

**Title:** Diurnal fluctuations of dissolved N<sub>2</sub>O concentrations and estimates of N<sub>2</sub>O emissions from a spring-fed river: implications for IPCC methodology.

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**Running title:** Diurnal changes in river N<sub>2</sub>O concentrations

## Abstract

There is uncertainty in the estimates of indirect nitrous oxide (N<sub>2</sub>O) emissions as defined by the Intergovernmental Panel on Climate Change (IPCC). The uncertainty is due to the challenge and dearth of *in situ* measurements. Recent work in a subtropical stream system has shown the potential for diurnal variability to influence the downstream N transfer, N form, and estimates of in-stream N<sub>2</sub>O production. Studies in temperate stream systems have also shown diurnal changes in stream chemistry.

The objectives of this study were to measure N<sub>2</sub>O fluxes and dissolved N<sub>2</sub>O concentrations from a spring-fed temperate river to determine if diurnal cycles were occurring. The study was performed during a 72 hour period, over a 180 m reach, using headspace chamber methodology. Significant diurnal cycles were observed in radiation, river temperature and chemistry including dissolved N<sub>2</sub>O-N concentrations. These data were used to further assess the IPCC methodology and experimental methodology used. River NO<sub>3</sub>-N and N<sub>2</sub>O-N concentrations averaged 3.0 mg L<sup>-1</sup> and 1.6 µg L<sup>-1</sup> respectively, with N<sub>2</sub>O saturation reaching a maximum of 664%. The N<sub>2</sub>O-N fluxes, measured using chamber methodology, ranged from 52-140 µg m<sup>-2</sup> h<sup>-1</sup> while fluxes predicted using the dissolved N<sub>2</sub>O concentration ranged from 13-25 µg m<sup>-2</sup> h<sup>-1</sup>. The headspace chamber methodology may have enhanced the measured N<sub>2</sub>O flux and this is discussed. Diurnal cycles in N<sub>2</sub>O % saturation were not large enough to influence downstream N transfer or N form with variability in measured N<sub>2</sub>O fluxes greater and more significant than diurnal variability in N<sub>2</sub>O % saturation. The measured N<sub>2</sub>O fluxes, extrapolated over the study reach area, represented only 6x10<sup>-4</sup> percent of the NO<sub>3</sub>-N that passed through the study reach over a 72 h period. This is only 0.1% of the IPCC calculated flux

## Introduction

Currently continental riverine N exports to the coastal zone are estimated to be 48 Tg N yr<sup>-1</sup> and 59 Tg N yr<sup>-1</sup> to all waters including the terrestrial inlands and dry lands (Boyer *et al.*, 2006). Much of this exported N originates from agricultural N leaching and runoff. The total global nitrous oxide (N<sub>2</sub>O) source from agricultural soils stands at 6.3 Tg N yr<sup>-1</sup> with indirect emissions accounting for 2.1 Tg N yr<sup>-1</sup> of this total (Mosier *et al.*, 1998). Biological cycling of both natural and anthropogenic N through aquatic ecosystems produces emissions of N<sub>2</sub>O via nitrification and denitrification. Nitrogen (N) leaching and runoff dominate the N<sub>2</sub>O indirect emission sources, accounting for over 75% of the estimated indirect emissions (Mosier *et al.*, 1998, Nevison, 2000). Modelling the rates and spatial distribution of N inputs to rivers and the subsequent N fate is challenging and further research is needed to better understand the processes controlling N transport in rivers (Boyer *et al.*, 2006).

The Intergovernmental Panel on Climate Change (IPCC) has defined a methodology (IPCC, 1997, Mosier *et al.*, 1998) where the mass of fertilizer and manure N lost through leaching and runoff per annum (NLEACH; kg NO<sub>3</sub>-N) is multiplied by an emission factor (EF5; kg N<sub>2</sub>O-N per kg NO<sub>3</sub>-N leached) to determine N<sub>2</sub>O emissions allied to N leaching and runoff. The value of EF5 is the sum of the N<sub>2</sub>O emission factors for N<sub>2</sub>O losses from i) groundwater and surface drainage (EF5-g = 0.015 kg N<sub>2</sub>O-N per kg NLEACH), ii) rivers (EF5-r = 0.0075 kg N<sub>2</sub>O-N per kg NLEACH), and iii) coastal marine areas (EF5-e = 0.0025 kg N<sub>2</sub>O-N per kg NLEACH). The rationale behind the development of the default values for EF5-g, EF5-r and EF5-e have been described previously (Mosier *et al.*, 1998, Nevison, 2000). Recently other studies have suggested further revision of these emission factors (Kroeze *et al.*, 2005, Reay *et al.*, 2005, Sawamoto *et al.*, 2005).

Only a few studies have actually directly measured N<sub>2</sub>O fluxes from aquatic river environments and information is sparse (MacMahon & Dennehey, 1999, Hasegawa *et al.*,

2000, Cole & Caraco, 2001, Reay *et al.*, 2003, Laursen & Seitzinger, 2004, Harrison *et al.*, 2005, Clough *et al.*, 2006). An assumption commonly made is that the N<sub>2</sub>O yield is 0.5% for both nitrification and denitrification (Mosier *et al.*, 1998, Seitzinger & Kroeze, 1998). Cole and Caraco (2001) measured N<sub>2</sub>O 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. Harrison and Matson (2003) found that the IPCC methodology overestimated their measured N<sub>2</sub>O emissions from drainage canals by 2 - 19 times. Clough *et al.* (2006) also found that the measured yields of N<sub>2</sub>O, from a spring-fed river, were significantly less than those calculated using the IPCC methodology. While recent suggestions call for a revision of the magnitude of the EF5 emission factor (Reay *et al.*, 2005, Well *et al.*, 2005) it is readily apparent that more data are required to credibly determine the role rivers play in the N<sub>2</sub>O budget (Cole & Caraco, 2001, Groffman *et al.*, 2002).

The occurrence of diurnal cycles of dissolved oxygen (DO) in rivers is well recognized with DO a function of river reaeration, plant and bacterial respiration and photosynthesis (Wilcock *et al.*, 1998). The dynamics of DO are linked to denitrification via the inhibition of denitrification by oxygen, mineralization of organic matter and the subsequent oxidation of ammonium to nitrate (Laursen & Seitzinger, 2004). Net fluxes of N<sub>2</sub>O have been noted as being generally higher at night than during the day for three small rivers in the U.S.A. (Laursen & Seitzinger, 2004). Recently, Harrison *et al.* (2005) investigated the effects of a diurnal oxygen cycle on N transformations and greenhouse gas emissions in a highly eutrophied subtropical stream and found that it could undergo complete

reduction and oxidation sequences in only a few hours. The ramifications of this in terms of N cycling were: decreased denitrification rates relative to daytime only measurements, increased downstream N transfer and a change in N form, and decreased estimates of in-stream nitrous oxide (Harrison *et al.*, 2005). A study by Wilcock *et al.* (1998) characterised diurnal DO cycles in 23 rural lowland streams and found that streams in shaded forest catchments were cooler with smaller deviations of DO from saturation compared with streams in open pasture. Previously Clough *et al.* (2006) measured N<sub>2</sub>O river surface fluxes, at the same time of day over several seasons, from a lowland river passing through open pasture, in order to assess the magnitude of EF5-r. Given the findings of Harrison *et al.* (2005), and the strong likelihood of a diurnal fluctuation in DO, we reinvestigated one site on the LII river, studied by Clough *et al.* (2006). We investigated the potential for diurnal cycles of dissolved N<sub>2</sub>O and the associated N<sub>2</sub>O fluxes, along with the possible implications for N dynamics and the calculation of an IPCC emission factor (EF5-r).

## **Materials and Methods**

This study was performed on the spring-fed LII river in Canterbury, New Zealand (Fig. 1). The LII commences at a spring (Latitude/Longitude 43.64673°S, 162.49677°E), 10 m above sea level where the shallow groundwater flow meets a confining aquitard (Bowden, 1986), and flows a distance of 12 km prior to discharging into Lake Ellesmere (Fig. 1). The source of the ground water feeding the spring has been previously described (Clough *et al.*, 2006). The sampling site for this study was 10 km downstream from the spring, previously described as ‘site 4’ by Clough *et al.* (2006). Prior to this site the river meanders, with a mean gradient of 0.08%, through land occupied by orchards, sheep and dairy farm operations. Due to the flat landscape the catchment and N loading, are not readily definable. No direct discharge of nitrogenous effluent into the LII occurs, with dairy farmers required to apply animal wastes

from the milking platform back onto pasture. The river bed comprises a silty mud with macrophytes, almost entirely *Elodea canadensis*, covering an estimated 85% of the river bed.

To determine the potential diurnal variability in dissolved N<sub>2</sub>O concentrations and headspace fluxes the following measurements were taken every 2 h for a 72 h period: water surface N<sub>2</sub>O fluxes using floating chambers, dissolved N<sub>2</sub>O concentrations, water and air temperatures, dissolved oxygen (DO), dissolved carbon (C), inorganic-N and sulphate, electrical conductivity, water pH, irradiance in the visible waveband, and wind speeds.

The floating chamber design, construction and operation have been previously noted (Clough *et al.*, 2006). To determine the river surface N<sub>2</sub>O flux five chambers were floated downstream for 15 minutes (180 m), on each sampling occasion. Chambers were deployed from the same location on each sampling occasion. The chamber headspace (4.2 L) was sampled (10 mL) using a glass syringe equipped with stopcocks (Part No. 2C6201, Baxter Healthcare Corp., Deerfield, IL, USA). The gas sample was injected into a previously evacuated (<0.01 atmosphere) 6 mL glass sample tube (Exetainer<sup>®</sup>, Labco Ltd, High Wycombe, UK). Ambient air samples were also taken on each sampling occasion to determine background N<sub>2</sub>O concentrations.

Analyses of the headspace gas samples, for N<sub>2</sub>O, were performed using a gas chromatograph (8610, SRI Instruments, CA.) interfaced to a liquid auto sampler (Gilson 222XL, Middleton, WI.). The auto-sampler had been specially modified for gas analysis by substituting a purpose-built (PDZ-Europa, Crewe, U.K) 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<sup>®</sup>) into the GC. The configuration of the GC and sample handling prior to analysis has been previously described (Clough *et al.*, 2006). A range of reference gases (0.363 to 35.2 μL L<sup>-1</sup>, BOC Ltd. Auckland) were used to determine the sample concentrations. River surface N<sub>2</sub>O fluxes were calculated

using the difference between the headspace N<sub>2</sub>O concentration, assuming a linear increase in the headspace concentration over time, the ambient air N<sub>2</sub>O concentration and the collection time.

Replicated water samples (3 x 50 mL) for dissolved N<sub>2</sub>O gases were collected in 100 mL glass digest tubes to determine dissolved N<sub>2</sub>O concentrations. A 2 L water bottle was filled 20 cm below the water surface 2 m out from the bank and then the water sample was rapidly decanted, avoiding bubbling, into a digest tube that had previously had 1 mL of mercuric chloride (MgCl<sub>2</sub>) added to it (20 µg L<sup>-1</sup> final concentration; (Kirkwood, 1992)). A gas-tight Suba-seal was then quickly fitted to the digest tube. Samples were transported back to the lab and shaken for 24 h to equilibrate N<sub>2</sub>O concentrations in the headspace and water phases. The digest tube headspace was then sampled and analysed in an identical manner to the floating chamber headspace N<sub>2</sub>O samples with allowances made for the pre-existing ambient N<sub>2</sub>O concentration. Concentrations of dissolved N<sub>2</sub>O in the river water samples were calculated according to Davidson and Firestone (1988) with appropriate Bunsen coefficients obtained for N<sub>2</sub>O (Young, 1981). Nitrous oxide equilibrium concentrations in the river water samples were determined using the ambient atmospheric N<sub>2</sub>O partial pressure (atm) and the appropriate solubility coefficient for N<sub>2</sub>O (mol L<sup>-1</sup> atm<sup>-1</sup>) for the temperature of the water sampled (Weiss & Price, 1980)). Dissolved N<sub>2</sub>O concentrations (µg N<sub>2</sub>O-N L<sup>-1</sup>) were also expressed in terms of percentage saturation based on the N<sub>2</sub>O equilibrium concentration (Weiss & Price, 1980).

An emission factor (EF5-r) was calculated according to the IPCC methodology and assumptions. We used the following data: a NO<sub>3</sub>-N concentration of 3.0 mg L<sup>-1</sup>, a river flow of 3.2 m<sup>3</sup> s<sup>-1</sup>, and an average river width of 13.5 m.

The process of gas exchange across the water-air interface is commonly described by either the 'stagnant-two-film' approach (Liss & Slater, 1974) or the 'surface renewal' model

(Danckwerts, 1951) both of which can be distilled into the following equation, which was used to model a predictive flux (Schwarzenbach *et al.*, 1993):

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

Where  $F_{N_2O}$  is the N<sub>2</sub>O flux (mole m<sup>-2</sup> s<sup>-1</sup>),  $V_{tot}$  is the combined transfer velocity (m s<sup>-1</sup>) for N<sub>2</sub>O that incorporates both a wind ( $V_{wind}$ ) and a water turbulence term ( $V_{water}$ ),  $C_w$  is the N<sub>2</sub>O concentration in the river water (mol m<sup>-3</sup>),  $C_a$  is the N<sub>2</sub>O concentration in ambient air (mol m<sup>-3</sup>), and  $K'_H$  is the dimensionless Henry's Law constant (mol m<sup>-3</sup><sub>a</sub> : mol m<sup>-3</sup><sub>w</sub>). The water turbulence contribution to  $V_{tot}$  was calculated using the river water velocity ( $U$ ; m s<sup>-1</sup>), average river depth ( $h$ ; m) and an N<sub>2</sub>O diffusion coefficient in water ( $D$ ; m<sup>2</sup> s<sup>-1</sup>) as follows, (O'Connor *et al.*, 1958, Schwarzenbach *et al.*, 1993):

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

Values for  $D$  were adjusted for river temperature (Jähne *et al.*, 1987). The wind contribution to  $V_{tot}$  was calculated as follows (Wanninkhof, 1992):

$$V_{wind} = 2.78E^{-6} k u_{10}^2 \left( \frac{Sc}{660} \right)^{\frac{1}{2}} \quad [3]$$

Where 2.78E-6 is a conversion factor (cm h<sup>-1</sup> to m s<sup>-1</sup>),  $k$  is a constant (0.31),  $u_{10}$  is the wind speed at a height of 10 m above the river, and  $Sc$  is the Schmidt number for N<sub>2</sub>O (Jähne *et al.*, 1987). The value of  $V_{tot}$  was calculated as the sum of  $V_{water}$  and  $V_{wind}$ . The wind speed at 10 m height above the river was calculated using the following equation (Israelsen & Hansen, 1962);

$$\frac{U_1}{U_2} = \log\left(\frac{Z_1}{Z_0}\right) \div \log\left(\frac{Z_2}{Z_0}\right) \quad [4]$$



Where  $Z_0$  equals the “effective roughness height”, assumed to be 0.001m, and  $U_1$  and  $U_2$  are the respective wind speeds at heights  $Z_1$  and  $Z_2$ . Where  $Z_1$  and  $Z_2$  are 10.0 and 0.1 m respectively.

Measurements of DO and water temperature were made in situ, using a portable hand held meter (YSI 550A, Ohio, USA), at 20, 40, 60 and 80 cm depths. Electrical conductivity was measured in situ using a hand held meter (HI98300/3, Hanna Instruments, Australia). Wind speeds above the water surface (0.1 m height) and on the river bank (0.3 m height) were measured using a hot-wire anemometer (TSI Incorporated, Minnesota, USA). Air temperature at the river site was measured using an Assmann psychrometer. Hourly average meteorological data, including wind speed (10 m height), wind direction, and rainfall were also made available from a near by (13 km) meteorological station.

Visible irradiance (400-700 nm) was also measured at the site every 2 h using a quantum sensor (LI-190, LI-COR Biosciences, Lincoln, Nebraska, USA). River flow measurements were performed by manually measuring the trapezoidal cross-sectional area of the river and determining the river’s velocity (Mosley *et al.*, 1992, Davie, 2003). At the measurement site the LII was 13.5 m wide with a mean depth of 1.2 m (range 0.4 - 1.7 m).

A further 100 mL water sample, sampled as above, was also collected for chemical analysis back in the laboratory. Water samples for chemical analysis were periodically transported back to the laboratory in an insulated styrofoam box and stored at 4°C until analysis within 24 h. Back in the laboratory the river water samples were subsampled and analyzed for ammonium ( $\text{NH}_4^+$ ), nitrite ( $\text{NO}_2^-$ ), nitrate ( $\text{NO}_3^-$ ), sulphate ( $\text{SO}_4^{2-}$ ), dissolved carbon, and pH. A colorimetric method with an auto-analyser (Alpkem FS3000 twin channel analyser; application notes P/N A002380 and P/N A002423) was used to analyse for  $\text{NH}_4\text{-N}$ . Detection limits for the inorganic-N species were 0.10, 0.01, and 0.01  $\text{mg L}^{-1}$  for  $\text{NO}_3\text{-N}$ ,  $\text{NO}_2\text{-N}$  and  $\text{NH}_4\text{-N}$  respectively. An ion chromatograph (DX-120, Dionex Corporation, USA)

was used to analyse water samples for  $\text{NO}_2^-$ ,  $\text{NO}_3^-$ , and  $\text{SO}_4^{2-}$ . Dissolved organic carbon (DOC) was calculated from the difference between the dissolved total carbon (DTC) and the dissolved inorganic carbon (DIC), i.e.  $\text{DOC} = \text{DTC} - \text{DIC}$ , using a Shimadzu TOC-Analyser fitted with a Shimadzu ASI-5000A auto sampler. Water pH was measured with a portable meter (Mettler-Toledo, Switzerland).

## Results

### *Meteorological data and river chemistry*

At the measurement site the cross sectional area of the river was  $16.2 \text{ m}^2$  with an average depth of 1.2 m. Average river velocity was  $0.2 \text{ m s}^{-1}$  with a mean flow of  $3.2 \text{ m}^3 \text{ s}^{-1}$ . There was no rainfall during the sampling period of the study. Wind speeds at the river sampling site averaged 0.3 (range 0- 1.0) and 1.3 (range (0- 4.0)  $\text{m s}^{-1}$  at the 0.1 and 0.3 m heights respectively (Fig. 2). The calculated 10 m height wind speed at the study site, based on the average wind speed at 0.1 m ( $0.3 \text{ m s}^{-1}$ ) and a roughness height of 0.05 m averaged  $2.3 \text{ m s}^{-1}$ . At the nearby meteorological station wind speed at a 10 m height averaged  $3.2 \text{ m s}^{-1}$  (range 0.2-6.0) with the predominant wind directions averaging  $48^\circ$  and  $175^\circ$  (Fig. 2). There was no relationship between wind speed and direction at the meteorological station site. Air temperature at the river study site followed a diurnal pattern and averaged  $14.8^\circ\text{C}$  (range 9.0 to  $24.6^\circ\text{C}$ ; Fig. 2). Regression analysis showed that there were significant relationships between wind speed at 0.1 and 0.3 m heights and air temperature at the study site,  $r^2 = 0.24$  ( $p < 0.01$ ) and  $r^2 = 0.19$  ( $p < 0.01$ ) respectively.

Irradiance received at the river surface reached a maximum value of  $2000 \mu\text{mol m}^{-2} \text{ s}^{-1}$  on day 2 (Fig. 3). Irradiance decreased with increasing water depth and the Beer's Law attenuation coefficient equalled  $1 \text{ m}^{-1}$  indicating that visibility in the water extended over a distance of approximately 5.5 m. River sediments and the aquatic macrophytes were clearly

visible on the river bed throughout the study period. There were no significant differences between DO concentrations at 20, 40, 60 and 80 cm depths or between water temperatures at these depths. Concentrations of DO followed a diurnal pattern (Fig. 3), ranging from 74 to 160 % saturation (7.5 to 15.5 mg L<sup>-1</sup>), and were significantly correlated with irradiance ( $r = 0.52, p < 0.001$ ) and water temperature ( $r = 0.89, p < 0.001$ ). The DO minima occurred around sunrise at ca. 06:00 h while DO maxima occurred at ca. 16:00-18:00 h, with sunset at 21:00 h. Mean water temperature, over all depths, followed a diurnal pattern ranging from 13.5 to 16.9 °C (Fig. 5b) that was significantly correlated with irradiance ( $r = 0.52, p < 0.001$ ) and air temperature ( $r = 0.68, p < 0.001$ ).

Concentrations of dissolved C were dominated by the DIC fraction which on average represented 87 % of the DTC fraction. The DIC concentrations averaged 12.4 mg L<sup>-1</sup> (SEM 0.1, range 11.2 to 13.5 mg L<sup>-1</sup>). DIC concentrations increased as DO saturation decreased ( $r^2 = 0.88, p < 0.01$ ; Fig. 3). The DOC concentrations averaged 1.9 mg L<sup>-1</sup> (SEM 0.2) and were generally below 3 mg L<sup>-1</sup> except on two occasions when they peaked at 6.8 and 4.0 g L<sup>-1</sup>, on the 1<sup>st</sup> December at 20:30 h and 2<sup>nd</sup> December 04:30 h respectively. River water pH averaged 8.1 (SEM 0.1, range 7.4-9.1) and followed a diurnal trend (Fig. 3) that was positively correlated with DO saturation ( $r = 0.97, p < 0.01$ ) and negatively correlated with DIC ( $r = -0.97, p < 0.01$ ).

Concentrations of NO<sub>3</sub>-N averaged 3.0 mg L<sup>-1</sup> (SEM 0.01, Fig. 4) while the SO<sub>4</sub><sup>2-</sup> concentrations averaged 3.3 mg L<sup>-1</sup> (SEM 0.01) but neither anion showed a significant relationship with DO. Based on the average NO<sub>3</sub>-N concentration and the river flow (3.2 m<sup>3</sup> s<sup>-1</sup>) the mass of NO<sub>3</sub>-N that moved out of the study reach equalled 34.6 kg h<sup>-1</sup> (829 kg d<sup>-1</sup>). The presence of NO<sub>2</sub>-N and NH<sub>4</sub>-N were not detected. Electrical conductivity averaged 180 μS (SEM 0.4) with no relationship to the other measured variables.

### *Dissolved N<sub>2</sub>O and N<sub>2</sub>O fluxes*

Dissolved N<sub>2</sub>O concentrations ranged from 1.3 to 2.0 µg N<sub>2</sub>O-N L<sup>-1</sup>, averaging 1.6 µg N<sub>2</sub>O-N L<sup>-1</sup> (SEM = 1). The ratio of N<sub>2</sub>O-N: NO<sub>3</sub>-N averaged 5.4x10<sup>-4</sup>, ranging from 4.2 x10<sup>-4</sup> to 6.5 x10<sup>-4</sup>, and showed no relationship to NO<sub>3</sub>-N concentrations (Fig. 4). Dissolved N<sub>2</sub>O expressed as a % saturation averaged 570% (SEM = 10, range 402 to 664%) and generally followed a diurnal pattern, increasing during the day and decreasing during the night, although the decrease was not apparent on the third night of the study (Fig. 5a). Dissolved N<sub>2</sub>O % saturation was positively correlated with DO % saturation ( $r = 0.34, p < 0.05$ ) and pH ( $r = 0.40, p < 0.05$ ) but negatively correlated with DIC ( $r = -0.38, p < 0.05$ ). Dissolved N<sub>2</sub>O % saturation did not correlate with Henry's Law constants and changes in water temperature (Fig. 5b).

The measured flux of N<sub>2</sub>O-N from the river surface averaged 89 µg m<sup>-2</sup> h<sup>-1</sup> (SEM = 3, range 52-140 µg m<sup>-2</sup> h<sup>-1</sup>, Fig. 5a), and correlated poorly with the dissolved N<sub>2</sub>O concentrations ( $r = 0.27, p = 0.10, n = 36$ ). However if flux measurements during periods of high wind speed ( $\geq 0.5 \text{ m s}^{-1}$  at the 0.1 m height) were removed from the data set the relationship improved significantly ( $r^2 = 0.29, p < 0.01, n = 24$ ; Fig. 6). Reasons for removing high wind speed flux measurements are made below. Predicted N<sub>2</sub>O-N fluxes averaged 20 µg m<sup>-2</sup> h<sup>-1</sup> (range 13-25 µg m<sup>-2</sup> h<sup>-1</sup>, Fig. 5a) and related well to measured fluxes when the high wind speed data were removed ( $r^2 = 0.22, p < 0.05, n = 24$ ). Calculated transfer velocity values for  $V_{wind}$ ,  $V_{water}$  and  $V_{tot}$  averaged 5.2x10<sup>-7</sup>, 4.1 x 10<sup>-3</sup>, and 4.1 x 10<sup>-3</sup> m s<sup>-1</sup> respectively. Integrating the measured N<sub>2</sub>O-N flux produced a cumulative flux of 6284 µg m<sup>-2</sup> over the 72 h period. Assuming that the loss of N<sub>2</sub>O-N during the water's transit through the study reach did not affect the magnitude of the subsequent flux downstream, then the absolute maximum mass of N lost as N<sub>2</sub>O-N was 0.015 kg over 72 h. Given that the average mass of NO<sub>3</sub>-N leaving the reach was 2621 kg over 72 h and that the EF5-r emission factor states that 0.0075

kg N<sub>2</sub>O-N should evolve per kg NO<sub>3</sub>-N leached then our N<sub>2</sub>O-N flux should have totalled 19.658 kg N<sub>2</sub>O-N over the 72 h period. Instead we only measured 0.015 kg N<sub>2</sub>O-N which is only 0.076% of the IPCC methodology estimate.

## **Discussion**

### *River chemistry*

The changes in DO and DIC concentrations were a measure of the net changes occurring in the river with inputs and outputs of O<sub>2</sub> and CO<sub>2</sub> taking place simultaneously. Inputs of O<sub>2</sub> included reaeration from the overlying air and O<sub>2</sub> release from photosynthetic organisms within the water body e.g. aquatic plants. Oxygen consumption occurred due to respiration within the river system e.g. plant and bacterial respiration, resulting in the subsequent release of CO<sub>2</sub>. During daylight hours O<sub>2</sub> production predominated with levels of O<sub>2</sub> increasing and decreasing depending on the intensity of the irradiance received, while during the nocturnal period O<sub>2</sub> concentrations decreased as respiration predominated. The diurnal range in O<sub>2</sub> observed in this study is comparable with previously reported diurnal O<sub>2</sub> variability in New Zealand streams (Wilcock *et al.*, 1998), where DO ranged from 3.7 to 12.2 mg L<sup>-1</sup> in a survey of 23 lowland streams in the Waikato region of New Zealand. However, the DO % saturation in our study (74-160%) contrasts strongly with the results of Harrison *et al.* (2005) who recorded a pronounced diurnal variation with O<sub>2</sub> going from > 300% to complete anoxia in only a few hours. Differences for this could be the relatively warm (28-36°C) eutrophic conditions in the subtropical stream study of Harrison *et al.* (2005), encouraging microbial function and greater respiration activity.

The diurnal variability we observed in river pH was also within the range reported by other studies (e.g. (Harrison *et al.*, 2005) with pH decline a function of increasing CO<sub>2</sub> inputs and vice versa. The lack of any significant difference between DO, CO<sub>2</sub> and temperature with

river depth, in our study, indicates a well-mixed water body. The inorganic-N concentrations and the advective flux of  $\text{NO}_3^-$  reported here, are consistent with those previously recorded for the LII river (Clough *et al.*, 2006). The lack of any diurnal variability in the inorganic-N concentrations may be due to their absence or because such fluctuations were below the levels of detection. If it is assumed that the changes in dissolved  $\text{N}_2\text{O}$ -N concentrations ( $1.2 - 2.0 \mu\text{g L}^{-1}$ ) occur as a result of microbial inorganic-N processing, then the corresponding shift in the  $\text{NO}_3^-$ -N or  $\text{NH}_4^-$ -N concentrations would be considerably less than the levels of detection for inorganic-N, as noted above.

#### *Dissolved $\text{N}_2\text{O}$*

Average dissolved  $\text{N}_2\text{O}$  concentrations and levels of  $\text{N}_2\text{O}$  saturation were more than double those previously measured at this site in non-summer seasons (Clough *et al.*, 2006). However,  $\text{N}_2\text{O}$  % saturation was much lower than the values recorded by (Harrison *et al.*, 2005) who measured values approaching 6000% during a 24 h period in a eutrophic subtropical stream. Clough *et al.* (2006) concluded that there were further inputs of  $\text{N}_2\text{O}$  entering the LII river, in addition to the antecedent  $\text{N}_2\text{O}$  present in the spring water. The diurnal cycle of  $\text{N}_2\text{O}$  % saturation recorded here supports this conclusion. The diurnal water temperature cycle means that the capacity of the water to absorb  $\text{N}_2\text{O}$  should also vary diurnally, all things being constant, but inversely to the temperature, according to Henry's Law (Fig.5b). However, what we actually observed were peak  $\text{N}_2\text{O}$  % saturation levels during the late afternoon when water temperatures were at their maximum, and  $\text{N}_2\text{O}$  % saturations declining overnight as the water temperature cooled, particularly over the first two nights. In fact the  $\text{N}_2\text{O}$  % saturation closely followed the DO and pH cycles as noted above. These factors suggest microbial activity was responsible for the diurnal cycle of  $\text{N}_2\text{O}$  % saturation. Microbial processes responsible for  $\text{N}_2\text{O}$  production include denitrification,

nitrification, coupled nitrification-denitrification, nitrifier denitrification (Wrage *et al.*, 2001), and dissimilatory nitrate reduction to ammonium (DNRA).

Had denitrification been the sole source of N<sub>2</sub>O we would not expect it to increase as DO levels increased. However, denitrification could have been occurring at anaerobic sediment surfaces (Petersen *et al.*, 2001) and been enhanced by the increased temperature and remained unaffected by changes in DO. Denitrification can also be enhanced due to coupled nitrification-denitrification in sediments. Typically half of the nitrate produced by nitrification is denitrified while the other half escapes to the water (Revsbech *et al.*, 2005). Coupled nitrification-denitrification can contribute to diurnal patterns of denitrification (Lorenzen *et al.*, 1998, An & Joye, 2001, Laursen & Seitzinger, 2004). The coupling of nitrification to denitrification can be due to the effect of light on photosynthetic activity of micro algal and the subsequent effects of this on oxygen supply. For example Lorenzen *et al.* (1998) determined that total denitrification was higher from stream sediment cores incubated during light conditions due to greater benthic micro algal production of oxygen. Alternatively the coupling of nitrification and denitrification may occur due to other factors that influence nitrification rates such as diurnal variability in water pH and temperature. For example, a study by Laursen and Seitzinger (2004) proposed that diurnal shifts in N<sub>2</sub>O concentrations on three small rivers were the result of temperature and pH effects on nitrification, since the rivers were too turbid for denitrification to have been regulated by the oxygen dynamics related to photosynthetic activity of micro algae. Harrison *et al.* (2005) also suggested that their results indicated coupled nitrification-denitrification processes as being responsible for day time increases in N<sub>2</sub>O with denitrification dominating during the nocturnal hours as DO levels decreased sharply. In the study of Harrison *et al.* (2005) this conclusion was supported by large decreases in NH<sub>4</sub>-N and large increases in NO<sub>3</sub>-N concentrations during daylight hours, followed by decreases in NO<sub>3</sub>-N during the nocturnal

period. Increases in water temperature, DO and pH would all have favoured enhanced nitrification activity in our study. An increase in pH during the day over the range 7.4 to 9.1, as observed in our study, would potentially see the nitrification rate increase by 50% of the maximum rate (Warwick, 1986). However, we do not have  $\text{NH}_4\text{-N}$  data to support this hypothesis. Future  $\text{NH}_4\text{-N}$  measurements will need to be made at lower levels of detection. The decline in  $\text{N}_2\text{O}$  % saturation during the nocturnal period may have been as a result of more anaerobic conditions leading to greater reduction of  $\text{N}_2\text{O}$  to  $\text{N}_2$  via denitrification or a decline in coupled nitrification-denitrification.

Nitrifier-denitrification, as defined by Wrage et al. (2001), is favoured under high N and low organic C loadings in association with low oxygen. Thus this process cannot be ruled out especially if it occurred near anaerobic sediment surfaces. The process of DNRA has been also been reported in fresh water sediments (Kelso *et al.*, 1999) and cannot be ruled out as a potential source of the  $\text{N}_2\text{O}$  production observed. Future *in situ* experiments using  $^{15}\text{N}$  labelled inorganic-N compounds are required to fully understand the  $\text{N}_2\text{O}$  % saturation dynamics. If in fact the warmer temperatures were enhancing microbial activity this may also explain why the measured  $\text{N}_2\text{O}$  fluxes were higher than in the other cooler seasons (Clough *et al.*, 2006).

### *N<sub>2</sub>O fluxes*

Our measured  $\text{N}_2\text{O}$  fluxes are only a very small fraction (0.01%) of what the IPCC methodology would estimate based on the  $\text{NO}_3\text{-N}$  loading and our results confirm earlier work indicating that the IPCC methodology overestimates  $\text{N}_2\text{O}$  fluxes from rivers.

The anticipated linear relationship between  $\text{N}_2\text{O}$  emissions, measured with floating chambers, and the dissolved  $\text{N}_2\text{O}$  concentrations was confined to relatively calm conditions as will be discussed below. After, removing the flux measurements made when the wind



speeds at 0.1 m height were  $\geq 0.5 \text{ m s}^{-1}$  the relationship between  $\text{N}_2\text{O}$  fluxes and the dissolved  $\text{N}_2\text{O}$  concentrations was significantly improved, and as expected the  $\text{N}_2\text{O}$  fluxes increased with increasing dissolved  $\text{N}_2\text{O}$  concentrations.

In oceans and lakes the dominant source of turbulence in the aqueous boundary layer is controlled by wind stress with transfer velocity a function of wind speed, while in shallow streams and rivers turbulence is created by water passing over the bottom and transfer velocity is a function of river depth and velocity (Raymond & Cole, 2001). The latter was obviously the case in our study where  $V_{wind}$  was several orders of magnitude less than  $V_{water}$ . Accounting, on average, for only 0.01% of  $V_{tot}$ . Increasing the wind speed over the range of 1 to  $7 \text{ m s}^{-1}$  only increased the predicted  $\text{N}_2\text{O-N}$  flux by an average of  $0.3 \mu\text{g m}^{-2} \text{ h}^{-1}$  (as noted above the predicted  $\text{N}_2\text{O-N}$  fluxes averaged  $20 \mu\text{g m}^{-2} \text{ h}^{-1}$ ). Thus if the chamber method used here did indeed overestimate the  $\text{N}_2\text{O}$  flux then the transfer velocity due to water turbulence must have been too large. To test this we conducted a visualisation experiment and placed a syringe, minus its plunger, through the gas sampling septa of a floating chamber. We then filled the syringe with dye and allowed this to drip out of the needle onto the water surface as we observed the chamber floating on the river surface. Under calm conditions over a 180 m long reach no dye ‘escaped’ from beneath the floating chamber. However, if wind gusts pushed the chamber, at a tangent away from the direction of the water flow, dye was seen to ‘escape’ from the chamber. Such wind effects would have caused enhanced water turbulence around the chamber-water boundary since the chamber projected 1 cm into the water. This could explain the higher measured fluxes when compared with the predicted fluxes and the subsequent lack of a good fit with measured fluxes and dissolved  $\text{N}_2\text{O}$ . Thus measurements made at a wind speed  $\geq 0.5 \text{ m s}^{-1}$ , at the 0.1 m height, were removed from the comparison of dissolved  $\text{N}_2\text{O}$  concentrations and the measured fluxes, and this greatly improved the relationship between the two variables. The effect of wind pushing the chamber against the

current direction is analogous to the chamber being moored. Previous work has found that mooring a floating chamber results in increased turbulence and enhanced gas fluxes (Hartman & Hammond, 1982). While chamber methods have shortcomings they are the only tool for assessing possible diurnal variation since traditional alternatives cannot provide data at appropriate time scales for diurnal ecological studies (Kremner *et al.*, 2003). The possibility that our measured fluxes were artificially high does not change a key finding of our study i.e. the emission of N<sub>2</sub>O-N from the river surface was grossly below that predicted by the IPCC methodology. Alternatively, it could also be argued that the model used for predicting  $V_{water}$  was generic and simplistic and needs to be further refined for the particular river conditions.

#### *Implications for IPCC methodology*

Diurnal cycles in dissolved N<sub>2</sub>O did not translate into measured diurnal N<sub>2</sub>O fluxes, using floating chambers, due to the variability in the measured flux being greater than any variability that the diurnal cycle in N<sub>2</sub>O % saturation might have caused in the N<sub>2</sub>O flux. Thus there are no implications, at least for this river, as to the time of day that N<sub>2</sub>O flux samples are taken. But if the N<sub>2</sub>O-N flux was determined solely from the dissolved N<sub>2</sub>O-N concentration then the diurnal variability needs to be accounted for. The magnitude of the diurnal N<sub>2</sub>O % saturation cycle in the LII river had no implications for increased downstream N transfer, unlike other studies (Harrison *et al.*, 2005), with N<sub>2</sub>O-N only accounting for a maximum of  $6 \times 10^{-4}$  % of the transient NO<sub>3</sub>-N flux. The N<sub>2</sub>O-N fluxes accounted for <0.01% of a calculated flux using the IPCC methodology which is consistent with earlier work at this site.

While the N<sub>2</sub>O-N flux data collected in this study support previous results from the LII river (Clough *et al.*, 2006) caution needs to be exercised in extrapolating the current results to other periods of the year and differing flow conditions. For instance Royer *et al.*

(2004) noted that the loss of  $\text{NO}_3\text{-N}$  was greater during periods of low flow and low  $\text{NO}_3\text{-N}$  concentrations which occurred mainly in the late summer and early autumn of a headwater agricultural stream in Illinois. However, the LII river base flow and  $\text{NO}_3\text{-N}$  concentrations vary little throughout the year with the exception of storm events (Clough *et al.*, 2006).

Clearly the mechanisms controlling in situ production of  $\text{N}_2\text{O}$  in rivers are complex and will vary depending on the conditions within individual rivers. For example, the rivers studied by Laursen and Seitzinger (2004) generally had higher net fluxes of  $\text{N}_2\text{O}$  at night than during the day and these rivers were turbid with the sediments only visible near the very edge of the river where the depth was  $<0.25$  m. Thus the diurnal patterns of denitrification observed by Laursen & Seitzinger (2004) were attributed to diurnal changes in river pH and temperature as opposed to changes in the light cycle. In our study visibility through the water, and thus light transmission, were relatively good. Thus the dissolved  $\text{N}_2\text{O}$  concentrations observed increasing during the day in our study were, as mentioned above, possible linked to photosynthetic effects on DO and coupled nitrification-denitrification mechanisms. Thus river conditions will influence the  $\text{N}_2\text{O}$  production mechanism.

How typical are the LII river results when compared with other river systems? River geometry and water residence times influence the potential for in-stream processing of inorganic-N (Petersen *et al.*, 2001) and the relatively short residence time of the water in the LII river (Clough *et al.*, 2006) limits the potential for the production of  $\text{N}_2\text{O}$ . Many of New Zealand's rivers are relatively short and well oxygenated. While the results reported here may be typical of short well oxygenated rivers, typical of New Zealand conditions, this may not necessarily be the case when river geometry, river length, river chemistry, water turbidity and water temperatures vary as noted above. This implies that the IPCC methodology should consider different coefficients for different classes of river based on both physical and chemical conditions.

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## Figure Legends

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

Fig. 2 (a) Wind speeds at 0.1 m above the water surface and 0.3 m above the bank, and air temperatures at the study site. (b) Wind speed and direction at a meteorological site 13 km from the study site. Shaded areas represent the nocturnal period.

Fig. 3 Diurnal cycles of irradiance, dissolved oxygen (DO), pH and dissolved inorganic carbon (DIC). Shaded areas represent the nocturnal period.

Fig. 4 Concentrations of  $\text{NO}_3\text{-N}$ ,  $\text{N}_2\text{O-N}$  and the resulting  $\text{N}_2\text{O-N}:\text{NO}_3\text{-N}$  ratio in the LII river over the study period. Shaded areas represent the nocturnal period.

Fig. 5 (a) Measured (error bars SEM,  $n=5$ ) and predicted  $\text{N}_2\text{O-N}$  fluxes (error bars SEM,  $n=3$  based on dissolved  $\text{N}_2\text{O}$  concentrations ( $C_w$ ) see Eq. 1) from the river surface along with the  $\text{N}_2\text{O}$  % saturation levels (error bars SEM,  $n=3$ ). (b) Graph showing Henry's constant, river temperature and the  $\text{N}_2\text{O}$  % saturation (error bars SEM,  $n=3$ ).

Fig. 6 Plot of measured  $\text{N}_2\text{O-N}$  fluxes (error bars SEM,  $n=5$ ) versus the dissolved  $\text{N}_2\text{O-N}$  concentrations (error bars SEM,  $n=3$ ). The regression line is plotted for data where wind speed was  $< 0.5 \text{ m s}^{-1}$  at the 0.1 m height, filled symbols ( $\bullet$ ). Empty symbols ( $\circ$ ) show data collected when wind speeds were  $\geq 0.5 \text{ m s}^{-1}$ .

Fig.1

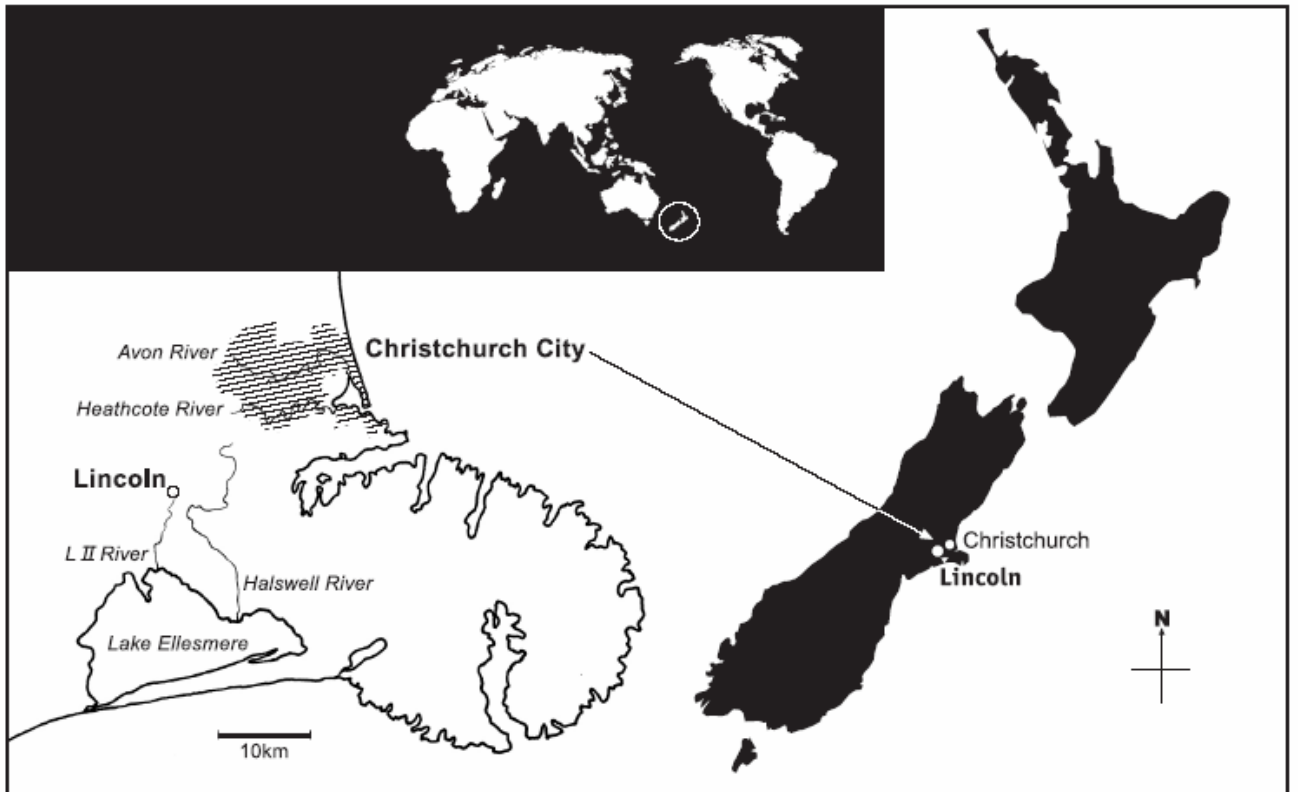
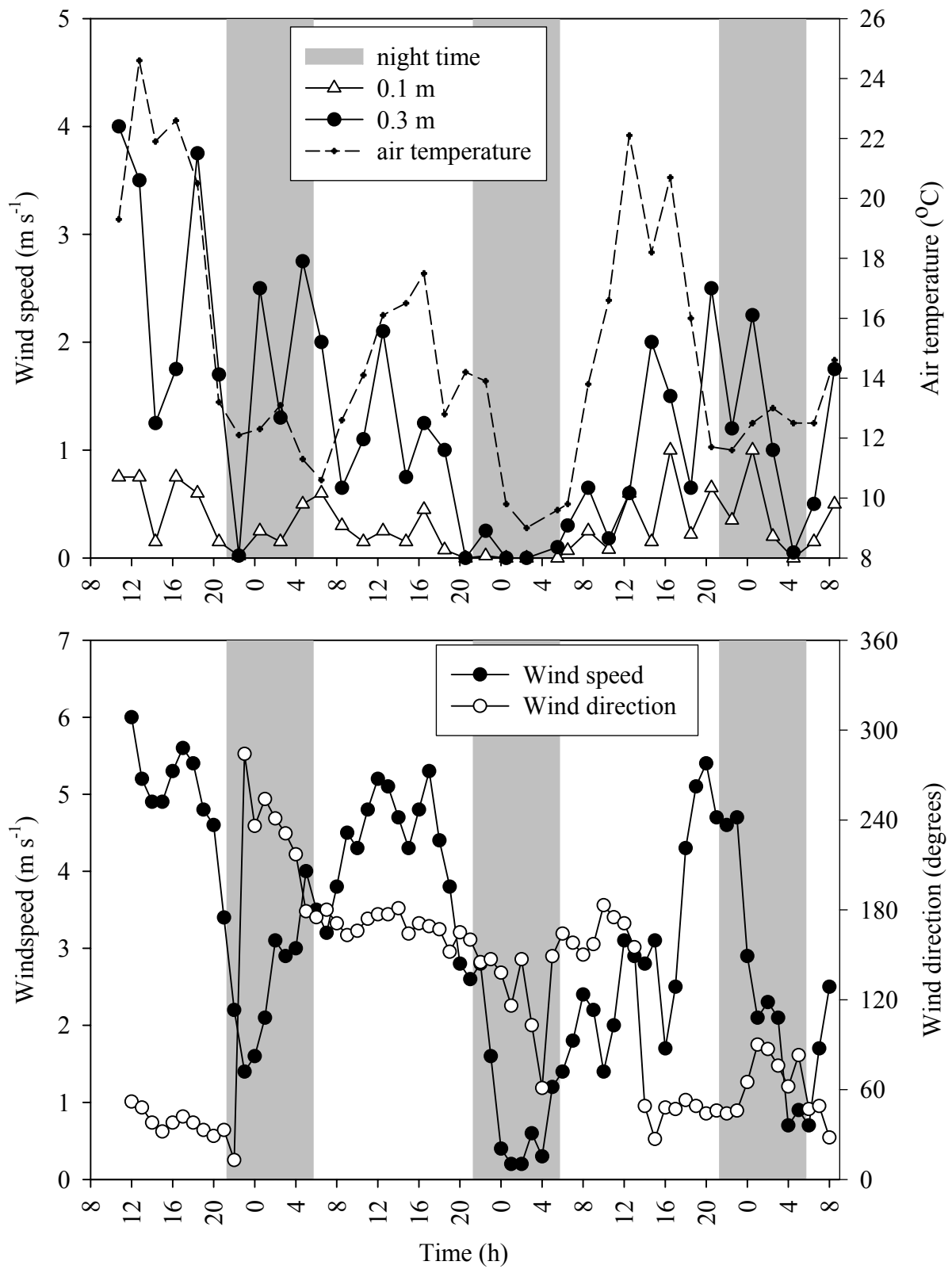
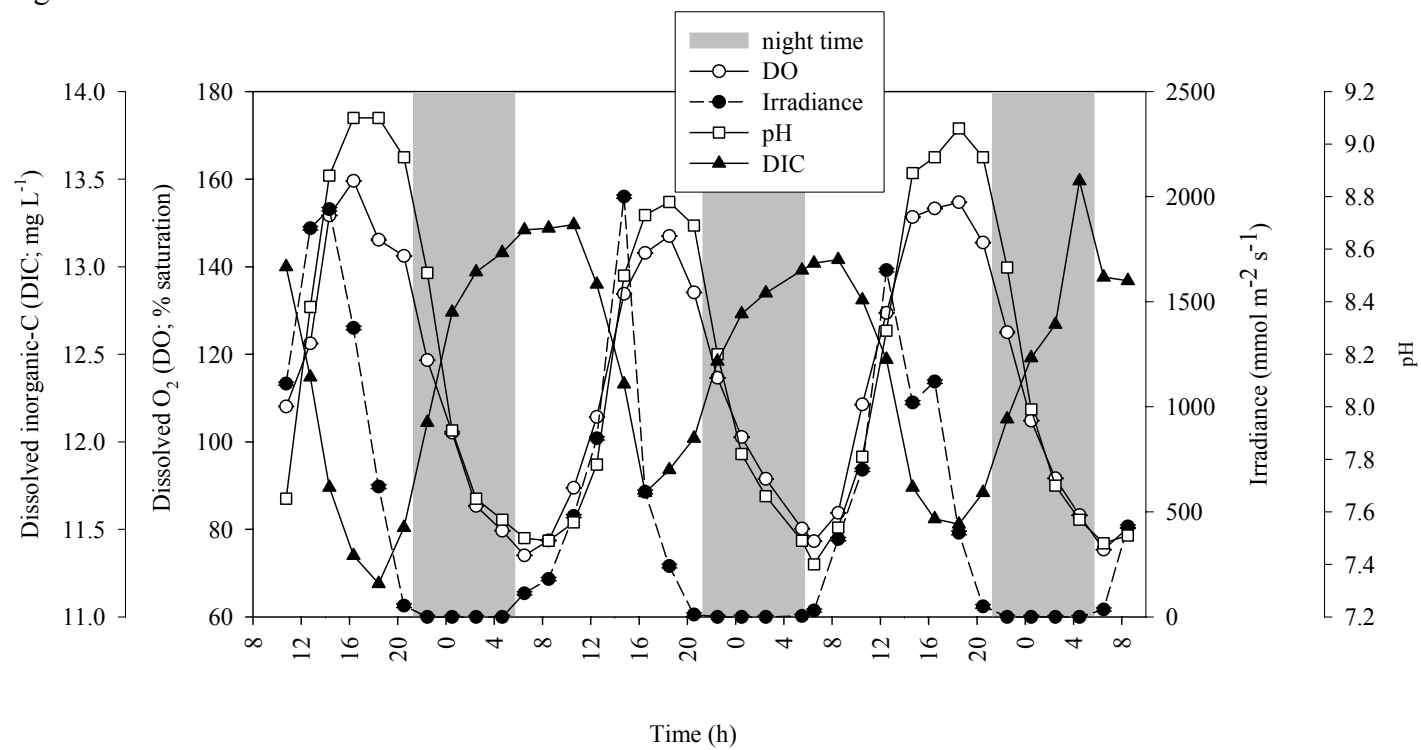


Fig. 2

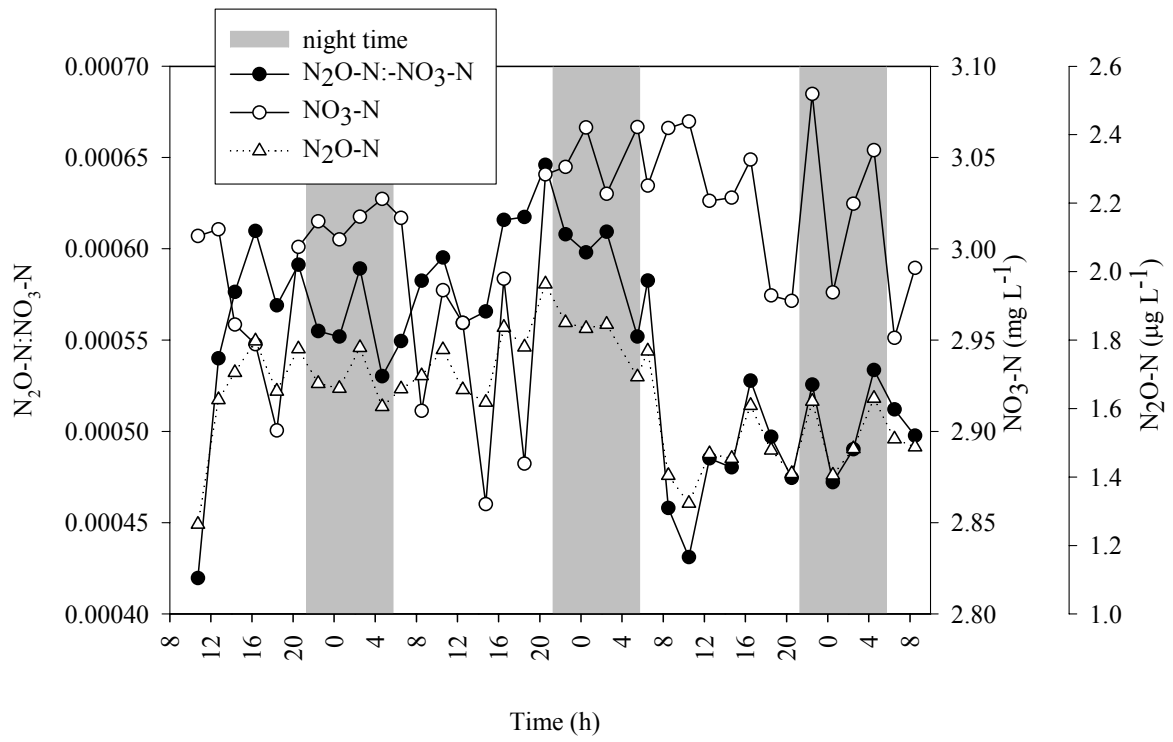


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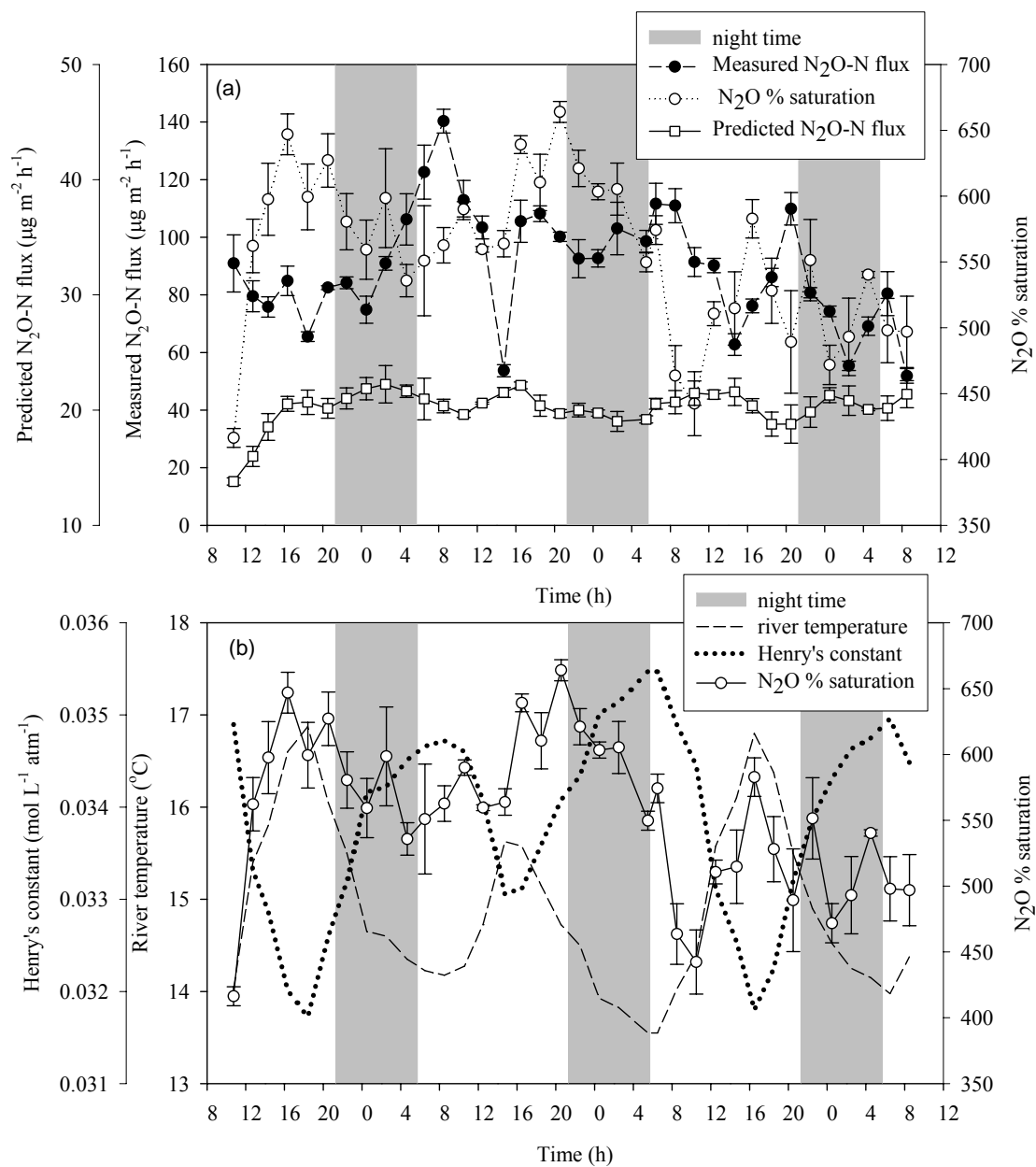
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4 Fig. 4



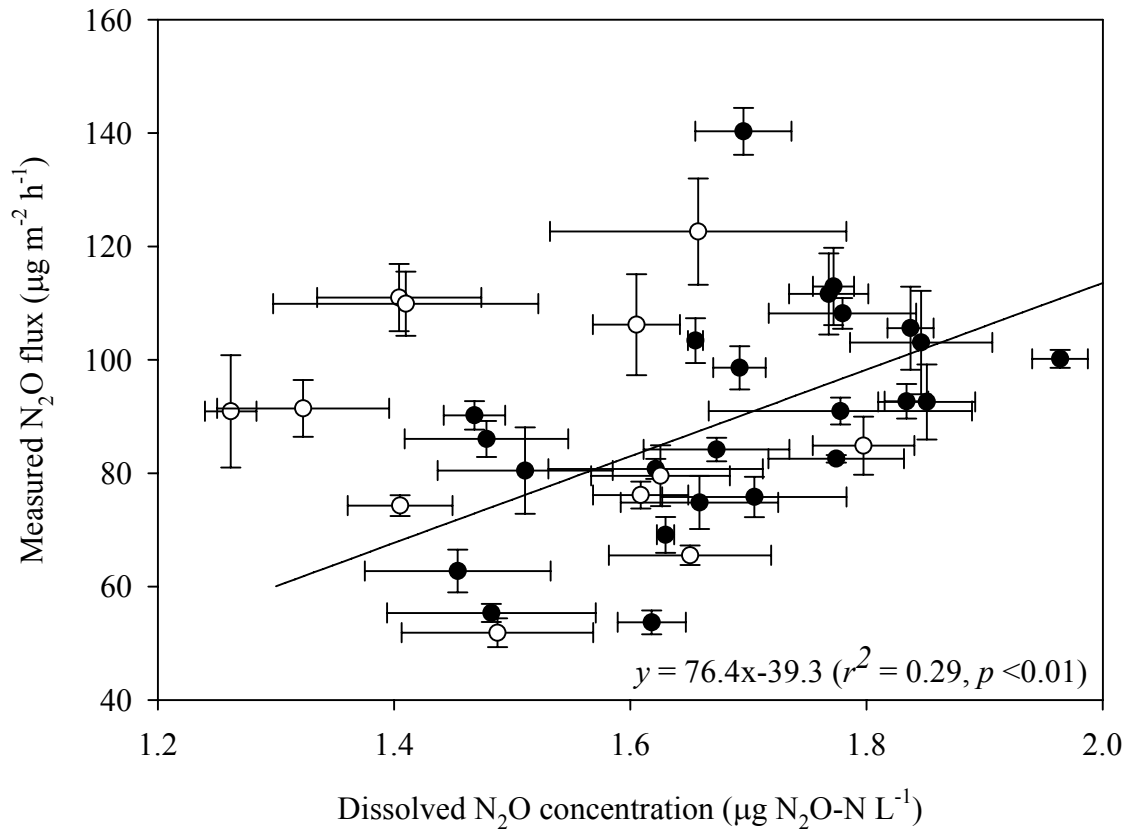
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7 Fig. 5



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10 Figure 6



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