



Methane and nitrous oxide sources and emissions in a subtropical freshwater reservoir, South East Queensland, Australia

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Abstract. Reservoirs have been identified as an important source of non-carbon dioxide (CO₂) greenhouse gases with wide ranging fluxes for reported methane (CH₄); however, fluxes for nitrous oxide (N₂O) are rarely quantified. This study investigates CH₄ and N₂O sources and emissions in a subtropical freshwater Gold Creek Reservoir, Australia, using a combination of water–air and sediment–water flux measurements and water column and pore water analyses. The reservoir was clearly a source of these gases as surface waters were supersaturated with CH₄ and N₂O. Atmospheric CH₄ fluxes were dominated by ebullition (60 to 99 %) relative to diffusive fluxes and ranged from 4.14×10^2 to $3.06 \times 10^5 \mu\text{mol CH}_4 \text{ m}^{-2} \text{ day}^{-1}$ across the sampling sites. Dissolved CH₄ concentrations were highest in the anoxic water column and sediment pore waters (approximately 5 000 000 % supersaturated). CH₄ production rates of up to $3616 \pm 395 \mu\text{mol CH}_4 \text{ m}^{-2} \text{ day}^{-1}$ were found during sediment incubations in anoxic conditions. These findings are in contrast to N₂O where no production was detected during sediment incubations and the highest dissolved N₂O concentrations were found in the oxic water column which was 110 to 220 % supersaturated with N₂O. N₂O fluxes to the atmosphere were primarily through the diffusive pathway, mainly driven by diffusive fluxes from the water column and by a minor contribution from sediment diffusion and ebullition. Results suggest that future studies of subtropical reservoirs should monitor CH₄ fluxes with an appropriate spatial resolution to ensure capture of ebullition zones, whereas assessment of N₂O fluxes should focus on the diffusive pathway.

1 Introduction

Methane (CH₄) and nitrous oxide (N₂O) are powerful greenhouse gases (GHGs) and are of emerging environmental concern. Their global warming potentials (GWPs) are 25 and 310 times that of carbon dioxide (CO₂), respectively, when calculated on a 100-year time horizon (IPCC, 2007). Man-made reservoirs, which include those for hydropower, agriculture or drinking water purposes, are now considered significant contributors of these GHGs, particularly CH₄ (Barros et al., 2011; Bastviken et al., 2011; St. Louis et al., 2000). The recognition of reservoirs as anthropogenic sources of GHGs has thus increased global interest in the measurement, monitoring and modelling of these emissions. The result is a discontinuous database of a large range of primarily CH₄ fluxes, of which studies in potentially important areas, such as the tropics and subtropics as well as whole continents like Australia, remain scarce (Mendonça et al., 2012; Ortiz-Llorente and Alvarez-Cobelas, 2012; St. Louis et al., 2000). Fewer studies conducted worldwide have analysed the contribution of N₂O to GHG emissions from reservoirs (Guerin et al., 2008; Mengis et al., 1997; Tremblay et al., 2005) despite N₂O having a higher GWP than CH₄. There are currently only two studies (Bastien and Demarty, 2013; Grinham et al., 2011) reporting CH₄ emissions and none for N₂O from reservoirs in Australia – a country with over 2300 reservoirs covering a surface area in excess of 5700 km² at full supply (Geoscience Australia, 2004).

Freshwater reservoirs in Australia cover a large surface area and are essential for drinking water supply and irrigation purposes. These reservoirs are typically closed systems

without continuous release through a dam but may have periodic release for environmental flows and drinking water supplies. These reservoirs enable storage and greater certainty of supply compared to river and groundwater sources in Australia. In reservoirs without continuous water release, the primary CH₄ emission pathways to the atmosphere are ebullition from sediments, diffusion over the water–air interface and plant-mediated transport from littoral zones (Bastviken et al., 2004). Ebullition has been shown to be the dominant CH₄ emission pathway in many tropical systems (DeISontro et al., 2011; Devol et al., 1988; Grinham et al., 2011; Joyce and Jewell, 2003; Keller and Stallard, 1994; Soumis et al., 2005). Factors controlling CH₄ ebullition in lake systems are relatively well known (Bastviken et al., 2004; Joyce and Jewell, 2003; Ortiz-Llorente and Alvarez-Cobelas, 2012); however, the dynamics and the spatial distribution of ebullition are not well understood (DeISontro et al., 2011; Ostrovsky et al., 2008; Ramos et al., 2006). CH₄ is typically produced by the process of methanogenesis under anoxic conditions (Canfield et al., 2005) as found in the sediment and hypolimnetic zones of a reservoir. However, zones within a reservoir may contain large gradients in dissolved oxygen (DO) availability (such as at the metalimnion under stratified conditions or upper layers of shallow sediments) and promote oxidation of dissolved CH₄ via methanotrophic bacteria (Guerin and Abril, 2007), which can greatly reduce diffusive emissions from the water surface.

N₂O production or consumption is also associated with these zones where large DO gradients occur. Under oxic conditions, as found in the epilimnion or metalimnion, N₂O is primarily produced as a byproduct of nitrification. At oxic–anoxic boundaries, N₂O is produced as an intermediate of denitrification (Mengis et al., 1997; Ward, 1996) or can be reduced to nitrogen gas during denitrification (Lipschultz et al., 1990; Mengis et al., 1997). In stratified reservoirs, the oxic–anoxic boundaries are found in the water column. In well-mixed systems or at shallow sites, DO can reach the sediment surface, and thus N₂O can be produced in the water column as well as in the upper layers of sediment.

The low-latitude reservoirs of Australia provide ideal conditions for GHG production, consumption and emissions. The generally higher temperatures experienced in tropical regions drive thermal stratification and a rapid deoxygenation of bottom waters (Barros et al., 2011; Tundisi and Tundisi, 2012). Irregular and heavy precipitation events can lead to the input of high organic carbon loads into the water body (Tundisi et al., 1993). The organic carbon loads together with elevated temperatures and deoxygenated bottom waters of these reservoirs will provide conditions that enhance CH₄ production and emissions (Demarty and Bastien, 2011; Fearnside, 1995; Galy-Lacaux et al., 1999). The steep oxygen gradients and high ammonium turnover found in subtropical reservoirs will likely favour N₂O production (Guerin et al., 2008).

There is recent emphasis to further study CH₄ emissions from freshwater reservoirs (Barros et al., 2011; Bastviken et al., 2011; Demarty and Bastien, 2011; St. Louis et al., 2000), and this has stimulated an increase of CH₄ monitoring. However, studies of N₂O emissions are lacking (Mengis et al., 1997; Seitzinger and Kroeze, 1998) despite N₂O being a more potent GHG than CH₄. Although GHG studies from reservoirs have recently increased, they remain limited, particularly in subtropical/tropical regions of the Southern Hemisphere (Mendonça et al., 2012; Ortiz-Llorente and Alvarez-Cobelas, 2012; St. Louis et al., 2000). Consequently, through this shortfall a large gap in the understanding of global CH₄ and N₂O emissions persists.

In our study we investigated CH₄ and N₂O emissions, production and consumption processes in the Gold Creek Reservoir in South East Queensland, Australia. The study consisted of two main parts. First, a detailed field investigation of the CH₄ and N₂O emission rates at two sites (one deep and one shallow) by measuring total water–air fluxes as well as water column and pore water concentrations. The detailed study also included sediment–water flux incubations of the shallow site which were conducted in the laboratory to gain further insight of the CH₄ and N₂O production or consumption processes. Secondly, a spatial emission field study focused on total flux (ebullitive and diffusive) measurements and estimated diffusive fluxes was performed to assess the CH₄ and N₂O emissions from shallow and deep sites of the reservoir. This study examined and validated the spatial and temporal representativeness of the CH₄ and N₂O emission data from the two sites of the detailed investigation.

2 Materials and methods

2.1 Site description

Gold Creek Reservoir (27°45′97″ S, 152°87′86″ E) is located in subtropical South East Queensland, 14 km west of the city of Brisbane, Australia. Completed in 1885, the reservoir is one of the oldest reservoirs in Australia and was built for the supply of drinking water to Brisbane (although currently not used for this purpose). Gold Creek Reservoir has a surface area of 19 ha and is near the median size for Australian reservoirs. The reservoir has a capacity of 820 000 m³ and maximum water depth of 11.75 m at full supply. Approximately 65 % of the total storage capacity is within the upper 2 m of the reservoir (Supplement Table S1). The reservoir's pristine catchment area is 10.5 km² and consists of 98 % open eucalyptus forest (Queensland Department of Science Information Technology Innovation and the Arts, 2012). These steep, forested catchments export high amounts of organic matter in the form of senescent leaves and woody material during intensive precipitation events (Tundisi et al., 1993). This material is generally deposited in the inflow points of

reservoirs where ebullition is frequently observed (Grinham et al., 2011).

In contrast to many temperate systems and reservoirs used for hydropower, Gold Creek Reservoir experiences water level increases mainly by intensive, irregular precipitation events and subsequent inflows especially during the summer months (e.g. 444 mm in 4 days, January 2013; Bureau of Meteorology, 2013). Water level decreases are caused by water evaporation due to the warm temperatures (annual mean temperature 26.4 °C; Bureau of Meteorology, 2013). As Gold Creek Reservoir has no regular release of water via dam outlets, the turbulent exchange of CH₄ and N₂O to the atmosphere is restricted to when the reservoir's capacity is exceeded and water is released over a spillway. The reservoir is steep-sided with limited colonisation of rooted macrophytes, limiting the importance of plant-mediated emission pathways. This means that the main emission pathways for Gold Creek Reservoir are ebullition from sediments and diffusion via the water–air interface.

Located in a subtropical region, Gold Creek Reservoir has relatively high water temperatures compared with many temperate systems. Monthly monitoring of water column profiles using a multi-parameter sonde (YSI 6600, YSI Inc., Yellow Springs, OH, USA) showed seasonal ranges of surface water temperature from 14 °C in winter (June to August) to 30 °C in summer (December to February) and bottom water temperatures ranging between 14 to 16 °C in all seasons. The water column was oxygenated in the upper 2 m during all seasons and stratified for 10 months of the year. Water column profiles of chlorophyll *a* were taken with a chlorophyll fluorometer (Seapoint Sensors Inc., Exeter, NH, USA). Sampling and experiments for this study were conducted in March 2012 and February 2014. During these periods, stratified conditions predominated, the reservoir was consistently filled to 90–100 % and experienced no overspill.

In the first part of our study, the detailed investigation was conducted at a shallow site (s4) and a deep site (d7) (Fig. 1; Supplement Table S2). CH₄ and N₂O total water–air fluxes and water column concentrations from both sites were measured as well as pore water concentrations from the shallow site s4. Additionally, laboratory incubations of sediments from sampling site s4 were conducted to determine CH₄ and N₂O production as this site was located at the oxycline zone.

The second part of this study investigated the spatial variability of emissions and focused on total flux measurements and diffusive flux estimates at several shallow sites (s1–s4) and deep sites (d5–d8) (Fig. 1; Supplement Table S2). The data obtained in this study were also used to validate the representativeness of water–air emission estimates from sites s4 and d7 of the detailed study. The average depth of the shallow sampling sites, located in the reservoir's sidearms, was 1.7 ± 0.5 m. The deep sampling sites, with an average depth of 7.9 ± 2.7 m, were generally located in the middle of the reservoir body.

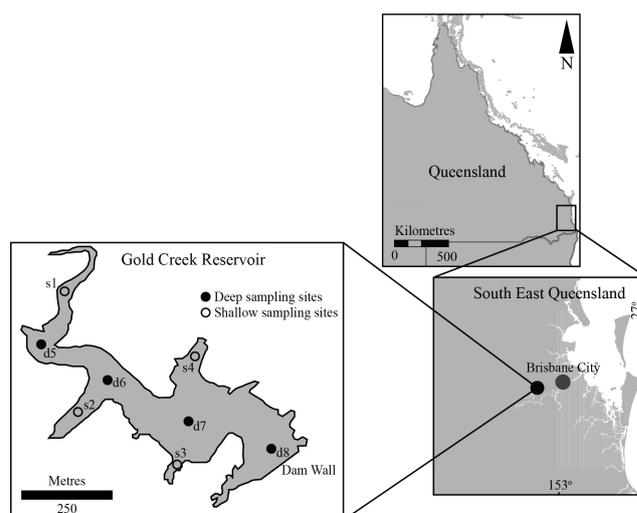


Figure 1. The location of the sampling sites at the Gold Creek Reservoir, South East Queensland, Australia. Sampling sites are numbered from the shallowest to deepest sites. Water depths were for the sites s1: 1.1 m, s2: 1.7 m, s3: 1.9 m, s4: 2.1 m, d5: 4.4 m, d6: 7.5 m, d7: 9.7 m, d8: 10.2 m during the spatial emission study. The detailed study was undertaken at sites s4 and d7.

2.2 Field measurements

2.2.1 Water–air flux measurements

Total CH₄ and N₂O emission fluxes (both ebullitive and diffusive fluxes) at the water–air interface were determined using anchored surface floating chambers. Gas accumulation of ebullitive and diffusive water–air fluxes in the chambers over time was used for rate calculations. Diffusive water–air fluxes were estimated using the thin boundary layer (TBL) model (Cole et al., 2010). Ebullitive emissions were calculated by the difference between total (floating chamber) and diffusive (TBL model) fluxes.

The surface floating chambers used are described in Grinham et al. (2011) and consisted of a floating platform with six small cylindrical PVC chamber units as replicates each with a volume of 0.00048 m³, and surface area of 0.00583 m². The chambers were stabilised in the water column by anchoring at two points to the reservoir's floor using an anchor system that was attached to each chamber at two opposite sides. The ropes used for this were connected to a sub-surface floating buoy which was again connected by ropes to an anchor on the reservoir ground. Sampling-induced disturbances to the water column and sampling-induced ebullition from the sediments were minimised by a careful approach and by maintaining boat speeds below 2.5 kn.

Headspace gas samples were taken from the floating chambers to determine emission rates after known deployment periods. During the detailed study at sites s4 and d7, gas samples were taken every 24 h from each of the six replicate units per floating chamber. After sampling, the surface

floating chambers were lifted out of the water and flushed with air. This sampling procedure was repeated 5 times over 5 consecutive days. During the spatial emission study, surface floating chambers with three replicate units per chamber were deployed at sites s1–s4 and at sites d5–d8. In this study, the chamber deployment time was 1 h. After taking gas samples from all chamber units, the chambers were also lifted out of the water and flushed with air. This sampling procedure was repeated 3 times at each site. Gas from the chambers was sampled using a 60 mL syringe with a 0.64 mm needle (Livingstone International Pty. Ltd., Rosebery, NSW, Australia) and transferred into 12 mL pre-evacuated borosilicate vials (Exetainer, Labco Ltd., Lampeter, UK).

Diffusive water–air fluxes were estimated using the equation:

$$F = k \times \Delta C = k \times (C_w - C_{eq}), \quad (1)$$

where F is the flux ($\mu\text{mol m}^{-2} \text{day}^{-1}$), k is the gas transfer coefficient (m day^{-1}) and ΔC is the difference between the gas concentration in the surface water (C_w) and the gas concentration in the surface water that is in equilibrium with the air (C_{eq}) (Cole et al., 2010).

The gas transfer coefficient k was estimated using the model, Eq. (2), developed by Wanninkhof (1992):

$$k = a \times U_{10}^2 \times (Sc/600)^{-x}, \quad (2)$$

where a is 0.31 for short-term winds or 0.39 for steady winds, U_{10} is the frictionless wind speed (m s^{-1}) normalised at 10 m, Sc is the Schmidt number for CH₄ and N₂O and x is a constant depending on the wind speed ($x = 0.66$ for wind speed $< 3 \text{ m s}^{-1}$ or $x = 0.5$ for wind speed $> 3 \text{ m s}^{-1}$). The Schmidt number Sc was calculated (Wanninkhof, 1992) using Eqs. (3) and (4) for CH₄ and N₂O, respectively:

$$Sc(\text{CH}_4) = 1897.8 - 114.28 \times t + 3.2902 \times t^2 - 0.039061 \times t^3, \quad (3)$$

$$Sc(\text{N}_2\text{O}) = 2055.6 - 137.11 \times t + 4.3173 \times t^2 - 0.054350 \times t^3, \quad (4)$$

where t is the temperature in Celsius. The frictionless wind speed U_{10} was normalised to a height of 10 m according to Crusius and Wanninkhof (2003):

$$U_{10} = 1.22 \times U_1, \quad (5)$$

where U_1 is the wind speed at 1 m height (m s^{-1}).

C_w was measured from a water sample (explained in the next section), whereas C_{eq} was calculated with the solubility approaches of Yamamoto et al. (1976) for CH₄ and Weiss and Price (1980) for N₂O and measured atmospheric concentrations before starting the chamber deployment times. A weather transmitter (WXT520, Vaisala, Vantaa, Finland) was installed during all sampling times at site d7 and the average

wind speeds were logged every minute (Supplement Figs. S1 and S2a). The wind speeds used for calculations were averaged over 24 h for each of the 5 consecutive measurement days for the detailed study and were averaged over the 1 h sampling intervals for the spatial emission study.

2.2.2 Water column sampling

Water column samples were taken at sites s4 and d7 to determine the concentrations of CH₄, N₂O and for the nutrient levels of ammonium (NH₄⁺), nitrate (NO₃⁻) and nitrite (NO₂⁻). Samples were taken from the epilimnion (20 cm below the water surface) and at the metalimnion depth (2 m) with a 4.2 L Niskin water sampler (Wildco, Wildlife Supply Company, Yulee, FL, USA) daily over the 5 consecutive days. At site d7, samples were also taken from the hypolimnion (8 m depth). All water samples were pressure-filtered through 25 mm diameter, 0.22 μm pore-size filters (Merck Millipore, Billerica, MA, USA). Water samples for CH₄ and N₂O analyses were injected into pre-evacuated borosilicate vials using a 12 mL syringe with a 0.64 mm needle, then equilibrated in an inflatable glove bag filled with ultra-high purity nitrogen gas (BOC, Brisbane, Australia) to atmospheric pressure and then stored at 4 °C until analysis. Water samples used for nutrient analyses were stored in sterile 10 mL vials (Sarstedt AG & Co., Nümbrecht, Germany) and frozen until analysis was carried out.

2.2.3 Pore water sampling

To investigate sediments as potential sources of CH₄ and N₂O, pore waters were extracted from sediment samples and analysed for CH₄ and N₂O concentrations at the shallow site s4. For this, six undisturbed sediment cores were taken with a gravity corer (Envco Environmental Equipment Suppliers, Australia), fitted with acrylic liners (69 mm inner diameter, 500 mm long) and sealed with PVC caps. The gravity corer used had a 2 m pole which limited the collection depth to a shallow site (i.e. site s4). However, Gold Creek Reservoir is generally shallow, with the main storage capacity being within the upper 2 m of the storage (Supplement Table S1). Therefore the oxycline of the reservoir is around the 2 m mark (Supplement Fig. S3a) and most sediments of the reservoir are exposed to oxygen. Thus, sediments of the chosen shallow site may be, at least in terms of oxygen exposure, representative for most of the reservoir's sediments.

Collected sediments in the cores had a height of 11.54 ± 2.34 cm. For the pore water analysis, sediment cores were pushed up to the top of the acrylic liners and 2 cm sediment layers were transferred into 50 mL test tubes (Falcon tubes, BD Biosciences, San Jose, CA, USA). Care was taken to ensure no headspace was formed. However, method drawbacks due to possible gas leakage from the vials would lead to an underestimation of pore water concentrations if the investigated gases are supersaturated. Upon arrival in the

laboratory, sediments in the test tubes were centrifuged (Eppendorf AG, Hamburg, Germany) for 20 min at 1500 g, without pressure or temperature changes. The pore water (supernatant) was removed and stored at 4 °C until analysis for CH₄, N₂O, NH₄⁺, NO₃⁻ and NO₂⁻. Sample handling as well as sample equilibration of the gases followed the same procedure as described previously for the water column samples.

2.3 Sediment incubation study

Sediment incubations were conducted in the laboratory to determine CH₄ and N₂O sediment–water fluxes from the shallow site samples (s4). For this, a second set of six undisturbed sediment core replicate samples were collected at site s4 with a gravity corer as described previously. The collected sediments had a height of 9.79 ± 1.12 cm with an overlying water column of 40.21 ± 1.12 cm. The covered sediment cores were transferred to the laboratory within 4 h, placed into incubators and the top PVC caps were removed. The incubators were filled with surface water from the respective site. The water was adjusted to the in situ temperature (24 °C) using water chillers. The open sediment cores were left to settle overnight while the water column above each sediment core was gently stirred using a magnetic stirring bar suspended in the water column and propelled by additional stirrer bars rotating at 18 rpm adjacent to the incubators. Results from in situ deployments of underwater light loggers (Odyssey photosynthetic active radiation recorders, Dataflow Systems Pty. Ltd., Christchurch, New Zealand) indicated strong light attenuation at the reservoir, with the photic zone being less than 1 to 0.5 m (Supplement Fig. S4). Consequently, for these sediment studies the incubators were covered with aluminum foil on the sides and light-blocking cloth at the top to mimic the reservoir's sediment conditions below the photic zone.

The sediment core liners were capped 15 h after sampling using plexiglas lids with O-rings taking care to exclude air bubbles. The lids contained three ports for sampling, refilling and for a dissolved oxygen probe (tip sealed against sampling port). One-way valves were attached to the tubing (Masterflex Tygon, John Morris Scientific Pty. Ltd., Chatswood, NSW, Australia) of the sampling and refilling ports, and a rubber stopper was used for the oxygen probe port if not used. Sampling and refilling with site water were carried out with 20 mL syringes. Dissolved oxygen and temperature of the water column above the sediment cores were monitored using an optical DO probe (PreSens, Precision Sensing GmbH, Regensburg, Germany) before the core liners were capped and every 24 h subsequently until the experiment finished. Cores were regularly inspected for signs of ebullition (bubble formation under the cap) throughout the incubation times. Samples from the overlying water of the sediment cores were taken for analysis of CH₄, N₂O and the nutrients NH₄⁺, NO₃⁻ and NO₂⁻ before the cores were capped and after 72, 120 and 288 h incubation. Daily fluxes were determined for CH₄, NH₄⁺, NO₃⁻ and NO₂⁻ over 288 h and for DO over

48 h. These were calculated from the rates of change in concentration and by taking the core volume and sediment surface area into account. CH₄, N₂O and nutrient sample handling as well as sample equilibration of the gases followed the same procedure as described previously for the water column samples.

2.4 Analyses

Both gaseous and liquid samples were analysed for CH₄ and N₂O concentrations using an Agilent GC7890A gas chromatograph (Agilent Technologies, Santa Clara, CA, USA). A flame ionisation detector and a micro-electron capture detector were used for the analysis of CH₄ and N₂O, respectively. The gas chromatograph was calibrated using standards with a range of 1.8 to 82 000 ppm for CH₄ and 0.5 to 50.53 ppm for N₂O which were prepared from certified gas standards (BOC gases, Brisbane, Australia). A Lachat QuickChem 8000 Flow Injection Analyzer (Lachat Instrument, Milwaukee, WI, USA) was used for the analysis of NH₄⁺, NO₃⁻ and NO₂⁻ concentrations.

Statistical analyses were performed with the program Statistica version 12 (StatSoft Inc., Tulsa, OK, USA), using one-way analysis of variances (ANOVAs). In order to evaluate differences amongst sampling sites, one-way ANOVAs were performed with sampling sites s4 or d7, sampling days 1–5 or the sampling depths (epilimnion, metalimnion, hypolimnion, pore water) as the categorical predictor and CH₄, N₂O or nutrients (NH₄⁺, NO₃⁻, NO₂⁻) as the continuous variables. Data were log transformed where necessary to ensure normality of distribution and homogeneity of variance (Levene's test) (Zar, 1984). Post hoc tests were performed using Fisher's LSD (least significant difference) test (Zar, 1984). The non-parametric Kruskal–Wallis (KW) test was used for data which failed to satisfy the assumptions of normality and homogeneity of data after being transformed.

3 Results

3.1 Water–air fluxes

Sites s4 (shallow) and d7 (deep) of the detailed study showed significantly different (KW-H_{1,60} = 41.2, *P* < 0.001) CH₄ emission rates, with the highest rates found at the shallow site s4 (Fig. 2a and c; Table 1). However, there was no significant difference (*P* > 0.05) found in N₂O emissions between the two sites (Fig. 2b and d; Table 1). Total CH₄ and N₂O fluxes across the 5 consecutive monitoring days were not significantly different (*P* > 0.05) at both sampling sites s4 and d7, apart from N₂O fluxes at site s4 between day 4 and day 5 (KW-H_{9,60} = 47.8, *P* < 0.01). Results of the detailed study (Fig. 2) showed that diffusive fluxes account for 12 to 40 % of the total CH₄ fluxes at site d7 and less than 3 % at site s4. However, diffusive fluxes estimated by the TBL model explain, in four out of 5 monitoring days, 82 to 100 % of total

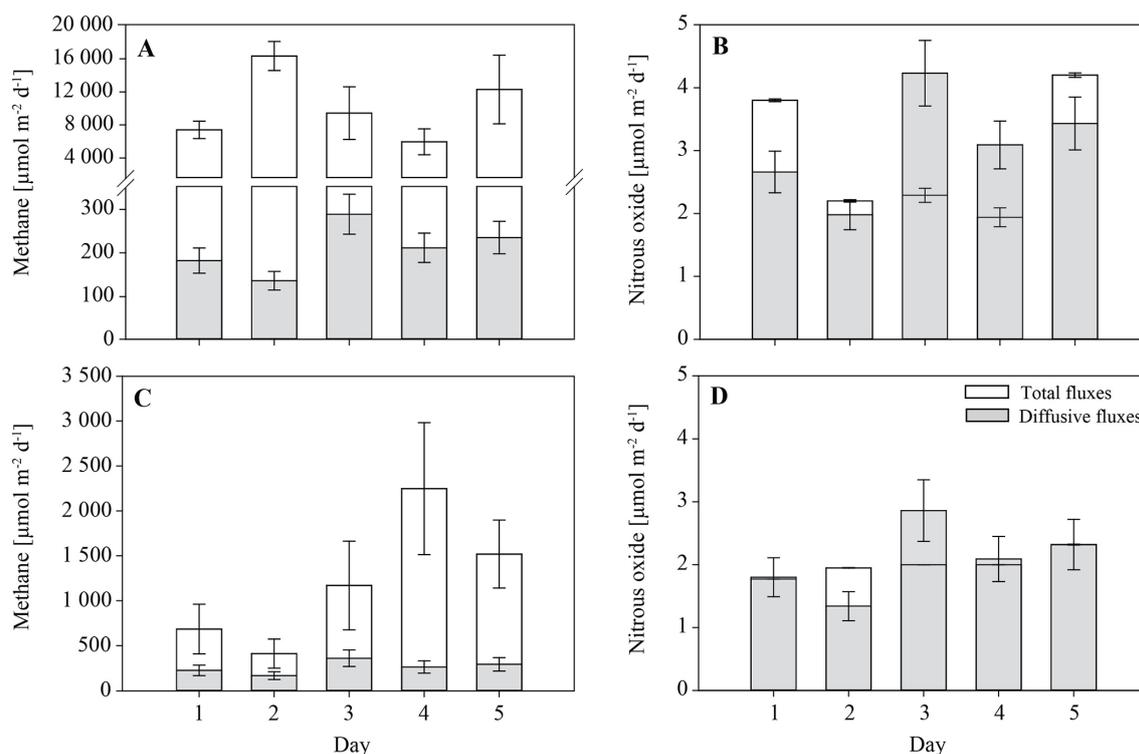


Figure 2. Total and diffusive methane and nitrous oxide fluxes at the shallow sampling site s4 (a, b) and the deep sampling site d7 (c, d) determined over 5 consecutive days. Total fluxes were determined from measurements using the anchored surface floating chambers, and diffusive fluxes were determined using the thin boundary layer model. Fluxes are given as averages \pm SE, $n = 6$.

Table 1. Total water–air methane and nitrous oxide fluxes at the shallow site s4 and the deep site d7 of the detailed study. Fluxes are given as the average determined over the 5 consecutive days \pm SE, $n = 30$.

Site	Total CH ₄ fluxes ($\mu\text{mol CH}_4 \text{ m}^{-2} \text{ day}^{-1}$)	Total N ₂ O fluxes ($\mu\text{mol N}_2\text{O m}^{-2} \text{ day}^{-1}$)
s4	10 423 \pm 1249	2.89 \pm 0.17
d7	1210 \pm 223	2.01 \pm 0.03

N₂O fluxes for both sites. Otherwise, the estimated fluxes exceed the measured fluxes by up to 80 % (Fig. 2b and d; discussed in Sect. 4.1).

The spatial emission study confirmed that the Gold Creek Reservoir is a source of both CH₄ and N₂O (Fig. 3; Table 2). However, the results show that CH₄ fluxes varied much more widely (6300 to 258 535 $\mu\text{mol CH}_4 \text{ m}^{-2} \text{ day}^{-1}$) than N₂O fluxes (0.73 to 1.40 $\mu\text{mol N}_2\text{O m}^{-2} \text{ day}^{-1}$). No significant trend was observed for flux differences between shallow and deep sites for either investigated gas, except that CH₄ emissions at the shallow site s1 exceeded the emissions of all other sites by 1–2 orders of magnitude. CH₄ emissions at site s1 were significantly different (KW- $H_{7,72} = 41.0$, $P < 0.05$) from all other sampling sites, while significant difference was

Table 2. Total water–air methane and nitrous oxide fluxes at sampling sites s1–s4 and d5–d8 of the spatial emission study. Rates are averaged over three surface floating chamber deployments. Sampling sites are numbered from shallowest to deepest site. Fluxes are given as an average \pm SE, $n = 9$.

Site	Total CH ₄ fluxes ($\mu\text{mol CH}_4 \text{ m}^{-2} \text{ day}^{-1}$)	Total N ₂ O fluxes ($\mu\text{mol N}_2\text{O m}^{-2} \text{ day}^{-1}$)
s1	258 535 \pm 37 087	0.73 \pm 0.06
s2	21 381 \pm 6695	1.24 \pm 0.08
s3	20 452 \pm 4164	1.40 \pm 0.06
s4	6726 \pm 2686	1.20 \pm 0.15
d5	28 597 \pm 5411	1.10 \pm 0.10
d6	30 274 \pm 13 023	0.87 \pm 0.05
d7	6300 \pm 932	1.17 \pm 0.08
d8	15 952 \pm 1896	1.22 \pm 0.08

not detected between emissions from the other sites s2–s4 and d5–d8 ($P > 0.05$). The highest CH₄ emissions from the deeper sites were detected at sites d5 and d6, which are both located in the north-western arm of the reservoir close to the shallow site s1. In contrast to this, no clear spatial pattern between sites was observed for N₂O fluxes. Similarly, N₂O fluxes measured amongst four sites, two shallow and two deep sites (s2, s4, d7 and d8), were not significantly

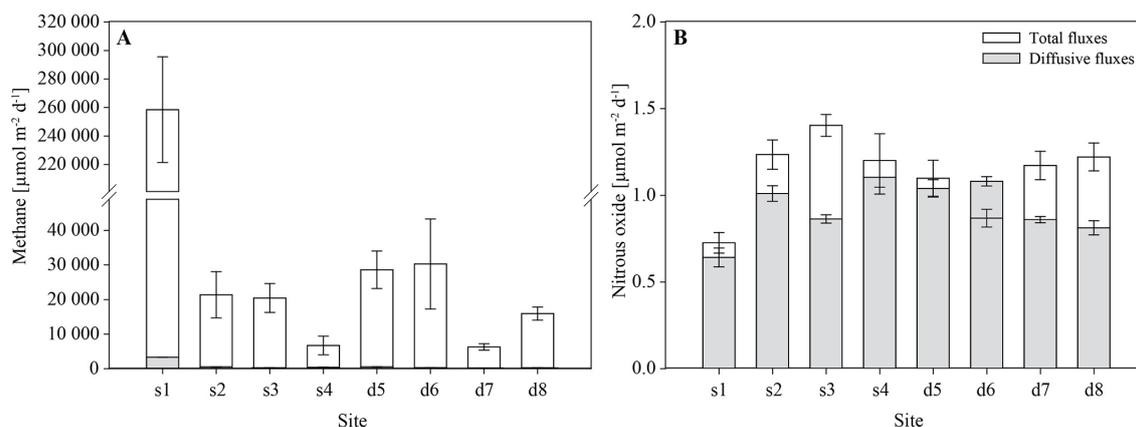


Figure 3. Total and diffusive methane (a) and nitrous oxide (b) fluxes at sampling sites s1–s4 and d5–d8. Total fluxes were determined using the anchored surface floating chambers, and diffusive fluxes were determined using the thin boundary layer model. Rates per site were averaged over three surface floating chamber deployments. Sampling sites are numbered from shallowest to deepest. Fluxes are given as average \pm SE, $n = 9$.

different ($P > 0.05$). However, N₂O fluxes from sampling site d6 were different than all other sites (KW-H_{7,72} = 31.2, $P < 0.01$) apart from s1 and d5 ($P > 0.05$). Interestingly, the lowest N₂O fluxes were measured at the shallow site s1. Comparing total fluxes with diffusive fluxes from all sampling sites showed that in the spatial emission study, diffusive fluxes accounted for 1 to 6 % of the total CH₄ fluxes (Fig. 3a). Diffusive fluxes explain, in five out of the eight sites, 82 to 100 % of total N₂O fluxes; although, at one site, d6, the diffusive flux exceeded (by up to 25 %) the measured total flux (Fig. 3b; discussed in Sect. 4.1).

Wind speed during the spatial emission study (Supplement Fig. S2a) conducted at sites s1–s4 and d5–d8 increased from the first ($1.8 \pm 0.8 \text{ m s}^{-1}$) to the second ($2.8 \pm 1.4 \text{ m s}^{-1}$) chamber deployment as well as from the second to the third ($4.0 \pm 1.2 \text{ m s}^{-1}$) chamber deployment (deployment interval for each floating chamber was 1 h). Averaged chamber N₂O fluxes increased at all sites with increasing wind speed; however, the increase was not significant ($P > 0.05$) (Supplement Fig. S2b). In contrast to this, averaged CH₄ fluxes at all sites did not increase with the increasing wind speed (Supplement Fig. S2c). Total chamber fluxes of each chamber deployment and per sampling site showed low variability for N₂O and high variability for CH₄.

Averaged total chamber CH₄ fluxes were not significantly different ($P > 0.05$) between the two conducted studies (detailed study from March 2012 and spatial emission study from February 2014) for the shallow site s4. However, at the deep site d7, total CH₄ fluxes differed significantly between the two studies (KW-H_{1,39} = 18.2, $P < 0.001$). The total N₂O fluxes at both sites, site s4 and site d7, differed significantly between the two studies (KW-H_{1,39} = 19.1, $P < 0.001$ and $F_{1,37} = 124.6$, $P < 0.001$, respectively).

3.2 Water column parameters

Water column CH₄, N₂O and nutrient concentrations at both sites s4 (Fig. 4a and b; Table 3) and d7 (Fig. 4c and d; Table 3) showed no significant difference ($P > 0.05$) amongst the 5 consecutive experiment days and thus were pooled. The reservoir was characterised by a clear stratification with respect to oxygen (Supplement Fig. S3a). Epilimnetic layers were fully oxic, while metalimnetic layers were suboxic and the hypolimnetic layer at the deep site d7 was anoxic.

The epilimnion at both sites s4 and d7 was supersaturated with CH₄ and N₂O. CH₄ metalimnion concentrations at site s4 were 1 order of magnitude higher than the epilimnion concentrations. At site d7, hypolimnion CH₄ concentrations were approximately 24 000 000 % supersaturated and 2–3 orders of magnitude higher than the meta- and epilimnion concentrations, respectively. N₂O concentrations were comparable for both sites s4 and d7 in the epilimnion and metalimnion. However, N₂O concentrations at site d7 were highest in the epilimnion, not in the hypolimnion. The epilimnetic and metalimnetic CH₄ and N₂O concentrations at site s4 were comparable to the measured concentrations at site d7.

NH₄⁺ concentrations at site s4 were not significantly different ($P > 0.05$) in epilimnion and metalimnion. NO₂⁻ and NO₃⁻ concentrations at site s4 showed slight increases between epilimnion and metalimnion. NH₄⁺ concentrations at site d7 were similar in the epilimnion and metalimnion but 2 orders of magnitude higher in the hypolimnion. NO₂⁻ and NO₃⁻ concentrations at site d7 were not significantly different ($P > 0.05$) within each of the three investigated water column layers. All analysed NH₄⁺, NO₂⁻ and NO₃⁻ concentrations in epilimnion as well as metalimnion were comparable between site s4 and site d7.

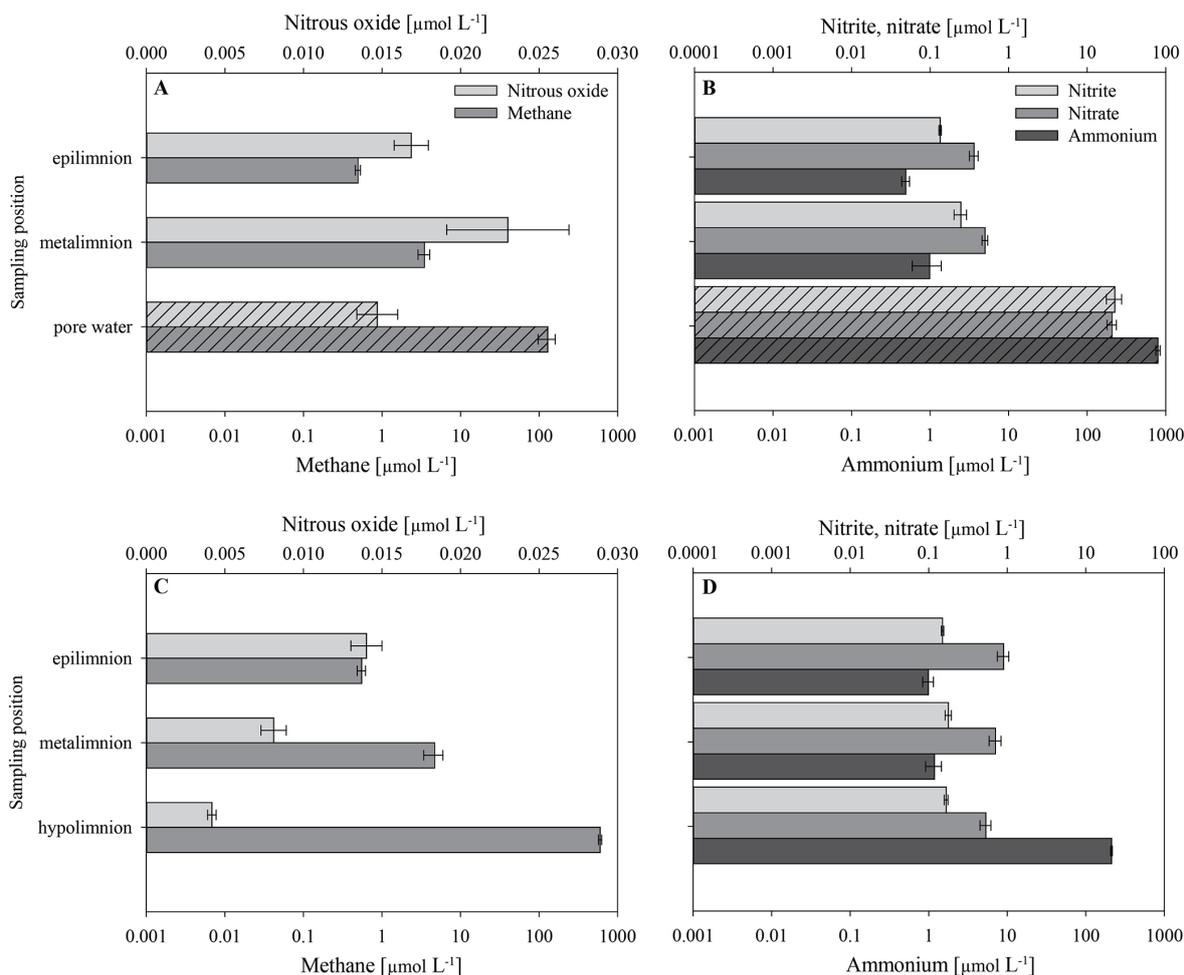


Figure 4. Levels of methane, nitrous oxide and nutrients determined at the shallow sampling site s4 (a, b) and at the deep sampling site d7 (c, d). Results are shown for the epilimnion, metalimnion and for pore water (bars with hatch pattern) at the shallow site s4 and for the epilimnion, metalimnion and hypolimnion at the deep site d7. Methane and nutrient concentrations are plotted on a log scale. Values represent averages \pm SE with the number of replicates being $n = 12$ for water column methane and nitrous oxide, $n = 15$ for nutrient water column samples, $n = 4$ for pore water methane and nitrous oxide and $n = 8$ for pore water nutrients.

3.3 Pore water parameters

The dissolved CH₄ pore water concentrations at site s4 (Fig. 4a; Table 3) were 2 orders of magnitude higher than the concentrations measured in the epilimnion as well as in the metalimnion. The pore waters were approximately 5 000 000 % supersaturated with CH₄ (pore waters were collected from the upper sediment layers and the saturation percent was calculated as done for the water samples). N₂O pore water concentrations at site s4 were comparable to measured concentrations in both investigated water column layers (epilimnion and metalimnion). NH₄⁺ pore water concentrations at site s4 (Fig. 4b; Table 3) were 3 orders of magnitude higher than in the epilimnion and metalimnion. Similarly, the pore water NO₂⁻ and NO₃⁻ concentrations were 2 orders of magnitude higher than in the water column.

3.4 Sediment–water fluxes

CH₄ was consistently produced during the incubations of the site s4 sediments (Fig. 5a, Table 4). N₂O concentrations indicated consumption had occurred; however, these levels were low and near the theoretical detection limit from 72 h onwards (Fig. 5a). Dissolved oxygen was rapidly removed (Table 4) from overlying waters and was not detected after 48 h (Fig. 5a). NH₄⁺ concentrations increased significantly ($F_{3,8} = 6.1$, $P < 0.01$) between the start and end (288 h) of the incubation study. NO₂⁻ concentrations were seen to have increased over time following the same pattern as NH₄⁺, while the NO₃⁻ levels decreased (Fig. 5b; Table 4).

Table 3. Measured methane, nitrous oxide and nutrient concentrations of the detailed study at the shallow site s4 in the epilimnion, metalimnion and pore water and at the deep site d7 in the epilimnion, metalimnion and hypolimnion. Values represent the average \pm SE: $n = 12$ for water column methane and nitrous oxide; $n = 15$ for water column nutrients; $n = 4$ for pore water methane and nitrous oxide and $n = 8$ for pore water nutrients.

Site	Measured parameter	Epilimnion concentration	Metalimnion concentration	Pore water concentration
s4	CH ₄	0.50 \pm 0.04 $\mu\text{mol CH}_4 \text{ L}^{-1}$	3.47 \pm 0.60 $\mu\text{mol CH}_4 \text{ L}^{-1}$	129 \pm 32 $\mu\text{mol CH}_4 \text{ L}^{-1}$
		21 986 \pm 2660 % saturation		
	N ₂ O	0.017 \pm 0.001 $\mu\text{mol N}_2\text{O L}^{-1}$	0.023 \pm 0.004 $\mu\text{mol N}_2\text{O L}^{-1}$	0.015 \pm 0.001 $\mu\text{mol N}_2\text{O L}^{-1}$
		168 \pm 12 % saturation		
	NH ₄ ⁺	0.49 \pm 0.06 $\mu\text{mol NH}_4^+ \text{-NL}^{-1}$	0.99 \pm 0.40 $\mu\text{mol NH}_4^+ \text{-NL}^{-1}$	798 \pm 51 $\mu\text{mol NH}_4^+ \text{-NL}^{-1}$
NO ₂ ⁻	0.13 \pm 0.00 $\mu\text{mol NO}_2^- \text{-NL}^{-1}$	0.25 \pm 0.04 $\mu\text{mol NO}_2^- \text{-NL}^{-1}$	23 \pm 5 $\mu\text{mol NO}_2^- \text{-NL}^{-1}$	
NO ₃ ⁻	0.36 \pm 0.05 $\mu\text{mol NO}_3^- \text{-NL}^{-1}$	0.50 \pm 0.04 $\mu\text{mol NO}_3^- \text{-NL}^{-1}$	21 \pm 3 $\mu\text{mol NO}_3^- \text{-NL}^{-1}$	
Site	Measured parameter	Epilimnion concentration	Metalimnion concentration	Hypolimnion concentration
d7	CH ₄	0.55 \pm 0.07 $\mu\text{mol CH}_4 \text{ L}^{-1}$	4.69 \pm 1.29 $\mu\text{mol CH}_4 \text{ L}^{-1}$	600 \pm 28 $\mu\text{mol CH}_4 \text{ L}^{-1}$
		19 722 \pm 1465 % saturation		
	N ₂ O	0.014 \pm 0.001 $\mu\text{mol N}_2\text{O L}^{-1}$	0.008 \pm 0.001 $\mu\text{mol N}_2\text{O L}^{-1}$	0.004 \pm 0.000 $\mu\text{mol N}_2\text{O L}^{-1}$
		206 \pm 14 % saturation		
	NH ₄ ⁺	0.99 \pm 0.15 $\mu\text{mol NH}_4^+ \text{-NL}^{-1}$	1.18 \pm 0.27 $\mu\text{mol NH}_4^+ \text{-NL}^{-1}$	212 \pm 6 $\mu\text{mol NH}_4^+ \text{-NL}^{-1}$
NO ₂ ⁻	0.15 \pm 0.01 $\mu\text{mol NO}_2^- \text{-NL}^{-1}$	0.18 \pm 0.02 $\mu\text{mol NO}_2^- \text{-NL}^{-1}$	0.17 \pm 0.01 $\mu\text{mol NO}_2^- \text{-NL}^{-1}$	
NO ₃ ⁻	0.90 \pm 0.15 $\mu\text{mol NO}_3^- \text{-NL}^{-1}$	0.71 \pm 0.12 $\mu\text{mol NO}_3^- \text{-NL}^{-1}$	0.53 \pm 0.08 $\mu\text{mol NO}_3^- \text{-NL}^{-1}$	

Table 4. Production and consumption rates of methane, nitrous oxide and nutrients during the sediment incubation study. Positive values indicate production and negative values indicate consumption. Rates are given as an average \pm SE, $n = 3$.

Measured parameter	Production/consumption rates
CH ₄	3616 \pm 395 $\mu\text{mol CH}_4 \text{ m}^{-2} \text{ day}^{-1}$
DO	-38 220 $\mu\text{mol O}_2 \text{ m}^{-2} \text{ day}^{-1}$
NH ₄ ⁺	3874 \pm 1129 $\mu\text{mol NH}_4^+ \text{-N m}^{-2} \text{ day}^{-1}$
NO ₂ ⁻	17 \pm 10 $\mu\text{mol NO}_2^- \text{-N m}^{-2} \text{ day}^{-1}$
NO ₃ ⁻	-8 \pm 5 $\mu\text{mol NO}_3^- \text{-N m}^{-2} \text{ day}^{-1}$

CH₄, NH₄⁺, NO₂⁻, NO₃⁻ production/consumption rates were determined between hour 0 and 288 of the incubation experiment. The DO rate was determined between hour 0 and 48 of the incubation experiment.

4 Discussion

4.1 Surface gas emissions and the dominance of CH₄ ebullition

The water–air flux measurements of the detailed study as well as the spatial emission study showed that the Gold Creek Reservoir was a source of CH₄ and N₂O. Overall CH₄ emissions emitted from the water surface were at least 1–2 (detailed study) or 2–4 (spatial emission study) orders of magnitude higher relative to N₂O in terms of CO₂ equivalents, despite N₂O being a more powerful GHG than CH₄.

The spatial emission study showed high variability of total CH₄ fluxes across and within (amongst chamber deployments) all sampling sites and low variability of total N₂O fluxes, indicating that fluxes were driven by ebullition and diffusion, respectively. These results agree with previous emission findings at sites s4 and d7 of the detailed study. High spatial variability of CH₄ fluxes driven by ebullition has

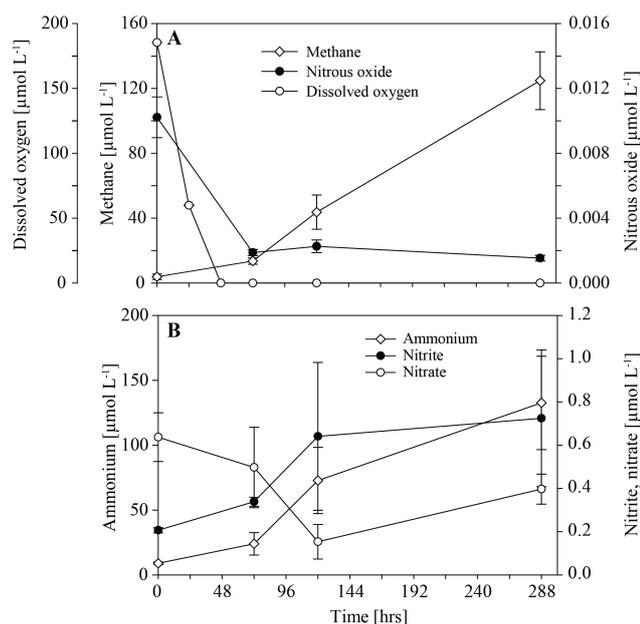


Figure 5. Sediment incubations of the shallow site s4: dissolved oxygen, methane, nitrous oxide (a) and nutrient production or consumption (b). Values represent averages \pm SE, $n = 3$.

been observed in other tropical reservoir studies (Bastviken et al., 2010; DelSontro et al., 2011; Grinham et al., 2011).

A comparison of the measured fluxes determined at the floating chambers and the estimated fluxes determined using the TBL model clearly showed that at all the sites the CH₄ fluxes were mainly driven by ebullition and the N₂O fluxes were mainly driven by diffusion. Our findings confirm those of previous studies, where ebullition has been shown to produce the largest CH₄ emissions compared to the pathways of diffusion and plant-mediated transport. This is especially the case under the conditions of shallow and warm water systems where high CH₄ production rates occur (DelSontro et al., 2011; Devol et al., 1988; Grinham et al., 2011; Joyce and Jewell, 2003; Keller and Stallard, 1994). Gold Creek Reservoir meets those conditions as it is a shallow system (maximum depth of 11.75 m) experiencing warm temperatures (Supplement Fig. S3b) throughout the year. Diffusion is the dominant pathway for N₂O emissions at Gold Creek Reservoir and this has been found in other tropical reservoirs (Guerin et al., 2008).

Estimated N₂O fluxes in some cases exceeded the fluxes measured by the floating chambers. It is likely this anomaly results from inherent errors in both these methods. The estimates were based on one exemplary model for the gas transfer coefficient, k (Wanninkhof, 1992). However, there are various models described that give over- or underestimations of measured fluxes and wide discrepancies in their results (Musenze et al., 2014; Ortiz-Llorente and Alvarez-Cobelas, 2012). In addition, modelled fluxes can be influenced by a number of factors that include rainfall on the water surface

(Guerin et al., 2007; Ho et al., 1997); spatial variations of wind speed (Matthews et al., 2003); heating and cooling of the water surface (Polensnaere et al., 2013; Rudorff et al., 2011); surrounding vegetation; and wind fetch (Cole et al., 2010). Emission rates in this study were modelled with averaged wind speeds for k over the deployment time of 24 h periods (detailed study) and for 1 h periods (spatial emission study). Diurnal changes in wind speed occurred with higher wind speeds during daylight which was when the spatial study was conducted. Therefore, the deployment periods do not provide the same study conditions and could introduce an error; consequently, comparisons of daily rates between the two studies should be treated with caution.

4.2 Factors controlling CH₄ ebullition

Both studies (detailed and spatial emission) showed that ebullition from anoxic sediments was the main contributor to the total CH₄ emissions in this subtropical reservoir. The detailed study showed that ebullitive CH₄ fluxes were higher at site s4 than at site d7. The spatial emission study revealed that ebullitive CH₄ fluxes at site s1 were significantly higher than at all deep sites. These results confirm findings from Bastviken et al. (2004) showing that CH₄ fluxes by ebullition are depth-dependent and higher at water depths of 4 m or less. Ebullition, and ultimately CH₄ emission, can be enhanced when the hydrostatic pressure is reduced which could be a result of current-induced bottom shear stress or the lowering of storage water levels (Joyce and Jewell, 2003; Ostrovsky et al., 2008). The already quite low hydrostatic pressure in the Gold Creek Reservoir (i.e. < 2 atmospheres) favours active ebullition there. The CH₄ in the gas bubbles can escape oxidation during the transport through the water column as CH₄ moves faster through the water column by ebullition than by diffusion (Joyce and Jewell, 2003). Interestingly, however, significantly higher ebullition rates were not found at the other shallow sites (s2–s4) as compared to the deeper sites. Highest CH₄ water–air fluxes of the spatial emission study were generally found at the shallow site s1 and the deep sites d5 and d6, located in the north-western arm of the reservoir. These three sites (s1, d5 and d6) are located where the main water inflow to the reservoir would occur, and these likely receive high amounts of organic matter compared to the other sites. Hence, higher CH₄ production resulting in higher fluxes would occur at these sites. This would also explain why CH₄ fluxes at the shallow sites s2–s4 did not support other findings of depth-dependent fluxes as they likely receive less organic matter than received in the north-western sidearm of the reservoir. The chlorophyll *a* profile indicated that phytoplankton was predominantly present in the upper 2 m of the water column (Supplement Fig. S3c). Phytoplankton were also present in the deeper aphotic layers, suggesting these are a source of organic carbon to the sediments. However, the spatial pattern in ebullition indicates that the major source of organic carbon is generated from the

surrounding catchment as the highest CH₄ flux rates were found adjacent to major inflows where there was intense forest litter deposition. This phenomenon has been observed in other storages within the region (Grinham et al., 2011) and highlights the importance of identifying ebullition hot spots to improve total emission estimates.

The CH₄ fluxes from Gold Creek Reservoir compare well with other reservoirs (Table 5) in the South East Queensland region (e.g. Little Nerang Dam (Grinham et al., 2011) and Baroon Pocket Dam (Grinham et al., 2012)) and even exceeded the rates of younger reservoirs (e.g. Lake Wivenhoe and Baroon Pocket Dam; Grinham et al., 2012). The age of a reservoir is described as one of the parameters affecting GHG fluxes as it is often described that fluxes tend to decline with the reservoir age (Abril et al., 2005; Galy-Lacaux et al., 1999). Barros et al. (2011) used published data from different hydroelectric reservoirs to show that the relationship between CH₄ flux and reservoir age is negatively correlated. However, CH₄ fluxes from reservoirs measured in South East Queensland (Table 5) significantly exceeded the fluxes analysed by Barros et al. (2011), and the older reservoirs in the region showed higher CH₄ emissions rates than the younger reservoirs. This may be explained by intensive, irregular precipitation events that occur in the region, and these would periodically flush high amounts of organic matter into the system. It is likely that these bursts of high organic loadings would allow the ebullitive pathways for CH₄ emissions to persist and maintain high fluxes over time.

4.3 Sources of CH₄ production

Generally, the highest CH₄ concentrations in the Gold Creek Reservoir were found in the hypolimnion and sediments, indicating the sediments as a main source of CH₄. The hypolimnetic CH₄ concentrations were comparable to concentrations found in other stratified, tropical reservoirs (Abril et al., 2005; Galy-Lacaux et al., 1999; Guerin and Abril, 2007). Epilimnetic CH₄ concentrations were 3 orders of magnitude lower than concentrations in the hypolimnion, indicating that a substantial portion of the CH₄ was oxidised by CH₄-oxidising bacteria before reaching the surface waters and the atmosphere, as has been suggested to occur in other tropical reservoirs (Guerin and Abril, 2007; Lima, 2005). These epilimnion concentrations were comparable (Guerin and Abril, 2007) or significantly lower (up to 3 orders of magnitude) than concentrations found in other stratified, tropical reservoirs (Abril et al., 2005). Despite lower CH₄ concentrations in the epilimnion, the reservoir was still supersaturated with CH₄ and a source to the atmosphere.

The laboratory incubations showed that the sediments of Gold Creek Reservoir were a consistent source of CH₄ as the CH₄ concentration steadily increased throughout the incubation period. This supports the findings of the field study where CH₄ sediment pore water concentrations were greatly elevated relative to the surface water concentrations. The

Table 5. The range of methane fluxes across selected reservoirs (covering shallow and deep sites) in South East Queensland.

Reservoir	Commission year	CH ₄ flux ranges (μmol CH ₄ m ⁻² day ⁻¹)
Baroon Pocket Dam (Grinham et al., 2012)	1988	505–251 750
Lake Wivenhoe (Grinham et al., 2012)	1984	95–78 500
Little Nerang Dam (Grinham et al., 2011)	1962	4230–1 403 250
Gold Creek Reservoir (this study)	1885	414–306 302

high methanogenesis rates in the sediments are thus likely driving a significant portion of the water–air CH₄ fluxes measured in this study. Past studies have demonstrated that sediments are a significant CH₄ source (Barros et al., 2011; Canfield et al., 2005). A recent study on a similar reservoir system clearly demonstrated the dominance of methanogenic archaea in the upper 15 cm of the sediment zone (Green et al., 2012). Given the high rates of organic matter loading in these systems, CH₄ production will be an important pathway for organic matter degradation in the sediments. The highly supersaturated concentrations of the pore waters of this relatively shallow reservoir means that any small changes in hydrostatic pressure, e.g. via bottom shear, would likely increase the ebullition rates (Joyce and Jewell, 2003). In comparison of the CH₄ sediment–water fluxes with the CH₄ water–air fluxes from the shallow site s4, it was evident that the sediment efflux (3616 ± 395 μmol CH₄ m⁻² day⁻¹) explained 67 % of the diffusive CH₄ emissions (5400 ± 1250 μmol CH₄ m⁻² day⁻¹) and 35 % of the total CH₄ emissions (10 423 ± 1249 μmol CH₄ m⁻² day⁻¹). This strongly indicates that the fluxes assessed during the sediment incubations in this study were underestimated. The most influential factor for this underestimation is likely the height of the incubated sediment core. With a height of only about 10 cm, the CH₄ production from deeper (also anoxic) sediment layers was not considered.

4.4 Sources of N₂O production or consumption

The sediment incubation study clearly showed that the anoxic sediments were the source of NH₄⁺ for the N₂O production (Fig. 5b). However, N₂O production through either the nitrification or denitrification pathway ultimately requires DO. Dissolved oxygen is introduced into the upper water layer through wind re-aeration or by photosynthetic production. The production of N₂O, therefore, suffers from twin limitations; below the oxycline DO is limiting, whereas above the oxycline, NH₄⁺ is limiting. This confines N₂O production to a narrow band within the water column in deep sites or to upper sediment layers in shallow sites and limits

the degree of supersaturation and, therefore, the likelihood of bubble production. The net result was that N₂O emissions from the water surface predominately occurred through the diffusive pathway.

Our measurements showed that the surface waters were supersaturated with N₂O so the system was acting as a N₂O source to the atmosphere. The elevated N₂O concentrations in the oxic zones (epilimnion and metalimnion) relative to the anoxic zones indicate that nitrification was the predominant production pathway. N₂O consumption occurs in the anoxic hypolimnion and sediments possibly via denitrification as found previously (Guerin et al., 2008; Mengis et al., 1997). The presence of NO₃⁻ within the anoxic zones further supports the likelihood of denitrification.

4.5 Implications

Intensive field and laboratory studies in Gold Creek Reservoir were undertaken to improve the understanding of production/consumption and emission rates of the non-CO₂ GHGs, CH₄ and N₂O. Our results clearly demonstrate that the Gold Creek Reservoir is a source of CH₄ and N₂O to the atmosphere although CH₄ is clearly the dominant gas even when expressed as CO₂ equivalents. N₂O flux rates were in fact much lower than those reported in other reservoirs with similar climates (N₂O fluxes from six reservoirs of three countries (Brazil, Panama, French Guiana) ranged between 3–157 μmol N₂O m⁻² day⁻¹ (Guerin et al., 2008); in comparison, the fluxes in this study range between 0.73–2.89 μmol N₂O m⁻² day⁻¹). Gold Creek Reservoir CH₄ fluxes, on the other hand (53 t CH₄ yr⁻¹; range between 7–290 t CH₄ yr⁻¹), were dominated by ebullitive emissions and were within the range reported for other tropical systems (St. Louis et al., 2000). The exception was the flux measured at the shallowest site (s1) which greatly exceeded even the higher-end range from the young (filled in 1994) Petit Saut Dam in French Guiana (Galy-Lacaux et al., 1997; St. Louis et al., 2000). Barros et al. (2011) determined that the relationship between CH₄ flux and latitude is significantly negatively correlated. CH₄ fluxes from Gold Creek Reservoir (spatial emission study range between 6300–258 535 μmol CH₄ m⁻² day⁻¹), situated at the latitude of 27°45'97" S, significantly exceeded the fluxes presented in that study, which were given to be in general less than 4167 μmol CH₄ m⁻² day⁻¹. The catchment of the Gold Creek Reservoir consists of 98% forest and experiences warm temperatures as well as intense precipitation events that potentially flush high amounts of organic matter into the reservoir throughout the year. These characteristics are in contrast to temperate systems and likely accelerate the CH₄ production in subtropical systems like the Gold Creek Reservoir. The high rates of CH₄ flux that we measured further highlight the importance of studies that focus on subtropical systems. Additionally, studies from tropical freshwater systems are also important as these experience higher

water temperatures than subtropical systems and are thus expected to exhibit even higher surface CH₄ fluxes (Barros et al., 2011). There is a lack of study of Australia's reservoirs in both the tropical and subtropical climate zones, and their contribution as significant CH₄ emitters is not recognised. Future emission studies of these systems would add to the limited knowledge of this region, which is important for inclusion in global GHG estimates.

The spatial variability results of our study further emphasise the importance of including a reasonable spatial resolution when monitoring GHG emissions from water bodies, particularly when measuring CH₄. In addition, monitoring efforts should include measuring CH₄ ebullition as it is the most dominant pathway in these systems. For N₂O, however, assessing only diffusive fluxes is likely sufficient. Our results also suggest that reservoir age is potentially not an important parameter affecting CH₄ fluxes in systems similar to Gold Creek Reservoir. Ultimately, the results presented here are likely to be globally relevant as an increasing number of large reservoirs are being constructed to meet growing water demand, particularly in tropical and subtropical zones, but also because subtropical systems can provide insight into the possible impacts that a warming climate will have on temperate reservoirs.

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