

Comparison of measured and EF5-r derived N₂O fluxes from a spring-fed river.

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Running title: River N₂O fluxes and EF5-r.

Abstract

There is considerable uncertainty in the estimates of indirect N₂O emissions as defined by the Intergovernmental Panel on Climate Change's (IPCC) methodology. Direct measurements of N₂O yields and fluxes in aquatic river environments are sparse and more data are required to determine the role that rivers play in the global N₂O budget.

The objectives of this research were to measure the N₂O fluxes from a spring-fed river, relate these fluxes to the dissolved N₂O concentrations and NO₃-N loading of the river, and to try and define the indirect emission factor (EF5-r) for the river.

Gas bubble ebullition was observed at the river source with bubbles containing 7.9 μL N₂O L⁻¹. River NO₃-N and dissolved N₂O concentrations ranged from 2.5 to 5.3 mg L⁻¹ and 0.4 to 1.9 μg N₂O-N L⁻¹ respectively with N₂O saturation reaching 404%. Floating headspace chambers were used to sample N₂O fluxes. N₂O-N fluxes were significantly related to dissolved N₂O-N concentrations ($r^2 = 30.6$) but not to NO₃-N concentrations. The N₂O-N fluxes ranged from 38-501 μg m⁻² h⁻¹, averaging 171 μg m⁻² h⁻¹ (± Std. Dev. 85) overall. The measured N₂O-N fluxes equated to an EF5-r of only 6.6% of that calculated using the IPCC methodology, and this itself was considered to be an over-estimate due to the degassing of antecedent dissolved N₂O present in the groundwater that fed the river.

Introduction

Atmospheric concentrations of N₂O, a greenhouse gas (GHG), have increased since pre-industrial times to the present (Prinn *et al.*, 1990, Rockmann *et al.*, 2003) and continue to rise at 0.2-0.3% yr⁻¹ (Nevison, 2000b). Due to the lack of any stabilization in atmospheric GHG concentrations, parties to the United Nations Framework Convention on Climate Change (UNFCCC) negotiated the Kyoto Protocol. This protocol sets targets for participating countries to reduce or take responsibility for their excess GHG emissions. An obligation of the parties that are signatories to the UNFCCC and the Kyoto protocol is the development and publication of an annual national inventory of all anthropogenic GHG emissions and removals. The IPCC methodology predicts that in many countries N₂O will comprise at least 10% or more of the aggregate GHG emissions (Nevison, 2000b); in New Zealand's case, N₂O emissions comprise 17% of the total aggregated GHG emissions per annum (New Zealand Climate Change Office, 2004).

Guidelines on how to construct inventories have been prescribed by the Intergovernmental Panel on Climate Change (IPCC) and include a number of "default" assumptions and data for use in the calculation of GHG emissions and removals (IPCC, 1997). The IPCC guidelines divide agricultural N₂O sources into three categories: direct emissions from agricultural land, emissions from animal waste systems, and indirect emissions associated with nitrogen (N) that is removed in biomass, volatilized, leached, or exported from the agricultural land (Mosier *et al.*, 1998). The aim of this methodology is to provide a standardized framework to account completely for the annual N₂O production associated with agricultural practice on a per country basis. Each of the three N₂O source categories typically contributes an equal 1/3 share of the total estimated agricultural N₂O source (Nevison, 2000b). However, approximately 2/3 of the uncertainty in the total

agricultural N₂O source is due to the wide range of estimates for indirect N₂O emissions (Nevison, 2000b).

The total global N₂O source from agricultural soils stands at 6.3 Tg N yr⁻¹ (Mosier *et al.*, 1998). Indirect emissions account for 2.1 Tg N yr⁻¹ of this total; nitrogen leaching and runoff dominate the indirect emission sources accounting for over 75% of estimated indirect emissions (Mosier *et al.*, 1998, Nevison, 2000b). Biological cycling of both the natural and anthropogenic N through aquatic ecosystems produces emissions of N₂O via nitrification and denitrification. N₂O production allied to N leaching and runoff is defined by the IPCC methodology as follows (IPCC, 1997, Mosier *et al.*, 1998):

$$\text{NLEACH} = (\text{NFERT} + \text{NEX}) * \text{FRACLEACH}$$

$$\text{N}_2\text{O(L)} = \text{NLEACH} * \text{EF}_5$$

Where NLEACH (kg N yr⁻¹) is the mass of fertilizer and manure N lost through leaching and runoff per annum, NFERT (kg N yr⁻¹) the mass of fertilizer used per annum, NEX (kg N yr⁻¹) the mass of manure N excreted by livestock per annum, and FRACLEACH the fraction of the fertilizer and manure N lost to leaching and surface runoff (range 0.1 - 0.8). The N₂O emissions due to agricultural N loss through leaching and runoff (N₂O(L)) are calculated by multiplying NLEACH by the emission factor (EF₅) for leaching and runoff. The value of EF₅ is the sum of the N₂O emission factors for N₂O losses from i) groundwater and surface drainage (EF_{5-g} = 0.015 kg N₂O–N per kg NLEACH), ii) rivers (EF_{5-r} = 0.0075 kg N₂O–N per kg NLEACH), and iii) coastal marine areas (EF_{5-e} = 0.0025 kg N₂O–N per kg NLEACH). The rationale behind the development of the default values for EF_{5-g}, EF_{5-r} and EF_{5-e} have been previously described (Mosier *et al.*, 1998, Nevison, 2000b).

As noted above, current estimates of the total agricultural sourced N₂O emissions equate to 6.3 Tg N yr⁻¹ which is greater than the observed atmospheric increase of 3.9 Tg N yr⁻¹. A simple explanation for this is that the IPCC methodology over-estimates the anthropogenic source (Nevison, 2000b). There is considerable discussion in the literature regarding the appropriate magnitude of the default factors for FRACLEACH and the components of EF5, with suggestions for possible improvements to the assumptions and the magnitudes of the default factors (Groffman *et al.*, 2000, Nevison, 2000b, Groffman *et al.*, 2002, Reay *et al.*, 2003). Actual measurements of N₂O yields in aquatic river environments are sparse (Nevison, 2000b, Cole & Caraco, 2001) and an assumption commonly made is that the N₂O yield is 0.5% for both nitrification and denitrification (Mosier *et al.*, 1998, Seitzinger & Kroeze, 1998). Cole and Caraco (2001) measured N₂O fluxes from the Hudson river and compared these with modelled estimates, determined using the model of Seitzinger and Kroeze (1998). They found the measured fluxes to be considerably lower than the modelled fluxes, as was the case for four out of seven other rivers, where measured values were also lower than modelled values. In the case of the Hudson river, the assumptions used in the model (Seitzinger & Kroeze, 1998) over-estimated denitrification and nitrification rates. More data are required to determine the role rivers play in the N₂O budget (Cole & Caraco, 2001, Groffman *et al.*, 2002).

This study presents N₂O flux data and associated river measurements from a spring-fed river that flows through an agricultural landscape. The data are used to examine the relationship between the measured fluxes and a component of the EF5 emission factor, EF5-r.

Materials and Methods

This study was carried out on the LII river, situated in the Canterbury region of the South Island, New Zealand (Fig. 1). In the Canterbury Plains area confined and unconfined aquifers

carry water from the Southern Alps eastwards towards the Pacific Ocean. Aquifers are primarily composed of gravels with small proportions of finer textured sands and silts. The lower the percentage of sand and silt the greater the permeability and yield of the aquifer. Aquifers high in sand and silt are lower yielding and are referred to as aquitards (Bowden, 1986). The uppermost water bearing layers over the inland plains have a high permeability and are referred to as unconfined aquifers. Rain water and river waters move into the unconfined aquifers and travel laterally towards the East Coast recharging the unconfined aquifers. Groundwater is vulnerable to contamination especially from associated land uses over the aquifers. In the coastal area around the city of Christchurch (Fig. 1) the groundwater flowing at shallow depth towards Christchurch city meets confining aquitards, and water is forced both below the aquitard and above the aquitard into the near-surface gravels and the spring-fed rivers (Bowden, 1986). Base flows in these spring-fed rivers are derived from the re-surfacing shallow groundwater (Bowden, 1986).

The LII is a spring-fed river, 12 km long, commencing 10 m above sea level near Lincoln township (Lat./Long. 43.64673S, 172.49677E), and flows in a south westerly direction for a distance of 12 km whereupon it discharges into Lake Ellesmere (Fig. 1). Four sampling sites were selected for this study. These were located evenly along the length of the river and had easy road access. Sites 1, 2, 3 and 4 were located at the 0, 4.4, 7.7 and 10 km from the spring. The LII river flows through land under agricultural stewardship that includes orchards, dairy, and sheep farms. The watershed area and N loading of the watershed are not readily definable. However, drainage ditches from the agricultural lands discharge into the LII at regular intervals. There are no direct point sources of effluent, such as dairy waste ponds, discharging into the LII. The river's mean gradient was 0.08%.

River flow measurements were performed using the velocity-area method (Mosley *et al.*, 1992, Davie, 2003). In brief this entailed calculating the trapezoidal cross-sectional area

of the river and measuring the river velocity with a timed float. River depth was monitored at sites 3 and 4 using pre-existing flow gauges that had been installed by the regional council. Meteorological data was collected at the Lincoln University climate station, a distance of 3 km from site 1.

Floating chambers were constructed from round polypropylene “cake” containers (Decor®, product No. 350, Australia). The container lids were discarded and the containers inverted so that the open side formed the chamber base. The containers were shaped like a conical frustrum (radii of 10.1 and 11.3 cm at the chamber roof and water surface respectively; an internal height from chamber roof to water surface of 11.7 cm). A styrofoam annulus (8.5 cm wide, 11.7 cm deep) was attached around the chamber. The polypropylene chamber projected 1.5 cm into the water when floating on the river surface. This was in addition to the internal chamber height of 11.7 cm. The resulting headspace volume of the floating chamber was 4.2 L. A rubber septum was placed in the roof of the plastic chamber to facilitate headspace gas sampling. The septa were from blood evacuation tubes (BD, Dickinson, NJ.). Laboratory testing of the floating chambers showed no N₂O production or consumption over a 60 minute period. Testing of the floating chambers on the LII river showed that N₂O concentrations increased in a linear manner for up to 60 minutes. This time was well in excess of the 15 minute sampling times used in the study (see below).

Unless otherwise stated 10 replicate chambers were used at each site during sampling of the river surface gas fluxes. To determine the river surface gas fluxes the chambers were placed on the water surface, linked with 1 m lengths of string and allowed to drift freely with the river current. A terminal chamber was linked via string to an observer on the river bank who walked alongside the river. Chambers were deployed at the same position, and in the same sequence, on each sampling occasion. Chamber capture was performed after 15 minutes

by gently pulling the chambers back to quiet water alongside the bank, where gas sampling occurred.

Glass syringes equipped with three way large bore stopcocks (Part No. 2C6201, Baxter Healthcare Corp., Deerfield IL.) were used to take gas samples while the chambers remained floating on the river surface. A gas sample of 10 mL was taken from the headspace chamber and flushed to waste, twice. On the third occasion the 10 mL sample was injected into a previously evacuated (<0.01 atmosphere) 6 mL glass sample tube with a screw cap and rubber septum (Exetainer®, Labco Ltd., UK.), creating an internal over-pressure. Ambient air gas samples were also taken at each site when chamber headspace samples were obtained.

Gas samples were analysed using a gas chromatograph (8610, SRI Instruments, CA.) interfaced to a liquid autosampler (Gilson 222XL, Middleton, WI.). The autosampler had been specially modified for gas analysis by substituting a purpose-built (PDZ-Europa, Crewe, UK) double concentric injection needle for the usual liquid level detector and needle. This enabled the entire gas sample to be flushed rapidly from its septum-sealed container (6 mL Exetainer®) into the GC.

The GC configuration was similar to that used by Mosier and Mack (1980) and included two 0.3 cm OD stainless steel columns packed with Haysep Q connected in series, oxygen-free dry nitrogen carrier gas (40 mL min^{-1}), and a ^{63}Ni electron capture detector at 320°C . Gas samples were analysed within 1 to 2 days of sampling. Immediately prior to analysis the over-pressurised samples were all brought to ambient atmospheric pressure, using a double-ended hypodermic needle. One end of the needle was placed at a constant depth (0.5 cm) just below the surface of some water in a small beaker while the other end pierced the Exetainer® septum. A brief flow of bubbles resulted and when these ceased, the gas in the Exetainer® was at ambient air pressure. Dissipating the excess gas pressure through the water medium not only gave a visual indication of when the samples were at

ambient air pressure, it also avoided any potential contamination of the sample with ambient air. Reference gases (0.363 to $35.2 \mu\text{L L}^{-1}$, BOC Ltd. Auckland) were prepared following the same over pressure-equilibration procedure as described above. Detection limits for N_2O analysis were considered significant if concentrations were $0.01 \mu\text{L L}^{-1} >$ than the ambient concentration.

Water samples for measurement of dissolved gases were collected in 500 mL glass reagent bottles. Bottles were first rinsed with river water and then submerged ca. 20 cm below the water surface and allowed to fill completely. Then a glass stopper was inserted, prior to the bottle's removal from the stream and its placement into a styrofoam insulated box, where it was stored until arrival back at the laboratory. River and air temperatures were measured *in-situ* using a portable pH meter fitted with a combination pH and temperature probe (HI9025, Hanna Instruments, Italy).

Gas ebullition at the spring was collected by placing an inverted plastic funnel, connected to a 2 L volumetric glass flask full of water, below the water surface. As the gas was collected the water in the flask was displaced. After 2 L of gas was collected a rubber septum was used to seal the flask prior to transporting it back to the laboratory for gas analyses.

Back in the laboratory the river water samples were subsampled and analyzed for dissolved oxygen (DO), inorganic-N ($\text{NH}_4\text{-N}$, $\text{NO}_2\text{-N}$, $\text{NO}_3\text{-N}$), dissolved total organic carbon (TOC), electrical conductivity (EC), pH, and dissolved N_2O . DO was measured using the iodometric titration method with an azide modification (Clesceri *et al.*, 1998). Inorganic-N concentrations were determined using colorimetric methods and an auto-analyser with a detection limit for $\text{NO}_3\text{-N L}^{-1}$, $\text{NO}_2\text{-N L}^{-1}$ and $\text{NH}_4\text{-N L}^{-1}$ of 0.10, 0.01, and 0.01 mg L^{-1} respectively (Alpkem FS3000 twin channel analyser; application notes P/N A002380 and P/N A002423). Dissolved TOC was calculated from the difference between dissolved total carbon

(TC) less dissolved inorganic carbon (TIC), i.e. $TOC = TC - TIC$. Dissolved carbon analyses were performed with a Shimadzu TOC-Analyser fitted with a Shimadzu ASI-5000A autosampler. The detection limit for dissolved organic carbon and inorganic was 1 mg L^{-1} . A conductivity meter (CDM83, Radiometer, Copenhagen) was used to measure the EC of the water samples.

Concentrations of dissolved gases in the river water samples were analysed according to Davidson and Firestone (1988) with appropriate Bunsen coefficients obtained for N_2O (Young, 1981). Initially a microbial inhibitor (mercuric chloride) was added to the water sample (Kirkwood, 1992). However, use of the inhibitor was discontinued when tests showed no difference in the dissolved N_2O results between inhibited and non-inhibited samples. Nitrous oxide equilibrium concentrations (nmol L^{-1}) in the river water were determined using an atmospheric N_2O partial pressure of $3.1 \times 10^{-7} \text{ atm}$ and the appropriate solubility coefficient for N_2O ($\text{mol L}^{-1} \text{ atm}^{-1}$) for the temperature of the water sampled (Weiss & Price, 1980)). Dissolved N_2O concentrations were then converted to units of $\mu\text{g N}_2\text{O-N L}^{-1}$.

An N_2O -N flux was calculated for the river reach between sites 1 and 4, according to the IPCC methodology and assumptions, using the following data: a NO_3 -N concentration of 2.8 mg L^{-1} , a river flow of $3.41 \text{ m}^3 \text{ s}^{-1}$, and an average river width of 10 m with a length of 10,000 m. A theoretical N_2O flux (F_{N_2O} ; $\text{mole m}^{-2} \text{ s}^{-1}$) was also calculated using the stagnant-two-film approach (Liss & Slater, 1974):

$$F_{N_2O} = -V_w^{N_2O} \left([N_2O] - \frac{p_{N_2O}}{K_H} \right)$$

Where K_H was the Henry's Law constant ($\text{atm. m}^3 \cdot \text{mole}^{-1}$), p_{N_2O} the partial pressure of N_2O in the atmosphere (atm.), $[N_2O]$ the concentration of N_2O in the water (mole m^{-3}), and $V_w^{N_2O}$ the transfer velocity (m s^{-1}). The value of $V_w^{N_2O}$ was estimated from the transfer velocity of a

reference gas, oxygen, as $V_w^{N_2O} = 0.913 \times V_w^{O_2}$ (Holmen & Liss, 1984). Transfer velocity of oxygen was assigned as discussed below in the results and discussion sections.

River surface N₂O flux measurements and associated water samplings were carried out on the LII river from autumn through to spring. Surface N₂O flux measurements were taken on the 3rd, 17th, and 31st May, 17th June, 8th July, 16th August, and the 10th September. Dissolved N₂O concentrations were measured on the same dates as the N₂O flux measurements and also on the 5th and 26th of April, and the 28th of July. Inorganic-N and dissolved carbon sample dates were the same as for the dissolved N₂O samples but also included the 5th and 19th of March, and 1st of October. To establish if these results were representative of other spring-fed rivers, N₂O flux and NO₃-N measurements were also taken from another agriculturally influenced spring-fed river approximately 10 km to the north of the LII, the 'Halswell'; and two other spring-fed rivers the 'Avon' and the 'Heathcote' that flow through the major urban centre of Christchurch, approximately 25 km away (Fig. 1). These other rivers were sampled on one occasion (18th August) using the same methods.

Results

Meteorological data and river chemistry

Average wind run, and air temperatures over the study period were 342 km d⁻¹ (range 84 to 689 km d⁻¹) and 9.2 °C (range 4.2 to 14.5 °C) respectively (Fig. 2). Maximum daily rainfall occurred in August with a maximum rainfall of 65 mm on August 6th (Fig. 2). The river flow ranged from 2.98 to 4.07 m³ s⁻¹ with the respective residence times of the water in the LII river ranging from 10.2 to 7.5 h (Table 1)

River water pH ranged from 6.2 to 7.6, and increased from site 1 (the source) to site 4 ($p < 0.05$). Site 1 had significantly lower EC values than the other sites ($p < 0.01$), averaging 160 μS cm⁻¹ [\pm Std. Dev. 8]. The average EC values at sites 2, 3 and 4 averaged 190 μS cm⁻¹

[\pm Std. Dev. 20] with no differences between these sites. At sites 2 to 4 the maximum EC values ($259 \mu\text{S cm}^{-1}$) occurred immediately after a large rainfall event on 6th August. No increase in EC was measured at site 1 at this time. Water temperatures were stable at site 1 ($13.1 \text{ }^\circ\text{C}$ [\pm Std. Dev. 0.3]) and differed significantly from sites 2 to 4 ($p < 0.01$), where changes in river water temperature (range $8.1 - 13.0 \text{ }^\circ\text{C}$) were driven by changes in air temperature. Correlations (r) between air temperature and water temperature for sites 2, 3 and 4 were 0.91, 0.87 and 0.89 respectively. At site 1 the DO concentrations averaged $6.9 \text{ mg O}_2 \text{ L}^{-1}$ [\pm Std. Dev. 0.3] and were significantly lower ($p < 0.05$) than concentrations at sites 2 to 4 where DO concentrations averaged $8.5 \text{ mg O}_2 \text{ L}^{-1}$. At sites 2 to 4 the DO concentrations decreased by $2 \text{ mg O}_2 \text{ L}^{-1}$ immediately following the high rainfall event in August for several days before returning to their previous levels.

Concentrations of $\text{NO}_3\text{-N}$ in the river at sites 1, 3 and 4 were quite stable throughout the study averaging 2.8 mg L^{-1} and remained within the range of 2.3 to 3.3 mg L^{-1} (Table 2). However, at site 2 concentrations of $\text{NO}_3\text{-N}$ were higher ($p < 0.01$) and ranged from 3.4 to 5.2 mg L^{-1} (Table 2). The $\text{NH}_4\text{-N}$ concentrations in the LII were an order of magnitude lower and constantly $< 0.2 \text{ mg L}^{-1}$ (Table 2) with peak concentrations occurring at the start of the study in March, mid-April for (sites 2 -4), mid-winter (all sites), and following the high rainfall event in mid-August (sites 2-4). Concentrations of $\text{NO}_2\text{-N}$ were generally below the level of detection (0.01 mg L^{-1}) except for sites 3 and 4 following the high rainfall event in mid-August when $\text{NO}_2\text{-N}$ concentrations were 0.02 and 0.04 mg L^{-1} respectively.

Total organic-C concentrations were approximately 3 mg L^{-1} at the start of the study and then decreased in early April to be $< 2 \text{ mg L}^{-1}$ where they stayed except for the rise in August following the high rainfall event when levels increased significantly at sites 2 - 4 (Fig. 3). Dissolved inorganic-C concentrations did not differ significantly between sites and were

lowest at the commencement of the study, mean concentrations ranging from 13 -14 mg L⁻¹ (Fig. 3).

Dissolved N₂O and N₂O fluxes

Gas ebullition was observed from the sediment at the spring (site 1). The concentration of N₂O in the evolved gas bubbles, measured in May, was 7.9 µL L⁻¹. The average concentrations of dissolved N₂O-N at the four sites, in the LII river, ranged from 0.43 to 1.89 µg N₂O-N L⁻¹ and decreased ($p < 0.01$) with increasing distance from the spring (Table 3). Significant differences between sites did not occur until 17th of June when the dissolved N₂O at sites 1 and 2 were significantly higher ($p < 0.01$) than at sites 3 or 4. This pattern continued until the end of the study. When averaged across all sampling times, the values of dissolved N₂O at sites 1, 2, 3, and 4 were 1.36 (0.40), 1.33 (0.41), 0.74 (0.23), and 0.67 (0.24) µg N₂O-N L⁻¹ respectively (numbers in brackets are standard deviations). These represent N₂O saturation levels for sites 1, 2, 3, and 4 of 404 (119), 395 (118), 223 (68), and 201 (74) %, respectively (numbers in brackets \pm Std. Dev.).

Ratios of dissolved N₂O-N: NO₃-N ranged from 0.00015 to 0.00067 across all sampling dates (Table 3). The mean ratio N₂O-N: NO₃-N, over all sampling dates, decreased from site 1 to 4 with values of 0.00049 (± 0.00011 Std. Dev.) to 0.00022 (± 0.00007 Std. Dev.) respectively. A regression analysis of this ratio against distance downstream from the site 1 was highly significant ($r^2 = 59.2\%$, $p < 0.01$).

The N₂O-N fluxes, from individual sampling dates, ranged from 38-501 µg m⁻² h⁻¹. Mean fluxes of N₂O-N at sites 1 and 2 were higher than those at sites 3 and 4 for the majority of sample dates (Table 4). When averaged over the entire period of the study the N₂O-N fluxes from sites 1, 2, 3 and 4 were 197(88), 241(86), 136(49), and 110(29) µg m⁻² h⁻¹ respectively (numbers in brackets \pm Std. Dev.), with the average fluxes from sites 1 and 2

significantly higher ($p < 0.01$) than those from sites 3 and 4. The overall mean $\text{N}_2\text{O-N}$ flux was $171 \mu\text{g m}^{-2} \text{h}^{-1}$ (\pm Std. Dev. 85). The N_2O fluxes and $\text{NO}_3\text{-N}$ concentrations measured from the LII river were typical of those measured from the other local agricultural and urban spring-fed rivers (Fig. 4a). Of the other rivers, which flow through Christchurch, the Avon river had the highest $\text{N}_2\text{O-N}$ flux ($973 \mu\text{g m}^{-2} \text{h}^{-1}$), 1 km from its source, and the lowest $\text{NO}_3\text{-N}$ concentrations (Fig. 4a).

The mean $\text{N}_2\text{O-N}$ fluxes and the mean dissolved N_2O concentrations showed no relationship to the corresponding $\text{NO}_3\text{-N}$ concentrations (Fig. 4a, 4b). The regression between the mean dissolved N_2O concentrations versus the mean $\text{N}_2\text{O-N}$ fluxes, for all sites, was significant ($r^2 = 0.31$, $p < 0.05$) and further improved if the additional data points of zero flux with a mean equilibrium $\text{N}_2\text{O-N}$ concentration of $0.34 \mu\text{g N}_2\text{O-N L}^{-1}$ were included ($r^2 = 0.58$, $p < 0.01$, Fig. 5). If data from site 1 were excluded, on the basis that some of the N_2O in the measured flux was almost certainly due to ebullition events, then the regression improved to $r^2 = 0.74$. Predicted N_2O fluxes, based on dissolved N_2O concentrations are plotted in Figure 5 based on oxygen transfer velocities of $0.5 \times 10^{-4} \text{ m s}^{-1}$ and $2.5 \times 10^{-4} \text{ m s}^{-1}$ and are discussed below.

The gross advective daily discharge of dissolved N_2O downstream from site 4 equalled $0.20 \text{ kg dissolved N}_2\text{O-N d}^{-1}$, based on an N_2O concentration of $0.67 \mu\text{g N}_2\text{O-N L}^{-1}$ and a mean flow of $3.41 \text{ m}^3 \text{ s}^{-1}$. This was less than the daily $\text{N}_2\text{O-N}$ flux of $0.41 \text{ kg N}_2\text{O-N d}^{-1}$ evolved from the 10 km reach of river leading to site 4, based on a mean river width of 10 m and a mean $\text{N}_2\text{O-N}$ flux of $171 \mu\text{g m}^{-2} \text{h}^{-1}$. The daily discharge of $\text{NO}_3\text{-N}$ downstream from site 4, equated to $825 \text{ kg NO}_3\text{-N d}^{-1}$, based on the mean $\text{NO}_3\text{-N}$ concentration of 2.8 mg L^{-1} and a mean flow of $3.41 \text{ m}^3 \text{ s}^{-1}$. Thus the daily mean loss of $\text{N}_2\text{O-N}$ was insignificant compared to the $\text{NO}_3\text{-N}$ lost, equalling just 0.07% of the $\text{NO}_3\text{-N}$ discharged from site 4.

The IPCC default value for EF5-r ($0.0075 \text{ kg N}_2\text{O kg}^{-1} \text{ NO}_3\text{-N}$) yielded a calculated daily flux of $6.2 \text{ kg N}_2\text{O-N d}^{-1}$ from the LII river whereas the average measured flux was $0.41 \text{ kg N}_2\text{O-N d}^{-1}$ i.e. just 6.6% of that calculated using the IPCC methodology.

Discussion

River chemistry

The values of pH, EC, and DO in the LII were typical of natural freshwater systems (Dojlido & Best, 1993). The measured values of temperature, pH, EC, TOC and DO were relatively constant at site 1 indicating that water chemistry at this site was predominately influenced by the water discharged from the spring and relatively unaffected by the climatic changes, physical, and/or biological inputs that subsequently influenced the LII river chemistry downstream from site 1. The observed increases in $\text{NH}_4\text{-N}$ at site one between April and August are not readily explainable but could be related to high populations of aquatic birdlife resident there during this time.

The high rainfall event in August followed a period of snowfall and the surrounding land was water-saturated. Due to the intensity of the rainfall event, overland flow of water occurred. This accounted for the increased levels of $\text{NH}_4\text{-N}$, EC and TOC, and the observed decrease in DO following the rainfall event. Interestingly the $\text{NO}_2\text{-N}$ levels also increased at this time, possibly indicating a period of denitrifying activity following the high rainfall event. Other studies have also found elevated TOC concentrations occurring from surface or near surface runoff following storm events (Inamder *et al.*, 2004). Dissolved oxygen levels indicated that the LII was generally well oxygenated throughout the study period.

Dissolved N_2O and $\text{NO}_3\text{-N}$

The higher $\text{NO}_3\text{-N}$ concentrations at site 2 were atypical. Further $\text{NO}_3\text{-N}$ addition(s) must have occurred either from drainage tributaries or from further groundwater flow(s), with high $\text{NO}_3\text{-N}$ concentration, between sites 1 and 2. Flows at sites 1 and 2 were not gauged but it was readily apparent, visually, that the river flow was greater at site 2 than at site 1. Additional work needs to be performed to clarify where and how this $\text{NO}_3\text{-N}$ input occurs.

Assuming nil production of N_2O in the river, and assuming no other inputs, there should have been a decrease in the dissolved N_2O concentration, due to N_2O degassing from the water surface between sites 1 and 2. This was not observed despite the relatively high N_2O fluxes measured. Thus additional inputs of N_2O occurred either via *in-situ* nitrification/denitrification processes or the further addition of water(s) containing high levels of dissolved N_2O . Additional N_2O inputs could have occurred as for $\text{NO}_3\text{-N}$, as described above. Dowdell *et al.* (1979) measured dissolved N_2O in agricultural drainage waters. Alternatively in-stream production of N_2O could also have occurred due to microbial processes. Denitrification as a source of N_2O cannot be ruled out, despite the well oxygenated status of the LII, because it could have been occurring at the interface between the anaerobic sediments and water-body (Petersen *et al.*, 2001).

The decrease in both the $\text{NO}_3\text{-N}$ and dissolved $\text{N}_2\text{O-N}$ concentrations between sites 2 and 3 could, again, have been due to dilution from water with lower $\text{NO}_3\text{-N}$ and dissolved $\text{N}_2\text{O-N}$ concentrations, or via consumption processes. Further additions of water to the LII between sites 2 and 3 occurred through a multitude of drainage ditches.

The observed drop in the dissolved N_2O concentration, between sites 2 and 3, was not maintained between sites 3 and 4, a distance of 2.3 km, despite the water still being over-saturated with N_2O (> 200%). This suggests that the N_2O flux from the river surface was matched by N_2O inputs over this reach of the river. Again further work is required to identify the source(s) and scale of the N_2O inputs. It was noticeable that over this stretch of the river

that the geometry of the river became shallower and broader thus there was a larger sediment area exposed per unit volume of water. This may have contributed to more anaerobic sediment surfaces for *in-situ* N₂O production (Petersen *et al.*, 2001). Alternatively it may be that the NO₃-N measurements were not sensitive enough to detect the possible transformation of NO₃-N to N₂O-N. As noted above the daily advective loss of N₂O-N from site 4 was only 0.07% of the NO₃-N discharged. Assuming the same fraction of NO₃-N was being transformed to N₂O-N would require a decrease in the NO₃-N concentration of only 0.002 mg NO₃-N L⁻¹. This is well below the level of detection for the NO₃-N analyses.

N₂O fluxes and IPCC calculations

As observed from the ebullition events and high levels of N₂O saturation in the water it can be concluded that N₂O was introduced into the river at its source, site 1. Furthermore, dissolved N₂O was probably introduced into the LII along the reach from site 1 to site 2 via other tributaries or possibly further groundwater flow. The EF5-g component of EF5 was formulated on the basis that the N₂O formed in surface soils undergoes transport with leaching water to the groundwater and eventually degasses to the atmosphere by upward diffusion or following entry of groundwater into surface waters (Mosier *et al.*, 1998). A study by Reay *et al.* (2003) demonstrated how rapidly N₂O degassing from drainage waters can occur. It is apparent that degassing of N₂O already present in the groundwater, hereafter referred to as antecedent N₂O, contributed significantly to the N₂O fluxes measured in our study, especially between sites 2 and 3, as can be seen from the following calculation. Based on an LII river velocity of 0.28 m s⁻¹ it requires 3.3 h for river water to travel between sites 2 and 3, through an estimated area of 33000 m². Assuming further, a river flow of 3 m³ s⁻¹, and the drop in dissolved N₂O was as measured i.e. 1.34 to 0.67 µg N₂O-N L⁻¹, then the calculated N₂O-N flux equates to 219 µg m⁻² h⁻¹, which is of quite similar magnitude to the

actual mean fluxes measured at sites 2 and 3 of $136 \mu\text{g m}^{-2} \text{h}^{-1}$ (49 Std. Dev.) and $110 \mu\text{g m}^{-2} \text{h}^{-1}$ (29 Std. Dev.) respectively. Thus in this study where the LII river is fed from an aquifer, and is of a relatively short length, degassing of antecedent N_2O appears to be a dominant component of the N_2O emissions.

The average $\text{N}_2\text{O-N}$ flux from the LII was intermediate in magnitude compared with other studies where *in-situ* N_2O surface fluxes have been physically measured from streams or rivers. Nitrous oxide fluxes from the Hudson river, Platte river, and a stream exiting a rice paddy area have been recorded as having $\text{N}_2\text{O-N}$ fluxes of 6, 6, and 240-56580 $\mu\text{g N}_2\text{O-N m}^{-2} \text{h}^{-1}$ respectively with corresponding $\text{NO}_3\text{-N}$ levels of 0.6, 0.1-11.2, and 20 $\text{mg NO}_3\text{-N L}^{-1}$ (MacMahon & Dennehey, 1999, Hasegawa *et al.*, 2000, Cole & Caraco, 2001). The ratios of $\text{N}_2\text{O-N}:\text{NO}_3\text{-N}$ measured in this study are within the range of values reviewed and quoted by Nevison (2000a) who found values of 0.0002 -0.0044 (groundwater) and 0.0005 - 0.01 (drainage ditches), with no strong difference between groundwater and drainage ditches. The lack of any significant relationships between the $\text{NO}_3\text{-N}$ concentrations dissolved $\text{N}_2\text{O-N}$, and the $\text{N}_2\text{O-N}$ fluxes supports the suggestion that degassing of the antecedent $\text{N}_2\text{O-N}$ load occurred without any concurrent transformation of the $\text{NO}_3\text{-N}$ load (Reay *et al.*, 2003).

We have made the assumption that all of the $\text{NO}_3\text{-N}$ in the LII was anthropogenic and calculated our “IPCC flux” using the EF5-r component of 0.0075. Our average measured $\text{N}_2\text{O-N}$ flux was only 6.6% of that calculated using the IPCC approach. In other words for the LII an EF5-r factor of 0.0005 was more appropriate. This is a large discrepancy and the possibility that our measurement method introduced significant bias needs to be considered. Our measured fluxes could possibly have underestimated the actual fluxes due to the headspace methodology used. The gas transfer velocity of a gas from water to the atmosphere is affected by both water turbulence and wind speed (MacIntyre *et al.*, 1995). Thus the water

surface turbulence under our headspace enclosures may have varied compared with that of the surrounding river. Likewise the lack of wind inside the headspace may also have caused lower fluxes; the wind run was significant (Fig. 2). In addition the bobbing motion of chambers on the water can create pressure fluctuations that may also influence the gas transfer velocity (MacIntyre *et al.*, 1995).

Predicted N₂O emissions, based on dissolved N₂O concentrations, were presented in Figure 5 using 2 arbitrary values of the transfer velocity. These values were chosen so that the predicted fluxes represented the upper and lower limits of the measured fluxes. The majority of the measured headspace flux data fell between these two arbitrary boundaries. The values of $V_w^{N_2O}$ used in Figure 5, 2.28×10^{-4} and $3.65 \times 10^{-5} \text{ m s}^{-1}$, correspond to oxygen transfer velocities of 2.5×10^{-4} and $4.0 \times 10^{-5} \text{ m s}^{-1}$ respectively. As noted above transfer velocity is dependent on wind flow. Our wind speed data was collected at a height of 10 m with the average daily wind run equal to 342 km d^{-1} or 3.95 m s^{-1} . Interpolating the data of Liss (1973) provides an oxygen transfer velocity of approximately $5 \times 10^{-5} \text{ m s}^{-1}$ at this wind speed. However, it is well recognized that wind speed decreases closer to the water surface via the usual logarithmic profile (Israelsen & Hansen, 1962). Conversion of the wind speed at 10 m (Z_1) to a wind speed at a height of 0.05 m above the water surface (Z_2) can be achieved using:

$$\frac{U_1}{U_2} = \log\left(\frac{Z_1}{Z_0}\right) \div \log\left(\frac{Z_2}{Z_0}\right)$$

Where Z_0 equals the “effective roughness height”, assumed to be 0.01 m, and U_1 and U_2 are the respective wind speeds at heights Z_1 and Z_2 . Thus the average wind speed at 0.05 m above the average water is calculated to equal 0.92 m s^{-1} . Given that this is the more likely wind speed at the water surface in our study then the transfer velocity for oxygen also decreases. If the data of Liss (1973) is extrapolated this value is approximately $1 \times 10^{-5} \text{ m s}^{-1}$. These

calculations suggest that our measured fluxes and methodology used were in general agreement with theoretically derived fluxes. These theoretically derived fluxes were dependent on the value of the oxygen transfer velocity assumed which was in turn highly dependent on wind speed. In future, experimentation should include wind speed measurements taken at the water surface so that more accurate transfer velocities can be calculated.

Given the above discussion on degassing it appears that the calculated IPCC flux is not only an overestimation but that the EF5-r factor for the LII was actually considerably < 0.0005 due to the dominant role played by degassing of antecedent N₂O. This is despite the potential for underestimating the flux with the chamber methodology used. In practice a discrete measurement of EF5-g is extremely difficult, requiring detailed and extensive resources to acquire knowledge on the presence of groundwater flows into a river and their respective dissolved N₂O concentrations. In most instances the antecedent N₂O contribution to a river flux measurement will be unknown. It has been previously indicated that denitrification in alluvial aquifers, where N₂O concentrations may be up to 100 times greater than the concentrations in the overlying river water, may contribute to dissolved N₂O concentrations in river water (MacMahon & Dennehey, 1999). Thus, as this study demonstrates, caution must be exercised in assigning N₂O fluxes from river surfaces solely to the EF5-r emission factor if contributions from EF5-g are present.

Of course river N₂O emissions could be treated as strictly that, i.e. the N₂O flux from the river system in question, since this is an easily definable area from which to take actual flux measurements. Then if the catchment's area and NO₃-N leaching load are known perhaps an amalgamated EF5 emission factor for the river system can be derived for the catchment concerned. In our study, neither the catchment's area nor the NO₃-N leaching load were readily definable due to the flat nature of the surrounding landscape and the unknown

groundwater contributions to the aquifer feeding the river. Further research needs to be performed to derive the exact origins and potential processing of the N₂O in the LII river and this could be performed using isotopic studies.

Previously the few river studies that have measured N₂O fluxes directly have been performed on either large rivers (MacMahon & Dennehey, 1999, Cole & Caraco, 2001) or on a small agricultural stream (Hasegawa *et al.*, 2000). Clearly water residence times and river geometries vary and these in turn will influence the potential for in-stream processing of NO₃-N (Petersen *et al.*, 2001). For example, the residence time in the Hudson river study averaged 0.15 yr (Cole & Caraco, 2001) while in our study the estimated residence time was < 11 h. This short residence time may help to explain the relatively conserved NO₃-N loading in the LII, despite the continual presence of water soluble organic carbon. Further work is also required to assess the *in-situ* NO₃-N transformations in rivers such as the LII.

Our results may have significant implications for New Zealand's river systems given that the rivers are relatively short, by world standards, and will have short residence times when compared to those of other studies e.g. MacMahon & Dennehey (1999).

This study also reinforces the comments made by Reay *et al.* (2003), who cautioned against making total N₂O flux estimates for drainage waters based on measurements at widely spaced sampling points. Had we measured fluxes at only site 1 or only site 4 we would have obtained a misleading result. The cumulative data from four sites provides a more informed appraisal of the variation and magnitude of the fluxes, but clearly demonstrates the need for spatially intensive sampling. Clearly a key factor in determining where to measure river N₂O fluxes is the possible presence of contributing groundwater flows that may contain antecedent dissolved N₂O. This will depend on the hydrological network of the river source. Aquifer-fed rivers may behave differently to those rivers where significant contributions come from overland flows. Our study highlights the suggestion made that the

IPCC methodology for assessing indirect N₂O emissions be at least partially spatially explicit (Groffman *et al.*, 2002). River factors such as the ratio of depth: width, speed, gradient, residence time, and water sources should perhaps be considered. Our results also support the hypothesis that the IPCC methodology over-estimates the anthropogenic source of N₂O (Nevison, 2000b), at least with respect to the EF5 emission factor.

In summary our flux measurements from the river surface indicate significant degassing of antecedent N₂O with a relatively conserved NO₃-N loading. The measured N₂O fluxes, concentrations of dissolved N₂O, and N₂O-N: NO₃-N ratios were all within the range of previously reported values. Calculation of an EF5-r factor, based on the LII river NO₃-N load and measured N₂O-N fluxes yielded a result that was approximately 6.6% of the IPCC default EF5-r value. However, included in this calculation is a contribution from antecedent N₂O that should really be included in an EF5-g emission factor. Further work is required to separate out the magnitude of the N₂O-N fluxes from these two sources.

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References

- Bowden MJ (1986) *The Christchurch Artesian Aquifers: a report prepared by the resources division of the North Canterbury Catchment Board and Regional Water Board.* Christchurch, New Zealand., 159 pp.
- Clesceri LS, Greenberg AE, Eaton AD (1998) *Standard Methods for the Examination of Water and Wastewater.* American Public Health Association, American Water Works Association, Water Environment Federation, Washington, D.C.
- Cole JJ, Caraco NF (2001) Emissions of nitrous oxide (N₂O) from a tidal, freshwater river, the Hudson River, New York. *Environmental Science & Technology*, **35**, 991-996.
- Davidson EA, Firestone MK (1988) Measurement of nitrous oxide dissolved in soil solution. *Soil Science Society of America Journal*, **52**, 1201-1203.
- Davie T (2003) *Fundamentals of Hydrology.* Routledge, London and New York, 169 pp.
- Dojlido JR, Best GA (1993) *Chemistry of water and water pollution.* Ellis Horwood, Chichester.
- Dowdell RJ, Burford JR, Crees R (1979) Losses of nitrous oxide dissolved in drainage water from agricultural land. *Nature*, **278**, 342-343.
- Groffman PM, Gold AJ, Addy K (2000) Nitrous oxide production in riparian zones and its importance to national emission inventories. *Chemosphere - Global Change Science*, **2**, 291-299.
- Groffman PM, Gold AJ, Kellog DQ, Addy K (2002) Mechanisms, rates and assessment of N₂O in groundwater, riparian zones and rivers. In *Non-CO₂ Greenhouse Gases: Scientific Understanding, Control Options and Policy Aspects. Proceedings of the Third International Symposium, Maastricht, The Netherlands.* (eds van Ham J, Baede APM, Guicherit R, Williams-Jacobse JGFM), pp. 159-166. Millpress, Rotterdam.

- Hasegawa K, Hanaki K, Matsuo T, Hidaka S (2000) Nitrous oxide from the agricultural water system contaminated with high nitrogen. *Chemosphere -Global Change Science*, **2**, 335-345.
- Holmen K, Liss PS (1984) Models for air-water gas transfer: an experimental investigation. *Tellus Series B-Chemical & Physical Meteorology*, **36**, 92-100.
- Inamder SP, Christopher SF, Mitchell MJ (2004) Export mechanisms for dissolved organic carbon and nitrate during summer storm events in a glaciated forested catchment in New York, USA. *Hydrological Processes*, **18**, 2651-2661.
- IPCC (1997) *Guidelines for National Greenhouse gas Inventories*. OECD/OCDE, Paris.
- Israelsen OW, Hansen VE (1962) *Irrigation Principles and Practices*. John Wiley and Sons Inc., New York.
- Kirkwood DS (1992) Stability of solutions of nutrient salts during storage. *Marine Chemistry*, **38**, 151-164.
- Liss PS (1973) Processes of gas exchange across an air-water interface. *Deep Sea Research*, **20**, 221-238.
- Liss PS, Slater PG (1974) Flux of gases across the air-sea interface. *Nature*, **247**, 184-184.
- MacIntyre S, Wanninkhof R, Chanton JP (1995) Trace gas exchange across the air-water interface in freshwater and coastal marine environments. In *Biogenic trace gas emissions: measuring emissions from soil and water*. (eds Matson PA, Harriss RC), pp. 52-97. Blackwell Science Inc., Cambridge, MA.
- MacMahon PB, Dennehey KF (1999) N₂O emissions from a nitrogen-enriched river. *Environmental Science & Technology*, **33**, 21-25.
- Mosier A, Kroeze C, Nevison C, Oenema O, Seitzinger S, Vancleemput O (1998) Closing the global N₂O budget: nitrous oxide emissions through the agricultural nitrogen cycle -

- OECD/IPCC/IEA phase ii development of IPCC guidelines for national greenhouse gas inventory methodology. *Nutrient Cycling in Agroecosystems*, **52**, 225-248.
- Mosier A, Mack L (1980) Gas chromatographic system for precise, rapid analysis of nitrous oxide. *Soil Science Society of America Journal*, **44**, 1121-1123.
- Mosley MP, Jowett I, Tomlinson AI (1992) Data, Information and Engineering Applications. In *Waters of New Zealand* (ed Mosley MP), pp. 29-61. New Zealand Hydrological Society Incorporated, Wellington.
- Nevison C (2000a) Good Practice Guidance and Uncertainty Management in National Greenhouse Gas Inventories. Indirect N₂O emissions from agriculture [Online]. [17 p]. Available at http://www.ipcc-nggip.iges.or.jp/public/gp/bgp/4_6_Indirect_N2O_Agriculture.pdf (modified 25 Feb. 2003; accessed April 2005) International Panel on Climate Change
- Nevison C (2000b) Review of the IPCC methodology for estimating nitrous oxide emissions associated with agricultural leaching and runoff. *Chemosphere - Global Change Science*, **2**, 493-500.
- New Zealand Climate Change Office (2004) *New Zealand's Greenhouse Gas Inventory 1990-2002: The National Inventory Report and Common Reporting Format Tables*. Ministry for the Environment, Wellington, 146 pp.
- Petersen BJ, Wollheim WM, Mulholland PJ, *et al.* (2001) Control of nitrogen export from watersheds by headwater streams. *Science*, **292**, 86-90.
- Prinn RG, Cunnold DM, Rasmussen RA, *et al.* (1990) Atmospheric emissions and trends of nitrous oxide deduced from 10 years of ALE/GAGE data. *Journal of Geophysical Research*, **95**, 18369-18385.
- Reay DS, Smith KA, Edwards AC (2003) Nitrous oxide emission from agricultural drainage waters. *Global Change Biology*, **9**, 195-203.

- Rockmann T, Kaiser J, Brenninkmeijer CAM (2003) The isotopic fingerprint of the pre-industrial and the anthropogenic N₂O source. *Atmospheric Chemistry and Physics*, **3**, 315-323.
- Seitzinger S, Kroeze C (1998) Global distribution of nitrous oxide production and N inputs in fresh water and coastal marine ecosystems. *Global Biogeochemical Cycles*, **12**, 93-113.
- Weiss RF, Price BA (1980) Nitrous Oxide Solubility in Water and Seawater. *Marine Chemistry*, **8**, 347-359.
- Young CL (1981) *Oxides of nitrogen*. Pergamon Press, Oxford.

Table 1 Water velocities, river flow and residence times of the LII river at Site 4

Season	Date	Average water velocity (m s ⁻¹)	River flow (m ³ s ⁻¹)	Residence time (h)
Fall	31-May	0.26	2.98	10.2
Winter	17-Jun	0.30	3.34	9.1
Winter	8-Jul	0.28	3.32	9.2
Winter	16-Aug	0.23	3.35	9.1
Spring	10-Sep	0.32	4.07	7.5

Table 2 Mean nitrate-N ($\text{NO}_3\text{-N}$) and ammonium concentrations ($\text{NH}_4\text{-N}$) in the LII river over time, standard error of the mean was < 0.01 in all cases (data not presented).

N form	Season	Date	Site 1	Site 2	Site 3	Site 4
$\text{NO}_3\text{-N}$ (mg L^{-1})	Fall	5th March	3.25	4.72	2.63	2.56
		19 th March	3.24	5.19	2.77	2.69
		5 th April	3.07	3.36	2.86	2.29
		26 th April	2.98	3.48	2.91	2.82
		3 rd May	2.83	3.71	2.85	2.81
		17 th May	2.88	3.59	2.95	2.95
	Winter	31 st May	2.85	3.82	3.05	3.06
		17 th June	2.83	4.11	2.95	2.88
		8th July	2.83	3.90	2.94	2.93
		28 th July	2.91	3.73	2.85	2.88
	Spring	16 th August	2.88	3.75	2.58	2.59
		10 th September	2.92	3.80	2.82	3.12
		1 st October	2.91	3.86	2.70	2.98
$\text{NH}_4\text{-N}$ (mg L^{-1})	Fall	5th March	0.06	0.06	0.12	0.06
		19 th March	0.01	0.01	0.06	0.03
		5 th April	0.00	0.05	0.03	0.04
		26 th April	0.01	0.05	0.05	0.05
		3 rd May	0.01	0.01	0.02	0.02
		17 th May	0.02	0.03	0.03	0.03
	Winter	31 st May	0.04	0.03	0.03	0.03
		17 th June	0.06	0.06	0.07	0.08
		8th July	0.04	0.02	0.04	0.04
		28 th July	0.01	0.01	0.01	0.01
	Spring	16 th August	0	0.02	0.08	0.11
		10 th September	0	0	0	0
		1 st October	0	0	0	0

Table 3 Mean dissolved N₂O-N concentrations ($\mu\text{g N}_2\text{O-N L}^{-1}$); $n = 3$ numbers in brackets are standard error of the mean) and dissolved N₂O-N: NO₃-N ratios.

	Season	Date	Site 1	Site 2	Site 3	Site 4	
Dissolved N ₂ O-N	Fall	5 th Apr.	1.37 (0.11)	1.09 (0.12)	0.77 (0.07)	0.54 (0.06)	
		26 th Apr.	1.43 (0.01)	1.08 (0.17)	1.06 (0.16)	1.10 (0.18)	
		3 rd May	1.04 (0.42)	1.27 (0.03)	0.74 (0.03)	0.65 (0.01)	
		17 th May	1.11 (0.46)	1.38 (0.06)	0.79 (0.04)	0.69 (0.01)	
		31 st May	1.26 (0.28)	0.76 (0.55)	0.68 (0.06)	0.49 (0.01)	
	Winter	17 th Jun.	1.89 (0.12)	1.88 (0.01)	0.88 (0.02)	0.73 (0.01)	
		8 th Jul.	1.35 (0.03)	1.12 (0.04)	0.51 (0.01)	0.45 (0.01)	
		28 th Jul.	1.21 (0.04)	1.12 (0.01)	0.52 (0.01)	0.43 (0.01)	
		16 th Aug.	1.49 (0.03)	1.94 (0.03)	0.81 (0.26)	0.94 (0.01)	
	Spring	10 th Sep.	1.68 (0.05)	1.50 (0.02)	0.65 (0.01)	0.52 (0.01)	
	Ratio N ₂ O-N: NO ₃ -N	Fall	5 th Apr.	0.00045	0.00032	0.00027	0.00024
			26 th Apr.	0.00048	0.00031	0.00036	0.00039
3 rd May			0.00037	0.00034	0.00026	0.00023	
17 th May			0.00039	0.00038	0.00027	0.00023	
31 st May			0.00044	0.00020	0.00022	0.00016	
Winter		17 th Jun.	0.00067	0.00046	0.00030	0.00025	
		8 th Jul.	0.00048	0.00029	0.00017	0.00015	
		28 th Jul.	0.00041	0.00030	0.00018	0.00015	
Spring		16 th Aug.	0.00052	0.00052	0.00032	0.00036	
		10 th Sep.	0.00057	0.00040	0.00023	0.00017	

Table 4. Mean dissolved N₂O-N fluxes ($\mu\text{g m}^{-2} \text{h}^{-1}$). Numbers in brackets are standard errors of the mean, $n = 3$.

Season	Date	Site 1	Site 2	Site 3	Site 4
Fall	3 rd May	307 (28)	173 (44)	179 (15)	90 (7)
	17 th May	109 (6)	223 (7)	151 (10)	119 (5)
	31 st May	299 (13)	320 (14)	78 (6)	89 (6)
Winter	17 th June	183 (12)	311 (30)	139 (9)	131 (7)
	8 th July	93 (8)	241 (12)	90 (2)	75 (2)
	16 th August	211 (10)	272 (4)	195 (6)	124 (9)
Spring	10 th September	188 (10)	173 (10)	106 (6)	138 (4)

Figure Legends

Fig. 1 Map showing global and regional locality of the study site.

Fig. 2 Meteorological data recorded at a distance of 3 km from site 1.

Fig. 3 Dissolved water soluble carbon concentrations in the LII river water over time at each site. Numerals in the legend refer to site number while OC and IC refer to organic and inorganic carbon respectively.

Fig. 4 The relationship between $\text{N}_2\text{O-N}$ fluxes and $\text{NO}_3\text{-N}$ concentrations for the LII river (sites 1 to 4), Avon, Heathcote and Halswell rivers, 7 sample dates (Fig 4a); and the relationship between dissolved N_2O and the $\text{NO}_3\text{-N}$ concentrations for the LII river, 10 sample dates (Fig. 4b)

Fig.5 Relationship between the mean $\text{N}_2\text{O-N}$ fluxes and mean dissolved N_2O concentrations for sites 1 to 4. Error bars are \pm standard error of the mean, y axis $n = 10$, x axis $n = 3$). Also shown are the equilibrium concentrations of N_2O in the river water and the predicted N_2O fluxes at N_2O transfer velocities (V^{N_2O}) of 2.28×10^{-4} (solid line) and $3.65 \times 10^{-5} \text{ m s}^{-1}$ (dotted line).

Figure 1

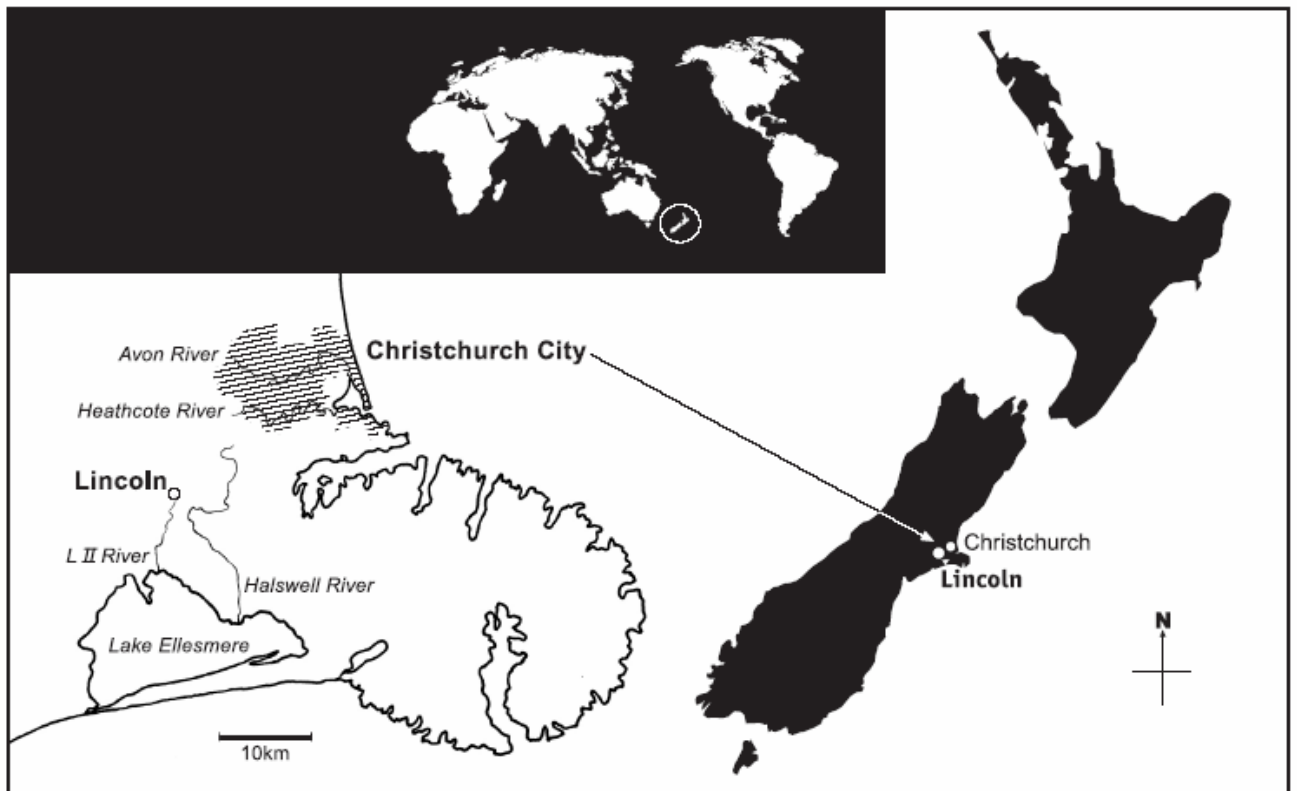
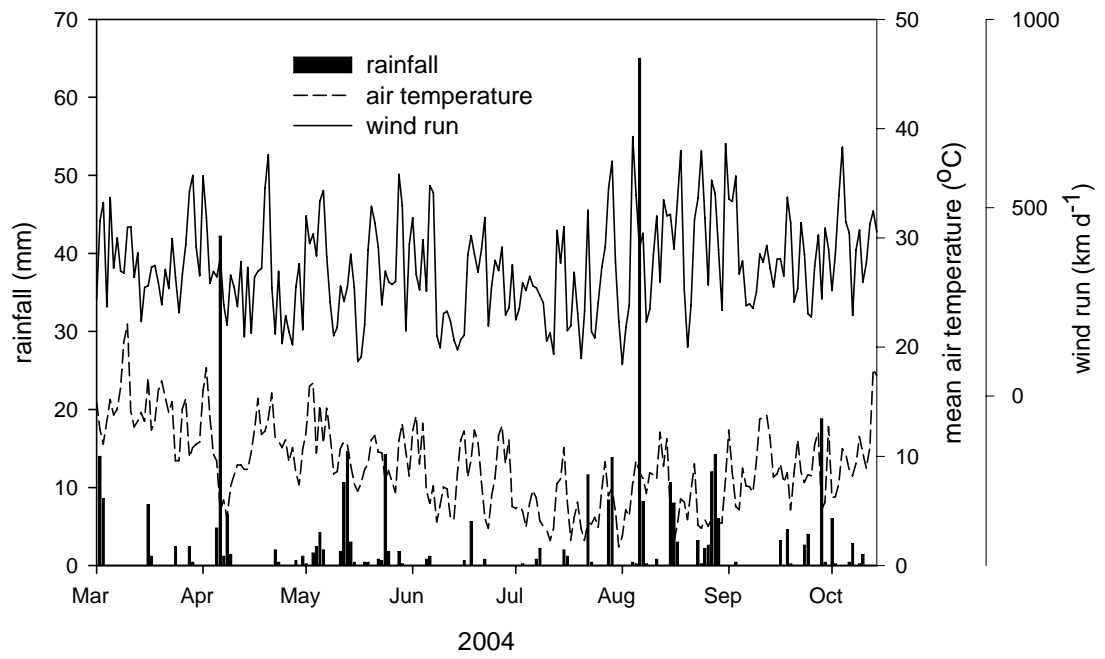


Figure 2



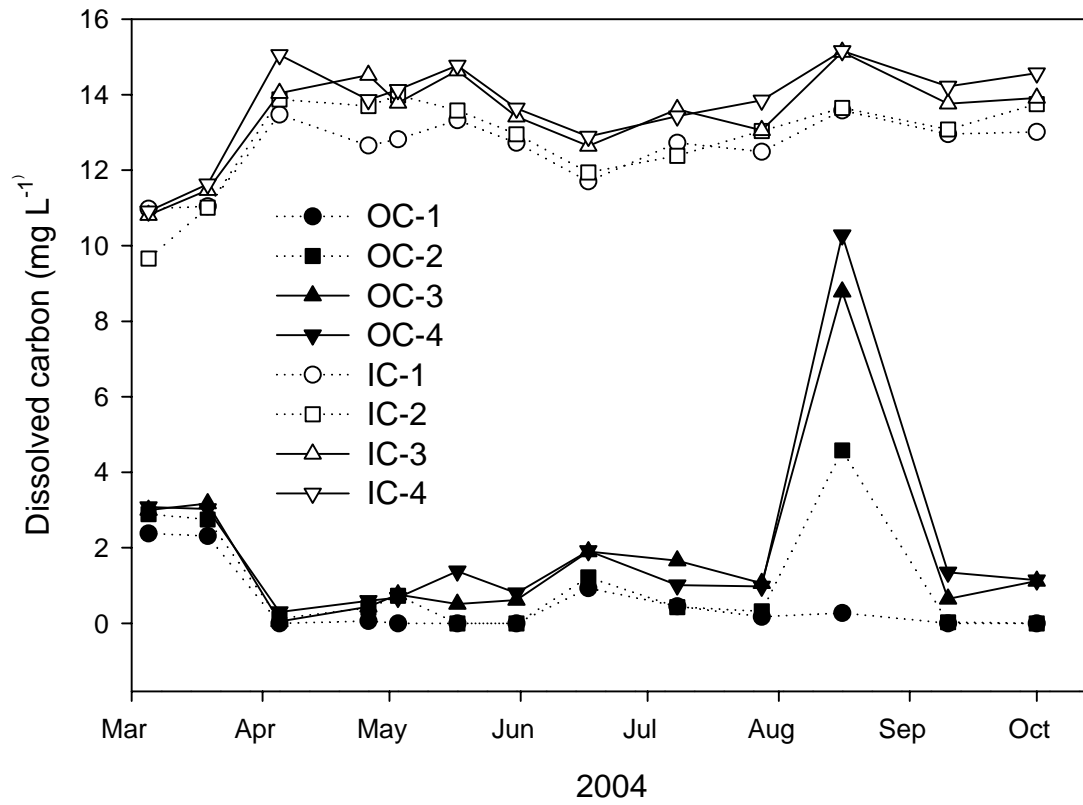


Figure 3

Figure 5

