Ministry for Primary Industries
Manatū Ahu Matua

Nitrous oxide emissions from waterways

MPI Sustainable land management mitigation and adaptation to climate change research programme

MPI Technical Paper No: 2013/05

Prepared by Professor T. J. Clough, Lincoln University, & Professor F. M. Kelliher, AgResearch
Peer reviewed by Dr Steve Thomas, Plant and Food Research
(CONT-24650-SLMACC-LIN LINX1101

ISBN No: 978-0-478-40581-1 (online)
ISSN No: 2253-3923 (online)

April 2013

New Zealand Government

Growing and Protecting New Zealand

Disclaimer

While every effort has been made to ensure the information in this publication is accurate, the Ministry for Primary Industries does not accept any responsibility or liability for error of fact, omission, interpretation or opinion that may be present, nor for the consequences of any decisions based on this information. Any view or opinion expressed does not necessarily represent the view of the Ministry for Primary Industries.

Requests for further copies should be directed to:
Publications Logistics Officer
Ministry for Primary Industries
PO Box 2526
WELLINGTON 6140

Email: brand@mpi.govt.nz

Telephone: 0800 00 83 33

Facsimile: 04-894 0300

This publication is also available on the Ministry for Primary Industries website at

http://www.mpi.govt.nz/news-resources/publications.aspx

Executive Summary

1. This document reports on completed and on-going work that examines nitrous oxide emissions from the Waikato River and assesses the results in comparison to previous New Zealand emission factors for indirect losses from rivers. The IPCC's default emission factor EF5-r currently has a value of 0.0025 kg N_2O-N per kg N in the 2006 guidelines[1].
2. In situ determinations of N_2O-N fluxes from the Waikato River were performed in December 2011 and February 2012 at dates when water temperatures would have optimised biological rates and minimised dissolved oxygen. The Waikato River is potentially two separate systems; waterways comprising lakes and the 'true' river downstream of Karapiro dam. Measured fluxes were of similar magnitude for each 'system'.
3. Measured N_2O-N fluxes were < 120 μg m^{-2} h^{-1} and when used in conjunction with the Waikato River's 10 year median values for nitrate concentrations and flow rates a calculated EF5-r value for the 'true' river (Karapiro to Waikato heads) equated to 0.0005 kg N_2O-N per kg N leached.
4. Using sites routinely sampled by Environment Waikato showed hot-spots of dissolved N_2O occurred. These included tailrace water from hydro dams and one site downstream of tributaries draining agricultural land.
5. There was no clear relationship between dissolved N_2O saturations and either nitrate concentrations or measured N_2O-N fluxes.
6. Isotopic studies using natural abundance nitrate isotopes indicate denitrification within the Waikato River especially downstream of the Ngaruawahia/Huntly reach. This is where the river becomes shallower, wider and the river bed is reported to hold more sediment.
7. An assessment of pelagic (in the water column) denitrification identified no significant activity for the water samples taken on the study day. Indications are that benthic (at the river bed water interface) denitrification in the river sediments may be the key determinant of N_2O flux. Other factors may dominate N cycling processes at the hydro-lake sites.
8. River length on its own is a poor determinant of a river's potential EF5-r 'value' and the Waikato chemistry/hydrology is a good example of why this is the case with its diverse catchment and water flows. An EF5-r value needs to be based on the factors that affect contact of the water body with the river bed i.e. the benthic community where denitrification is likely to be at its highest rate.
9. Given the results of this study and past New Zealand specific work it is advocated that a New Zealand specific EF5-r value should be implemented, equal to 0.0025 kg N_2O-N/kg NO_3^--N leached. This would make the EF5 value (EF5-r + EF5-g + EF5-e) equal to 0.0075 kg N_2O-N/kg NO_3^--N leached and New Zealand's indirect N_2O emissions from leaching and runoff would reduce by 3.62 Gg N_2O.

[1] 2006 IPCC Guidelines for National Greenhouse Gas Inventories. Chapter 11. Page 24. Footnote 23.

Disclaimer

Contents

1. Introduction

As a consequence of New Zealand's commitment to the Kyoto Protocol it must ensure that the average emissions (less removals by forestry meeting Article 3.3 forestry definitions) over the first commitment period of the Kyoto protocol (2008-2012) are less than or equal to emissions in 1990 as reported in New Zealand's initial report under the Kyoto Protocol, or take responsibility for the excess emissions. The ability to correctly account for the sources of N_2O is crucial in determining New Zealand's subsequent responsibility under the first commitment period of the Kyoto Protocol and beyond. In 1990, New Zealand's total greenhouse gas emissions were 59,797.2 Gg carbon dioxide equivalents (CO_2-e). In 2010, total greenhouse gas emissions (excluding Land Use Land-use change and forestry) had increased by 11,860.0 Gg CO_2-e (19.8 per cent) to 71,657.2 Gg CO_2-e (MfE 2012).

New Zealand has a unique emissions profile compared with other developed countries, where agriculture often makes up ≤ 10% of their total emissions. Emissions of CO_2 make up approximately 80% of most developed countries' greenhouse gas emissions. Since New Zealand exports predominantly agricultural goods and has a relatively low population, with low CO_2 emissions per capita, the agricultural emissions of methane (CH_4) and nitrous oxide (N_2O) comprise almost half of New Zealand's total emissions (47% in 2010). New Zealand's greenhouse gas inventory 1990-2010 notes that in 2010, emissions of N_2O from agricultural soils equated to 31.95 Gg. Sources of N_2O, and the amounts emitted in 2010, include direct soil emissions that are dominated by fertiliser inputs (5.60 Gg), pasture, range and paddock manure (18.22 Gg), and indirect emissions (8.13 Gg).

Losses of synthetic fertiliser and manure nitrogen can lead to indirect emissions of N_2O via volatilisation and subsequent atmospheric deposition of ammonia (NH_3) and nitrogen oxides (NO_x), and from nitrogen leaching and runoff. In 2010, New Zealand's indirect emissions sources from agricultural soil comprised of 'atmospheric deposition' (2.96 Gg) along with 'nitrogen leaching and runoff' (5.17 Gg). While higher indirect N_2O emissions occurred from 'nitrogen leaching and runoff' the actual loss of nitrogen (131.6 Gg N yr^{-1} in 2010) was lower than the N associated with atmospheric deposition (188.3 Gg N yr^{-1} in 2010). The difference was due to the emission factors that are used to calculate the N_2O emissions, with 'nitrogen leaching and run off' having a higher prescribed emission factor per kg of N.

The fraction of N lost (FRACLEACH) to leachate and runoff can be determined using a default factor supplied by the Intergovernmental Panel on Climate Change (IPCC) and this has an uncertainty of 0.1–0.8 with a default value of 0.3 kg N leached per kg of N input as fertiliser and excreta (IPCC 2006). Alternatively, a country specific emission factor can be used. New Zealand uses a country specific factor for FRACLEACH that is equal to 0.07 (Thomas et al. 2005) and which can be further adjusted to take into account modifiers of N leaching fluxes e.g. nitrification inhibitor use (MfE 2012 Table 4.Ds1).

In order to apply the FRACLEACH factor the total amounts of N fertiliser [NFERT] and N excreta [NEX] are determined for agricultural soils and then these variables are used to calculate the amount of N leached (NLEACH) as follows:

NLEACH = [NFERT + NEX] * FRACLEACH

The sum of the indirect N_2O emissions attributed to NLEACH can subsequently be determined, once N_2O emission factors for this NLEACH pool have been assigned. Indirect emissions of N_2O may occur as a result of leached N cycling in groundwater, rivers and estuaries. For groundwater it is assumed that NLEACH is in the nitrate (NO_3^-) form and a default emission factor of 0.015 (EF5-g) was initially recommended (Mosier et al. 1998) with N_2O emitted from groundwater once groundwater enters surface waters or by upward diffusion. If nitrogen enters rivers as NO_3^- the possibility exists for the N to be assimilated into biomass and subsequently released as ammonia, which can then be nitrified releasing N_2O. Alternatively there is also the possibility that NO_3^- undergoes denitrification during transport in the river. The emission factor for NLEACH in rivers (EF5-r), due to nitrification and denitrification, was initially set to equal 0.0075 (Mosier et al. 1998). The final component of EF5 is the term EF5-e that pertains to NLEACH discharged by rivers into estuaries where, again, nitrification and denitrification of NLEACH leads to N_2O emissions, and this value was initially set to equal 0.0025 kg N_2O–N kg^{-1} N leached. Thus the combined EF5 term (EF5-g +EF5-r + EF5-e) equalled 0.025 kg N_2O–N kg^{-1} N leached in the 1996 IPCC guidelines for inventories.

Subsequently, however, in the most recent IPCC Guidelines for National Greenhouse Gas Inventories (IPCC, 2006) the values for EF5 emission factors have been updated. The previously used emission factor EF5-g (0.015) was considered too high and was reduced to 0.0025 kg N_2O–N kg^{-1} N leached, and the EF5-r value was also reduced to 0.0025 kg N_2O–N kg^{-1} N leached, while the value for EF5-e remained unchanged. Thus, the overall combined value of EF5 was decreased from 0.025 to 0.0075 kg N_2O–N kg^{-1} N leached. However, there is still considerable uncertainty with regard to this value, range 0.0005 -0.025, (IPCC, 2006).

When the EF5-r value was revised there were even lower reported values available for the EF5-r component that ranged from 0.0003 to 0.0005 (Dong *et al.*, 2004; Clough *et al*, (2006)). These lower values had, however, been determined on shorter river systems and the authors of the IPCC 2006 guidleines stated that there still remained the possibility that higher values might apply to longer river systems. Thus, EF5-r was not decreased any further than 0.0025 kg N_2O–N kg^{-1} N leached despite these lower values having been reported. However, uncertainty still surrounds the EF5-r factor with more recent work reporting EF5-r values equal to the original EF5-r emission factor. Beaulieu et al. (2011) examined 72 headwater streams across the USA, showing that N_2O formation in streams

increased with NO_3^--N loading and that 0.75% of dissolved inorganic-N inputs were transformed to N_2O.

To date, published peer-reviewed work on determining N_2O fluxes from New Zealand's waterways has focused on a lowland stream, the LII in Canterbury, (Clough et al. 2006; Clough et al. 2007) and a braided river (Ashburton) in Canterbury, both in the South Island (Clough et al. 2011). The water residence time in these rivers was < 15 hours. The results of these studies tend to justify a lowering of the EF5-r value for New Zealand. However, it has been mooted that the N_2O fluxes so far determined for New Zealand water ways might be higher if there was more time for the embodied NO_3^- to be assimilated and nitrified and/or denitrified. The longest river in New Zealand is the Waikato River in the North Island. This has been chosen as an extreme example of a 'long New Zealand river'.

1.1 The Waikato River

If the entire catchment is considered the Waikato River is the longest in New Zealand. The Waikato River commences on the slopes of Mount Ruapehu in the central North Island at an elevation of 2797 m above mean sea level (amsl) as the Waikato stream which flows into the Tongariro River and then Lake Taupo (357 amsl). Lake Taupo (623 km^2) is the largest freshwater lake in the Southern hemisphere with water taking an average 10 years to transit through the lake.

The Waikato River, proper, leaves Lake Taupo at the 'Taupo gates' and travels a distance of 182 km to the Karapiro dam (22 amsl) which under summer flow conditions (100 cumecs at Taupo gates) and winter (225 cumecs at Taupo gates) takes between 875 to 315 hours, respectively (Brown et al. 2005). But this is only just over half way by distance because the river continues, unimpeded by any further hydro dams, another 148 km to discharge into the Tasman sea at the Waikato heads which takes a further 86 to 58 hours depending again on summer (250 cumecs) and winter (570 cumecs) flows at Mercer (Figure 1.1), respectively (Brown et al. 2005). Thus the river travels a total of 330 km from Taupo Gates taking approximately 373 to 961 hours depending on season. If the entire catchment is considered i.e. Lake Taupo and its headwaters, the Waikato River is considered to be 425 km long with a catchment area of approximately 14,500 km^2.

This report covers completed and on-going work to assess the magnitude of the N_2O flux from the Waikato River and an EF5-r value. Reported on here are the data, collected to date, that pertain to the river chemistry and dissolved N_2O concentrations, measured N_2O fluxes, results of isotopic determinations of NO_3^- in the Waikato River, and a laboratory study to examine the potential for collected waters to denitrify NO_3^-. This work is put into context with other New Zealand data and the case for a New Zealand specific EF5-r is considered.

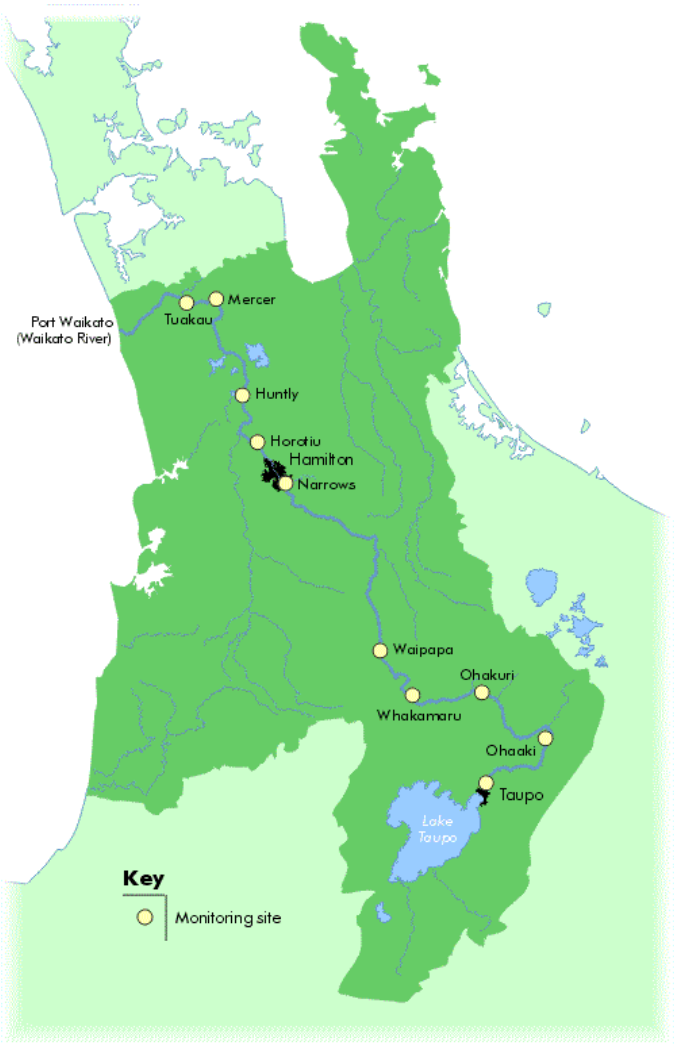


Figure 1.1 Map of Waikato River also showing showing the location of Environment Waikato's ten water quality sampling sites (Figure from: http://www.waikatoregion.govt.nz/Environment/Natural-resources/Water/Rivers/Waikato-River/map/)

2. In situ determination of Waikato River N_2O fluxes

During the 12th to 13th December 2011, and 29th February to 1st March 2012 headspace chambers were floated, tethered within 10 m of the bank, at 15 sites on the Waikato River commencing at the Taupo gates (the outlet from Lake Taupo) and finishing at Port Waikato. Floating chambers were constructed from round polypropylene containers supported by a styrofoam annulus (8.5 cm wide, 11.7 cm deep) attached around the chamber. The polypropylene chamber projected 1.5 cm into the water when floating on the river surface with a resulting headspace volume of 4.2 L (Clough et al. 2006).

Seven sites were sampled on the first day and eight on the subsequent day commencing at ca. 12:30 p.m. to 6 p.m. from Taupo to Lake Karapiro and then 7:00 a.m. to 4:00 p.m. between Hamilton and Port Waikato. Sites were chosen to provide a geographical spread and ease of access while also sampling varying hydrological features i.e. lakes versus river. Sample occasions are hereafter referred to as the 12th December 2011 and the 29th February 2012. Six chambers (n = 6) were floated at each site for a period of 13 minutes. Preliminary tests with these chambers had shown that the headspace sizes were sufficient for changes in headspace N_2O concentration to be linear over time for over one hour. Chambers were floated for 13 minutes at each site. Concentrations of N_2O were determined according to Clough et al. (2009).

River water temperatures and dissolved oxygen concentrations were measured at each N_2O flux measurement site, 10 cm depth, using a portable hand-held meter (model 550A; YSI, Yellow Springs, OH). This data was recorded during N_2O flux measurements along with air temperature, using a hand held thermometer. Water samples (n=3) were also taken for water NO_3^- determinations, 10 cm below the surface at N_2O flux sites, on the 29th February 2012 and for dissolved N_2O concentrations on both dates. Determination of dissolved N_2O is described in section 5.2.

Dissolved oxygen concentrations, measured *in situ*, at the sites sampled ranged from 8.1 to 11.0 mg l^{-1} over the two sampling periods with no relationship to water temperatures, dissolved N_2O, or N_2O fluxes. River water temperatures were relatively constant over the sampling periods but tended to be 1.0 to 1.5°C warmer between the Taupo Gates and Lake Karapiro sites, a reach of the river dominated by hydro lakes, during the sampling on 29th February (Figure 2.1). There was no relationship between river water temperature and the N_2O flux evolved on either the 12th December 2011 (r = 0.34, p = 0.21) or the 29th February 2012 (r = -0.10, p = 0.73).

Table 2.1: Site locations where chambers were floated on the Waikato River during 12th December 2011 and 29th February 2012.

Site	Grid reference (NZMG)
A. Taupo Gates	2776619E, 6275117N
B. Mihi Road Bridge	2797107E, 6296800N
C. Lake Ohakuri Dam	2779850E, 6305748N
D. Whakamaru	2755749E, 6304907N
E. Lake Waipapa	2744532E, 6319378N
F. Arapuni Landing	2740922E, 6341028N
G. Lake Karapiro	2733598E, 6360820N
H. Horotiu Bridge	2704816E, 638706N
I. Ngaruawahia	2699644E, 6391159N
J. Ohinewhai	2700805E, 6410239N
K. Rangiriri Bridge	2698787E, 6416786N
L. Mercer	2691723E, 6433802N
M. Tuakau Bridge	2682765E, 6432163N
N. Tauranganui Marae[a]	2670621E, 6429570N
O. Downstream of Tauranganui Marae[b]	2667341E, 6426865N
P. Port Waikato	2663668E, 6426616N

[a] 29th February 2012 only, [b] 12th December 2011 only

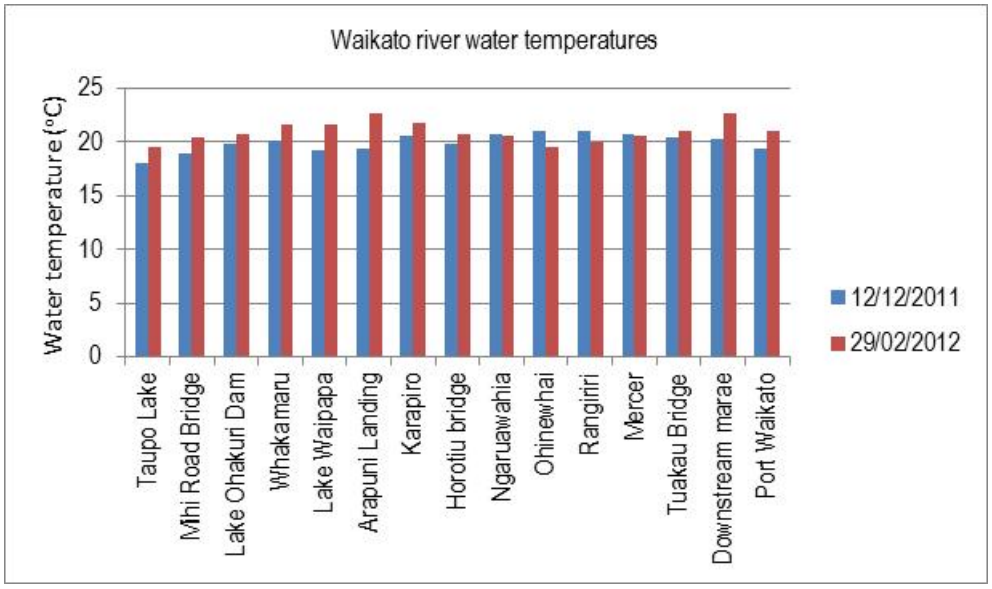


Figure 2.1: River temperatures on 12th December 2011 and 29th February 2012.

River water NO_3^--N concentrations were determined using flow injection analysis. Sample concentrations, taken on the 29th of February 2012, varied by site ($P < 0.01$). They were lowest at the Taupo Gates site and remained ≤ 0.2 μg ml^{-1} until the Horotiu bridge. After this point they increased to be 0.3 μg ml^{-1} and then decreased prior to an increase at Port Waikato. Of note and of relevance to other isotopic measures is the decrease in the NO_3^--N concentration downstream of Ngaruawahia (see section 3).

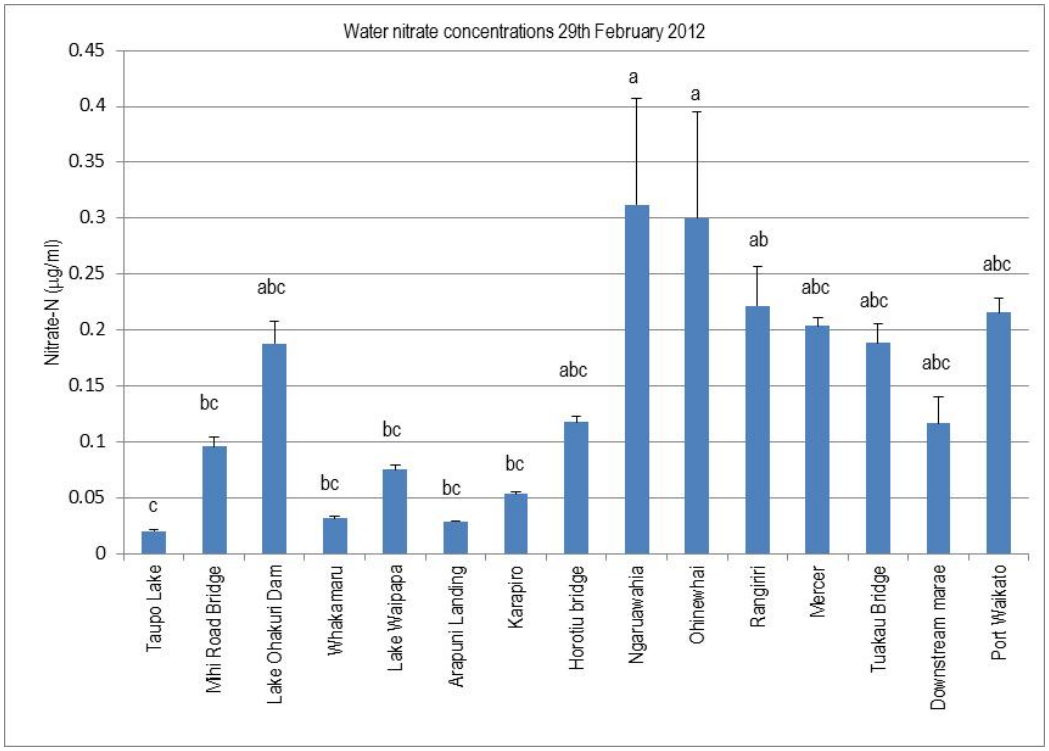


Figure 2.2: River nitrate-N concentrations on 29th February 2012. Values are means of 3 replicates, error bars are plus one s.e.m. Lower case letters indicate significant differences between means (Tukey's test, $p < 0.05$).

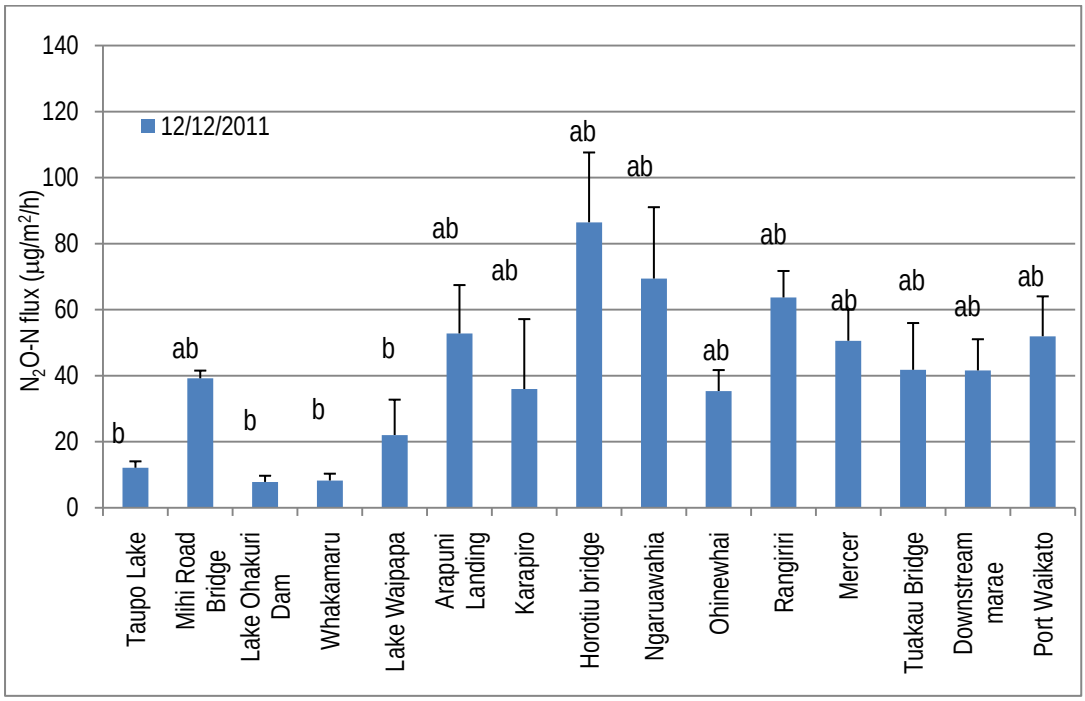


Figure 2.3: River N_2O-N fluxes measured on 12th December 2011. Values are means of 6 replicates, error bars are plus one s.e.m. Lower case letters indicate significant differences between means (Tukey's test, $p < 0.05$).

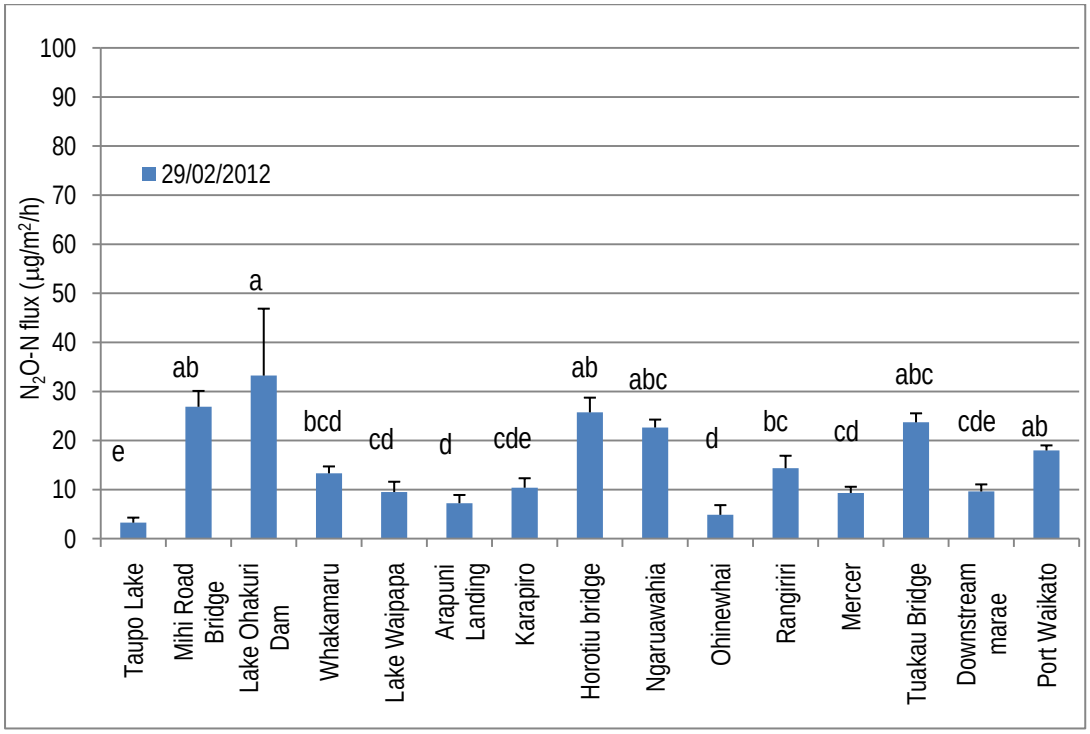


Figure 2.4: River N_2O-N fluxes measured on 29th February 2012. Values are means of 6 replicates, error bars are plus one s.e.m. Lower case letters indicate significant differences between means (Tukey's test, $p < 0.05$).

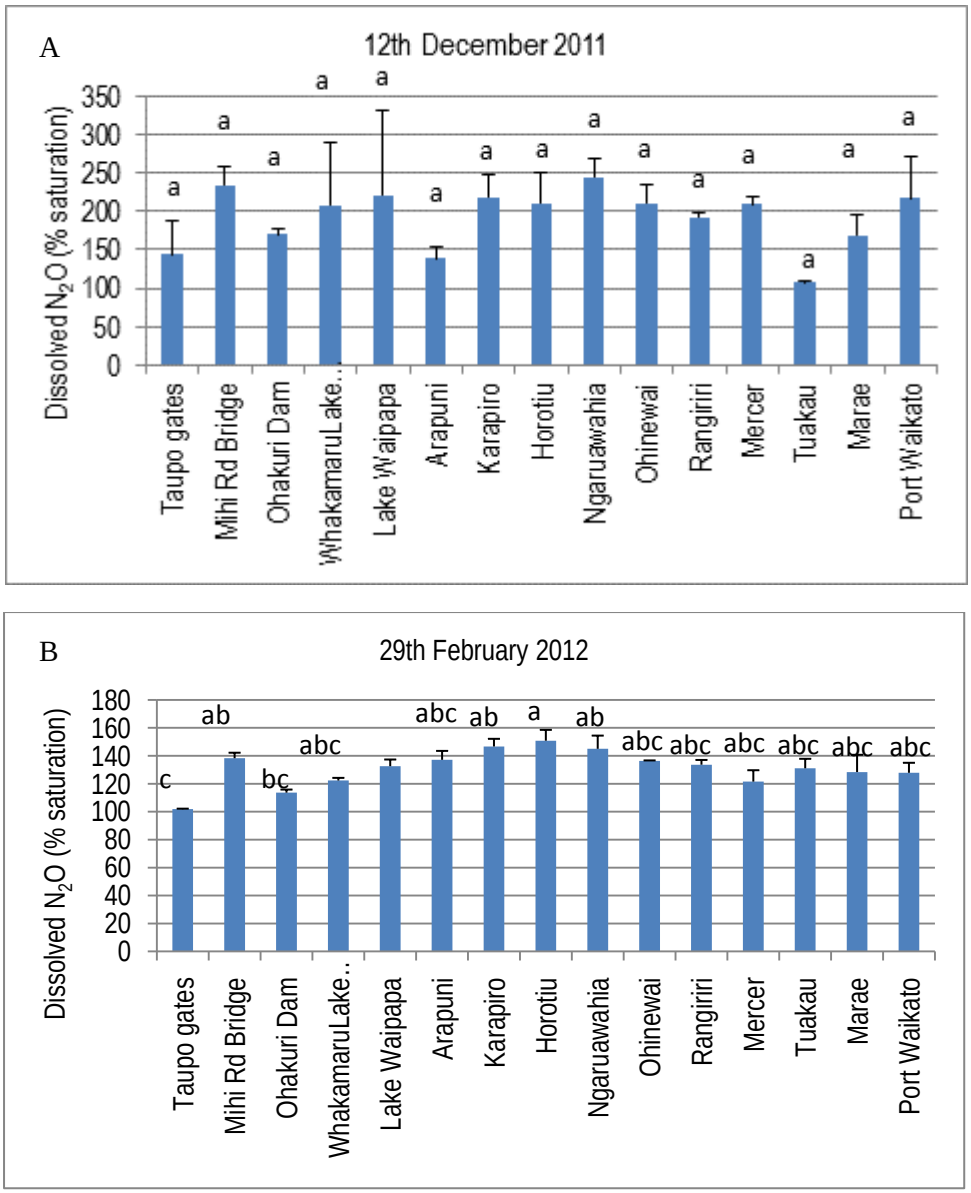


Figure 2.5: Dissolved N_2O-N concentrations on 12th December 2011 (A) and 29th February 2012 (B). Values are means of 2 replicates, error bars are plus one s.e.m, for each site, lower case letters indicate significant differences between means (Tukey's test, $p < 0.05$).

Dissolved N_2O concentrations showed no variation by site on the 12th December 2011 ($p=0.673$) but they did vary ($p < 0.01$) by site on the 29th of February 2012 (Figure 2.5). Pooling all dissolved N_2O data showed that there was no effect of site but that sampling date was significant ($p < 0.012$) with average values on the 12th December 2011 and the 29th of February 2012 equal to 192 and 131% saturation, respectively.

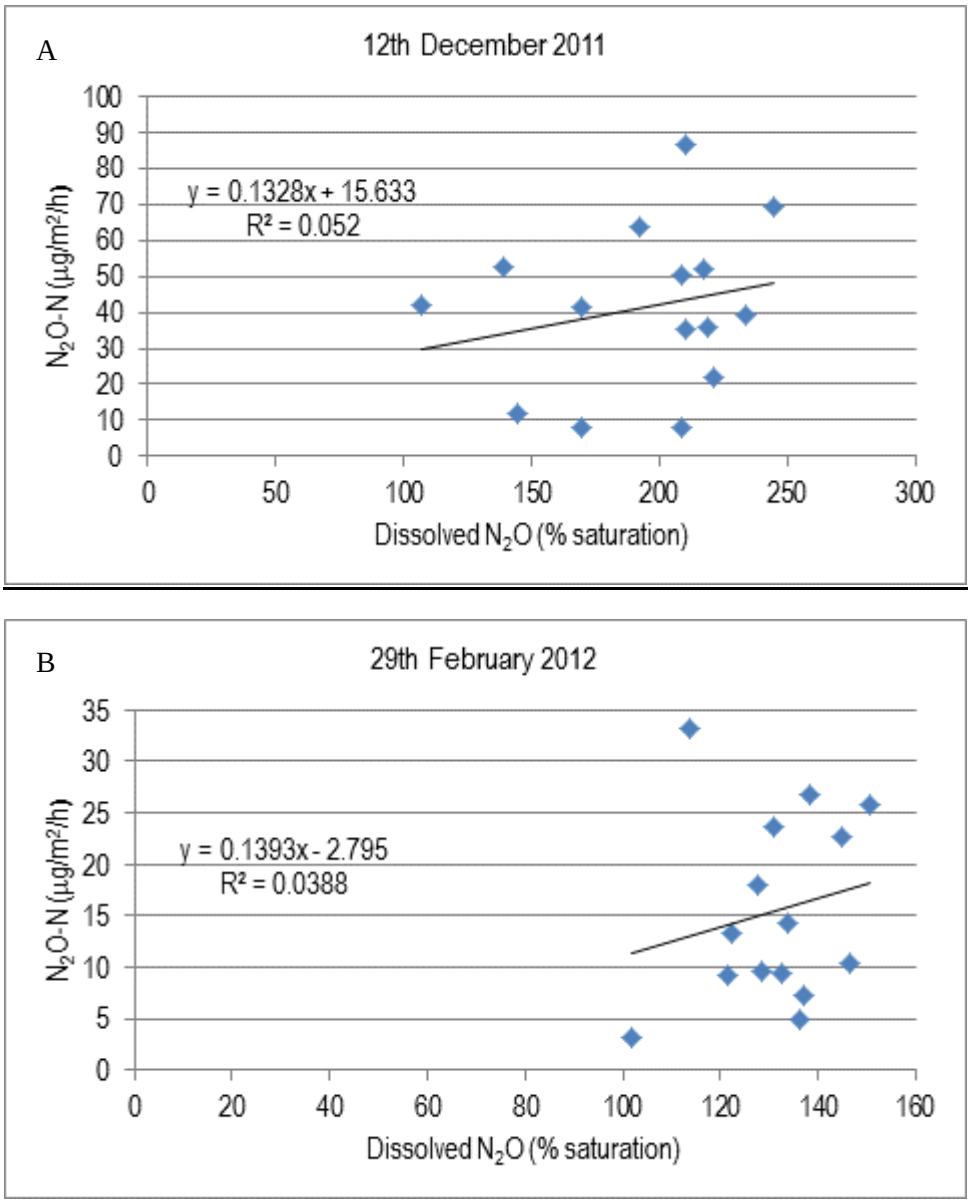


Figure 2.6: Plots of mean river N_2O-N fluxes versus mean dissolved N_2O concentrations on 12 December 2011 (A) and 29th February 2012 (B).

When plotting all N_2O-N fluxes against dissolved N_2O saturation no relationships were observed despite the close proximity of sampling (Figure 2.6). When considering correlations between dissolved N_2O and N_2O-N fluxes on the 29th February 2012 there was no relationship ($r = 0.197$, $p < 0.401$) but on the 12th December 2012 the N_2O-N flux was correlated with dissolved N_2O ($r = 0.385$, $p < 0.05$). Similar significant, yet weak, correlations were observed for the LII spring-fed stream where measured fluxes were a similar order of magnitude (Clough et al., 2007). Possible reasons for poorer than expected correlations between these variables were discussed in Clough et al. (2007) and predominately include the effects of wind creating artefacts. The study by Clough et al. (2007) found

that wind could push chambers across the water surface and lead to enhanced N_2O emissions presumably as a result of turbulence at the chamber-water interface enhanced gas release from the water.

3. Stable isotope analysis of the nitrate in the Waikato River.

3.1 Introduction

There are two stable isotopes of nitrogen (N): ^{14}N and ^{15}N. The relative abundance of ^{15}N in air is constant and the ratio of $^{15}N/^{14}N = 0.003676$. Nitrogen isotopes values are reported relative to an international standard (air) in units of permil (‰), relative to N_2 in atmospheric air, using the standard delta (δ) definition. In biological processes organisms preferentially use the lighter isotopic species since less energy is required. This preferential selection results in fractionation of the substrate (which gets heavier i.e. more ^{15}N) while the product gets lighter (i.e. less ^{15}N). Nitrogen compounds have a wide range of oxidation states as a consequence of several biological reactions and there is thus a wide range of reactions that can cause isotopic fractionation. One reaction, denitrification, causes the $\delta^{15}N$ of the residual NO_3^- to increase as the NO_3^- concentration decreases. Oxygen has 3 stable isotopes (^{16}O, ^{17}O and ^{18}O). Of interest here is ^{18}O, which is reported as ‰ relative to the standard V-SMOW (Vienna-standard mean ocean water). Like N, the oxygen isotopes on the NO_3^- molecule are fractionated from their original source compositions (water and atmospheric oxygen) during NO_3^- transformation. During denitrification increases in both the $\delta^{15}N$ and $\delta^{18}O$ values of the residual NO_3^- occur. In many cases the ratio of the enrichment of oxygen to nitrogen is close to 1:2 and thus a plot of $\delta^{15}N$ vs. $\delta^{18}O$ produces a slope of about 0.5 which is indicative of denitrification (Kendall, 1998) assuming no other reactions or mixing occurs. Thus the method can show, or be indicative of, denitrification taking place in a water body if a slope of 0.5 is seen in a plot of $\delta^{15}N$ vs. $\delta^{18}O$. The isotopic method tells us nothing about nitrification. Further information on the use of isotopes in catchment hydrology can be found in Kendall (1998).

3.2 Initial assessment of Waikato river nitrate stable isotope values.

To gauge the potential of using NO_3^- stable isotope analyses as indicators of denitrification in the Waikato River, NO_3^- in water samples was analysed for $\delta^{15}N$ and $\delta^{18}O$. On the 4th of May 2012 and 1st February 2012 water samples were obtained from 10 sites along the Waikato River (these sites are the Environment Waikato Regional Council's monitoring sites (Table 3.1). These samples were initially sent to Lincoln where dissolved nitrous oxide values were obtained. Then the samples were frozen and subsequently sent to GNS Science for NO_3^- isotope analysis.

Nitrate samples were converted to nitrite (NO_2^-) using cadmium, then to nitrous oxide (N_2O) using sodium azide in an acetic acid buffer. The N_2O was then purged from the water sample, and passed through a series of chemical traps to remove H_2O and CO_2, prior to it being cryogenically trapped under liquid nitrogen. After being cryofocused in a second trap, the N_2O was passed through a GC column and into an Isoprime Isotope Ratio Mass Spectrometer to determine its nitrogen and oxygen isotopic signatures. The method was modified from McIlvin and Altabet (2005). Results are reported with respect to AIR for $\delta^{15}N$ and VSMOW for $\delta^{18}O$, normalized to the international standards; USGS 34 (-1.8‰ for $\delta^{15}N$ and -27.9‰ for $\delta^{18}O$), IAEA-NO3 (4.7‰ for $\delta^{15}N$ and 25.6‰ for $\delta^{18}O$) and to the internal standard; KNO3b (10.7‰ for $\delta^{15}N$ and 11.7‰ for $\delta^{18}O$). The analytical precision for these measurements was 0.3‰ for $\delta^{15}N$ and for $\delta^{18}O$.

The results of these analyses are shown in Table 3.1 and plotted in Figure 3.1 which includes all hydro lake data and river data. In Figure 3.2 the plot is repeated, but only for those sites downstream of the hydro lakes.

Table 3.1: Isotopic values of nitrate, concentrations of nitrate and distance from Taupo Gates at ten sites along the Waikato River on two sampling dates. Shaded portion represents water in lakes in the hydro region of the river.

Site[a]	River Distance	Map Ref. (NZMG)		1st February 2012			4th May 2012		
				Nitrate	$\delta^{18}O$	$\delta^{15}N$	Nitrate	$\delta^{18}O$	$\delta^{15}N$
	(km)	Easting	Northing	(µg/ml)	(‰)	(‰)	(µg/ml)	(‰)	(‰)
Taupo Gates	0	2777133	6275733	0.02	0.9	62.2	0.01	2.5	23.4
Ohaaki Br[a]	37	2798071	6291450	0.04	11.4	-	0.07	0.4	17.6
Ohakuri Tr- Br	74	2779596	6306083	0.20	2.4	25.3	0.12	-0.5	1.4
Whakamaru Tr[b]	103.5	2755134	6305593	0.19	7.6	16.6	0.20	1.1	11.4
Waipapa Tr	125.5	2745012	6320697	0.20	-1.3	4.2	0.17	0.6	3.3
Narrows Brp[c]	203.5	2716821	6371002	0.17	3.9	10.7	0.30	1.7	5.9
Horotiu Br	228.5	2704815	6387066	0.11	1.9	14.5	0.60	2.5	6.4
Huntly-Tainui Br	250.5	2700546	6401768	0.19	7.6	16.6	0.38	2.1	7.0
Mercer Br	290.5	2691787	6433612	0.30	6.1	50.8	0.32	1.9	6.8
Tuakau Br	301.5	2682750	6432184	0.38	0.8	9.4	0.34	1.1	6.5

[a]Br = bridge, [b]Tr = tailrace, [c]Brp = boatramp

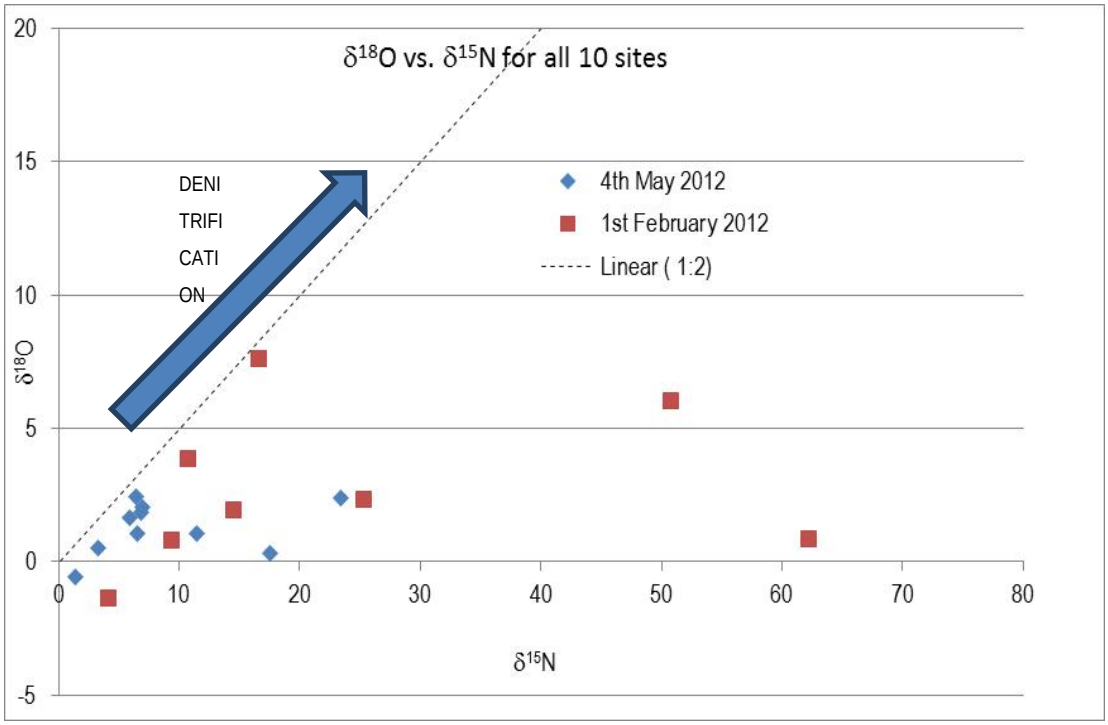


Figure 3.1: Plot of $\delta^{18}O$ vs. $\delta^{15}N$ for all ten sites on both sampling dates along with the linear 1:2 line.

If only denitrification was perturbing the isotopic signal of the $\delta^{15}N$ and $\delta^{18}O$ of the NO_3^- molecule, as NO_3^- moved downstream, the data should plot along the 1:2 line with data values increasing with distance downstream. The data was split into hydro-affected areas and non-hydro areas and is presented in Figure 3.2.

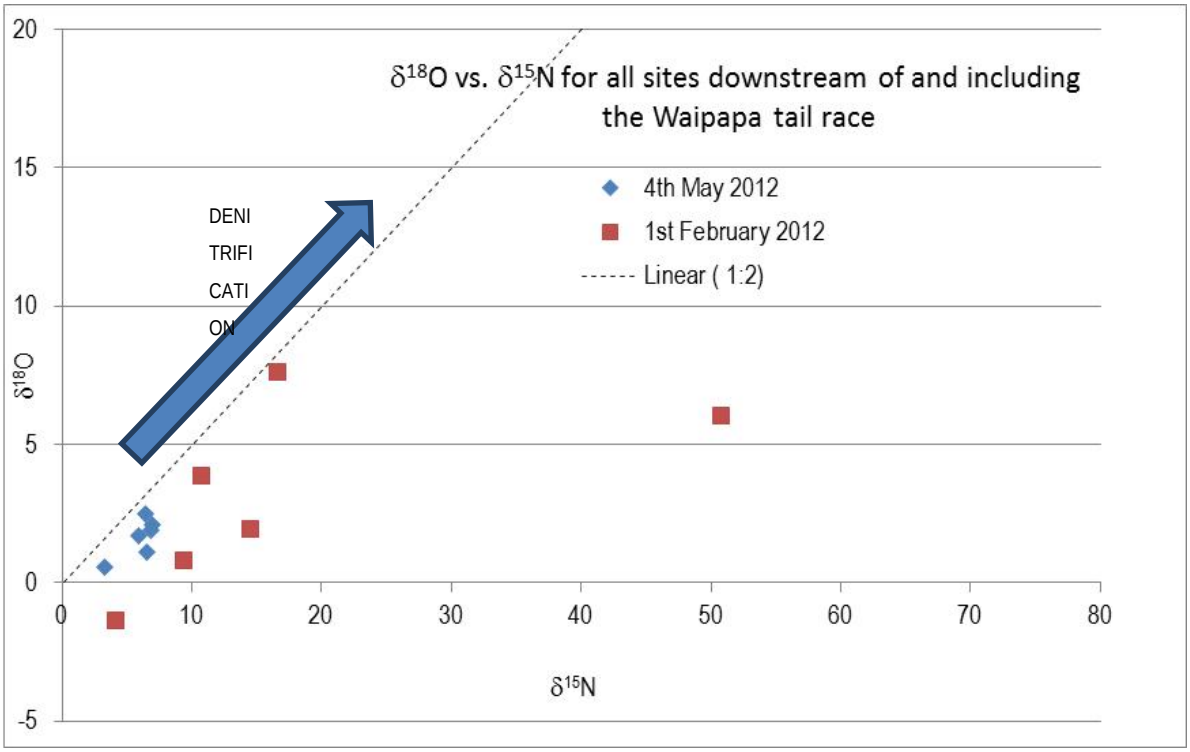


Figure 3.2: A plot of $\delta^{18}O$ vs. $\delta^{15}N$ for six sites on both sampling occasions, downstream of the hydro-lakes from the Narrows site. Also shown is the linear 1:2 line. Data plotting on this line would be indicative of denitrification.

With the exception of an extreme $\delta^{15}N$ value for the Mercer Br site, data begin to follow a more linear trend. However, values are still below the theoretical 1:2 line. Reasons for this may include further additions of NO_3^- of lower isotopic enrichment, as the river moves downstream. Such an effect would lead to dilution of the isotopic signal. If the plot of NO_3^- concentration over distance is considered (Figure 3.3) it can be seen that NO_3^- concentrations in the Waikato River do in fact increase throughout the river's journey to the sea (also see section 5).

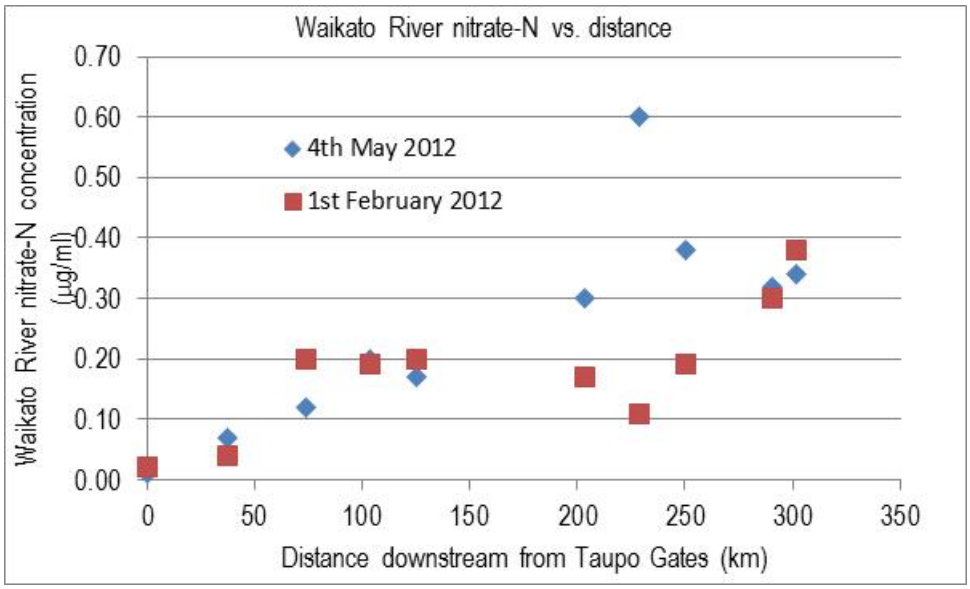


Figure 3.3: Nitrate-N concentrations versus river distance from Taupo Gates.

A further compounding factor when considering the interpretation of these isotopic values is the uptake and release of nitrogen within the river by other organisms such as algae. Because both N and phosphorus increase as water moves downstream (Beard, 2010), so too do algae as indicated by chlorophyll pigment measurements (Figure 5.4). These algae will, in turn, affect N cycling within the river by taking up N and releasing N as they decompose, affecting fractionation of N and the associated isotopic values of NO_3^-, and some species will also be capable of fixing N which in turn can affect isotopic values of embodied N. Thus it can be concluded from this initial isotopic data that denitrification is definitely occurring downstream of the Waipapa tailrace site, with isotopic values generally becoming heavier as would be expected if denitrification was the sole transformation of NO_3^-, but due to the relationship observed between $\delta^{18}O$ and $\delta^{15}N$, there are other N processes also operating to dilute or recycle NO_3^--N.

Above the Waipapa tailrace no clear conclusions can be drawn from the isotopic values. Denitrification will certainly occur, but the isotopic values of the NO_3^- are inconsistent and large when compared with other published works (Kendall, 1998). This may be due to the long residence time of the water in the hydro-affected reach of the Waikato River with water taking in excess of 800 h (c. 1 month) to transit the reach. This time allows for considerable transformation and cycling of the nitrogen and may explain the observed high values. However, further detailed studies are required to fully understand the reasons for these values.

4. Generation of nitrous oxide within the water body.

4.1 Introduction

The data from section 2 clearly show that nitrous oxide (N_2O) is clearly being produced either within the Waikato river water body itself (pelagic zone) or at the river-bed interface with the overlying water (benthic zone). Alternatively a proportion of the N_2O may also derive from N_2O dissolved in hyporheic inputs of water to the river system. As discussed above N_2O may be formed via nitrification or denitrification, which are aerobic and anaerobic processes, respectively. The purpose of this experiment was to assess if N_2O was being made solely within the water body (pelagic production) from NO_3^-. Given that monthly Waikato River water samples were relatively aerobic in nature with almost all samples $\geq$ 90% saturation (Figure 5.3A) it was hypothesised that the generation of N_2O would be low within the water body but that if anaerobic conditions occurred then potentially pelagic production may increase.

4.2 Methods

Samples were collected from eight sites along the Waikato River on 14th May 2012. These sites were the same as listed in Table 2.1 (G, H, I, J, K, L, M, N) and covered the reach from Lake Karapiro to the Tuaranganui Marae. At each site water was collected in 5 litre containers and immediately shipped in chilly bins to Lincoln University. Upon arrival water samples (50 ml aliquots) were placed into 150 ml glass bottles. Potassium NO_3^-, enriched with ^{15}N (10 atom % ^{15}N), was the added to the river water to raise the concentration by 1.0 μg ml^{-1}. This was to provide a ^{15}N labelled NO_3^- substrate for potential denitrification. Any denitrification of the substrate would result in ^{15}N labelled N_2O and/or N_2 production. The head spaces of the bottles were then either left aerobic or purged with argon to remove oxygen. Bottles were gently shaken for 24 hours at 20^oC, a temperature representative of summer conditions in the Waikato River. Then the headspace of each bottle was sampled for N_2O by gas chromatography (Clough et al. 2009) and N_2O and N_2 ^{15}N enrichment using mass spectrometry (Stevens et al. 1993).

4.3 Results and Discussion

After 24 hours the dinitrogen (N_2) concentration in the headspace of the aerobic and anaerobic treatments was 78 and 13% respectively with no differences due to site. No ^{15}N enrichment of the N_2 gas occurred with an overall mean enrichment of 0.3663 atom % ^{15}N demonstrating that no ^{15}N labelled NO_3^- had been converted to N_2. The presence of N_2 in the anaerobic treatment, along with it being non-enriched in ^{15}N, indicates the bottles were not totally purged when being made anaerobic with Ar, possibly as a result of dissolved gases. However, oxygen levels of the water would still have been considerably less than those observed in situ (see Figure 5.3). The N_2O concentrations varied

due to oxygen status and were higher ($P<0.01$) under the aerobic conditions (mean 0.381 μl l^{-1}) than anaerobic (mean 0.163 μl l^{-1}) but with no differences in enrichment (0.373 atom % ^{15}N). This indicates that the lower N_2O concentrations under anaerobic conditions were due to dilution of antecedent N_2O. Antecedent N_2O would have been present as a result of N_2O in the headspace of the bottle and/or any dissolved N_2O in the water sample. The lack of any ^{15}N enrichment in the N_2O demonstrates that, under the experimental conditions employed, pelagic denitrification is not likely to be a significant contributor to the N_2O fluxes observed. Given the relatively high dissolved oxygen conditions observed in the Waikato River it is thus more likely that the benthic zone is the 'hot-spot' for N_2O production via denitrification in the river-bed sediments. This view is supported by Seitzinger et al. (2006) who noted that denitrification requires suboxic conditions (<0.2 mg O_2/l) and that denitrification occurs at the oxic/suboxic interface (river bed). Of course if a nocturnal decline in dissolved oxygen concentrations occurred there may possibly be some induction of pelagic denitrification if sufficient carbon substrate and microorganism numbers were available.

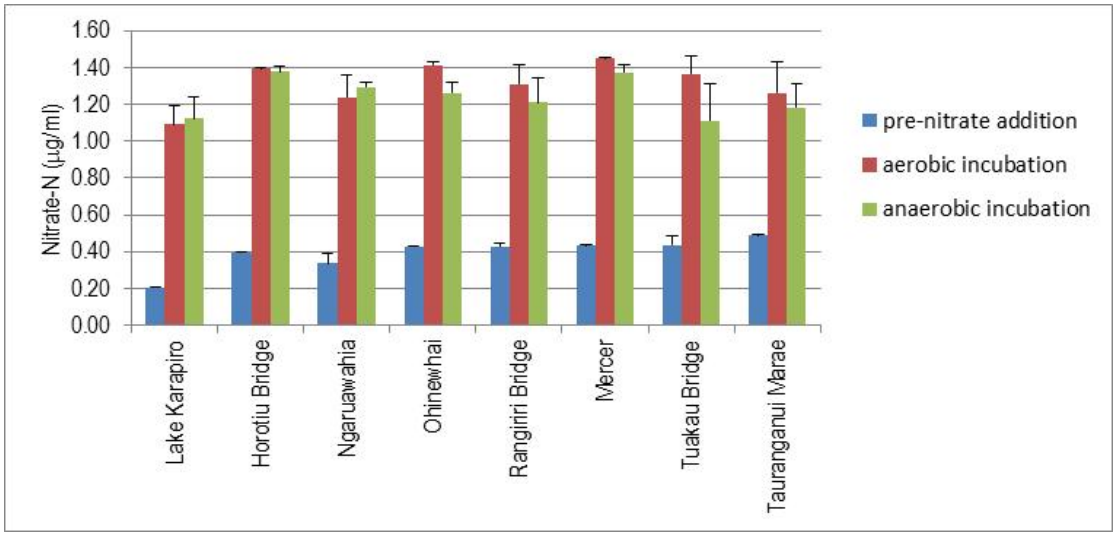


Figure 4.1: Nitrate-N concentrations in river water samples pre-nitrate addition and incubation, and after increasing nitrate-N concentrations by 1 μg ml^{-1} and after a 24 h incubation under either aerobic or anaerobic conditions.

Nitrate-N concentrations in the incubated sample bottles did not differ significantly with aerobic or anaerobic treatment (Figure 4.1). Pelagic N_2O production cannot be ruled out based solely on this one experiment since the condition of the river at time of sampling may have influenced potential microbial numbers and species and these were not evaluated here. Significant pelagic N_2O production has been observed in a large impounded river, the Ohio, but this was determined to be a result of waste water treatment discharge and its associated high ammonium-N content (Beaulieu et al. 2010)

5. Monthly sampling of river water chemistry and dissolved nitrous oxide.

5.1 Introduction

The Waikato Regional Council collects environmental information to comply

with its obligations under Section 32 of the Resource Management Act 1991. The

Environmental Monitoring Programme is ISO 9001:2008 registered through Telarc New Zealand for the supply of environmental information and services, including water quality, biological sampling, air quality, land and rating information and geographical information systems (Beard, 2011). Sample collection is undertaken monthly, at ten sites, as two sampling runs (5 sites per day on successive days) with the upper catchment sampled on the first day (Taupo to Waipapa) and the lower catchment on the second (Narrows to Tuakau). Sample locations are listed in Table 5.1 and shown in Figure 1.1. Water quality of the Waikato River is assessed by measuring up to 40 parameters (27 routinely) either in the field or the laboratory using standard methods (Beard, 2010). Trends in the Waikato River water quality are published as technical reports (e.g. Beard, 2010) by Environment Waikato on line:

http://www.waikatoregion.govt.nz/Services/Publications/Technical-Reports/TR-201103/

Table 5.1 Environment Waikato's ten sampling sites. Also see Figure 1.1.

Location	Distance[1]
Taupo Control Gates	0.1
Ohaaki Br	36.5
Ohakuri Tailrace Br	75.8
Whakamaru Tailrace	105.0
Waipapa Tailrace	126.1
Narrows Boat Ramp	202.2
Horotiu Br	225.6
Huntly-Tainui Br	246.5
Mercer Br	286.3
Tuakau Br	296.8

[1]distance from Lake Taupo outlet

5.2 Methodology

Water samples were collected monthly, at the same time during the day each month, by the Environment Waikato team according to their normal routine (see Table 5.2 for sample dates) with a further water sample taken and placed in gas-tight-glass 110 ml bottles equipped with aluminium screw on caps, lined with rubber septa. Three water samples were taken at each site. These were shipped to Lincoln University in insulated containers where, upon arrival, dissolved N_2O was analysed.

The sample bottles had 50 ml of water extracted in a gas-tight manner, with ambient air replacing the water volume, and these were immediately capped and then shaken for 5 minutes to allow the dissolved N_2O in the water to equilibrate with headspace ambient air. The 50 ml of water originally extracted was immediately injected into another glass bottle and equilibrated with headspace air in a similar manner. Thus a total of three replicates (analysed in duplicate) were available for each sampling site at any given time.

After equilibration headspace gas samples (10 ml) were taken and placed in pre-evacuated Exetainers® and analysed for N_2O as described in Clough et al. (2009). The total N_2O in the water sample was calculated using the following equation (Tiedje, 1983):

$$M=C_g \times [V_g + (V_l \times \alpha)]$$

Where M is the total N_2O present in the bottle minus N_2O introduced in ambient air (μl), C_g is the headspace volume (μl l^{-1}), V_g is the volume of gas (l), V_l is the volume of liquid (l) and α is the Bunsen coefficient based on the laboratory temperature of equilibration (20°C).

The concentration of N_2O in the water (dissolved N_2O) was then calculated as follows (Davidson and Firestone, 1988):

$$\text{Concentration of } N_2O \text{ in water} = M/V_l$$

Where M and V_l are defined as above.

Dissolved N_2O was expressed as percentage saturation by dividing the concentration of N_2O in the water sample by the theoretical equilibrium concentration of N_2O in air at the given river water temperature at time of sampling. The latter was calculated using the water temperature of the river at time of sampling, and a Henry's Law constant (the concentration of N_2O expected in water at the

given river temperature if N_2O in the water was in equilibrium with the ambient air N_2O concentration).

5.3 Results and Discussion

Dissolved N_2O concentrations are depicted by site and by date of sampling in Figure 5.2. When comparing dissolved N_2O between sampling dates the months of December and February had the highest concentrations of dissolved N_2O (Figure 5.2 (A)). There was a notable reduction in N_2O saturation at the January sampling time. Methodologies were the same at all sampling times. This leads us to question other environmental variables and substrate supply. Dissolved oxygen remained relatively constant over sites and throughout time (Figure 5.3 (A)) but varied with water temperature ($r = -0.34$; $P < 0.01$). Water temperatures in the Waikato River are influenced by season and the injection of warm water due to cooling of generating equipment at thermal power stations (Wairakei and Huntly) and the discharge of geothermal water. Thus increases in water temperature are observed between the Taupo Gates and Ohaki Bridge sites and downstream of Huntly at Mercer. But overall no decrease in temperature was observed between December 2011 and February 2012 (Figure 5.3 (B)). What is noticeable, however, is a significant change in denitrification substrate concentration (assuming denitrification is responsible for N_2O production) with river water NO_3^--N concentrations decreasing for the month of December 2011 (Figure 5.3 (C)). Supporting this theory are coinciding increases in dissolved organic carbon (DOC), a substrate supporting denitrification (Figure 5.4 (B)), increases in turbidity (Figure 5.4 (C)), and declines in dissolved oxygen (Figure 5.3 (A)). It may be that the decline in N_2O saturation was due to more complete denitrification as DO was lowered and DOC increased. Looking at rainfall records for the Hamilton meteorological station (Clifo, station number 26117), downstream of the Narrows site, there was an extended period of soil moisture deficit in early December, where the deficit was in excess of 100 mm. This was alleviated with runoff occurring on the 18th and 19th December 2011 with an 88 mm rain event, where after the deficit resumed until further rainfall, when 50 mm of rainfall fell over the 6 days immediately prior to the 5th January 2012 sampling. The Waikato River depth at the Hamilton gauging station also increased by ca. 2 m over this time with river flow at the Narrows site increasing from 167 $m^3 s^{-1}$ on 2nd December 2011 to 332 $m^3 s^{-1}$ by 6th January 2012 (Environment Waikato provisional data). River flows at Mercer were 246 and 577 $m^3 s^{-1}$, respectively. The measure of algal biomass (chlorophyll *a)* also decreased in response to the high river flow (Figure 5.4 (A)). Thus, the large dynamic in the dissolved N_2O saturations during December 2011, January 2012 and February 2012 may indeed be due to dynamics in river flow and associated water chemistry. Nitrous oxide could have been more fully reduced to dinitrogen, its rate of production may have decreased or it may have been diluted. It is not possible to prescribe exact mechanism(s) for the dynamics with time which can only be speculated upon, and while the data strongly indicate changes in conditions favouring denitrification the

oxidation of ammonium-N cannot be ruled out as a contributing source of dissolved N_2O. Ammonium-N was present at both hydro and river sampling sites (Figure 5.4 (D)).

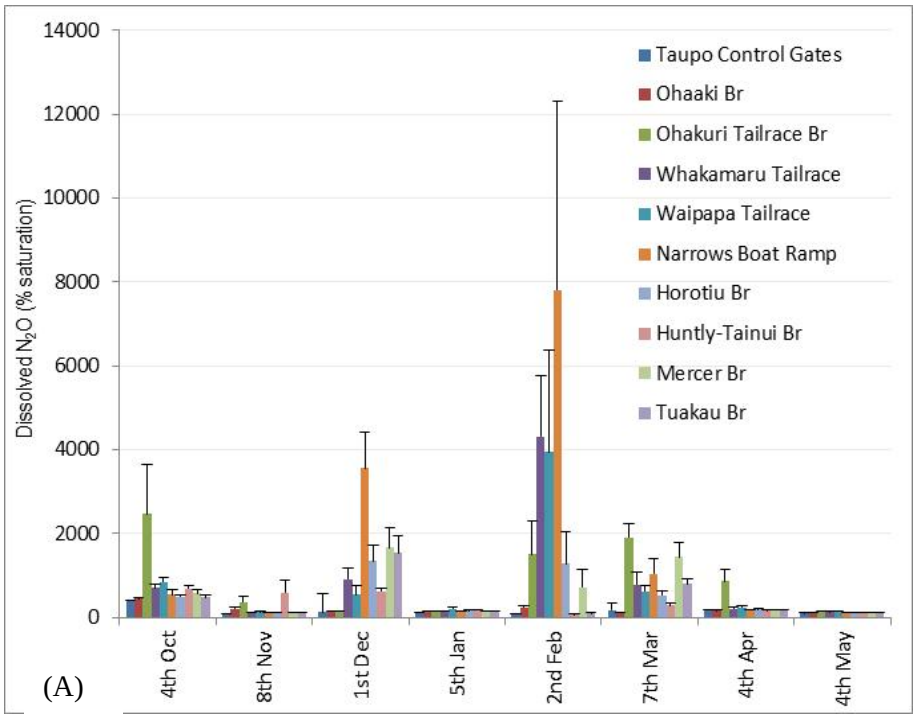
When comparing dissolved N_2O concentrations between sampling sites (Figure 5.2 (B)) there were differences between sites on all dates sampled ($P < 0.05$).Water sampled from the tailraces (Ohakuri and Waipapa) generally had consistently higher dissolved N_2O with the exception of the Narrows site. The Narrows site is well downstream of the final hydro dam (Karapiro). However, between Karapiro and the Narrows sample site there are surface water inputs from the Karapiro stream, the Mangawhero Stream (visually estimated from topographic maps to be draining in excess of 50 km^2 of farmland) approximately 8 km upstream of the Narrows site, and then a further injection of water approximately 2 km upstream of the Narrows site from Mystery Creek. The tributaries of Mystery Creek (Te Maire Stream, Nihokeke Stream) and Mystery Creek itself are visually estimated to be draining $\geq$ 30 km^2 of farmland. Notably, *Escherichia coli* numbers also increase dramatically at the Narrows site with the 5 year median value being 8 cfu ml^{-1} at the Waipapa tailrace and 40 cfu ml^{-1} at the Narrows site, indicating pollution from faecal sources (Beard, 2011). The concentration of NO_3^--N, a denitrification substrate, also increases at this site (Figure 5.3 (C)).

Reasons for the high dissolved N_2O concentrations at tailrace sites can be speculated upon. It may be due to high rates of N cycling in the hydro-lakes, since algal numbers are higher in these lakes than in the rivers (Beard, 2011). Nitrogen uptake and remineralisation of organic matter to form ammonium-N may lead to higher nitrification rates and subsequent N_2O release. Ammonium-N was elevated in the Waipapa tailrace water (Figure 5.4 (D)). Alternatively, water exiting through the tailrace comes from the bottom of the reservoir near the base of the dam, which in the case of the Karapiro dam is a depth of approximately 30 m. It may be that the water is more saturated in N_2O due to this water coming from near the benthic surface of the hydro-lake. Without knowing the profile of N_2O with depth it cannot be concluded why tailrace water has more N_2O.

While measuring lake depth profiles was outside the scope of this work there is pre-existing work that supports conditions being more anaerobic towards the sediment bed of the hydro lakes. A study by Magadza (1979) examined six of the Waikato river hydroelectric lakes between 1970-1972. It was found that weak thermoclines could occur in the deepest lake (Ohakuri) and that generally the bottom of the lakes were, on average, about 20% less saturated in oxygen than the surface waters (% saturation) with the exception of the deeper Ohakuri lake which had mean decreases of 43-49% depending on season, and which reached 0% saturation on the lake bed in February 1970, possibly as a result of weed management (Magadza, 1979).

Lower oxygen concentrations will slow nitrification of ammonium, and this may explain the elevated ammonium-N concentrations observed in the Waipapa and Ohakuri tailrace samples. Denitrification of impounded waters will also be favoured by lower oxygen levels and the lower oxygen levels near the lake beds may explain the observed elevated N_2O concentrations found in tailrace samples. The fact that tailrace samples then showed reduced N_2O concentrations during January is not readily explainable but may possibly be due to the spilling of surface waters (fresh runoff) causing dilution of the tailrace waters (yet to be verified for these dates). Of note, is a study by Mengis et al. (1997) who found meso- to eutrophic lakes had high levels of N_2O saturation in subsurface waters, up to 597% saturation (+/- 308 stdev).

What can be noted here, however, is the fact that dissolved N_2O concentrations of the surface water samples taken in December 2011 and February 2012 were not higher than at other sites (Figure 2.5(A) & 2.5(B)), again suggesting that deeper waters in the lake may be more saturated in N_2O. The dissolved N_2O concentrations at the tailrace and Narrows sites are very high but also extremely variable. Further detailed analysis to verify these sites as hot-spots and the extent of the hot-spot over distance would be useful. Then the relative impact of these hot-spots on the Waikato River's over all N_2O-N flux could be assessed.



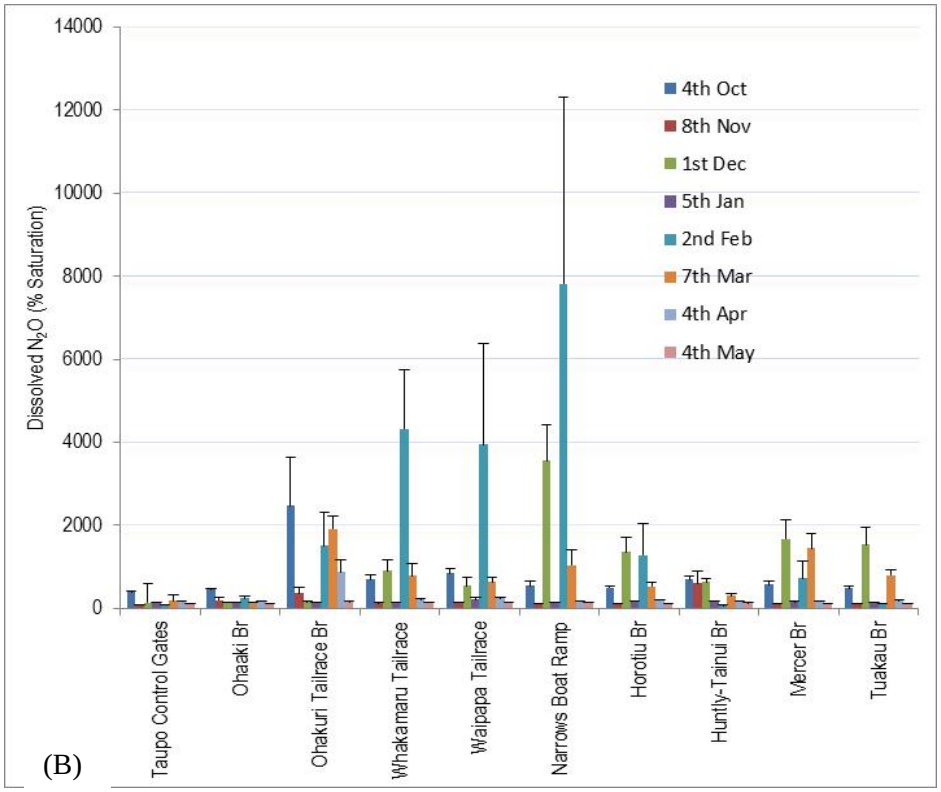


Figure 5.2: Average dissolved N_2O concentrations by sample date (A) and by site (B). Error bars are plus one s.e.m (n = 3).

Figure 5.3: Waikato River dissolved oxygen (A), water temperature (B) and nitrate-N (C) by site vs. time. Provisional data from Environment Waikato (*n*=1).

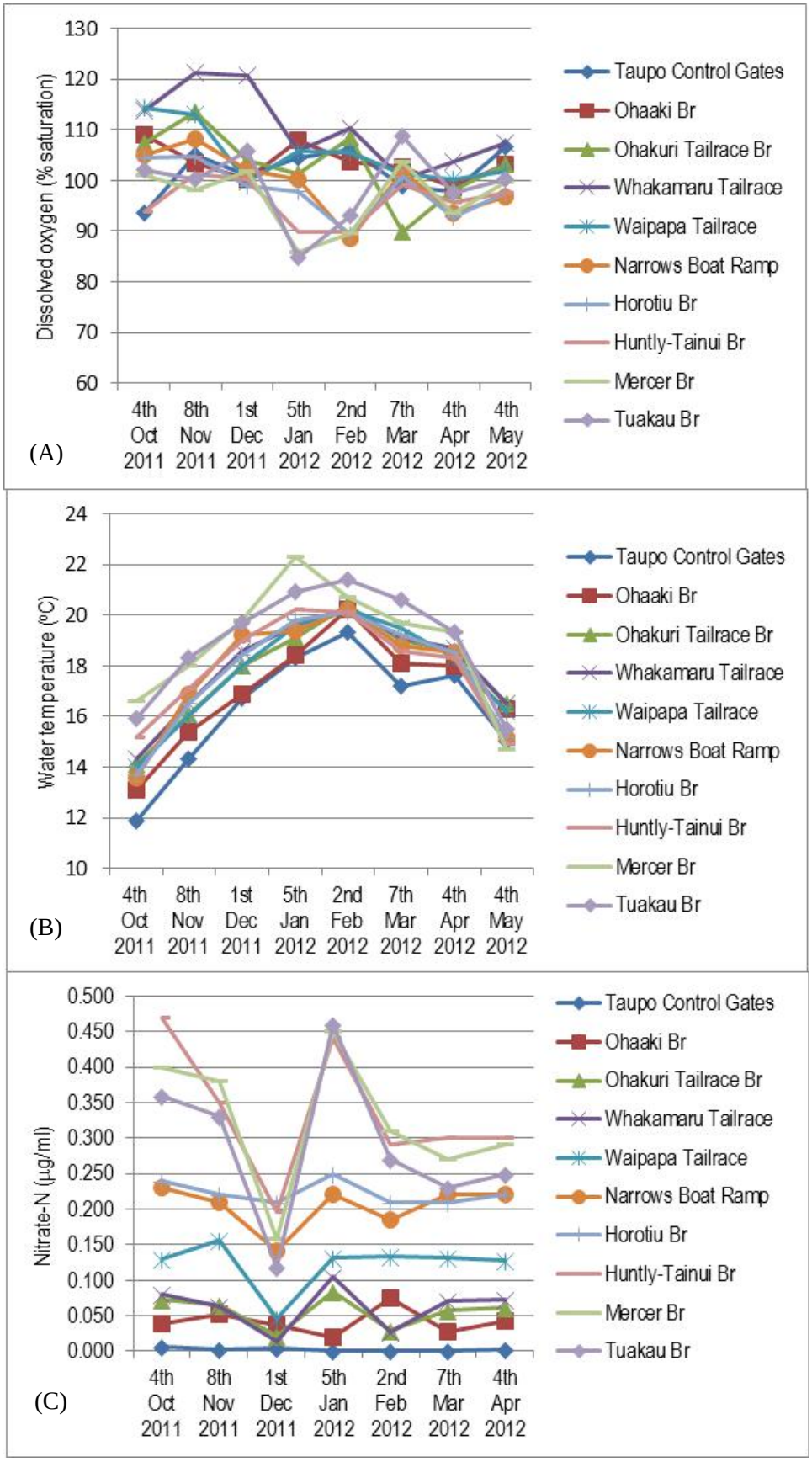
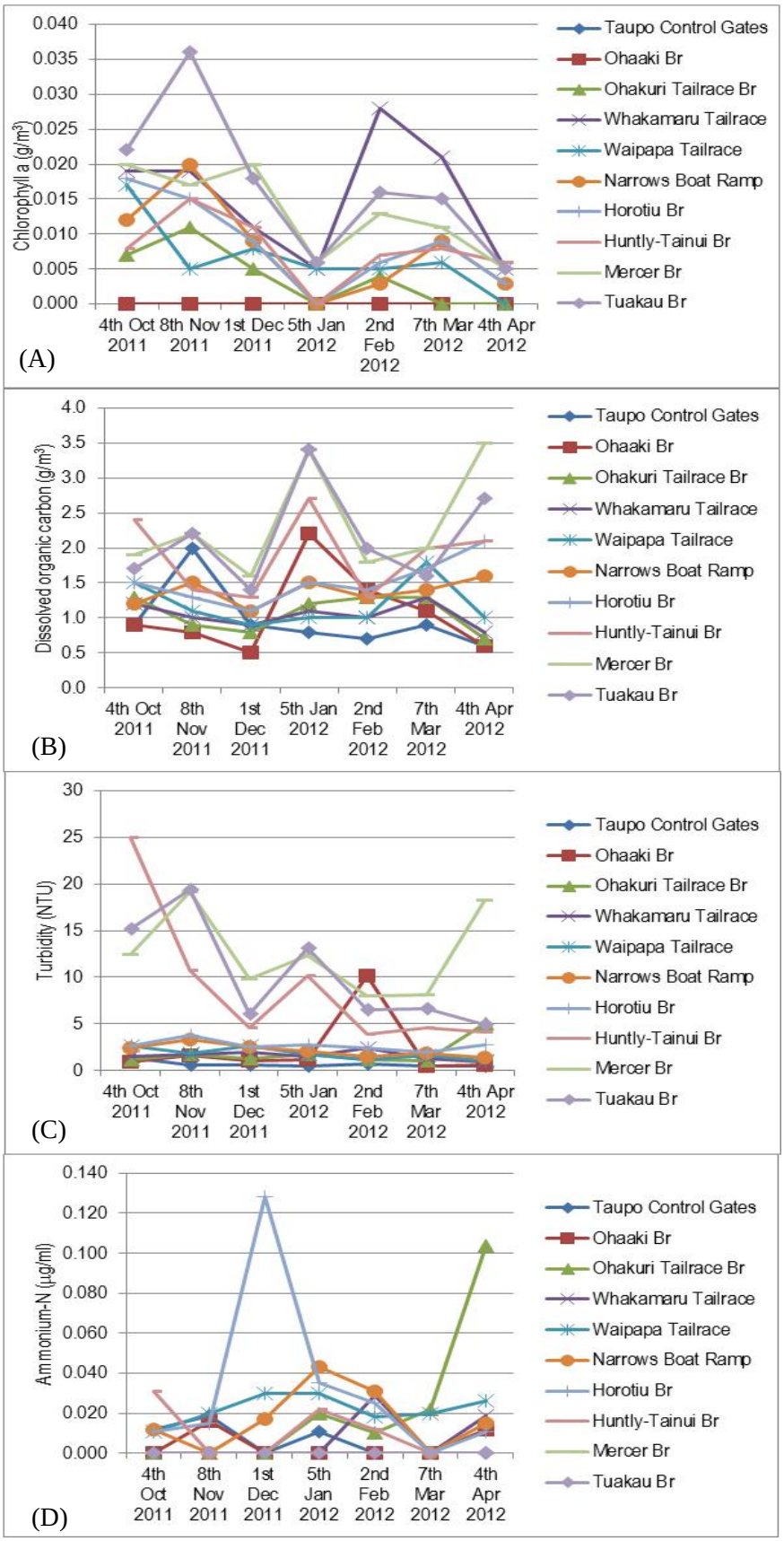


Figure 5.4: Waikato River chloropyll a (A), dissolved organic carbon (B) turbidity (C) and ammonium-N (D) by site vs. time. Provisional data from Environment Waikato (*n*=1).



6. Estimating an EF5-r value for the Waikato River

6.1 Introduction

As noted above the EF5-r emission factor is the proportion of N_2O-N emitted relative to the amount of N leached. In order to assess the relative magnitude of EF5-r this section takes either predicted N_2O-N fluxes based on gas exchange across the water-air interface or the measured N_2O-N fluxes in order to derive an EF5-r value based on NO_3^- loads in the Waikato river. Sites where tailrace waters were sampled are not considered in this section since there are several unanswered questions as to what this water represents and the N_2O dynamics of the hydro-lake system.

6.2 Methodology

The prediction of the gas fluxes was based on the process of gas exchange across the water-air interface and modelled using the following equation (Schwarzenbach et al. 1993).

$$F_{N_2O} = V_{tot}^{N2O}\left(C_w - \frac{C_a}{K'_H}\right) \quad [1]$$

Where F_{N2O} is the N_2O flux (mole m^{-2} s^{-1}), V_{tot}^{N2O} is the combined transfer velocity (m s^{-1}) for N_2O that incorporates both a wind (V_{wind}) and a water turbulence term (V_{water}). The value of V_{tot}^{N2O} was determined from the diffusion coefficient of oxygen in water and is equal to $0.913V_{tot}^{O2}$ (Holmen and Liss, 1984). The term C_w is the N_2O concentration in the river water (mol m^{-3}), C_a is the N_2O concentration in ambient air (mol m^{-3}) and K'_H is the dimensionless Henry's Law constant. The water turbulence term was calculated as follows (O'Connor and Dobbins, 1958)

$$V_{water} = \sqrt{\frac{DU}{h}} \quad [2]$$

Where U is the river water velocity (m s^{-1}), h is the average river depth (m), and D is the O_2 diffusion coefficient in water (m^2 s^{-1}) calculated by extrapolating data contained in Wise and Houghton (1966). The wind term contributing to V_{tot} was calculated as follows (Schwarzenbach et al. 1993).

$$V_{wind} = 2.87E^{-6}ku_{10}^2\left(\frac{Sc}{660}\right)^{1/2} \quad [3]$$

Where $2.78E^{-6}$ is a conversion factor (cm h^{-1} to m s^{-1}), k is a constant (0.31), u_{10} is the wind speed at a height of 10 m above the river (taken from the meteorological data), and Sc is the Schmidt number for oxygen (Wanninkof, 1992). Windspeed data were taken from the Hamilton meteorological station (Cliflo No. 26117) where the annual median 3 hourly wind speed value was 3.5 m/s).

Modelled fluxes of N_2O-N were calculated, using equation [1] as previously performed (Clough et al. 2011) and dissolved N_2O concentrations from six river sites and one lake site that were collected on 29th February 2012 during actual measurement of N_2O fluxes. Data for the Waikato River water

flows were from Brown et al. (2005) and depths were estimated from Environment Waikato gauging information (Table 6.1). If gauging stations did not coincide with sites where fluxes were sampled then data were interpolated between gauging sites. Lake flow (velocity) was estimated using data on water transit times and distances from Table 4 in Brown (2005). Travel times and distances were obtained using information in Brown (2005).

Data in Table 6.1 portray the data used to establish the predictive N_2O-N fluxes based on the methodologies above. Lake Karapiro was used as an assessment site for predictive fluxes from hydro lakes and it was based on a water speed of 0.04 m s^{-1} (based on a length of 15760 m and a cumulative time of 140 hours for water to move through the lake (Brown, 2005)), a water depth of 20 m, and a lake area of 7.7 km^2.

Table 6.1: Data used to establish predicted N_2O-N fluxes downstream from Karapiro dam.

	Velocity (m/s)[1]		River depth[2]	Intermediate distance[1]	Cum. distance	Cum. distance	Cum. hours @	Cum. hours @
Site	250 m^3/s	570 m^3/s	(m)	(m)	(m)	(km)	250 $m3/s^3$	570 $m3/s^3$
Karapiro dam	1	1.15	12.5	80	0	0	0	0
Narrows Brp	1	1.15	12.5	80	23207	23.2	6	6
Horotiu Br	0.8	0.85	12.5	80	23654	46.9	14	12
Huntly Br	0.65	0.8	7.4	100	21072	67.9	23	19
Mercer Br	0.55	0.9	2.2	200	40290	108.2	44	33
Tuakau Br	0.35	0.6	1.2	200	11393	119.6	53	38
Waikato heads	0.15	0.25	1.2	200	27843	147.5	86	58

[1]Travel times and distances from Table 2, Section 4.1 Brown (2005). [2]River depths estimated from Environment Waikato river gauging stations. [3]Discharge rates are reference flows at Mercer based on 15th and 85th percentile flows, 570 and 250 m3/s, respectively. The 15th percentile represents high flow conditions which are equalled or exceeded 15% of the time, while the 85th percentile represents low flow conditions which are equalled or exceeded 85% of the time

6.3 Results and Discussion

Using the data and assumptions outlined above the N_2O-N fluxes were predicted for the sites on the Waikato River downstream of the Karapiro dam using two wind velocities (3.5 and 5 m s^{-1}) and adjusting river velocities in accordance with changes in given flows. Data are shown in Table 6.2. It

can be seen that as expected, the predicted fluxes increase with wind speed. However, at the Lake Karapiro site the predicted fluxes were 462 (18) and 641 (31) μg/m^2/h (s.e.m in brackets) at wind speeds at 10 m height of 3.5 and 5 m s^{-1}.

Table 6.2: Predicted N_2O-N fluxes downstream from Karapiro (μg/m^2/h).

Site	Reference flow 250 m^3/s		Reference flow 570 m^3/s	
	Wind speed (m/s)		Wind speed (m/s)	
	3.5	5.0	3.5	5.0
Narrows Brp	546 (22)	737 (38)	572 (23)	763 (39)
Horotiu Br	618 (23)	794 (37)	650 (23)	827 (38)
Huntly Br	589 (26)	766 (38)	602 (26)	779 (38)
Mercer Br	682 (17)	853 (27)	682 (17)	853 (27)
Tuakau Br	957 (20)	1113 (29)	1138 (22)	1295 (31)
Waikato heads	985 (22)	1142 (32)	1148 (25)	1304 (34)

For the same dissolved N_2O concentrations used here, as collected in February 2012, the measured N_2O-N fluxes ranged from 10 to 26 μg/m^2/h, an order of magnitude lower than predicted here. Thus there is a large discrepancy between predicted N_2O fluxes and measured N_2O fluxes. The most challenging component of the equation [1] for predicting N_2O flux is V_{tot} (Beaulieu et al., 2012) which ranged from 4.7 to 9.4 cm h^{-1} at a wind speed of 3.5 m s^{-1} at a reference flow of 570 m^3 s^{-1}. This is well within the range reported by Beaulieu et al., (2012) and who found that for an impounded area of a large river (Ohio) values were on average equal to 14.8 ± 6.8 cm h^{-1} for wind speeds < 1 m s^{-1}, flow of 0.31 m s^{-1} and mean depth of 8 m. So the value of V_{tot} obtained here is not excessive, although Beaulieu et al., (2012) considered their values high compared to those from a study on the Amazon River, where the transfer velocity was equal to 9.6 ± 3.8 cm h^{-1}.

Raymond and Cole (2001) concluded that wind or bottom stress would dominate in rivers < 10 m deep with wind the dominate factor determining fluxes in deeper systems. At a wind speed of 3.5 m s^{-1} the V_{water} component of equation [1] dominates, contributing 60 to 80% of V_{tot} for the river and 65% in Lake Karapiro. However, if the wind speed was increased to 5 m s^{-1} the V_{water} component contribution reduced to 50-75% on the river but only 50% on the Lake Karapiro. Thus given the relative depths and water speeds of the river reach and hydro lakes the wind speed is going to be a significant factor in determining N_2O-N fluxes from impounded waters.

Predicting N_2O fluxes is notoriously difficult. While the measure of dissolved N_2O is relatively straight forward it is the measure of V_{water} and V_{wind} that is more problematic. The equations used here are not the only ones available for calculating V_{tot} and there is scope to further refine the predicted fluxes. For example, McJannet et al. (2012) have recently published formulae for estimating open water evaporation using land-based meteorological data which consider the surface area of the water body, adjust wind speeds to those expected at 2 m height, and allow for fetch (distance wind travels over water before meeting an obstacle) and surface roughness. Similarly, Raymond et al. (2012) have very recently performed a metadata analysis on 563 gas tracer release experiments, examining gas transfer velocities. As expected the value of the transfer velocity scaled with velocity but also slope.

While no strong emphasis can be placed on the predictive fluxes, at this time, they were used to assess a possible EF5-r value for the 'true-river' section of the Waikato River. Taking the predicted fluxes and multiplying the fluxes by the area of the river downstream of Karapiro the N_2O-N fluxes were determined as a percentage of the NO_3^--N load discharging past Mercer, based on a median 10 year flow (354 m^3/s) and the average river water NO_3^--N concentration of 0.55 g m^{-3} at Mercer, which gave a total of 59994 kg of NO_3^--N discharging over an 86 h period (the transit time from Karapiro to Waikato heads). The N_2O-N fluxes as a percentage of this NO_3^- load ranged from 2.38 to 3.11% of the NO_3^--N discharged (0.024 to 0.031 kg N_2O-N per kg N leached) using the predicted fluxes and a calculated river surface area of 21.8 km^2. **However, when placing the actual measured fluxes into the same scenario the EF5-r equated to 0.05% (0.0005 kg N_2O-N per kg N leached) of the NO_3^--N load over 86 h.**

Using Lake Karapiro as an example of the hydro-lakes and estimating a mean NO_3^--N concentration of 0.18 g m^{-3}, an average discharge of 150 m^3 s^{-1} and a residence time of 140 hours for Lake Karapiro then the N_2O-N flux coming off the 7.7 km^2 area equates to 2.7% of the NO_3^--N leaving the dam if a predicted flux of 347 $\mu g/m^2/h$ is used based on a 1 m s^{-1} wind speed. Under these same conditions a measured flux of 10 $\mu g/m^2/h$ equated to only 0.0008 kg N_2O-N per kg N leached or 0.08%.

Nitrous oxide emissions resulting from agricultural runoff entering lakes are not currently considered in the IPCC inventory process and relatively few studies have examined N_2O emissions from lakes.

This work identifies apparent hot-spots on the Waikato River where point sources of N_2O exist. These may also be seasonal in nature. Clearly the tailrace waters are elevated in the summer months as are the tributaries draining into the Waikato River that transit through farmland. However, further intensive sampling over time in conjunction with lake profile measurements is required to verify the

transient nature and causes of the tailrace dissolved N_2O-N increases. Likewise the dissolved N_2O-N entering from tributaries needs to be characterised in terms of seasonality and influencing variables. Are tributaries seasonally influenced e.g. by warmer summers or rainfall patterns? Rainfall events are shown in this study to affect dissolved N_2O-N. A further question unanswered is the impact of these hot spots relative to the overall river flux.

7. The case for a New Zealand specific EF5-r value.

7.1 Prior work

The original IPCC value for EF5-r (0.0075 kg N_2O-N/kg N leached; uncertainty range 0.0005 - 0.025) was originally based on a suggestion that there was a constant ratio (0.005) for N_2O-N emissions relative to denitrification (N_2-N production) in rivers (Mosier et al. 1998). This was revised in the 2006 IPCC guidelines, which currently provide an EF-r value of 0.0025 kg N_2O-N/kg N leached following the results of several studies that implied the EF5-r value was too high. However, the exact rationale for arriving at this new value is not clear other than it being based on the studies showing lower values. No precise information is given as to why exactly 0.0025 kg N_2O-N/kg N leached was chosen. The rationale for not having a lower value still was the supposition that longer rivers may have higher emissions of N_2O.

A recent study by Beaulieu et al. (2011) used a ^{15}N tracer method to study the N_2O yield following nitrate addition to 72 headwater streams finding that $8.9x10^{-3}$ kg N_2O-N was produced per kg nitrate leached. Then they developed a global river N_2O production model where 0.25% of anthropogenic N inputs to river networks were converted to N_2O via denitrification, they also adopted the IPCC assumption that nitrification converts twice as much anthropogenic N to N_2O as denitrification (i.e. 0.5%) and inferred an EF5-r value of 0.75%. However, it needs to be noted that dissolved organic carbon was high in many cases and the river flows in the agricultural rivers studied by Beaulieu et al. (2011) were extremely slow, quoted as being 0.2 – 190 litres per second ($2x10^{-4}$ to 0.19 m^3/s), relative to New Zealand conditions and this would have provided considerable time for denitrification and further processing of nitrate.

Taking the actual measured fluxes of the current study the calculated emission of N_2O-N was 20% of the 2006 IPCC recommended guidelines EF5-r value (i.e. 0.0005 vs. 0.0025) and the measured fluxes were comparable to fluxes previously measured *in situ* in spring-fed streams where nitrate concentrations were higher Clough et al. (2007). Studies to date on New Zealand rivers, on the

Ashburton River (Clough et al. 2011) and the LII River (Clough et al. 2006, 2007), have all derived EF5-r values less than the current value derived for the Waikato river.

As discussed below (7.2) a key determinant of denitrification in water ways is the time the water is in contact with the river sediments. As rivers get faster and the water body gets deeper this contact time is reduced and less of the water volume is in contact with the sediment.

Given the results of this current study and past New Zealand specific work it is advocated that a New Zealand specific EF5-r value should be implemented which is at least equal to the current value advocated in the 2006 revised guidelines i.e. 0.0025 kg N_2O-N/kg NO_3^--N leached. Work to date in New Zealand from actual measured fluxes has shown no EF5-r value higher than this.

Currently, in 2010, there are 1,508,379,670 kg N excreted on to 'pasture, range and paddock', and given a $FRAC_{LEACH}$ value of 0.07, then 131,648,736 kg of N is then leached or runoff (MfE Greenhouse gas inventory 1990-2012). This equates to 5.17 Gg N_2O if the 1990 IPCC EF5 value of 0.025 is used. If the 2006 guidelines are followed and an EF5 (= EF5-r + EF5-g + EF5-e) value of 0.0075 was used (where EF5-r is 0.0025) it would equate to 1.55 Gg N_2O being emitted.

Implementing an EF5-r value of 0.0025 kg N_2O-N/kg NO_3^--N leached would reduce inventory indirect emissions by 3.62 Gg N_2O, equivalent to 1079 Gg of CO_2 if a GWP potential of 298 over a 100 year period is used to convert Gg N_2O to Gg CO_2.

7.2 Does length make a difference?

In the revised IPCC guidelines (De Klein, 2006) the rationale for not reducing the EF5-r value further was studies showing low EF5-r factors were based on rivers of short length. It was considered that longer rivers might have higher emission rates. Such an argument requires certain assumptions to be made. If a 'short-river' was theoretically extended and the extension was identical to the original 'short' length in terms of NO_3^- attenuation and IF no other NO_3^- inputs occurred along the 'extension' to the short river then there would be increased sink capacity, assuming the extension denitrified at the same rate (thus EF5-r would be higher). However, if the 'extension' behaves as the original 'short' river section and not only emits N_2O but also receives NO_3^- then the status quo may well result – no change in emission factor regardless of length.

The longer a river is the larger the catchment becomes, and the potential contribution for NO_3^- inputs from runoff and/or hyporheic sources may also increase accordingly. Using the Waikato River as a case in point it can be seen that NO_3^--N concentrations increase as the river distance increases. The catchment area also increases in this case with the river distance.

Thus river length is not, on its own, a good discriminating factor for considering an EF5-r value and should not in our opinion be used. With river velocity changing with slope over a river's distance as is the case in the Waikato a term such as 'water residence time' is more useful but still not adequate when nitrate is being injected along the length of a river. In effect different inputs of nitrate have different 'river lengths' to travel or 'differing residence times'.

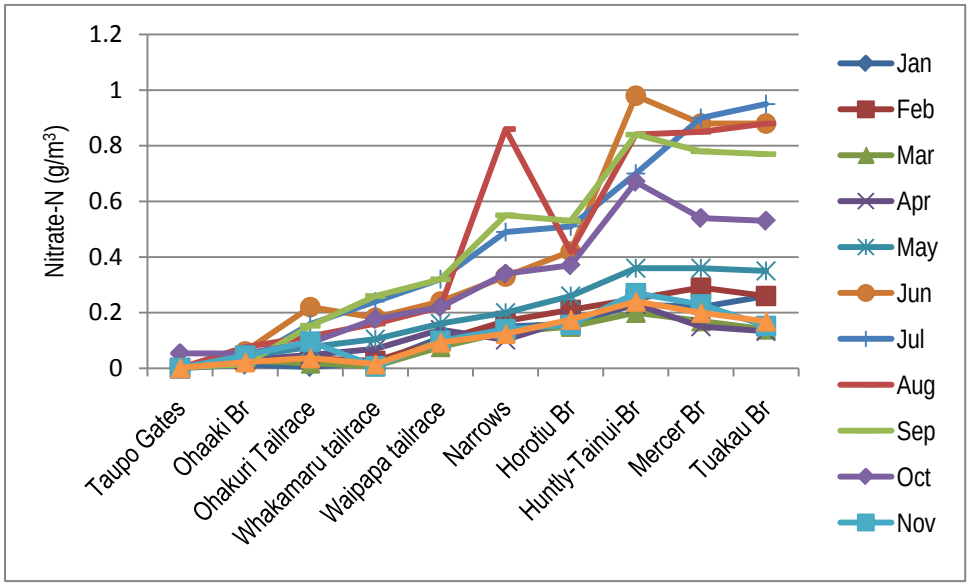


Figure 7:1 Change in nitrate- N concentration by site from Taupo Gates to Tuakau Bridge. [Source Waikato Regional Council Technical Report 2011/03 (Beard, 2011)].

Figure 7:2 Change in nitrate- N concentration by distance from Taupo Gates (0 km) to Tuakau Bridge (302 km). [Source Waikato Regional Council Technical Report 2011/03 (Beard, 2011)].

Previously, a relationship has been developed showing that the percentage of N removal increases with increases in the water residence time (Seitzinger et al. 2006) but the relationship described does not consider further N inputs with increased residence time.

Beaulieu et al. (2011) also found no effect of catchment area (which they describe as a surrogate for river network length), a fact that was presumed to be due to variation in N inputs, temperature, runoff conditions, and the presence of lakes and reservoirs within the river networks.

What is potentially more important than river length is the ratio of the cross sectional area of the river to the width of the river bed (i.e. depth). Shallow, slow moving, wide reaches provide a greater opportunity for embodied NO_3^- to react with benthic sediments and be denitrified. Deep fast waters provide less opportunity. In the case of the Waikato river greater opportunities for benthic denitrification exist downstream from Huntly as the river begins to become shallower and widens. Seitzinger et al. (2006) also develop a relationship (from several studies) that shows higher N removal occurs when the depth: water residence time ratio decreases (i.e. shallow slow moving water will denitrify a higher percentage of embodied nitrate) but again this percentage of removal was not discussed with respect to dynamics in N loads.

Sediments will also have a maximum rate of denitrification and if surplus NO_3^- substrate exists there may not necessarily be an increase in N_2O-N evolved if denitrifiers are saturated with substrates (nitrate and carbon) or limited by lack of another substrate such as available carbon.

Interestingly the levels of NO_3^--N in the Waikato River taken during February sampling (Figure 2.2) show a decline in NO_3^- concentration from Ngaruawahia, just upstream of Huntly, to Tuakau. This is the area of the river where higher denitrification should theoretically exist if benthic denitrification processes dominate. Further examination of sediment samples and associated denitrification rates would assist in explaining this observed trend, and determining maximum rates of denitrification.

Wetland areas or deltas associated with rivers may vary with river size. In many instances these are now confined. But a river with a large hydraulic load will potentially spread, if allowed, over a wider area and have shallower depth which may assist in enhancing denitrification and EF5-r. But any enhancement will depend on this area as a percentage of the river area.

Thus, we believe denitrification rates and N_2O fluxes should be more closely examined in relation to river geomorphology (depth, residence time), hydrology (residence time and flow), and the dynamics of the nitrate load over distance and time. Potentially there will be further scope to assess this once an annual data set on nitrate load and flows is compiled for the Waikato River.

8. References

Beaulieu JJ, Shuster WD, and Rebholz JA. 2010. Nitrous Oxide emissions from a Large, Impounded River: The Ohio River. Environmental Science and Technology. 44:7527-7533.

Beaulieu JJ, Tank JL, Hamilton SKL, Wollheim WM, Hall RO Jr, Mulholland PJ, Peterson BJ, Ashkenas LR, Cooper LW, Dahm CN et al. 2011 Nitrous oxide emission from denitrification in stream and river networks. Proceedings of the National Academy of Sciences. 108:214-219.

Beaulieu JJ, Shuster WD, and Rebholz. 2012. Controls on gas transfer velocities in a large river. Journal of Geophysical research. 117:1-13.

Beard S. 2011. Waikato River Water Quality Monitoring Programme: data Report 2010. Waikato Regional Council Technical Report 2011/03. Waikato Regional Council document # 1931299.

Brown 2005. Hydraulic Travel Times of Major Waikato Rivers. Waikato Regional Council Technical Report 2005/04. Waikato Regional Council document # 973399.

Clough TJ, Bertram JE, Sherlock RR, Leonard, and Nowicki BL. 2006. Comparison of measured and EF5-r-derived fluxes from a spring-fed river. Global Change Biology. 12:352-363.

Clough TJ, Buckthought LE, Kelliher FM, and Sherlock RR. 2007. Diurnal fluctuations in dissolved N_2O concentrations in a spring-fed temperate river: Implications for measuring N_2O fluxes and IPCC methodology. Global Change Biology. 13:1016-1027.

Clough TJ, Ray JL, Buckthought LE, Calder J, Baird D, O'Calaghan M, Sherlock RR, Condron LM. 2009. The mitigation potential of hippuric acid on N_2O emissions from urine patches: An *in situ* determination of its effect. Soil Biology and Biochemistry. 41:2222-2229.

Clough TJ, Buckthought LE, Casciotti KL. Kelliher FM, and Jones PK. 2011. Nitrous oxide Dynamics in a Braided River System, New Zealand. Journal of Environmental Quality 40:1532-1541.

Davidson EA, and Firestone MK. 1988. Measurement of nitrous oxide dissolved in soil solution. Soil Science Society of America Journal. 52:1201-1203.

Dong LF, Nedwell DB, Colbeck I, Finch J. 2004. Nitrous oxide emission from some English and Welsh rivers and estuaries. Water Air and Soil Pollution: Focus. 4:127-134.

Ivens WPMF, Tysmans DJJ, Kroeze C, Lohr AJ, and van Wijnen J. 2011. Modeling global N_2O emissions from aquatic systems. Current Opinion in Environmental Sustainability. 3: 350-358.

Kendall C. 1998. Tracing Nitrogen Sources and Cycling in Catchments. Chapter 16 in Isotope Tracers in Catchment Hydrology. Edited by Kendall C. & McDonnell JJ. Elsevier Science, Amsterdam.

Matthew R. McIlvin and Mark A. Altabet - Chemical Conversion of Nitrate and Nitrite to Nitrous Oxide for Nitrogen and Oxygen Isotopic Analysis in Freshwater and Seawater. Anal. Chem., 2005, 77 (17), pp 5589–5595.

Magadza CHD. 1979. Physical and chemical limnology of six hydroelectric lakes on the Waikato Rover, 1970-72. New Zealand Journal of Marine and Freshwater Research. 13:561-572.

McJanet DL, Webster IT and Cook FJ. 2012. An area-dependent wi9nd function for estimating open water evaporation using land-based meteorological data. Environmental Modelling and Software. 31:76-83.

Mengis M., Gächter R and Wehrli B. 1997 Sources and sinks of nitrous ocide (N_2O) in deep lakes. Biogeochemistry 38:281-301.

Mosier AR, Kroeze C, Nevison C, Oenema O, Seitzinger S, van Cleemput O. 1998. Closing the global N_2O budget: nitrous oxide emissions through the agricultural nitrogen cycle. Nutrient Cycling in Agroecosystems 52:225-248.

O'Connor DJ, and Dobbins WE. 1958. Mechanisms of reaeration in natural Streams. Transactions ASCE. 123:43.

Outram FN, and Hiscock KM. 2012 Indirect Nitrous Oxide Emissions from Surface Water Bodies in a Lowland Arable Catchment: A Significant Contribution to Agricultural Greenhouse Gas Budgets? Environmental Science and Technology 46:8156-8163

Raymond PA, and Cole JJ. 2001. Gas exchange in rivers and estuaries: Choosing a gas transfer velocity. Estuaries Coasts 24:312-317.

Raymond PA, Zappa CJ, Butman D, Bott TL, Potter J, Mulholland P, LAursen AE, McDowell H, Newbold D. 2012. Scaling the gas transfer velocity and hydraulic geometry in streams and small rivers. Limnology and Oceanography: Fluids and Environments 2:41–53

Schwarzenbach RP, Gschwend PM, and Imboden DM. 1983. Environmental organic chemistry. John Wiley & Sons, New York.

Seitzinger S, Harrison JA, Böhlke JK, Bouwman AF, Lowrance R, Peterson B, Tobias C, van Drecht G. 2006. Denitrification across landscapes and waterscapes a synthesis. Ecological Applications 16:2064-2090.

Stevens RJ, Laughlin RJ, Atkins GJ, and Prosser SJ. 1993. Automated determination of nitrogen-15 labelled dinitrogen and nitrous oxide by mass spectrometry. Soil Science Society of America Journal 57:981-988.

Tiedje JM. 1983. Denitrification. In: Methods of Soil Analysis. Page et al. (ed). Part 2. 2nd Edition. Agronomy 9:1011-1026.

Thomas, S.M., S.F. Ledgard, and G.S. Francis. 2005. Improving estimates of nitrate leaching for quantifying New Zealand's indirect nitrous oxide emissions. Nutrient Cycling in Agroecosystems 73:213–226.

Wanninkhof R. 1992. Relationship between wind speed and gas exchange over the ocean. Journal of Geophysical Research. 97:7373-7382.

Appendix 1: Reviewer's comments and response.

Reviewer's Comment	Authors' Response
It is a really interesting study and you are accumulating some very interesting information, albeit challenging to understand due to system complexity. I think you justify your interpretation well. I have made a number of comments in the draft. These are minor and largely suggestions to help the reader (e.g. a map of the site locations for your flux measurements would be helpful). In a number of cases I have suggested you provide more information about the sampling methodology. In some cases you have described them but they appear later in other sections of the report. It could probably do with some editorial tweaking, but it is in the main is easily readable.	These are much appreciated and have been acted upon.
I have made one comment about reporting of reps for your determination of dissolved N2O that I don't believe is correct. You are essentially analyzing the same water sample twice (n=3), and don't have 6 individual samples.	These are pseudo-replicates to be more accurate.
I am not sure about your calculations/assumptions of the emission factor for the river. My comment relates to the calculation of the N input (NLEACH value). Should your N input value be higher? You calculate your emission factor below Karapiro but use the N discharge values for Mercer and below. If you get denitrification of N above Mercer you would underestimate N input.	Correct, but a value has to be taken somehow. If we take the value at e.g. Karapiro we significantly under estimate N load in the river which is dynamic (it increases as the catchment gets larger, as you move downstream of Karapiro). This value was taken because it represented a median 10 year value based on a median 10 year flow rate from which total N loading could be judged. If we look at the change of nitrate within the river the value at Mercer differs little from the Huntly-Tainui/Tuakau sites and these are always elevated compared to the sites further upstream (Fig. 5.3). So I do not think we have underestimated the N load taking the available data – which is for Mercer – because good hydrology data are also available here over time.
Determination of transfer velocities using tracer measurements (e.g. SF 6 or others) – see Laursen, A.E.; Seitzinger, S.P. 2002: Measurement of denitrification in rivers: an integrated, whole reach approach. Hydrobiologia	Yes, but for the size of the Waikato river this is not a simple exercise. I realize it has been performed on the Hudson river in New York State but it is a major project in its own right. To use a tracer method you need to be able to inject a tracer and have it well mixed in a very short

485: 67-81. They used tracers for determination of denitrification in whole reach studies	distance. I think this type of approach is very valid but should first be tried on lowland streams of small flows and perfected there.
Have you thought about using the NIWA River Environment Classification (REC) and Estuarine Environment classification tool http://www.mfe.govt.nz/environmental-reporting/about/tools-guidelines/classifications/freshwater/rec-user-guide-2010.pdf ? It divides streams/rivers into segments through its hierarchical classification system. I saw an opportunity to use this to identify "typical" catchment reaches – contains information about climate, topography, and land use. Can be used with GIS too. I think it has information about stream cross sections. If you can characterize typical segments then use the GIS to upscale? Not sure how these fit in with EW sample sites – they will know about the REC.	This may be something for a future study to consider. From what I have read of this "Each of the REC's six hierarchical classification levels is defined by one of six controlling factors (referred to as factors). These factors are Climate, Source-of-Flow, Geology, Land-Cover, Network-Position and Valley-Landform. There is an increasing number of potential classes moving down the REC hierarchy." There is no factor based on nitrogen loading – although land-cover may be useful here. Maybe measures of N2O fluxes should, in future, be made based on this network classification system.