitrification and so actual denitrification equals maximum denitrification (50 kgN ha<sup>-1</sup> y<sup>-1</sup>). This means that denitrification and nitrous oxide emission increase linearly with wetland area. Nitrogen delivery to streams also always exceeds the maximum stream denitrification and so actual denitrification equals maximum denitrification (25 kgN ha<sup>-1</sup> y<sup>-1</sup>). Because stream area remains constant so does stream emission. Total emission increases linearly. Scenario 1 illustrates two points.

Point 1: if denitrification in headwater streams is small compared with the flux from the catchment, then wetland and stream denitrification and nitrous oxide emission are uncoupled. In this situation encouraging wetlands will increase nitrous oxide emissions and there will be no compensating reduction in stream emissions. This point is discussed further in Scenario 2.

Point 2: if nitrogen yield from the catchment exceeds the denitrification potential of wetlands then encouraging wetlands will increase nitrous oxide emissions. This point is addressed in Scenario 3.

Scenario 2 is identical to Scenario 1 except that stream area is 20% of the catchment area. This mimics denitrification in downstreams rivers, floodplains, lakes and estuaries. In this situation, encouraging wetlands increases wetland emission. However, nitrogen export from wetland no longer exceeds the denitrification potential of the downstream waterways

and emissions from wetlands and streams are now coupled. As wetland area increases, nitrate input to streams decreases and so stream emission decreases. The total emission remains the same – all that changes is the place where those emissions occur.

Point 3: if denitrification in streams, rivers, floodplains, lakes and/or estuaries is large compared with the flux from the catchment, then wetland and stream denitrification and nitrous oxide emission are coupled. In this situation encouraging wetlands will increase nitrous oxide emissions but there will be compensating reductions in emissions from downstream waterways.

Scenario 3 is identical to Scenario 1 except that catchment yield is  $20 \text{ kgN ha}^{-1} \text{ y}^{-1}$  – a typical value for sheep/beef pasture. Once wetlands reach 4% of catchment area, wetlands and streams denitrify 100% of the catchment yield and thereafter emissions remain constant. For wetland areas between 0-4%, wetland input always exceeds maximum wetland denitrification. Consequently, wetland denitrification equals maximum denitrification ( $25 \text{ kgN ha}^{-1} \text{ y}^{-1}$ ) and denitrification and emission both increase linearly with wetland area. For wetland areas between 0-1.5%, wetland output exceeds maximum stream denitrification. Consequently stream denitrification equals maximum stream denitrification and since stream area is constant, stream emission is also constant.

Point 4: coupling between wetland and stream emissions is more likely when wetland and stream denitrification potential are high compared with catchment yield.

	Scenario 1	Scenario 2	Scenario 3	ha
catchment				
area	20	20	20	ha
yield	50	50	20	$\text{kgN ha}^{-1} \text{ y}^{-1}$
% to wetlands	10	10	10	%
% direct to streams	0	0	0	%
wetlands				
area	0-1	0-1	0-1	ha
denitrification	50	50	50	$\text{kgN ha}^{-1} \text{ y}^{-1}$
N <sub>2</sub> O:denitrification	10	10	10	%
headwater streams				
area	1	4	1	ha
denitrification	25	25	25	$\text{kgN ha}^{-1} \text{ y}^{-1}$
N <sub>2</sub> O:denitrification	10	10	10	%

Table 4. Coefficients used to predict nitrous oxide emissions from wetlands and headwater streams in a hypothetical catchment.

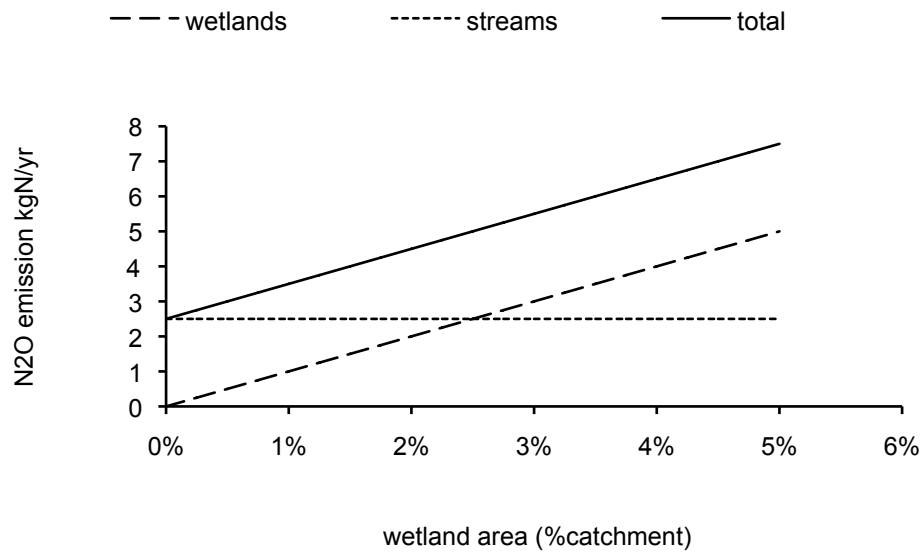


Fig. 15A. Predicted nitrous oxide emissions from wetlands and headwater streams in a hypothetical catchment. Scenario 1.

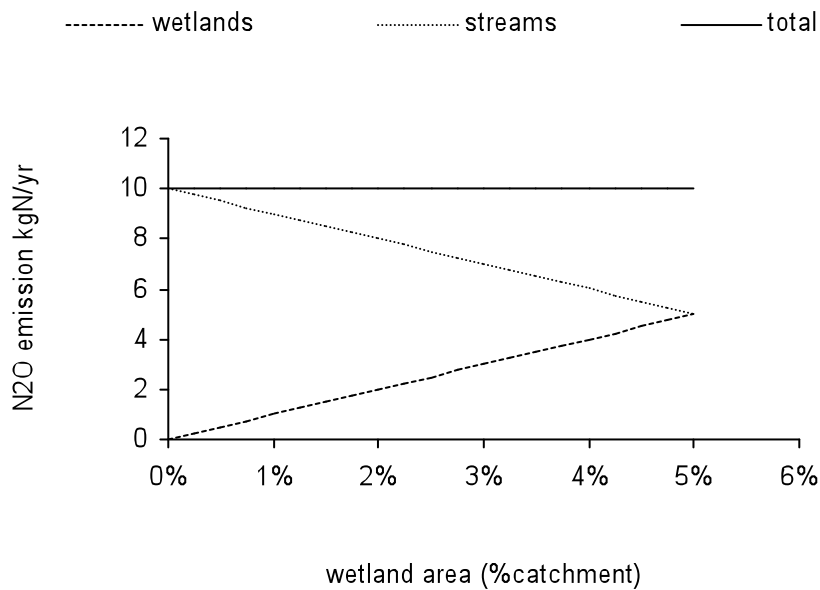


Fig. 15B. Predicted nitrous oxide emissions from wetlands and headwater streams in a hypothetical catchment. Scenario 2.

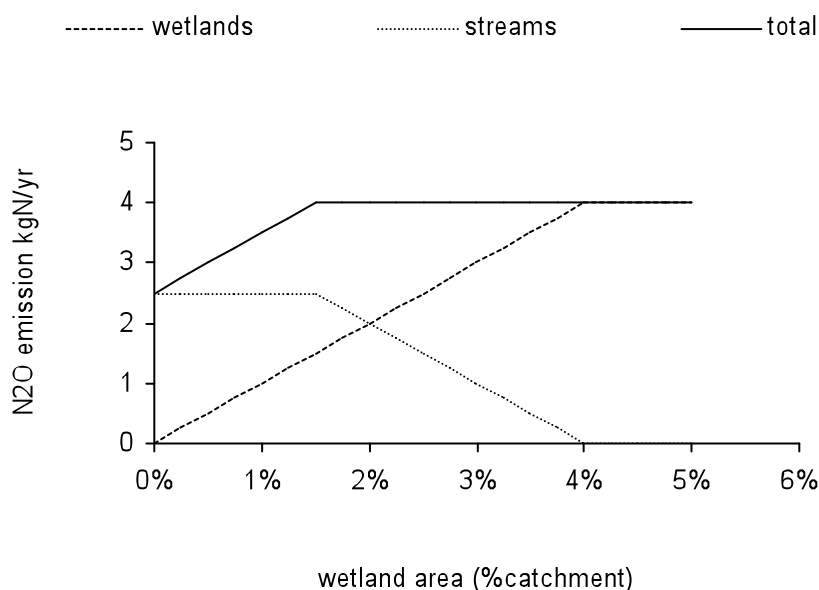


Fig. 15C. Predicted nitrous oxide emissions from wetlands and headwater streams in a hypothetical catchment. Scenario 3.

### 3.4 Discussion

If the nitrous emission rate in wetlands is comparable with or less than the rate in other parts of the catchment then increasing the area of wetlands will not significantly increase the total nitrous oxide emission from the catchment. Conversely if wetlands have a significantly higher emission rate than other parts of the catchment then increasing the area of wetlands will significantly increase the total nitrous oxide emission from the catchment.

The available data for pasture nitrous oxide emissions are included in Table 2. Zaman et al., (2007) report rates  $158\text{--}195\text{ kgN ha}^{-1}\text{ y}^{-1}$  during 90 day trials involving urea and urine application. These values may over-estimate annual average values. de Kleine et al., (1994) estimated annual average emissions in the range  $20\text{--}50\text{ kgN ha}^{-1}\text{ y}^{-1}$  based on short-term experiments involving application of synthetic urine. Zaman's control value of  $18\text{ kgN ha}^{-1}\text{ y}^{-1}$  is similar de Kleine's lower bound. Saggar et al. (2006) used the DNDC model to predict annual average emissions of  $\sim 4\text{ kgN ha}^{-1}\text{ y}^{-1}$  for sheep pasture and  $\sim 10\text{ kgN ha}^{-1}\text{ y}^{-1}$  for dairy pasture. Wilcock & Sorrell (2008) report maximum pasture emissions of  $\sim 4\text{ kgN ha}^{-1}\text{ y}^{-1}$ .

Reported nitrous oxide emissions for NZ pasture lie in the range  $4\text{--}50\text{ kgN ha}^{-1}\text{ y}^{-1}$  with mean and median values of 10 and  $4\text{ kgN ha}^{-1}\text{ y}^{-1}$  respectively. By comparison, published overseas data for nitrous oxide emissions from wetlands (Table 1) range from  $0\text{--}84\text{ kgN ha}^{-1}\text{ y}^{-1}$  with mean and median values of 14 and  $5\text{ kgN ha}^{-1}\text{ y}^{-1}$  respectively. This suggests that nitrous oxide emissions are rather similar in pasture and wetlands.

Schipper et al. (1993) measured nitrous oxide emissions in forest wetlands irrigated with sewage of  $290 \pm 20\text{ kgN ha}^{-1}\text{ y}^{-1}$ . Cooper (1990) measured denitrification rates averaging  $26 \pm 5.2\text{ tN ha}^{-1}\text{ y}^{-1}$  near the upstream edge of a pasture wetland. Assuming a

N<sub>2</sub>O:denitrification ratio of 5% (a likely minimum estimate) this equates to a N<sub>2</sub>O emission of  $1300 \pm 260 \text{ kgN ha}^{-1} \text{ y}^{-1}$ . These rates are 1-2 orders of magnitude higher than reported emission rates for pasture. In four other published studies, nitrate removal rate lay in the range  $18\text{--}913 \text{ kgN ha}^{-1} \text{ y}^{-1}$  (see Table 1). Assuming a N<sub>2</sub>O:denitrification ratio of 10%, this equates to a N<sub>2</sub>O emission of  $40 \pm 20 \text{ kgN ha}^{-1} \text{ y}^{-1}$ . This is slightly higher than the reported mean of  $10 \text{ kgN ha}^{-1} \text{ y}^{-1}$  for nitrous oxide emissions from NZ pasture.

#### Main points

1. there are very few measurements of nitrous oxide emission from NZ wetlands and to confidently estimate their role as nitrous oxide emitters
2. wetland denitrification rates measured in four NZ studies (Sukias, 2006; Nguyen, pers. comm.; Sukias & Collins, in press; Rutherford & Nguyen, 2003) are similar to published values from overseas studies and this suggests that nitrous oxide emissions from these wetlands are similar to published emission rates from overseas studies
3. the estimated emission rates in these wetlands are similar to estimated emissions from pasture
4. however, measured nitrous oxide emissions from a wetland draining a forested sewage spray irrigation site are orders of magnitude higher than any published values from overseas studies (Schipper et al., 1993)
5. in addition, measured denitrification rates in one study of a pasture wetland are orders of magnitude higher than any published values from overseas studies (Cooper 1990) which suggests that nitrous oxide emissions may be very high
6. therefore, it is possible that there are 'hot spots' of denitrification and nitrous oxide emission in NZ wetlands
7. it is possible that nitrous oxide emission rates expressed on an areal basis ( $\text{kgN ha}^{-1} \text{ y}^{-1}$ ) are comparable in wetlands and pasture in much of the NZ landscape
8. where this occurs wetlands will not be 'hot spots' for nitrous oxide emission (viz., encouraging wetlands will not significantly increase nitrous oxide emissions)
9. however, it is also possible that nitrous oxide emissions are very high in some wetlands, or some parts of wetlands
10. if this is the case then those wetlands, or parts of wetlands, could be 'hot spots' for nitrous oxide emission
11. we cannot confidently predict whether nitrous oxide emissions in ecosystems downstream of pasture catchments emit significantly more (or less) nitrous oxide than that emitted from the pasture, wetlands, and streams within the catchment.

## 4 Conclusions and next stage

This review has highlighted the key processes leading to  $\text{N}_2\text{O}$  emission from wetlands. It has also shown that while reported  $\text{N}_2\text{O}$  emissions from riparian wetlands are highly variable, the highest rates are associated with high external  $\text{NO}_3^-$  loads. There have not been, as yet, any systematic measurements of  $\text{N}_2\text{O}$  emissions from riparian wetlands in New Zealand pasture catchments. However, there is other evidence that suggests that they may be at the high end of the range reported in the literature. This evidence includes:

1. A plentiful (in general)  $\text{NO}_3^-$  supply from the pasture catchment,
2. Very high rates of in situ denitrification reported (1 study), and,
3. Significant concentrations of dissolved  $\text{N}_2\text{O}$  in lowlands streams draining pasture catchments (1 study).

There is, therefore, a justifiable need to obtain some reliable measurements of  $\text{N}_2\text{O}$  production from New Zealand riparian wetlands. This will confirm or deny the circumstantial evidence that they are a focal point for  $\text{N}_2\text{O}$  emissions in pasture catchments; not only because they 'process' the majority of the  $\text{NO}_3^-$  rich leachate generated within the pasture, but also because they provide optimal conditions for denitrification.

Together with estimates of the area of wetlands within pasture catchments, such measurements will also enable us to make a more robust estimate of total  $\text{N}_2\text{O}$  emissions from wetlands compared to the emissions from their pasture catchments. There is no national inventory of wetlands suitable for this purpose. The WERI (wetlands of ecological and representative importance) database maintained by Department of Conservation focuses on those wetlands that are representative of the natural diversity. Thus small wetlands or seepage areas are not generally included and it is these areas that are likely to be the most important sources of  $\text{N}_2\text{O}$ .

Estimating wetland area within pastoral catchments is a difficult task and, to the best of our knowledge, has only been achieved within the Lake Taupo catchment, where there is much interest in finding ways of reducing nitrogen input to the lake. McKergow et al. (2007) modelled the extent of Taupo wetlands using terrain indices based on slope factors and predictors of soil saturation in the small agricultural Tutaeuaua catchment (6.6 km<sup>2</sup>) that drains to the north western shore of Lake Taupo. The model results were validated by field surveys and aerial photography and showed that > 5% of the farmed area in the Tutaeuaua catchment is wetland. The spatial pattern of wetlands predicted generally agreed with the mapped wetlands, particularly along the larger valley bottoms. Although it is not possible to extrapolate the results of the Tutaeuaua catchment to all agricultural catchments in New Zealand, it does provide an indication that wetland areas are significant, and are consistent with the areas chosen from empirical modelling (Section 3). If, however, there is a distinct gradient in  $\text{N}_2\text{O}$  emissions across riparian wetlands, then simply calculating an average emission factor from wetlands may mask very high rates occurring over very small areas,



which could be amenable to interventions that reduce overall emissions from pasture catchments.

Completing objectives 3 and 3 of our original proposal is necessary to refine our understanding of N<sub>2</sub>O production and emission across riparian wetlands, calibrate and validate a deterministic model, and provide robust estimates of N<sub>2</sub>O emissions from wetlands within NZ pasture catchments.

We propose selecting a number of example wetlands, each with relatively straightforward hydrology and good agricultural information (e.g., farm type, stocking rate, fertiliser use, effluent management). Field work will focus on measuring net N<sub>2</sub>O emission rates, and examining key nitrification-denitrification processes affecting N<sub>2</sub>O emissions along transects from aerobic zones near the edges to anerobic zones in saturated wetland soils. This will establish whether there are predictable gradients in N<sub>2</sub>O production across wetlands in pasture catchments. Key variables measured will include seasonal nitrate concentrations in shallow groundwater, temperature, dissolved oxygen and Eh. We will measure N<sub>2</sub>O emission rates and N<sub>2</sub>O:N<sub>2</sub> ratios using standard enclosure methods and GC-ECD methodology. We will use this data to calibrate a deterministic model that predicts N<sub>2</sub>O emission as a function of the environmental conditions prevailing across riparian wetland transects from the boundary with the pasture to the boundary with the stream. We will use the model piloted by McKergow et al. (2007) to estimate the total wetland area within each catchment and couple this with improved understanding of spatial variability to estimate total N<sub>2</sub>O emission rates from wetlands within the chosen catchments. Depending on the error associated with these estimates, we may then be able to estimate total N<sub>2</sub>O emissions from agricultural wetlands nationally.

Completion of objectives 3 and 4 will enable us to make recommendations about (i) the significance of pastoral wetlands as source of N<sub>2</sub>O, and (ii) ways of managing wetlands to reduce N<sub>2</sub>O emissions and optimise their function for water treatment and greenhouse gas abatement.

Through this review we have been able to extract and highlight a plethora of information that enable us to understand the processes and conditions leading to N<sub>2</sub>O production, emission and loss to streams. However, because of the lack of data from New Zealand wetlands we are unable to answer definitively, the question as to whether NO<sub>3</sub><sup>-</sup> load reduction is offset by significantly higher N<sub>2</sub>O emissions to the atmosphere; so called 'pollution swapping'.

If NO<sub>3</sub><sup>-</sup> load is the main driver of N<sub>2</sub>O emissions from riparian wetlands then minimization of N<sub>2</sub>O emissions will only be possible if riparian zone management is combined with source-directed measures designed to drastically reduce the nitrate concentration in subsurface runoff (Franken et al., 1992; Hefting et al., 2006).

It may of course be argued that from a GHG perspective it doesn't matter whether more or less N<sub>2</sub>O is emitted from riparian wetlands because it will ultimately be processed and emitted in 'downstream' ecosystems including rivers, estuaries, and the ocean (Seitzinger et al., 2000; Hernandez & Mitsch, 2006). However there are many pathways in the nitrogen cycle, which could assimilate pasture-sourced N as well as physical processes that can result in deposition and burial (effectively removing it from biogenic processes). It is therefore not at all obvious that nitrogen not lost to the atmosphere through denitrification in wetlands will ultimately be emitted in downstream ecosystems.

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