Methane and nitrous oxide sources and emissions in a subtropical freshwater reservoir, south east Queensland, Australia

K. Sturm¹, Z. Yuan¹, B. Gibbes², and A. Grinham¹,²

¹Advanced Water Management Centre (AWMC), The University of Queensland, Level 4, Gehrmann Building, Brisbane, Queensland 4072, Australia
²School of Civil Engineering, The University of Queensland, Level 5, Advanced Engineering Building, Brisbane, Queensland 4072, Australia

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Correspondence to: A. Grinham (a.grinham@uq.edu.au)

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Abstract

Reservoirs have been identified as an important source of non-CO$_2$ greenhouse gases, especially methane (CH$_4$). This study investigates CH$_4$ and nitrous oxide (N$_2$O) sources and emissions in a subtropical freshwater reservoir Gold Creek Dam, Australia using a combination of water–atmosphere and sediment–water flux measurements, water column sampling and pore water analysis. The reservoir was clearly a net source as surface waters were supersaturated with CH$_4$ and N$_2$O. CH$_4$ flux rates were one to two orders of magnitude higher than N$_2$O rates when expressed as CO$_2$ equivalents. Atmospheric CH$_4$ fluxes were dominated by ebullition (> 60 %) relative to diffusive fluxes and ranged from 165 to 6526 mg CO$_2$ eq m$^{-2}$ d$^{-1}$. Dissolved CH$_4$ concentrations in sediment pore waters were approximately 5 000 000 % supersaturated. However, dissolved N$_2$O concentrations were 140 to 220 % supersaturated and generally confined to the water column greatly reducing the likelihood of ebullition. The flux measurements from this study support past findings that demonstrate the potential important contribution of emissions from subtropical reservoirs to overall GHG budgets. Results suggest future efforts to monitor and model emissions that concentrate on quantifying the ebullition pathway for CH$_4$ as this was dominant relative to diffusive fluxes as well as total N$_2$O emissions.

1 Introduction

Methane (CH$_4$) and nitrous oxide (N$_2$O) are powerful greenhouse gases (GHG) and are of emerging environmental concern. Their global warming potentials are 21 and 310 times, respectively, that of carbon dioxide (CO$_2$), seen on a 100 yr time horizon (IPCC, 2007). Reservoirs were shown to be important contributors to GHG emissions, particularly CH$_4$, with wide ranging reported fluxes around the world (St. Louis et al., 2000; Barros et al., 2011; Bastviken et al., 2011) increasing global interest in their measurement, monitoring and modelling GHG concentrations and emissions.
In reservoirs without water release through the dam, the primary \( CH_4 \) emission pathways to the atmosphere are ebullition from sediments, diffusion at the water–air interface and plant-mediated transport from littoral zones (Bastviken et al., 2004). \( CH_4 \) is typically produced by the process of methanogenesis under anaerobic conditions (Canfield et al., 2005) as found in the sediment and hypolimnic zones of a reservoir. However, a mid-water metalimnion in a reservoir is generally associated with large gradients in dissolved oxygen availability that promotes oxidation of \( CH_4 \) via methanotrophic bacteria, which greatly reduces diffusive emissions. \( N_2O \) is primarily produced under oxic conditions (e.g. in epilimnion zone) as a byproduct of nitrification or under anoxic conditions as an intermediate of denitrification (Ward, 1996), which generally occurs in the metalimnion. Therefore both the zone of \( N_2O \) production and dissolved \( CH_4 \) consumption depend on how stratified the aquatic systems are and the location of the oxic–anoxic interface. Processes that lead to \( CH_4 \) and \( N_2O \) generation are relatively well known (Bange, 2006), however, processes controlling \( CH_4 \) and \( N_2O \) water–air fluxes are poorly understood and need further investigation (De Wilde and De Bie, 2000; Dong et al., 2002; Harrison et al., 2005).

Ideal conditions for investigating greenhouse gas emissions are provided by subtropical reservoirs. The generally higher temperatures drive thermal stratification and a rapid deoxygenation of bottom waters (Tundisi and Tundisi, 2012) that enables intensive \( CH_4 \) accumulation and potentially immense emissions (DelSontro et al., 2011). Intermittent and heavy rainfall events can cause high organic matter loads into the water body. This organic matter settles to the benthic zone and together with steep gradients in dissolved oxygen availability in overlying water, provides ideal conditions for the production and transformation processes of \( CH_4 \) and \( N_2O \).

Freshwater reservoirs in Australia are essential for drinking water supply and irrigation purposes as they allow for more storage and greater certainty of supply compared to river and ground water sources. There are over 2300 reservoirs in Australia concentrated in tropical and subtropical zones covering a surface area in excess of 5700 km\(^2\) at full supply (Geoscience Australia, 2004). Despite their prevalence, studies of green-
house gas cycling in subtropical water bodies, particularly in the Southern Hemisphere, are limited (Bastviken et al., 2011). This represents an important gap in our understanding of global emissions as the higher temperatures experienced in the subtropics will likely accelerate greenhouse gas production and consumption. Critical to understanding the net impact of these accelerated rates are detailed studies of representative systems within this region.

The results of an investigation of freshwater reservoir, Gold Creek Dam in southeast Queensland, Australia are presented. The combined investigation of water–atmosphere and sediment–water fluxes, water column sampling and pore water analysis improve the understanding of production and emission rates of CH$_4$ and N$_2$O. Further, the magnitude of the benthic sediment contribution of CH$_4$ and N$_2$O to the water column is examined.

2 Materials and methods

2.1 Site description

Gold Creek Dam (27°45′97″ S, 152°87′86″ E) is located in subtropical south east Queensland, 14 km west of the city Brisbane, Australia. Gold Creek Dam is a medium-size and steep-sided reservoir with limited colonisation of rooted macrophytes, limiting the importance of plant mediated emission pathways. The reservoir has a capacity of 820 000 m$^3$, a surface area of 19 ha and maximum water depth of 11.75 m at full supply. The reservoir’s storage curve showed that approximately 65% of the total storage capacity is within the upper 2 m (Supplement Table S1). Completed in 1885, the reservoir is one of the oldest reservoirs in Australia and was built for the supply of drinking water to Brisbane. The pristine catchment area is 10.5 km$^2$ and consists of 98% of open eucalyptus forest (Queensland Department of Science, 2012) providing high amounts of organic matter in the form of senescent leaves and branches. In contrast to many temperate systems, Gold Creek Dam experiences intensive, intermittent pre-
cipitation events and subsequent inflows especially during the summer months (e.g. 444 mm in 4 days, January 2013, Bureau of Meteorology, 2013). Large quantities of organic matter in the form of forest litter from the surrounding steep catchment, are supplied during these precipitation events. Located in a subtropical region, Gold Creek Dam 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 to 30 °C in summer and bottom water temperatures between 14 to 16 °C at all seasons. The water column was oxygenated in the upper 2 m during all seasons and stratified for ten months a year. Sampling for this study was conducted in March 2012 (autumn), which represented stratified conditions after summer inflows during sampling.

To capture the different deep and shallow zones of the reservoir, two sampling sites (Fig. 1) were chosen for in-situ water–air flux measurements, water column sampling and sediment core sampling for laboratory pore water studies. A deep sampling site was chosen with a water depth of 9 m and was situated in the middle of the reservoir (water depth profile of dissolved oxygen and water temperature, Supplement Fig. S1). A shallow sampling site was located in the northern side arm of the reservoir with a water depth of approximately 2 m. The water columns at both sites incorporated the epilimnion and the upper part of the metalimnion (dissolved oxygen < 1 mg L⁻¹ at 2 m water depth). The shallow sampling site was additionally used for sediment incubation studies in the laboratory with sediment cores from the oxycline zone. During the course of the field experiment water level remained relatively constant at approximately 100 % capacity.
2.2 Field measurements

2.2.1 Water–air flux measurements

Total CH$_4$ and N$_2$O emission fluxes (both ebullitive and diffusive fluxes) at the water–air interface were estimated using anchored surface floating chambers over 5 consecutive days. Gas accumulation of ebullitive and diffusive water–air fluxes in the chambers over time was used for rate calculations. Headspace gas samples for total rates were sampled every 24 h using 12 mL pre-evacuated borosilicate vials (Exetainer, Labco Limited, Lampeter, UK) and a 60 mL syringe with a 23 G × 1.25”, 0.64 mm needle (Livingstone International Pty Ltd, Rosebery, NSW, Australia). The surface floating chambers used are described in Grinham et al. (2011a) and consisted of a floating platform with six small cylindrical PVC chamber units as replicates (volume 0.00048 m$^3$, surface area 0.00583 m$^2$).

Diffusive water–air fluxes were additionally estimated using the thin boundary layer (TBL) model with the equation:

$$F = k \cdot \Delta C = k \cdot (C_w - C_{eq})$$  \hspace{1cm} (1)

where $F$ is the flux (e.g. mmol m$^{-2}$ d$^{-1}$), $k$ is the piston velocity (e.g. m d$^{-1}$) and $\Delta C$ is the gas concentration difference across the water ($C_w$) and air-equilibrium ($C_{eq}$) interface (Cole et al., 2010). Ebullitive emissions were calculated by the difference between total (floating chamber fluxes) and diffusive (TBL model) fluxes. Wind data measurements were logged on the reservoir.

2.2.2 Water column sampling

Water column samples were taken to determine the water column concentrations of CH$_4$ and N$_2$O. Nutrient samples were additionally taken to support the understanding of CH$_4$ and N$_2$O production or consumption pathways. Water samples for GHG (CH$_4$, N$_2$O) and nutrient (ammonia, nitrate, nitrite) analysis were sampled from the epilimnion.
(20 cm below the water surface) and metalimnion (2 m depth) with a 4.2 L Niskin water sampler (Wildco, Wildlife Supply Company, Yulee, FL, USA) over 5 consecutive days. At the deep site, samples were also taken from the hypolimnion (8 m depth). Dissolved GHG were sampled into pre-evacuated borosilicate vials using a 12 mL syringe with a 0.64 mm needle, equilibrated with nitrogen gas to atmospheric pressure and stored at 4 °C until analysis. Nutrient samples were stored in sterile 10 mL vials (Sarstedt AG & Co., Nümbrecht, Germany) and frozen until analysis was carried out. CH$_4$ and N$_2$O as well as nutrient samples were pressure-filtered through 25 mm diameter, 0.22 µm pore-size filters (Merck Millipore, Billerica, MA, USA) before filling the samples in vials.

2.2.3 Pore water sampling

Pore water analyses were carried out to investigate CH$_4$ and N$_2$O concentrations and identifying if the pore waters contribute to GHG sources or emissions, supporting the sediment incubation study (Sect. 2.3). According to the reservoirs storage curve, sediments were collected at the oxycline zone (2 m depth), representing the main storage and oxygenated sediments of the Gold Creek reservoir. Six undisturbed sediment cores from the shallow site 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 corer used had a 2 m pole which limited the collection depth to the shallow site. Collected sediments had a height of 11.54 ± 2.34 cm with an overlying water column of 38.46 ± 2.34 cm. For the pore water analysis, sediment cores were pushed up to the top of the acrylic liners and sediment layers of 2 cm from up to five depths were transferred without headspace into 50 mL test tubes (Falcon tubes, BD Biosciences, San Jose, CA, USA). Upon arrival in the laboratory sediments in the test tubes were spun down in a centrifuge (Eppendorf AG, Hamburg, Germany) for 20 min at 1500 g and the pore water was sampled for nutrient analysis (ammonia, nitrate, nitrite) and GHG (CH$_4$, N$_2$O) concentrations (sampling as described previously).
2.3 Sediment incubation study

To determine the magnitude of the benthic sediment contribution of CH$_4$ and N$_2$O to the water column, sediment incubations were conducted in the laboratory. Six replicates of undisturbed sediment core samples were collected at the shallow site with a gravity corer as described previously. 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 brought in a short amount of time (< 4 h) to the laboratory, 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 by 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 system hanging from the top of the liner (movement propelled by additional magnetic stirrer bars rotating at the outside of the cores). Long term underwater light loggers (Odyssey photosynthetic active radiation recorders, Dataflow Systems Pty Limited, Christchurch, New Zealand) were deployed in situ at approximately 0.25 m intervals ranging from above water surface to 1.25 m depth. Results from in situ deployments helped to determine the light conditions that the cores should be incubated within and revealed strong light attenuation with the photic zone less than 1–0.5 m (Supplement Fig. S2). Therefore, the incubators sides were covered with aluminum foil and light blocking cloth at the top during the experiments to mimic the sediment collection conditions of below the photic zone.

The top cover of the incubators was only removed for sampling purposes. The core liners were capped 15 h after sampling using plexiglas lids with O-rings excluding air bubbles. The lids contained three ports for sampling, refilling the amount of sample water with site water and oxygen measurements (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. Oxygen and temperature of the water column above all sediment cores were monitored using an optical dissolved oxygen probe (PreSens, Precision Sensing GmbH, Regensburg, Germany) before the core liners were capped and every subsequent 24 h until the experiment finished. GHG (CH$_4$, N$_2$O) and nutrient (ammonia, nitrate, nitrite) samples were taken before the sediment cores were capped and after 72, 120 and 288 h. Daily flux rates were determined from the rate of change in the concentration and corrected for the core volume and sediment surface area.

### 2.4 Analyses

Both gaseous and liquid samples were analysed for CH$_4$ and N$_2$O concentrations by 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 CH$_4$ and N$_2$O, respectively. The gas chromatograph was calibrated using standards with a range of $1.8 \pm 0.02$–$249.8 \pm 1.3$ ppm for CH$_4$ and $0.5 \pm 0.01$–$50.53 \pm 0.51$ ppm for N$_2$O which were prepared from certified gas standards (BOC gases, Brisbane, Australia). A Lachat QuickChem 8000 Flow Injection Analyser (Lachat Instrument, Milwaukee, WI, USA) was used for the analysis of ammonia, nitrate and nitrite concentrations.

Statistical analysis 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 between sampling sites one-way ANOVAs were performed with the two sites or different sampling days as the categorical predictor and CH$_4$, N$_2$O or nutrients as the continuous variables. Post hoc tests were performed using Fisher’s LSD (least significant difference) Test (Zar, 1984).
3 Results

3.1 Water–air flux measurements

The Gold Creek Dam was a source of CH$_4$ and N$_2$O. Total in-situ CH$_4$ (deep site: 20 ± 12 mg m$^{-2}$ d$^{-1}$; shallow site: 167 ± 64 mg m$^{-2}$ d$^{-1}$) and N$_2$O (deep site: 0.09 ± 0.01 mg m$^{-2}$ d$^{-1}$; shallow site: 0.13 ± 0.05 mg m$^{-2}$ d$^{-1}$) floating chamber flux rates were similar across the monitoring days and showed significantly different ($F_{1,8} = 43.2$, $p < 0.001$) CH$_4$ rates, with highest rates at the shallow site, but no significantly different N$_2$O rates between the shallow and deep site. Total floating chamber and diffusive TBL emissions expressed as CO$_2$ equivalents showed that CH$_4$ flux rates (Fig. 2a) were one order of magnitude higher than N$_2$O (Fig. 2b) for the deep site and two orders of magnitude higher for the shallow site. Results from the deep site showed that diffusive fluxes account for 12–41% of the total CH$_4$ fluxes and 68–100% for total N$_2$O fluxes. However, the shallow site showed that diffusive fluxes explain less than 3% of the total fluxes for CH$_4$ but 70–100% for N$_2$O.

3.2 Water column and pore water sampling

Water column greenhouse gas and nutrient results at both sites showed no significant difference among the 5 consecutive experiment days and thus were pooled. Samples from the epilimnion (Figs. 3a and 4a) experienced oxic conditions; however, samples from the metalimnion at both sites (Figs. 3b and 4b) had low oxic conditions and samples from the hypolimnion (8 m depth) at the deep site (Fig. 3c) as well as pore water at the shallow site (Fig. 4c) anoxic conditions. The deep site had epilimnic concentrations comparable to the shallow site of CH$_4$ (deep site: 551 ± 221 nmol L$^{-1}$, shallow site: 494 ± 137 nmol L$^{-1}$) and N$_2$O (deep site: 14 ± 4 nmol L$^{-1}$, shallow site: 17 ± 4 nmol L$^{-1}$). The epilimnion at both sites was supersaturated with CH$_4$ (deep site: 19 722 ± 5,480 saturation%, shallow site: 21 986 ± 8,821 saturation%) and N$_2$O (deep site: 206 ± 53 saturation%, shallow site: 168 ± 39 saturation%).

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At the deep site, hypolimnion \( \text{CH}_4 \) concentrations \((600\ 237 \pm 111\ 552\ \text{nmolL}^{-1})\) were 2 to 3 orders of magnitude higher than the mete- and epilimnion concentrations, respectively. However, \( \text{N}_2\text{O} \) concentrations at the deep site were highest in the epilimnion \((14 \pm 4\ \text{nmolL}^{-1})\), not in the hypolimnion \((4 \pm 1\ \text{nmolL}^{-1})\). Ammonia concentrations at the deep site were similar in the epilimnion and metalimnion but two orders of magnitude higher in the hypolimnion. Nitrite and nitrate concentrations at the deep site were not significantly different in all three investigated reservoir layers.

\( \text{CH}_4 \) metalimnion concentrations \((3467 \pm 2313\ \text{nmolL}^{-1})\) at the shallow site were one order of magnitude higher than the epilimnion concentrations. However, the dissolved \( \text{CH}_4 \) pore water concentrations \((128\ 788 \pm 63\ 119\ \text{nmolL}^{-1})\) at the shallow site were two orders of magnitude higher than the metalimnion concentrations and approximately 5,000,000 % supersaturated (pore waters were collected from the upper sediment layers and saturation percent calculated as per water samples.). \( \text{N}_2\text{O} \) concentrations at the shallow site in all water column layers (epilimnion and metalimnion, no hypolimnion) and pore waters were comparable, but variable (140–220 %). Ammonia concentrations at the shallow site were not significantly different in epilimnion and metalimnion but two orders of magnitude higher in the pore waters.

### 3.3 Sediment incubation study

Sediment incubations (Fig. 5a) at the shallow site showed that the sediments were consistently producing \( \text{CH}_4 \) \((151 \pm 29\ \mu\text{molm}^{-2}\ \text{h}^{-1})\). \( \text{N}_2\text{O} \) concentrations indicated consumption but were already under the theoretical detection limit at the analysis of the 72 h incubation samples. Changes in dissolved oxygen and nutrient concentrations followed similar patterns with each replicate core incubation. Dissolved oxygen was rapidly removed \((-51\ \mu\text{gO}_2\ \text{m}^{-2}\ \text{h}^{-1})\) from overlying waters with zero oxygen concentration at measurement after 48 h (Fig. 5a). Ammonia \((161 \pm 81\ \mu\text{molm}^{-2}\ \text{h}^{-1})\) concentrations increased significantly between start and end of the incubation study \((F_{3,8} =\)
Nitrite (0.69 ± 0.72 µmol m⁻² h⁻¹) concentrations increased slightly over time whilst nitrate (−0.32 ± 0.35 µmol m⁻² h⁻¹) decreased (Fig. 5b).

4 Discussion

4.1 Water–air flux measurements

It was shown that ebullition from anoxic sediments was the main contributor main contributor of total CH₄ emissions, while diffusive fluxes were dominant for N₂O emissions. However, ebullitive CH₄ fluxes were higher at the shallow site confirming findings from Bastviken et al. (2004) showing that CH₄ flux rates by ebullition are depth-dependent and higher at water depths of 4 m or less. Despite N₂O being a more powerful greenhouse gas than CH₄, overall the dominant non-CO₂ greenhouse gas emitted from the water surface in terms of carbon dioxide equivalents (CO₂ eq) was CH₄ by at least one order of magnitude for the deep site and two orders of magnitude for the shallow site. Future studies that monitor and model non-CO₂ greenhouse gas emissions should concentrate on quantifying the ebullition pathway for CH₄ as this was the dominant pathway relative to diffusive fluxes and CH₄ showed 1 to 2 orders of magnitude higher emissions than N₂O. The methane flux rates measured in this study (deep site: 165–900 mg CO₂ eq m⁻² d⁻¹, shallow site: 2458–6526 mg CO₂ eq m⁻² d⁻¹) were within the ranges for other tropical reservoirs reported in the literature (e.g., Barros et al., 2011). The CH₄ fluxes from Gold Creek reservoir compare well with other reservoirs (Table 1) in south east Queensland (i.e., Little Nerang Dam in Grinham et al., 2012) and even exceeded rates of younger reservoirs (i.e., Baroon Pocket dam; Grinham et al., 2012). The age of a reservoir is described as one of the parameters affecting greenhouse gas fluxes with the often described expectation that fluxes tend to decline with reservoir age (Abril et al., 2005; Barros et al., 2011; Galy-Lacaux et al., 1999). The older reservoirs examined in south east Queensland however, showed higher CH₄ emissions rates than younger reservoirs, suggesting that reservoir emissions in this
study region are not related to an increasing reservoir age. It is likely the high organic loading allows the ebullitive pathways for CH$_4$ emissions to persist and maintain high flux rates over time.

4.2 Water column and pore water sampling

The deep sampling site showed clear accumulation of CH$_4$ in the 8 m deep hypolimnion zone. Epilimnic CH$_4$ concentrations were three orders of magnitude lower than in the hypolimnion, indicating that a substantial portion of the CH$_4$ was oxidised by methane-oxidising bacteria before reaching the surface waters and the atmosphere. The shallow sampling site indicated that the production of CH$_4$ was in the sub-oxic metalimnion and especially in the pore waters. Generally, highest CH$_4$ concentrations in the Gold Creek Dam were found in the hypolimnion and sediments, indicating the sediments as a main source of CH$_4$. Despite lower CH$_4$ concentrations in the epilimnion, the reservoir was supersaturated with CH$_4$ and a source to the atmosphere. Ammonia concentrations at the deep site were two orders of magnitude higher in the anoxic hypolimnion than in epilimnion and metalimnion. Studies showed that the release of ammonia from sediments is controlled by the concentration of dissolved oxygen present in the overlying water column and is highest from anoxic sediments (Beutel, 2006).

Ammonia release from anoxic reservoir sediments can be explained by the inhibition of nitrification, thus resulting in the accumulation of ammonia in pore water released to the overlying water column and ammonia assimilation (Rysgaard et al., 1994; Beutel et al., 2008). The production zone of N$_2$O was found in the oxic epilimnion zone. Results indicated N$_2$O consumption in the anoxic hypolimnion and sediments. N$_2$O concentrations were generally confined to the water column thus greatly reducing the likelihood of ebullition. All samples showed that the surface waters were supersaturated with N$_2$O, acting as N$_2$O sources to the atmosphere. Mengis et al. (1997) found in a comprehensive study of prealpine lakes examining N$_2$O sources and sinks, that N$_2$O concentrations were strongly correlated to oxygen consumption. The study showed that N$_2$O production zones were found to be in all oxic parts of epilimnion and metalimnion. The
lower concentrations of N$_2$O in the anoxic zones were likely due to diffusion dilution and/or by N$_2$O reduction to nitrogen gas (Mengis et al., 1997). N$_2$O emissions appear to be limited to the diffusive pathway as the production of N$_2$O suffers from twin limitation, below the oxycline dissolved oxygen is limiting whilst above the oxycline ammonia becomes limiting. This confines N$_2$O production to a narrow band within the water column/sediment continuum and limits the degree of supersaturation and, therefore, the likelihood of bubble production.

### 4.3 Sediment incubation study

Sediment incubations at the shallow site showed that the sediments of Gold Creek Dam were a consistent source of CH$_4$, supporting the findings of the pore water analysis. Green et al. (2012) analysed the bacterial and archaeal sediment community in the subtropical Lake Wivenhoe (south east Queensland), located in close distance to the Gold Creek Dam. They found based on their 16S rRNA sequence studies archaea related to methanogens (*Methanomicrobiales, Methanoseta, Methanobacterium*) and suggested that the sedimentary CH$_4$ production of Lake Wivenhoe is due to methanogenic hydrogen/carbon dioxide reduction and acetoclastic methanogenesis. These findings could also explain the CH$_4$ production of the Gold Creek Dam and suggest including analyses of sediment communities in future studies for further insight. However, the study also demonstrated limited production of N$_2$O occurred from sediments. The rapidly removed dissolved oxygen from overlying waters showed rates at least 3 times higher than observed in other monitored water reservoirs (i.e. Lake Wivenhoe, Little Nerang Dam) of south east Queensland (Grinham et al., 2011b). The sediment incubation study showed significant increases in ammonia. Sediment remineralisation of organic matter under anaerobic conditions provides the basis of N$_2$O emission indirectly through the high rates of ammonia diffusion towards the oxycline. Whilst the sediments are not a direct source of N$_2$O they play a crucial role in its formation.
5 Conclusions

Intensive field and laboratory studies of two sites of the Gold Creek Dam were undertaken to improve the understanding of production and emission rates of the non-CO₂ GHG, CH₄ and N₂O from the sediments through the water column and to the atmosphere. These results clearly demonstrated that the Gold Creek Dam was a source of CH₄ and N₂O with CH₄ up to two orders of magnitude higher when expressed as CO₂ equivalents, despite N₂O having a higher global warming potential. The present study adds to the limited but conclusive body of knowledge that tropical reservoirs are important as a GHG source, especially of CH₄. The investigated reservoir has shown to be a subtropical stratified system with high CH₄ concentrations in the hypolimnion and sediment pore waters, indicating high CH₄ production levels, and thus leading to CH₄ being the dominant GHG released. Sediment incubations of this study showed clear CH₄ effluxes supporting that the sediments are a consistent source of CH₄. This is in contrast to N₂O where highest concentrations were from the aerobic water zone and fluxes to the atmosphere were controlled by diffusion. These study findings emphasise the importance of future studies which should focus on modeling and further monitoring of CH₄ fluxes by ebullition and N₂O fluxes by diffusion, especially in subtropical water systems. Comparisons to other regional, subtropical water bodies suggest that the reservoir age is not a key parameter affecting greenhouse gas fluxes in this region. The presented results are likely to be globally relevant as an increasing number of large dams are being constructed to meet the growing water demand. Moreover, within a warming climate, subtropical systems can provide insight into future changes likely to occur in temperate systems.

Supplementary material related to this article is available online at http://www.biogeosciences-discuss.net/10/19485/2013/bgd-10-19485-2013-supplement.pdf.
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Table 1. Range of methane emission rates from reservoir sites located in south east Queensland. Flux ranges presented as carbon dioxide equivalents.

| Reservoir             | Commission year | Methane flux ranges (mgCO₂ m⁻² d⁻²) |
|-----------------------|-----------------|-------------------------------------|
| Baroon Pocket Dam     | 1988            | 202–259                             |
| Lake Wivenhoe         | 1984            | 38–379                              |
| Little Nerang Dam     | 1962            | 1692–5310                           |
| Gold Creek Dam        | 1885            | 2458–6526                           |
Fig. 1. Map with the sampling sites at Gold Creek Dam, south east Queensland, Australia.
Fig. 2. Total and diffusive methane (A) and nitrous oxide (B) emissions from both monitoring sites of the Gold Creek Dam over five consecutive days. Values represent average ± SD, n = 6 and are plotted on a log scale.
Fig. 3. Epilimnion (A), metalimnion (B) and hypolimnion (C) greenhouse gas and nutrient results from the deep monitoring site. Methane, ammonia, nitrite and nitrate values are plotted on a log scale. Values represent average ± SD, \( n = 12 \) for GHG/\( n = 15 \) for nutrient water column results.
Fig. 4. Epilimnion (A), metalimnion (B) and pore water (C) greenhouse gas and nutrient results from the shallow monitoring site. Methane, ammonia, nitrite and nitrate values are plotted on a log scale. Values represent average ± SD, \( n = 12 \) for GHG, \( n = 15 \) for nutrient water column results and \( n = 4 \) for GHG, \( n = 8 \) for nutrient pore water results.
Fig. 5. Sediment incubation greenhouse gas, dissolved oxygen (A) and nutrient (B) study results from the shallow monitoring site of the Gold Creek Dam. Values represent average ± SE, \( n = 3 \).