Do wetland or denitrifying bioreactor systems designed to remove nitrate lead to pollution swapping?

Priscila Simon & Cecile de Klein

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Contents

1.	Exe	Executive Summary1							
2.	Intro	Introduction2							
	2.1	Bad	ckground	2					
	2.2	Ob	jectives	3					
3.	Met	hod		4					
	3.1	Lite	erature review	4					
	3.1	1.1	Constructed wetlands	4					
	3.1	1.2	Natural wetlands	4					
	3.1	1.3	Denitrifying bioreactors	4					
	3.2	Est	timating nitrous oxide emission factors	5					
4.	Res	ults	and Discussion	6					
5.	Conclusions								
6.	Acknowledgements								
7.	Refe	References							
8.	Appendix13								

1. Executive Summary

The use of wetlands (natural and constructed) and denitrifying bioreactors within agricultural catchments can reduce nitrate losses (Schipper et al. 2010). A potential unintended consequence of using these systems is that nitrous oxide emissions may increase, given that the process of nitrate removal (denitrification) is also a pathway for nitrous oxide production. However, nitrate that is lost to water can subsequently be emitted as nitrous oxide from waterbodies (groundwater, rivers, estuaries). Therefore, wetlands and bioreactors will only cause pollution swapping (an increase in one pollutant as a result of a measure introduced to reduce a different pollutant), if the proportion of nitrate that is lost as nitrous oxide emission factor for nitrate that had already entered waterbodies.

The purpose of this review was to assess the potential for pollution swapping between nitrate and nitrous oxide loss from wetlands and denitrifying bioreactors in agricultural systems. We undertook a literature review to collate data and information from peer-reviewed publications where nitrous oxide emissions from these systems were measured. We then compared the measured or estimated nitrous oxide emission factors from wetlands and denitrifying bioreactors with the nitrous oxide emission factor values used in global and national methodologies for estimating nitrous oxide emissions. The Intergovernmental Panel on Climate Change (IPCC) and the New Zealand Inventory recommend an emission factor (EF₅) for nitrous oxide emissions from waterbodies of 0.75% (IPCC 2006), although a recent revision of international greenhouse gas inventory guidelines has suggested an EF₅ of 1.1 % (IPCC 2019). This emission factor includes three components: EF_{5g}, EF_{5r} and EF_{5e} representing emissions from ground water and surface drainage, rivers and estuaries, respectively. For the IPCC 2006 EF₅ value of 0.75% each component contributes 0.25%, while for the IPCC 2019 EF5 value of 1.1% the components contribute 0.6 % (g), 0.25% (r) and 0.25% (e) (IPCC 2019).

To our best knowledge, there have been no New Zealand studies measuring nitrous oxide emissions from wetlands within agricultural catchments, and only a few studies measuring nitrous oxide emissions from denitrifying bioreactors. Our study is, therefore, mainly based on results from the international literature. Studies of nitrous oxide emissions from natural wetlands represented the smallest number of studies found in the literature (7 studies), compared with studies on constructed wetlands (22 studies) and denitrifying bioreactors (11 studies).

We reveiwed N₂O emission and emission factors from the structures themselves, but also estimated an overall EF₅ value, by including N₂O emissions from rivers and estuaries (each at 0.25%) for any nitrate that was not removed in the systems. We either used the nitrate reduction rates measured in the different studies, or, for studies where the nitrate reduction rate was not provided, assumed an average NO₃⁻ reduction efficiency of 70%.

The main findings of this review were:

- The majority of the nitrous oxide emission factors reported for wetlands and denitrifying bioreactors were below the 0.75% IPCC value for nitrous oxide emissions from leached nitrate.
- Denitrifying bioreactors were the only systems for which a number of studies reported values above 1.1%. These were all from laboratory studies with high rates of nitrate inflow.

- Natural wetlands had the lowest nitrous oxide emissions, with EF_{5g} values ranging from 0.08 to 0.55% (median value of 0.19%), followed by constructed wetlands from 0.003 to 1.15% (median value of 0.10%) and denitrifying bioreactors with EF_{5g} values ranging from 0.003 to 1.4% (median value of 0.29%).
- However, when estimating an overall EF_{5 (g+r+e)}, by using the measured or assumed nitrate reduction rates, the lowest emissions were from constructed wetlands with values ranging from 0.004 to 1.5 (average 0.21 and median 0.11), followed by natural wetland, ranging from 0.14 to 0.94 (average 0.41 and median 0.39), and bioreactors, ranging from 0.15 to 1.6 (average 0.58 and median 0.51).

The results of our review suggest that the potential for pollution swapping in wetlands and denitrifying bioreactors is unlikely.

2. Introduction

2.1 Background

To reduce risks of nitrate leaching to water, landowners could consider protecting or installing wetlands and denitrifying bioreactors that can remove nitrate from water via denitrification, a biological process that converts nitrate into gaseous nitrogen (N) forms. The two main gases released through denitrification are environmentally benign dinitrogen gas (N₂), and the greenhouse gas nitrous oxide.

Natural and constructed wetlands intercept and process nitrate in surface or subsurface flow from pasture as it is transported towards streams. There have been numerous studies that have demonstrated that riparian wetlands can remove large amounts (> 100 kg N ha⁻¹ y⁻¹) of nitrate -N and most studies suggest that denitrification is the mechanism responsible (Hill 1996; Cooke et al. 2018).

Denitrifying bioreactors vary in their designs according to the solid carbon (C) sources utilized (e.g. woodchips, cardboard and pine needles), the hydrologic connection between water containing nitrate and C source, and the ratio of source area: treatment area (Schipper et al. 2010). Bioreactors can be classified into denitrification walls and denitrification beds.

Denitrification walls are systems where solid C material is incorporated vertically into shallow groundwater perpendicular to the flow. Darcian flow, saturated hydraulic conductivity, hydraulic gradient and the flow paths intercepted by the walls, are factors which control the flux of nitrate into the walls (Robertson & Cherry 1995; Schipper et al. 2010).

Denitrification beds are compartments that are filled with wood chips and receive nitrate in concentrated discharges either from a range of wastewaters (Schipper et al. 2010) or tile/drain discharge (Robertson & Merkley 2009). Denitrification beds can also be installed into existing stream beds or drainage ditches and are specifically referred to as "stream bed bioreactors" (Robertson & Merkley 2009). The source area: treatment area ratio for beds is usually much greater than in wall designs, due to either natural or artificial drainage networks that intercept and funnel groundwater inputs to the bioreactor. Retention and creation of wetlands and denitrifying bioreactors within agricultural landscapes are promoted as a means of reducing the nitrate load to surface waters (Cooke et al. 2018). Given that the nitrate removal process, denitrification, can result in

nitrous oxide emissions, there is a risk of pollution swapping. However, as nitrate can also denitrify to nitrous oxide once it is in a waterbody (groundwater, rivers, estuaries; Figure 1), wetlands and bioreactors will only cause pollution swapping if the proportion of nitrate that is denitrified in these structures is greater than that in waterbodies.



Figure 1: Schematic representation of direct and indirect nitrous oxide emissions from leached N. (adapted from de Klein et al. (2008)).

Under current inventory frameworks, estimates of a farm's nitrous oxide emissions include emissions that occur from nitrate *after* it is lost from the farm through leaching. This is referred to as an *indirect* source of nitrous oxide. The emission factor used to estimate these indirect emissions is known as EF_5 and incorporates three components (Figure 1): an emission factor for groundwater and surface drainage (EF_{5g}), an emission factor for rivers (EF_{5r}), and an emission factor for estuaries (EF_{5e}).

The value for EF_5 used in New Zealand's inventory methodology is 0.75% (% nitrous oxide-N lost per unit of nitrate-N leached), with the three components contributing 0.25% each (MfE 2020). A recent revision of international greenhouse gas inventory guidelines suggests that EF_5 is 1.1%, with EF_{5g} , EF_{5r} and EF_{5e} contributing 0.6, 0.26 and 0.26% respectively (IPCC 2019). Therefore, if the nitrous oxide emission factor of wetlands or denitrifying bioreactors is equal to or less than 1.1% of the N entering these structures, then any nitrous oxide produced from intercepted nitrate is not additional to the farm's total direct and indirect nitrous oxide emissions, and does not result in any pollution swapping. However, if the emission factor is greater than 1.1% pollution swapping will occur. There is a need to quantify the nitrous oxide emission factor of wetlands and denitrifying bioreactors ensure any pollution swapping can be assessed.

2.2 Objectives

The aims of this project were:

1. Provide a summary of the literature on nitrous oxide emissions from wetlands and denitrifying bioreactors, and a summary of the basis for the 0.75% emission factor used in the NZ Inventory, and relevance of updated IPCC value (1.1%).

2. For published studies that provide the results as 'emission factors' or provide enough information for EF_5 to be calculated, compare the nitrous oxide emission factors from wetlands or denitrifying bioreactors with the IPCC default emission factor for N that is lost to waterways.

3. If the nitrous oxide emission factors of wetlands or denitrifying bioreactors are greater than 0.75% or 1.1%, assess the increase in emissions relative to the total nitrous oxide losses from other on-farm activities and the farm enterprise.

4. Provide a description of the methodology used and assumptions made

5. Provide a 1-2 page 'farmer-friendly' summary of findings specifically addressing farmer concerns regarding pollution swapping.

3. Method

3.1 Literature review

The data were collected from studies published and reported in the database "Scopus - multidisciplinary" indexed by Elsevier. The key words searched were: ("Wetlands", "Natural wetlands", "Constructed wetlands", "Denitrifying bioreactors", "Bioreactors", "Denitrification beds", "Nitrous oxide", "N₂O", "Nitrate leaching", "Pollution swapping").

Data originated from studies that, (i) used constructed wetland, (ii) natural wetlands or (iii) denitrifying bioreactors to reduce nitrate leaching, and also had measured losses of nitrous oxide. The studies were separated by system, as described below:

3.1.1 Constructed wetlands

Studies undertaken in wetlands constructed under 3 different designs: VSSF (Vertical subsurface flow), HSSF (Horizontal subsurface flow), and FWS (Free water surface) constructed wetlands.

3.1.2 Natural wetlands

Studies undertaken in natural riparian wetlands with measurements of surface nitrous oxide fluxes.

3.1.3 Denitrifying bioreactors

Field and laboratory studies with different designs (denitrification beds or denitrification walls), using woodchip as the C substrate. Studies evaluating different C substrates (woodchips, cardboard, pine needles or barley straw), under distinct hydraulic retention times (HRTs) (2, 3, 8, 5 or 10 hours) were also reviewed. Unfortunately, these studies did not provide enough information to calculate EF values and we could therefore not use them for the current assessment. However, for completeness, we have included a summary of the results as an appendix.

3.2 Estimating nitrous oxide emission factors

When emission factors were not provided in the publications, values were estimated based on the measured nitrous oxide emission and other information provided. For estimating EF values, we calculated the proportion of cumulative nitrous oxide loss as a proportion of the amount of nitrate that entered the system. This included both the amount of nitrous oxide emitted to the atmosphere (surface fluxes) as well as nitrous oxide that was diluted in water leaving the wetland or bioreactor:

EF₅ wetland/bioreactor =

[(nitrous oxide-N_{emitted} + nitrous oxide-N_{diluted})/nitrate-N_{in}] x 100. (Eq. 1)

The various studies presented the nitrous oxide fluxes in different units, and we therefore converted the results to standardised units (mg N/m²/h; g N/m²/d or mg N/L). For the studies where there was not enough information provided to estimate the nitrous oxide EF, we recorded the results as presented in the paper, i.e. the amount of nitrous oxide emitted from the surface, or the concentration of nitrous oxide diluted in water, and proportion of nitrous oxide lost from the nitrate removed.

Since wetlands and bioreactor systems generally do not denitrify the total amount of nitrate entering the system, in studies where the rate of nitrate reduction was provided, we estimated the potential losses of nitrous oxide downstream (rivers and estuaries, $\text{EF}_{5r,e}$). When the nitrate reduction rate was not provided, we considered an average value of 70% for these systems.

When the rate of nitrate reduction was provided, the EF_{5r,s} is estimated as follows:

kg nitrous oxide-N downstream =

$$[EF_{5r,e} (0.005) \times (kg nitrate-N_{in} - kg nitrate-N_{removed})]$$
(Eq. 2.1)

When the rate of nitrate reduction was not provided, the $EF_{5r,s}$ is estimated as follows: kg nitrous oxide-N downstream =

$$[EF_{5r,e} (0.005) x (kg nitrate-N_{in} - (kg nitrate-N_{in} x 0.70))]$$
(Eq. 2.2)

To estimate the overall EF₅, we then added the estimated cumulative nitrous oxide emissions downstream to the nitrous oxide cumulative emissions/diluted from wetlands/bioreactors and divided it by the total amount of nitrate-N entering the system (equation 3):

 $EF_5=$

[(kg nitrous oxide-N_{wetl/bior} + kg nitrous oxide-N_{downstream})/ kg nitrate-N_{in}] x100 (Eq.3)

4. Results and Discussion

The results obtained from this literature review show that nitrous oxide emissions from the systems increased in the following order: natural wetlands, ranging from 0.08 to 0.55% (Table 1), followed by constructed wetlands (0.003 to 1.1%; Table 2), and denitrifying bioreactors (0.003 to 1.4%; Table 3). When estimating the overall EF_{5 (g+r+e)}, by using either the measured or assumed nitrate reduction rates, the lowest emissions were from constructed wetlands with values ranging from 0.004 to 1.5 (average 0.21 and median 0.11), followed by natural wetland, ranging from 0.14 to 0.94 (average 0.41 and median 0.39), and bioreactors, ranging from 0.15 to 1.6 (average 0.58 and median 0.51).

Studies of nitrous oxide emissions from natural wetlands represented the smallest number of studies found in the literature (7 studies), followed by denitrifying bioreactors (12 studies) and constructed wetlands (16 studies). Of the bioreactor studies, 8 included measured EF values, and 4 studies only measured cumulative emissions. The literature data are summarised in Figure 2.

The majority of the indirect nitrous oxide emission factors found in the three systems were below the 0.75% IPCC EF_5 value for indirect nitrous oxide emissions from nitrate leaching. Denitrifying bioreactor was the only system where a few studies observed EF_5 values above 0.75% (Figure 2).

The boxplot comparisons demonstrate that the overall EF_5 for both natural and constructed wetland systems all (but two outliers) were below IPCC EF_5 values (0.75 or 1.1%). For the bioreactor studies, the data presented a large variability, with some overall EF_5 values above the 0.75% and 1.1% IPCC values. However, the majority of the results are under the 0.75% EF_5 . This suggests that although the use of bioreactors can vary in terms of effectiveness, it is unlikely that the indirect nitrous oxide emissions from this system will be above the IPCC 2019 default of 1.1%, and with a low chance to be above the 0.75% IPCC 2006.



Figure 2: Average nitrous oxide emission factors (EF_{5g+r+e}) from bioreactors, constructed wetlands and natural wetlands collected from 8, 16 and 7 studies, respectively. The nitrous oxide EFs from wetlands and bioreactors are compared with the IPCC default values (EF_5) of 0.75% (IPCC 2006) and the revised value of 1.1% (IPCC 2019) for indirect nitrous oxide emissions from nitrate leaching.

Reference	Country	System	Nitrate inflow	Nitrous oxide flux	EF _{5g}	Overall EF₅
			g N/m²/y	g N/m²/y	(%)	(%)
Hefting (2003)	The Netherlands	Forested riparian zone	630	2	0.32	0.47*
		Grassland riparian zone	270	0.3	0.11	0.26*
Muelherr and Hiscock, 1997	England	Wetland			0.15	0.30*
Hiscock et al. (2003)	England	Wetland			0.19	0.34*
	England/Scotland	Wetland			0.17	0.32*
Ueda et al. (1991)	Japan	Wetland			0.23	0.38*
Ronen et al. (1988)	Israel	Wetland			0.25	0.40*
Minami and Ohsawa (1990)	Japan	Wetland			0.08	0.23*
Dowdell et al. (1979)	England	Wetland			0.55	0.70*

Table 1. Summary of published results on inflow nitrate-N loading, nitrous oxide emissions and the nitrous oxide emission factor (EF(%)= nitrous oxide flux/nitrate inflow x 100%) of natural wetlands. *Overall EF_5 estimated assuming 70% of nitrate reduction efficiency.

 EF_{5g} = emission factor of nitrous oxide, represented by the nitrous oxide emitted to the atmosphere (surface fluxes) as well as nitrous oxide that was diluted in water leaving the wetland or bioreactor.

Overall EF_5 = emission factor of nitrous oxide, represented by sum of the nitrous oxide emitted/diluted in water leaving the wetland or bioreactor (EF_{5g}), with the nitrous oxide lost downstream in rivers and estuaries, ($EF_{5r,e}$ of 0.25% each).

N₂O emissions from wetlands/bioreactors Priscila Simon & Cecile de Klein

Table 2	2. Summary of published results on inflow nitrate-N loading, nitrous oxide er	nissions and the nitrous oxide emission factor (EF(%)= nitrous oxic
flux/nit	rate inflow x 100%) of different constructed wetland systems. VSSF=vertica	l subsurface; HSSF=horizontal subsurface; FWS=free water surfac
* Overa	all EF₅ estimated assuming 70% of nitrate reduction efficiency.	

Reference	Country	System	Nitrate inflow mg N/L	Nitrous oxide flux mg N/m²/h	EF _{5g} (%)	Overall EF (%)
Teiter and Mander (2005)	Estonia	VSSF	50.9	0.225	0.02	0.17*
Mander et al. (2003)	Estonia	HSSF	109	0.186	0.45	0.60*
Søvik and Kløve (2007)	Norway	FWS	38	0.130	0.13	0.28*
Johansson et al. (2003)	Sweden	FWS	8	0.112	0.17	0.32*
Søvik et al. (2006)	Finland	FWS	59.7-66.1	0.057	0.08	0.23*
	Finland	FWS	1.4	0.001	0.07	0.22*
	Finland	HSSF	1.8	0.005	0.47	0.62*
	Norway	FWS	43.4	0.068	0.04	0.19*
	Norway	VSSF	52.6	0.200	0.01	0.16*
Ström et al. (2007)	Sweden	FWS	75	0.230	0.11	0.26*
Gui et al. (2007)	Japan	FWS	73.5	0.079	0.06	0.21*
	Japan	VSSF	73.5	0.123	0.10	0.25*
Zhou et al. (2020)	China			0.480	0.11	0.26*
Liu et al. (2009)	USA	FWS	100	0.200	0.12	0.27*
	Japan	VSSF	100	0.073	0.04	0.19*
Wu et al. (2009)	China	FWS	49-55	0.350	0.25	0.40*
VanderZaag et al. (2010)	Canada	FWS	306	0.250	0.12	0.27*
	Canada	HSSF	306	0.396	0.20	0.35*
Inamori et al. (2007)	Japan	VSSF	307	0.022	0.003	0.15*
Inamori et al. (2008)	Japan	VSSF	308	0.287	0.01	0.16*
Wang et al. (2008)	Japan	VSSF	309	0.072	0.04	0.19*
Liikanen et al. (2006)	Finland	HSSF	310	0.017	1.15	1.30*
Fey et al. (1999)	Germany	HSSF	73	0.133	0.07	0.22*

Table 3. Summary of published results on inflow nitrate-N loading, nitrous oxide emissions, dissolved nitrous oxide and the nitrous oxide emission factor (EF(%)= nitrous oxide flux/nitrate inflow x 100%) of different bioreactor systems. WS= Woodchip on the surface; SS= Soil on the surface. *Overall EF_5 estimated assuming 70% of nitrate reduction efficiency.

Reference	Country	System	Nitrate inflow	Nitrous oxide flux	Nitrous oxide dissolved	EF _{5g} (%)	Overall EF₅ (%)
Greenan et al. (2009)	EUA	Woodchip wall	580 mg N/kg wood	0.019 mg N/kg wood		0.003	0.15*
		Woodchip wall	1320 mg N/kg wood	0.085 mg N/kg wood		0.006	0.16*
		Woodchip wall	1390 mg N/kg wood	0.299 mg N/kg wood		0.022	0.17*
		Woodchip wall	3080 mg N/kg wood	0.236 mg N/kg wood		0.008	0.16*
Moorman et al. (2010)	USA	Woodchip wall	10 mg N/L (77% efficiency)			0.62	0.85
		Soil Control	10 mg N/L (51% efficiency)			0.39	0.88
Elgood et al. (2010)	Canada	Woodchip bed	2.8 mg N/L (92% efficiency)		0.0064 mg N/L	0.23	0.31
Christianson et al. (2013)	USA	Woodchip bed/WS Woodchip bed/ SS	1250 mg N/h (56% efficiency) 1250 mg N/h (56% efficiency)	0.055 mg N/h 0.0025 mg N/h	0.675 mg N/h 0.065 mg N/h	0.13 0.01	0.57 0.45
Warneke et al. (2011)	NZ	Woodchip bed	132 kg N	99.58 g N/d	362 g N/d	0.35	0.50*
Rivas et al. (2020)	NZ	Woodchip Woodchip	3-8.5 mg N/L (96% efficiency) 6.4-23.4 mg N/L (80% efficiency)	0.06 mg N/L 0.04-0.307 mg N/L		1.0 1.4	1.04 1.60
Burbery et al. (2020)	NZ	Woodchip	6 -7 mg N/L		0.006-0.008 mg N/L	0.11	0.26*
Bock et al. (2018)	USA	Woodchip	0.052 g N/d	0.00024 g N/d		0.46	0.61*
		Woodchip	0.026 g N/d	0.00011 g N/d		0.43	0.58*
		Woodchip	0.013 g N/d	0.00012 g N/d		0.91	1.06*

5. Conclusions

The results obtained in this review show that the nitrous oxide emission factors from wetlands and bioreactors are very low, and well below the default EF₅ values suggested by IPCC for nitrous oxide emissions from leached nitrate. The results of our study therefore suggest that the potential for pollution swapping in wetlands and denitrifying bioreactors is unlikely.

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8. Appendix

Summary of published results on nitrate inflow loading, nitrous oxide fluxes and dissolved nitrous oxide dissolved in different bioreactor systems (HRT=hydraulic retention time).

Reference	Country	System	Nitrate inflow	Nitrous oxide flux	Nitrous oxide dissolved
Healy et al. (2012)	Ireland	Woodchip bed	19.5 - 32.5 mg N/L	Nil	1.24 g N/m²/d
		Cardboard bed		Nil	0.08 g N/m²/d
		Pine needles bed		3.21 g N/m²/d	0.17 g N/m²/d
		Barley straw bed		0.72 g N/m²/d	0.47 g N/m²/d
		Soil - control		1.56 g N/m²/d	0.39 g N/m²/d
Healy et al. (2015)	Ireland	Woodchip bed- 3h HRT	20 - 29.6 mg N/L	0.57 g N/m²/d	
		Cardboard bed- 3h HRT		0.04 g N/m²/d	
		Pine needles bed - 3h HRT		0.1 g N/m²/d	
		Barley straw bed - 3h HRT		0.22 g N/m²/d	
		Woodchip bed - 5h HRT		1.48 g N/m²/d	
		Cardboard bed - 5h HRT		0.02 g N/m²/d	
		Pine needles bed - 5h HRT		0.09 g N/m²/d	
		Barley straw bed - 5h HRT		0.13 g N/m²/d	
		Woodchip bed - 10h HRT		3.29 g N/m²/d	
		Cardboard bed - 10h HRT		0.69 g N/m²/d	
		Pine needles bed - 10h HRT		4.11 g N/m²/d	
		Barley straw bed - 10h HRT		0.02 g N/m²/d	
Woli et al. (2010)	USA	Woodchip bed	2.80 -18.9 mg N/L	0.01 - 0.13 mg N/m²/h	0.004% of NO ₃ ⁻ removed
Davis et al. (2019)	USA	Woodchip bed - 2h HRT		478.4 mg N/m³/d	5.19% of NO ₃ ⁻ removed
		Woodchip bed - 8h HRT		28.9 mg N/m ³ /d	0.35% of NO ₃ ⁻ removed
		Woodchip bed- 16h HRT		36.6 mg N/m³/d	0.52% of NO ₃ ⁻ removed