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Quantifying groundwater carbon dioxide and methane fluxes to an urban freshwater lake using radon measurements

Mahmood Sadat-Noori, Helen Rutlidge, Martin S. Andersen, William Glamore

Water Research Laboratory, School of Civil & Environmental Engineering, UNSW Sydney, NSW 2052, Australia

Corresponding author:

Mahmood Sadat-Noori, Water Research Laboratory, School of Civil & Environmental Engineering, UNSW Sydney, 110 King St., Manly Vale, NSW, 2093, Australia

Email: m.sadat-noori@unsw.edu.au

Tel: (+61) 2 8071 9879

Abstract

Freshwater lakes can play a significant role in greenhouse gas budgets as they can be sources or sinks of carbon to the atmosphere. However, there is limited information on groundwater discharge being a source of carbon to freshwater lakes. Here, we measure CO_2 and CH_4 in the largest urban freshwater lake in the metropolitan area of Sydney (Australia) and quantify groundwater discharge rates into the lake using radon (^{222}Rn, a natural groundwater tracer). We also assess the spatial variability of radon, CO_2 and CH_4 in the lake, in addition to surface water and groundwater nutrient and carbon concentrations. Results revealed that the lake system was a source of CO_2 and CH_4 to the atmosphere with fluxes of 113 ± 81 and 0.3 ± 0.1 mmol/m^2/d, respectively. These calculated CO_2 fluxes were larger than commonly observed lake fluxes and the global average flux from lakes. However, CH_4 fluxes were lower than the average global value. Based on the radon mass balance model, groundwater discharge to the lake was 16 ± 10 cm/d, which resulted in groundwater-derived CO_2 and CH_4 fluxes contributing 25 and 13% to the overall greenhouse gas emissions from the lake, respectively. Radon, CO_2 and CH_4 maps showed similar spatial distribution trends in the lake and a strong relationship between radon, NO_3 and NH_4 suggested groundwater flow was also a driver of nitrogen into the lake from the western side of the lake, following the general regional groundwater flow. This work provides insights into groundwater and greenhouse gas dynamics in Sydney's largest urban freshwater lake with two implications for carbon budgets: to incorporate urban lakes in global carbon budgets and to account for, the often ignored, groundwater discharge as a source of carbon to lakes.

Keywords: Groundwater discharge, greenhouse gasses, wetland, nutrient, carbon budget, DIC, DOC, lakes.

1 Introduction

Freshwater lakes occupy ~2% of the earths land surface (Lehner and Döll, 2004; Raymond et al., 2013), yet they contribute around 10% of the total global carbon dioxide (CO_2) emissions to the atmosphere (Deng et al., 2011). Although they constitute a small fraction of the land surface, lakes also emit large amounts of methane (CH_4) to the atmosphere, potentially equal to 25% of the global terrestrial carbon sink (Bastviken et al., 2011). Due to the disproportionate contribution of greenhouse gas evasion from lakes, relative to size, in the global carbon cycle, further assessment to reduce uncertainties regarding their contribution is warranted (DelSontro et al., 2018; Tranvik et al., 2009). This can be investigated by quantifying dissolved CO_2 and CH_4 concentrations throughout the water column, which ultimately provides the quantification of the total diffusive CO_2 and CH_4 evasion to the atmosphere (Gonzalez-Valencia et al., 2014).

Despite increasing evidence of the large quantities of greenhouse gas evasions from lakes, estimated evasions are still subject to uncertainty mainly due to a paucity of data (Regnier et al., 2013). Current literature indicates that direct measurements of pCO_2 and pCH_4 for lakes are necessary worldwide and the vast majority of reported gas flux measurements were made during warm seasons (DelSontro et al., 2018). Additional studies that are representative of winter CO_2 and CH_4 flux measurements are particularly needed as they could be different than during other seasons due to changes in processes controlling carbon cycling in lakes, such as variations in temperature and surface water runoff (Holgerson and Raymond, 2016; Kortelainen et al., 2006; Raymond et al., 2013). Assessments and quantification of greenhouse gases are not distributed evenly across the globe, with most studies biased towards Europe and North America (Cole et al., 2007; Raymond et al., 2013). Hence, Southern Hemisphere temperate and tropical locations are widely under-represented in global estimates (Gerardo-Nieto et al., 2017; Maher and Eyre, 2012; Staehr et al., 2012). As such, it is important to provide estimates from data-limited regions which will improve global estimations of greenhouse gas fluxes from freshwater lakes and feed into global climate models (Li et al., 2018; Sadat-Noori et al., 2017).

Freshwater lakes are typically supersaturated in CO_2 and CH_4, relative to equilibrium with the atmosphere. These elevated greenhouse gas concentrations are associated with organic matter that are respired in-situ (Cole et al., 1994; Marcé et al., 2015; Regnier et al., 2013). Sources of organic carbon in lakes can be autochthonous, especially in eutrophic lakes, where large amounts of nutrient input contributes to organic matter production (Grasset et al., 2018). On the other hand, surface water runoff is typically considered the primary source of allochthonous organic matter input to lakes (Aufdenkampe et al., 2011). However, recent studies have revealed that groundwater discharge can also act as a hidden pathway for delivering dissolved organic and/or inorganic carbon to inland and aquatic systems (Jahangir et al., 2012; Lupon et al., 2019; Sadat-Noori et al., 2016a). As such, groundwater inputs may drive surface water systems towards increased CO_2 and CH_4 concentrations and consequently high water-air fluxes.

Groundwater discharge into surface waters is usually volumetrically smaller than surface water runoff, however, groundwater usually contains higher concentrations of dissolved constituents making minor volumetric inputs potentially significant (Kessler and Harvey, 2001; Monger et al., 2015). Despite its influence, groundwater discharge is usually overlooked in carbon budgets, due to challenges in identifying groundwater discharge locations and quantifying inputs as groundwater discharge is spatially variable and patchy or has a diffusive nature (Burnett et al., 2006; Sadat-Noori and Glamore, 2019). Natural groundwater tracers, such as radon (^{222}Rn), are useful tools that can overcome such challenges, by enabling investigation of groundwater discharge both spatially and quantitatively (Burnett et al., 2006; Burnett and Dimova, 2012; Peterson et al., 2019). Radon's noble gas characteristics make it chemically very inert. Because it is a gas and has a low half-life of 3.8 days, it typically has distinctly higher concentrations in groundwater compared to surface water. Therefore, if detected in surface waters, it implies recent (within days) groundwater discharge (Burnett, 2008). These properties make radon tracing an effective tool for tracing groundwater discharge and its associated inputs into surface waterbodies such as lakes (Dimova et al., 2013; Sadat-Noori et al., 2016b).

In this study we measure CO_2 and CH_4 in Sydney's largest urban freshwater lake, (Manly, NSW, Australia) and quantify fluxes of CO_2 and CH_4 at the water-air interface. Through continuous measurements of surface water radon and greenhouse gases and groundwater sampling of carbon, nutrient, greenhouse gases at several locations across the lake, we quantify groundwater discharge and its contribution to the overall greenhouse gas evasion fluxes from the lake. We show that groundwater discharge in our instance plays an important role in driving greenhouse gas fluxes. This is likely to be the case for other lakes with groundwater discharge.

2 Material and Method

2.1 Study site

The study site is located in Sydney, New South Wales, Australia, (34°46’3’’ S, 151°14’52’’ E). The lake has an elevation of 35 meters (Australian Height Datum, AHD), a volume of 16×10^5 m^3, a catchment area of 5.5 km^2 and a surface area of about 0.3 km^2 (Warringah Council, 2015). The location has a temperate climate with a long-term average daily minimum and maximum temperature ranging from 13.8 °C to 21.8 °C. The area receives an average annual rainfall of 1213 mm. The geological formation of the area is mainly the Middle Triassic Hawkesbury sandstone and local thin lacustrine deposits within the lake. Most of the catchment (70 %) is covered by native Australian Eucalyptus forest with over 300 native plant species. Pollution from residential development around the upper catchment (10 %) and a golf course (11 %) are of concern as green algae blooms are observed most of the year (Smith et al., 2003).

2.2 Surface water sampling

Fieldwork was carried out in June and July 2019 (Austral winter) to measure water quality parameters, radon, carbon, nutrients, and greenhouse gases. An automated radon-in-air-detector (RAD7, Durridge Co.) modified for water measurements, was used to sample radon concentrations at 10 min intervals giving 2σ uncertainties of 20–30% for each data point. An Ultraportable Greenhouse Gas Analyzer (UGGA, Los Gatos Research) was used to measure dissolved pCO_2 and fCH_4 in-situ with data averaged over 1 min intervals and 2σ uncertainties of <5%. The instrument reports partial pressure of CO_2 (pCO_2) and methane fugacity.

All instruments were mounted on a canoe and transported along the banks of the lake at a slow speed < 1 km/h. A Garmin handheld GPS was used to mark the location of each discrete sampling point and track movement. Continuous and discrete samples were taken along the lake edge where average water depth was approximately 1 m. To measure radon and greenhouse gases, a continuous flow of surface water was pumped at about 2.5 litres per minute from 30 cm below the surface into a gas equilibration device (GED) (Dulaiova et al., 2005). Dissolved gasses (e.g., radon) and air reach equilibrium in the GED and a pump transfers the equilibrated air through drierite before it is passed through the RAD7 and the UGGA and then returned to the GED. In this set up, an equilibrium time of around 5, 20 and 30 minutes is required for CO_2, CH_4 and radon, respectively (Santos et al., 2012; Webb et al., 2016).

The partitioning of radon between the gas and the liquid phase is calculated based on surface water salinity and temperature (Schubert et al., 2006). The concentration of radon in the air-phase is determined by counting the positively charged alpha emitting Po-218 and Po-214, detected by a silicon detector. The Po-218 has a half-life of 3.04 minutes and reaches secular equilibrium in around 15 minutes, making it an ideal tracer for spatial measurements of groundwater discharge/seepage (Schubert et al., 2012). The fugacity of CH_4 was converted to concentrations based on the solubility coefficient of water estimated as a function of salinity and temperature (Wiesenburg and Guinasso Jr, 1979).

A calibrated water quality multiparameter sonde (YSI EXO_2) was set to measure surface water physical and chemical parameters, every 10 minutes, including water temperature (±.01 °C), conductivity (±0.001 mS/cm), dissolved oxygen (±0.2 mg/L) and pH (±0.1 units). Additionally, the concentrations of fluorescent dissolved organic matter (fDOM), in relative fluorescence units (RFU), were measured using the same EXO_2 and was used as a proxy for dissolved organic matter distribution in the surface water of the lake.

Ten surface water grab samples were collected at various locations around the lake. A polypropylene syringe was used to collect samples in 60 ml falcon tubes for dissolved carbon and nutrients after filtering through 0.45 µm cellulose acetate filters. The falcon tubes were filled to exclude headspace and samples were immediately placed in an insulated container filled with ice and processed for carbon and nutrients within 3 days of collection following standard protocols (Rutlidge et al., 2014). Spatial maps were created by interpolation of point data in Esri, Arc GIS 10.5. The Inverse Distance Weighted (IDW) model was used for interpolation as it outperforms other interpolation models such as kriging, cokriging, and Thin Plate Spline (Sadat Noori et al., 2013) .

2.3 Radon diffusion from sediments and ingrowth

To calculate radon diffusion from the sediments a depth-independent approach following Equation (1) was used (Corbett et al., 1998).

$$J_{dif} = (\lambda D_s)^{0.5}(C_{eq} - C_W) \tag{1}$$

where, λ is the radon decay constant (0.181/day); D_s is the effective wet bulk sediment diffusion coefficient in sediment (m^2/day); C_{eq} and C_W are the average radon concentration in groundwater and surface water (Bq/m^3). The D_s parameter was calculated as a function of temperature, $D_s = \phi\left(10^{\,-[(980/T)+1.59]}\right)$ (Schaefer et al., 2012), while porosity was considered

0.3 for the sediment type (sandstone) of the study site (Manger, 1963). To estimate the contribution of radon due to the decay of its parent isotope (radium-226), two 40 L containers were collected from the lake and filtered through columns with 15 – 20 g of manganese oxide fibre which absorb radium-226 (Moore, 2003). The fibres were sealed after sampling and after 5 half-lives analysed for radium-226 concentrations following the method by Kim et al. (2001).

2.4 Groundwater sampling

Eight shallow groundwater samples were collected using a push point piezometer inserted 0.5 – 1.2 m below the sediment surface, avoiding any contamination by surface water (Charette and Allen, 2006). After purging the bores with a peristaltic pump and field parameters stabilising, a sample was collected. Prior to sampling the tubing was flushed with the sample water. For each groundwater sample, a calibrated handheld HACH multiprobe (HQ40d) was used to measure electrical conductivity, dissolved oxygen, temperature, and pH. Grab samples were collected for dissolved carbon and nutrient analysis following a similar procedure described for surface water samples. Samples for radon, CO_2 and CH_4 were collected in gas tight 250 ml glass bottles. Each bottle was connected to a RAD H_2O gas extraction device before the extracted gases were led into the RAD7 for radon measurements and the UGGA for CO_2 and CH_4 measurements in a closed loop system. Each sample was given at least two hours of processing time to reach equilibrium (Lee and Kim, 2006).

2.5 Radon mass balance

A steady state radon mass balance model was developed to estimate the discharging groundwater into the lake. The model is described in detail by Burnett and Dimova (2012), but briefly, the model accounts for known sources and sinks of radon entering and leaving the system and assumes the missing radon to balance the model is delivered by groundwater discharge. Input sources include radon from groundwater discharge, diffusion from sediments and radon ingrowth from parent isotopes while losses consist of radioactive decay and atmospheric evasion of radon gas. The mass balance model applied is as below:

$$\left(Q_{gw} \times Rn_{gw}\right) + \left(D_{dif} \times A\right) + \left({}^{226}Ra \times \lambda_{222} \times V\right) = \left(Rn_{Sw} \times \lambda_{222} \times V\right) + J_{atm} \qquad (2)$$

where, Q_{gw} is groundwater discharge (m^3/d), Rn_{gw} is the radon concentration in groundwater (Bq/m^3), D_{dif} is radon diffusion from sediments (Bq/m^2/d), A is the lake surface area (m^2), ${}^{266}Ra$ is radium concentration in surface water (Bq/m^3), λ_{222} is radon decay constant (0.181/day) and V is lake water volume (m^3). Rn_{Sw} is radon concentration in lake surface water

(Bq/m^3) and $Rn \times \lambda_{222} \times V$ is radon decay (Bq/d) and J_{atm} is radon atmospheric evasions (Bq/d). To estimate the groundwater discharge to the lake, the average surface water radon concentration value from the area weighted radon interpolation map was used to avoid bias resulting from areas with high radon concentration.

Radon atmospheric evasions across the air-water interface depends on the concentration gradient and the intensity of turbulent gas transfer caused by molecular diffusion and was estimated using Equation (3). Uncertainty for each parameter was propagated into the radon mass balance model and the overall groundwater discharge uncertainty was calculated following the basic rules of error propagation.

2.6 Greenhouse gas fluxes quantification

Water to air fluxes of greenhouse gases were calculated using the equation of Wanninkhof (1992):

$$F = K\alpha\,(C_{Water} - C_{air}) \tag{3}$$

where, F is the flux of CO_2 or CH_4 in units of mmol/m^2/day or radon in Bq/m^2/d, C_{Water} is the partial pressure of CO_2, CH_4 or radon in water and C_{air} is the partial pressure of CO_2, CH_4 or radon in air, in units of µatm, or Bq/m^3 for radon. The background or atmospheric concentrations of radon, CO_2 and CH_4 were assumed to be 10 Bq/m^3, 410 and 1.8 µatm, respectively. Similar to radon, the average area weighted surface water CO_2 and CH_4 concentrations obtained from the interpolation maps were used to avoid bias from sampling areas with high concentrations. The solubility coefficient, α, is calculated as a function of salinity and temperature by using the constants of Weiss (1974) and Wiesenburg and Guinasso Jr (1979) for CO_2 and CH_4, respectively. To derive a reasonable range of flux rates, the gas transfer velocity at the water-air interface, K, was calculated using multiple methods in the literature, from six authors defining K as a function of wind speed for lake ecosystems (Cole et al., 2010; Cole and Caraco, 1998; Crusius and Wanninkhof, 2003; MacIntyre et al., 1995; McGillis et al., 2001; Wanninkhof, 1992). The gas transfer velocity equation in each method rely on wind speed (u) at a height of 10 m (m/s) and the gas specific Schmidt number (Sc) as a function of salinity and temperature (Wanninkhof, 1992). Greenhouse gas fluxes at the water - air boundary were calculated using average daily wind speeds obtained from a local weather station (Seaforth, NSW) approximately 1.5 km from the site.

2.7 Laboratory analysis of dissolved species

A DOC-LABOR Liquid Chromatography-Organic Carbon Detection size exclusion chromatography system (LC-OCD) and customised software program (ChromCALC, DOC-LABOR, Karlsruhe, Germany) was used for total dissolved organic carbon (DOC) analysis as well as 6 different size fractions based on mass (Huber et al., 2011). Alkalinity was determined by the Gran titration method (Stumm and Morgan, 1981) on a 25 ml subsample using a HACH digital titrator. Samples were kept sealed, dark and cool, and were titrated on the same day of collection. DIC was calculated in a PHREEQC (Parkhurst and Appelo, 1999) speciation based on pH and alkalinity, assuming that alkalinity is equal to HCO_3^-. This assumption is reasonable considering the range of pH values (7.2 to 7.6) in the samples (Appelo and Postma, 2005). For the nutrient analysis, phosphate was analysed by a Dionex Ion chromatography system and nitrate and ammonium was analysed by a Lachet Flow Injection Analyser (FIA). Phosphate was consistently below detection levels and hence is not reported here. All samples were analysed at the Solid State & Elemental Analysis Unit at Mark Wainwright Analytical Centre, University of New South Wales (UNSW, Sydney) following standard laboratory procedures.

3 Results

3.1 Surface water observations

During the field campaigns there was no rainfall events, and the area did not receive any rainfall in the 2 weeks prior to field work. Surface runoff is known to occur following rain events through several small intermittent creeks, however, during the field investigation no surface runoff into the lake was observed, and hence this term is zero for the radon mass balance for the field data considered here. Average surface water EC and pH were 550 ± 80 µS/cm and 7.5 ± 0.1, respectively, indicative of a fresh water and a neutral pH system (Figure 2). Temperature and DO ranged from 9.7 to 15.3 (°C) and 5.8 to 10.8 mg/L indicating for most parts of the lake mild water temperatures and close to DO saturation but with distinctly lower DO concentrations observed in the northern parts of the lake. Average wind speed during sampling was 7.4 ± 3.3 m/s. Radon concentration ranged from 0.2 to 69 Bq/m^3 with an average of 15 ± 10 Bq/m^3. NO_3 and NH_4 had average concentrations of 0.2 ± 0.1 and 0.01 ± 0.006 mg/L, respectively. fDOM, DOC and DIC had average concentrations of 8.8 ± 1.0 RFU, 0.6 ± 0.2, and 0.8 ± 0.8 mmol/L, respectively. The two greenhouse gases (CO_2, and CH_4) were above atmospheric equilibrium (~410 ppm for CO_2 and 2 nmol/L for CH_4), indicating the lake was a source of CO_2 and CH_4 to the atmosphere. Partial pressure of CO_2 varied from 649 to 3,725 ppm with an average of 1,323 ppm. CH_4 ranged from 21 to 578 nmol/L with an average of 142 ± 131 nmol/L.

The spatial distribution of pH did not vary significantly, with lower values generally located along the western side of the lake, while temperature and DO showed distinctly lower values at the northern end of the lake (Figure 2). Radon distribution varied spatially with the highest concentrations observed along a small creek on the north western side and towards the northern end of the lake (Figure 2). Similar distributions were observed for NO_3 and NH_4 with highest concentrations recorded around the aforementioned creek. The spatial distribution of DOC and DIC was very similar to each other with the same creek being the one noticeable location of high concentration (Figure 3). Maps of fDOM, CH_4 and pCO_2 also indicated higher concentrations toward the upper northern half of the lake, with pCO_2 and CH_4 trends being similar to the radon distribution trends. Overall, the small creek was identified as a hot spot for high activities of radon, NO_3, NH_4, pCO_2, CH_4, and DIC concentrations.

3.2 Groundwater observations

Average groundwater EC was 437 ± 125 (µS/cm) and slightly (0.8-fold) lower than average surface water values (Table 1). Average groundwater pH (5.65 ± 0.49) and DO (0.74 ± 0.42 mg/L) were also lower than surface water pH and DO concentrations. The average groundwater radon concentration was 69 ± 71 Bq/m^3, 3.5-fold higher than average surface water observations (Table 2). Average NO_3 (1.4 ± 1.7 mg/L) and NH_4 (1.1 ± 1.7 mg/L) concentrations were 5- and 62-fold higher than those observed in surface water. The average DIC concentration in groundwater (3.0 ± 2.3 mmol/L) was 3.6 times higher than surface water observations, while groundwater DOC concentration (0.4 ± 0.3 mmol/L) was 0.7 times lower. The average pCO_2, and CH_4 in groundwater were 7,656 ± 7,665 µatm and 238 ± 300 nmol/L, respectively, and 2 and 6 times higher than the average surface water concentrations (Figure 4).

3.3 Groundwater discharge estimates

The steady state radon mass balance model indicated that groundwater was discharging into the lake at a rate of 16 ± 10 cm/d (Table 3). Estimated radon diffusive fluxes were 4.0 ± 1.8 Bq/m^2/d which was less than 10% of the estimated groundwater discharge contribution from the mass balance model, implying that groundwater was the major contributor of radon to the lake rather than diffusion. Radon production from its parent isotope (^{226}Ra) was low (6.0 ± 2.5 Bq/m^3) and had a minor contribution to the mass balance model. Generally, ^{226}Ra concentrations are low in freshwater environments (Dimova et al., 2013). Previous studies have also reported sediment diffusion and ^{226}Ra to be minor components of the radon mass balance in lakes that received groundwater discharge (Ji et al., 2017; Perkins et al., 2015; Sadat-Noori et al., 2016b; Wallace et al., 2020).

3.4 Greenhouse gas fluxes

The average gas transfer velocity calculated using the various available methods for lake ecosystems was 3.0 ± 2.1 m/d. (Table 4). The highest greenhouse gas fluxes, as a result of the highest K, was estimated when using the equation proposed by McGillis et al. (2001), while the lowest fluxes and gas transfer velocity was estimated when the Cole et al. (2010) empirical equation was used. The average CO_2 and CH_4 flux from surface water to the atmosphere were calculated to be 113 ± 81 and 0.3 ± 0.1 mmol/m^2/day, respectively (Table 4).

4 Discussion

4.1 Freshwater lakes sources of greenhouse gases to the atmosphere

Our observations revealed supersaturation of CO_2 and CH_4 in the studied freshwater lake system, which made the lake a source of carbon to the atmosphere. Most previous studies on lake atmospheric greenhouse gas emissions have been conducted in the Northern Hemisphere and in subarctic climate zones. When compared to CO_2 flux estimates from studies conducted in Europe and the Americas, our estimates are an order of magnitude larger (Table 5). Studies from temperate climate zones are limited in the literature, however, greenhouse gas fluxes from lakes in these regions can be significantly higher than lakes in high latitudes. This is because in the cold conditions of subarctic climate zones, carbon is preserved in lake sediment, whereas organic carbon mineralization increases in regions with warmer temperatures and enhances fluxes of carbon to the atmosphere (Gudasz et al., 2010; Marotta et al., 2014).

Eucalyptus forests located in low to mid latitudes can play an important role in the global carbon cycle (Keith et al., 2009; Schimel, 1995). Such forests are carbon sinks due to their significant levels of CO_2 uptake, respiration, biomass accumulation and sediment burial (Leuning et al., 2005). Here, the lake was surrounded by dense eucalyptus forests however, due to the lake being a source of carbon to the atmosphere, it acts as a hotspot in terms of greenhouse gases emissions in the landscape. This indicates that other lakes in eucalyptus catchments can be large emitters of greenhouse gases within their environment. Australia has approximately 100 million hectares of eucalyptus forests with numerous lakes situated within these forest environments (Department, of Agriculture and Water, 2018). Further carbon sampling and gas flux quantification in such catchments can help determine the role of lakes in the carbon cycle and reduce uncertainties and imbalances in regional and potentially global carbon budgets.

The studied lake also had a $p\mathrm{CO}_2$ value and CO_2 evasion rate higher than global average estimates from freshwater lakes. The global average $p\mathrm{CO}_2$ from inland lakes is estimated to be 800 µatm with a corresponding ~ 7 mmol/m^2/d evasion rate (Raymond et al., 2013). In our case, the average $p\mathrm{CO}_2$ values were double and CO_2 evasion fluxes were ~40-fold higher than the global average estimate. This was largely related to elevated $p\mathrm{CO}_2$ levels in the lake (1,323 µatm). These $p\mathrm{CO}_2$ values seem common for tropical and temperate regions in the Southern Hemisphere. For example, Perkins et al. (2015) reported similar average $p\mathrm{CO}_2$ values (1,910 µatm) and a maximum CO_2 evasion flux of 82.7 mmol/m^2/d from a subtropical freshwater lake in Australia (Lake Ainsworth, NSW). Marotta et al. (2010) also reported an average CO_2 flux of 137 mmol/m^2/d from three lakes in tropical areas of Brazil. Here, estimated fluxes are conservative as sampling was conducted during the day. Night-time CO_2 is expected to be higher when algae are respiring rather than photosynthesising (Gómez-Gener et al., 2021; Podgrajsek et al., 2016). Overall, results suggest CO_2 evasions from freshwater lakes in the Southern Hemisphere can be important sources of carbon to the atmosphere and should be accounted for in global carbon budgets.

There is a significantly lower number of studies reporting concentrations and flux estimates of CH_4 from lakes, with 50-times more studies on CO_2 fluxes reported in the literature (Tranvik et al., 2009). In a review of CH_4 evasion from freshwater lake systems, Kayranli et al. (2010) showed large variations in flux estimates ranging from 0 - 475 mmol/m^2/d. Here, CH_4 flux estimates (0.3 mmol/m^2/d) fall within the lower range of fluxes reported in the literature. The average global CH_4 evasion from lakes is estimated to be 5.9 mmol/m^2/d, which is ~20-fold larger than CH_4 estimates observed in this study (Bastviken et al., 2011). Our CH_4 fluxes were also lower than the range observed for the Northern Hemisphere (Table 5). A potential explanation for such lower fluxes in this study can be the large content of iron-oxides in the Hawkesbury sandstone formation (sediment of the lake). Iron-oxide reduction by natural organic matter can delay the onset of methanogenesis along flow paths (Appelo and Postma, 2005).

The wide range of estimates for CH_4 evasions in the literature highlights that CH_4 evasions are not as well constrained as CO_2 fluxes (Tranvik et al., 2009). Although CH_4 fluxes are usually lower than CO_2 fluxes, CH_4 is a more potent greenhouse gas and has a global warming potential 45 times higher compared to CO_2 over 100 years which is the time CH_4 will remain in the atmosphere once emitted (Jackson et al., 2019). Therefore, all CH_4 evasion fluxes regardless of their magnitude should be taken into account as they can have a significant effect in local and regional greenhouse gas budgets.

4.2 Groundwater as a source of greenhouse gases to the lake

Studies in the literature have utilised radon as a groundwater tracer in lake ecosystems (Dabrowski et al., 2020; Perkins et al., 2015). Here, by simultaneously measuring radon, pCO_2, and CH_4, similarities with previous studies were observed where radon correlated with CO_2 and CH_4 distributions (Dabrowski et al., 2020; Macklin et al., 2014). In this study, groundwater was enriched in pCO_2 and CH_4, and radon had a significant positive relationship with pCO_2, and CH_4 (Figure 5), suggesting groundwater as a significant source of greenhouse gases to the lake. Groundwater discharge can contribute to the overall lake greenhouse gas evasion in two ways, by directly delivering dissolved pCO_2 and CH_4 to lake surface water and/or indirectly by delivering nutrients and DOC (Martinez-Cruz et al., 2020). A recent global review of groundwater DOC concentrations and its controls revealed that groundwater DOC is affected by global warming and increases with urbanisation (McDonough et al., 2020). Increases in groundwater DOC will increase inorganic carbon (DIC and CH_4) groundwater fluxes by direct mineralisation and by driving dissolution of carbonate minerals (Appelo and Postma, 2005). Additionally, direct groundwater inputs of DOC can boost carbon respiration within lake systems (Maher et al., 2015; Sanders et al., 2015). Similarly, groundwater nutrient fluxes, particularly nitrogen, is predicted to increase due to fertiliser use and leaky sewer systems (Burkart and Stoner, 2008; Wakida and Lerner, 2005). Nutrient inputs can boost algae growth and, when they die, can lead to secondary organic matter mineralisation and CO_2 and CH_4 production. Because of the links between lake fluxes of carbon and greenhouse gases with catchment land-use and groundwater processes, fluxes from freshwater lakes need to be understood in their catchment context for prediction of future fluxes and management to mitigate unwanted carbon feedback loops.

One of the main objectives of this study was to quantify the contribution of groundwater discharge as a pathway for dissolved greenhouse gases to the freshwater lake. Previous studies rarely account for this source when developing carbon budgets for lake ecosystems, as shown in Table 5. Here, the radon mass balance model provided quantitative estimates of groundwater fluxes of greenhouse gases to the lake, supporting the correlation analysis (Figure 5). Groundwater-derived CO_2 and CH_4 were 29 ± 18 mmol/m^2/d and 40 ± 29 μmol/m^2/d and contributed 25 and 13% to the overall CO_2 and CH_4 atmospheric evasion from the lake surface water, respectively (Table 6). Studies quantifying groundwater-derived greenhouse gas fluxes to lakes are very limited. Perkins reported groundwater-derived CO_2 fluxes ranging from 10 to 152 mmol/m^2/d, which contributed around 13% of annual CO_2 outgassing in a freshwater lake on the east coast of Australia (Lake Ainsworth, NSW). Similar results were also observed in Sweden where groundwater discharge contributed up to 8% of lake CO_2 emissions (Einarsdottir et al., 2017). Much larger groundwater CH_4 fluxes (7-24 mmol/m^2/d) have been reported in a subarctic lake in Alaska (Dabrowski et al., 2020). Overall, the contribution of groundwater discharge to greenhouse gases (and nutrient) delivery can be significant due to the large concentration of solutes and dissolved gasses in groundwater and because discharge may occur over long periods of time and a large area (Lewandowski et al., 2015)

Studies have shown that higher concentrations of dissolved organic or inorganic carbon, which regulate microbial respiration, can have a significant effect on pCO_2 variations in lake ecosystems, even more than temperature variations (Sobek et al., 2005 and references therein). Here, a strong negative relationship between DO and pCO_2 suggests that microbial respiration contributed to CO_2 gas evasion. The respiration process is indirectly fuelled by nutrient input to the lake, which create large areas covered with algae as visually observed during sampling. The source of nutrients to the lake is thought to be a nearby golf course with groundwater discharge being the main pathway for transporting nutrients. This is also supported by the significant positive correlation between NO_3 and radon (groundwater tracer) (Figure 5). Additionally, the radon spatial variation map depicts a clear alignment between elevated NO_3 and NH_4 concentrations within the lake (Figure 2).

Maintaining golf course turfgrass requires intensive management and regular use of fertilisers which can become a source of nutrient loading to surface water bodies (Bachman et al., 2016). Losses of inorganic nutrient species through leaching into groundwater are known to be much larger than surface water runoff in golf course sites with a sandstone geological formation underneath (Bock and Easton, 2020). Previous studies have shown the negative effects of nutrient leaching from golf course turfgrass on nearby surface water bodies and its environmental impacts (Lei and Guoyang, 2018; Williams et al., 2000).

A significant source of uncertainty for determining the groundwater discharge rate using a radon mass balance model is the variability of the radon activity in groundwater. Generally, radon groundwater variability is due to the variability in the secular equilibrium for most residence times (except very short resident times < 1 month). The decay term is fixed and the secular equilibrium is therefore mostly controlled by the radon emanation which in turn is controlled by mineral composition and the ratio of sediment area to pore volume (e.g., effectively controlled by grain size and porosity) (Duque et al., 2019b). Here, large variability in groundwater radon activity and nutrients was observed which was mainly due to the natural heterogeneity and characteristics of the aquifer. Such variability in radon concentrations is common when using radon as a natural groundwater tracer even at a meter scale and has previously been observed and discussed in detail (Duque et al., 2019b). On the other hand, the variability in nutrients is controlled by land-use (land surface fluxes) and biogeochemical processes attenuating or releasing nutrients along flow paths (Duque et al., 2019a).

While additional spatial and temporal groundwater sampling would help better constrain groundwater endmembers, it is often limited by the number of available monitoring bores. Focusing the investigation effort on characterising the composition of shallow groundwater on the shore (and out in the lake sediments as far as practicable) with push-point mini-piezometers, is a cost-effective alternative and may reduce the need for characterising the catchment groundwater variability, as the net result of subsurface processes are integrated at the groundwater discharge zone (Sadat-Noori et al., 2021; Unland et al., 2013).

The lake bottom sediment can also be a source of local CH_4 and or CO_2 production which is then emitted to the lake surface water through ebullition and diffusion. Our radon sediment diffusion rate indicated that advective, rather than diffusion processes, play a stronger role as a driver of dissolved material to the lake. However, the top sediment layer of the lake may contain a high content of labile organic matter, but not necessarily release much radon (because of low mineral content). Therefore, concentration gradients and diffusive fluxes may be larger for CO_2 and CH_4 than for radon. To fully understand the sediment-water-air CH_4 dynamics, benthic and floating chamber sampling and carbon isotope analysis may be required.

4.3 CO_2-equivalent greenhouse gas emissions

The global warming potential of different greenhouse gases is significantly different. To evaluate the total contribution of the two greenhouse gases, CH_4 was converted to CO_2-equivalent evasions from the lake surface water assuming a 20 and 100-year sustained-flux global warming potential. On a mass basis, CH_4 is 96 and 45 times more powerful in capturing heat over a 20 and 100-year time frame, respectively (Neubauer and Megonigal, 2015). Here, on a 20-year time frame, CH_4 evasion accounted for 15% of the total CO_2-equivalent evasion in the lake surface water and 10% on a 100-year time frame (Figure 7). Therefore, not accounting CH_4 evasions in greenhouse gas assessments could underestimate the overall global warming potential caused by freshwater lakes or any ecosystem under investigation. Our approach, combining measurements of CO_2 and CH_4 offers an improved understanding of their drivers but, more importantly, can assist with constraining local, regional and possibly global greenhouse gas budgets.

5 Conclusions

We present the first comprehensive survey of radon, carbon dioxide, and methane in surface and groundwater for the largest urban freshwater lake system in Sydney, Australia. The results demonstrated the importance of investigating groundwater discharge and how it relates to greenhouse gas emissions in freshwater lake environments. By simultaneously measuring radon and greenhouse gases, site specific groundwater discharge hotspots were located and found to be a significant contribution to lake pCO_2 and CH_4 concentrations and contributors to CO_2 and CH_4 water-to-air fluxes. The freshwater lake system was a net source of CO_2 and CH_4 to the atmosphere during our survey with CO_2 and CH_4 evasion rates ranging from 6 to 230 and 0.02 to 0.67 $mmol/m^2/d$, respectively. Groundwater discharge contributed 25% and 13% to CO_2 and CH_4 flux from the lake. CO_2 fluxes were driven by primary production fuelled by nutrient-rich groundwater inputs demonstrated by a positive correlation between radon, NH_4 and NO_3 and supported by groundwater discharge estimates. The nutrient-rich groundwater inputs potentially contribute to additional primary production (algae growth) and subsequent decomposition of organic matter and increase in situ respiration. Constraining CO_2 and CH_4 fluxes in freshwater lakes is particularly important due to their poor representation in global datasets. We recommend groundwater discharge and associated carbon species fluxes to be quantified and accounted for, to better understand greenhouse gas dynamics and the role of groundwater discharge as a driver of greenhouse gas in freshwater lakes. This is also important for predicting future greenhouse fluxes via groundwater due to global warming and changes in land-use and hence, deriving informed land and water management.

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Table 1. Groundwater sampling locations and physio-chemical observations.

ID	Date/time	Latitude	Longitude	Depth of sampling (m)	EC (µS/cm)	pH	Temperature (C)	Dissolved Oxygen (mg/L)
GW1	6/06/2019 10:45	-33.782066	151.253207	0.9	627	4.81	15.8	0.24
GW2	6/06/2019 13:20	-33.777473	151.249280	0.8	292	6.17	16.9	0.55
GW3	6/06/2019 14:40	-33.776738	151.246867	1.2	481	6.03	17.4	0.14
GW4	3/07/2019 10:34	-33.776683	151.246901	0.8	437	6.15	12.6	0.27
GW5	3/07/2019 11:46	-33.774101	151.245616	0.3	500	5.33	12.5	1.01
GW6	3/07/2019 12:39	-33.773083	151.243966	0.9	255	5.21	13.7	1.03
GW7	3/07/2019 13:18	-33.772133	151.242066	0.6	455	5.95	15.6	0.88
GW8	3/07/2019 14:12	-33.770933	151.242083	0.5	481	5.46	12.5	1.01
Average					437	5.65	15.1	0.74
Std. dev.					125	0.49	1.94	0.42

Table 2. Groundwater radon, carbon, nutrient, and greenhouse gases concentrations.

ID	Radon (Bq/m^3)	NO_3 (mg/L)	NH_4 (mg/L)	DOC (mmol/L)	DIC (mmol/L)	Alkalinity (mmol/L)	CH_4 (nmo/L)	pCO_2 (µatm)
GW1	63	0.5	0.1	0.3	4.1	0.1	88	8412
GW2	82	1	0.2	0.5	1.6	0.7	153	4021
GW3	36	0.6	0.1	0.1	0.4	0	88	4260
GW4	58	5.4	4.0	0.5	7.5	2.5	148	25410
GW5	18	1.3	0.2	0.2	1.9	0.2	73	7530
GW6	220	1.5	3.6	0.3	4.8	1.9	969	10254
GW7	40	0.8	0.4	0.9	1.4	0.4	153	2531
GW8	26	0.1	0.4	0.7	2.2	0.2	239	4012
Average	69	1.4	1.1	0.4	3.0	0.7	238	7656
Std. dev.	71	1.7	1.7	0.3	2.3	0.9	300	7665

Table 3. Radon mass balance model input and output parameters and groundwater discharge rates.

Mass balance parameters	Value
Average SW Radon (Bq/m^3)	15 ± 19.5
Average GW radon (Bq/m^3)	69 ± 71.1
Average Depth (m)	4 ± 0.6
Average area (km^2)	0.37 ± 0.074
Volume (m^3)	$167 \times 10^4 \pm 334 \times 10^3$
Average wind speed (m/s)	7 ± 2
Radon decay (Bq/m^2/d)	12 ± 3.5
Radon evasion (Bq/m^2/d)	9 ± 4
^{226}Ra ingrowth (Bq/m^2/d)	6 ± 2.5
Radon diffusion (Bq/m^2/d)	4 ± 1.8
GW discharge (cm/d)	16 ± 10
GW % of lake water volume	4 ± 3

Table 4. CO_2 and CH_4 fluxes from lake surface water quantified using multiple methods available in the literature. Uncertainties indicate 1 standard deviation. K is the gas transfer velocity (m/d), u is the wind speed (m/s) at a height of 10 m and Sc is the Schmidt number of CO_2 at in situ temperature and salinity.

Number	Equation	Average K (m/d)	Average CO_2 Flux (mmol/m^2/d)	Average CH_4 Flux (mmol/m^2/d)	Reference
1	$K = 0.31u^{2} (Sc/660)^{-1/2}$	3.7	140	0.41	Wanninkof (1992)
2	$K = 0.45u^{1.6} (Sc/660)^{-1/2}$	2.2	81	0.25	MacIntyre et al. (1995)
3	$K = 0.215u^{2.2} (Sc/660)^{-1/2} + 2.07$	1.5	56	0.17	Cole & Caraco (1998)
4	$K = 0.026u^{3} (Sc/660)^{-1/2} + 3.3$	6.0	230	0.67	McGillis et al. (2001)
5	$K = 0.228u^{2.2} + 0.168 (Sc/660)^{-1/2}$	4.3	163	0.46	Crusius & Waninnkhof (2003)
6	$K = 0.0064u1.8^{3} (Sc/660)^{-1/2} + 0.497$	0.2	6	0.02	Cole et al. (2010)
	Average	3.0 ± 2.1	113 ± 81	0.3 ± 0.1	

Table 5. A synthesis of freshwater lake CO_2 and CH_4 atmospheric fluxes from the literature. The majority of the studies are conducted in the Northern Hemisphere and neglect groundwater discharge as a source of dissolved gases to the lake.

Site name	Location	Hemisphere	Climate	Area (km^2)	Ave. depth (m)	CO_2 atmospheric flux ($mmol/m^2/d$)	GW contribution (%)	CH_4 atmospheric flux ($mmol/m^2/d$)	GW contribution (%)	Reference
Donghu	China	Northern	Subtropical	27.9	3.5	7.6	-	-	-	Xing et al. (2005)
948 lakes	USA	Northern	Subtropical	<198	<5	20.4	-	-	-	Lazzarino et al. (2009)
Paajarvi	Finland	Northern	Subarctic	13.4	14	42.7	-	-	-	(López Bellido et al., 2009)
Landing Lake	Alaska	Northern	Subarctic	0.36	1.5	-	-	1.8	100	Dabrowski et al. (2020)
3 Lakes	Russia	Northern	Subarctic	0.23	1.5	70.5	-	3.8	-	Repo et al. (2007)
Lake Stortjärn	Sweden	Northern	Subarctic	0.65	2.7	67.5	-	0.4	-	Denfeld et al. (2020)
Stordalen Mire (3 lakes)	Sweden	Northern	Subarctic	0.06	4.2	8.8	-	1.4	-	Jansen et al. (2019)
Stordalen Mire	Sweden	Northern	Subarctic	0.17	1	19.1	-	5	-	Jammet et al. (2017)
40 ponds	Sweden	Northern	Subarctic	0.001	-	17.1	-	1.9	-	Peacock et al. (2019)
Lake Tämnaren	Sweden	Northern	Subarctic	38	1.3	9.5	-	0.7	-	Podgrajsek et al. (2016)
Lake Dagow	Germany	Northern	Subarctic	0.24	9.5	5.9	-	1.2	-	Martinez-Cruz et al. (2020)
Dendre stone pit lake	Belgium	Northern	Temperate	0.032	15	-	-	6.6	-	Roland et al. (2017)
Lake Erie	USA/Canada	Northern	Temperate	25744	19	-	-	1.4	-	Townsend-Small et al. (2016)
Garcas, Barrinha and Rabalo	Brazil	Southern	Tropical	5	<1	137	-	-	-	Marotta et al. (2010)
Lake Ainsworth	Australia	Southern	Subtropical	0.12	4.4	6.7	13	-	-	Perkins et al. (2015)
Manly	Australia	Southern	Temperate	0.35	5	113	25	0.3	13	This study

Table 6. Groundwater-derived greenhouse gas fluxes and their relative contribution to the overall lake atmospheric greenhouse gas emissions.

Greenhouse gas fluxes	GW discharge (cm/d)	CO_2 (mmol/m^2/d)	CH_4 (μmol/m^2/d)
	16 ± 10		
Groundwater-derived		29 ± 18	40 ± 29
Atmospheric		113 ± 81	300 ± 100
Groundwater contribution		25%	13%

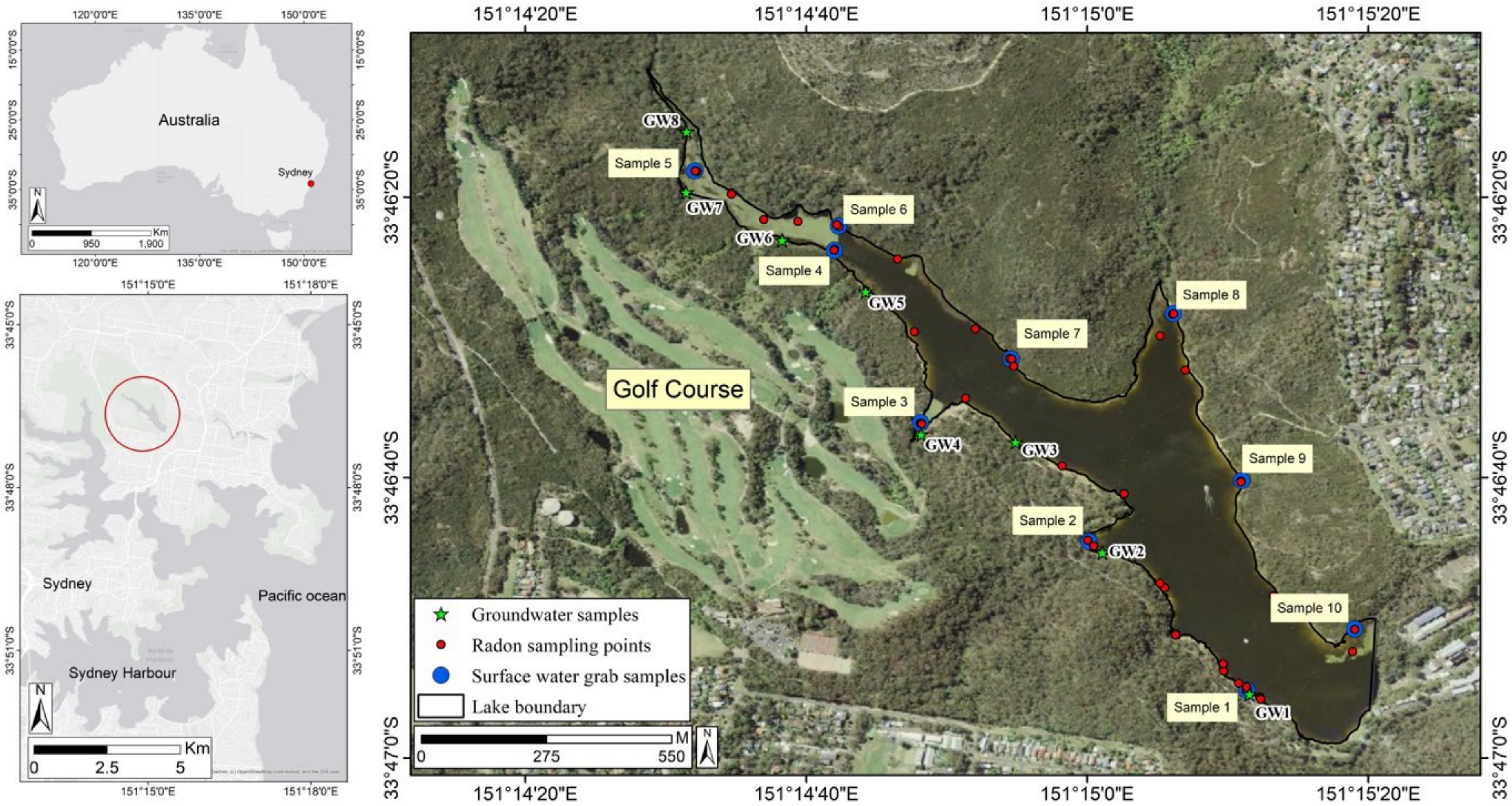

Figure 1. Map of the study area showing water sampling location with radon, CO_2 and CH_4 measured with automated instruments and surface water grab samples collected for water quality parameters.

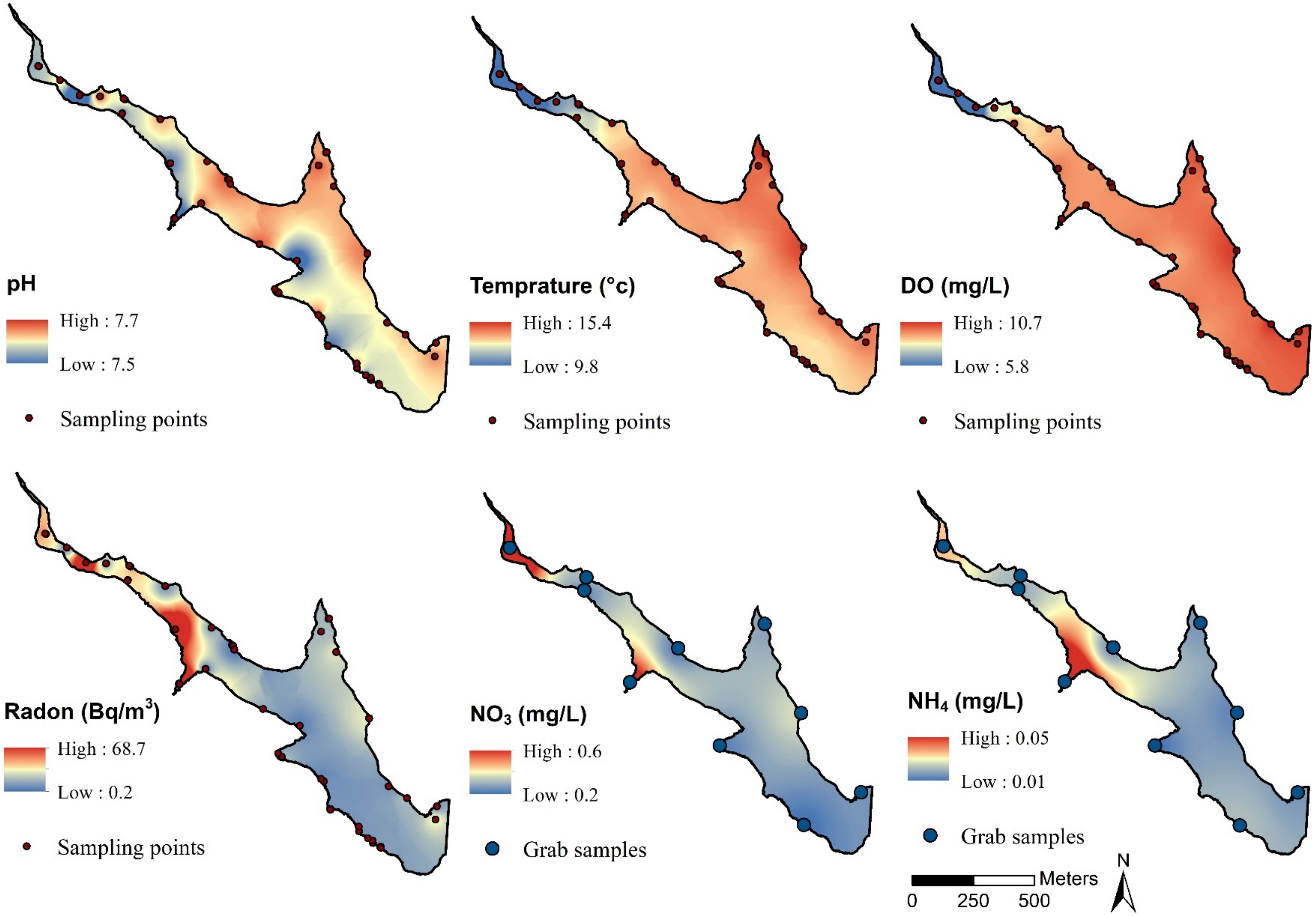

Figure 2. Spatial survey maps of physico-chemical parameters, radon and nitrogen species at the site illustrating similar trends for radon (groundwater tracers) and nitrogen in the lake.

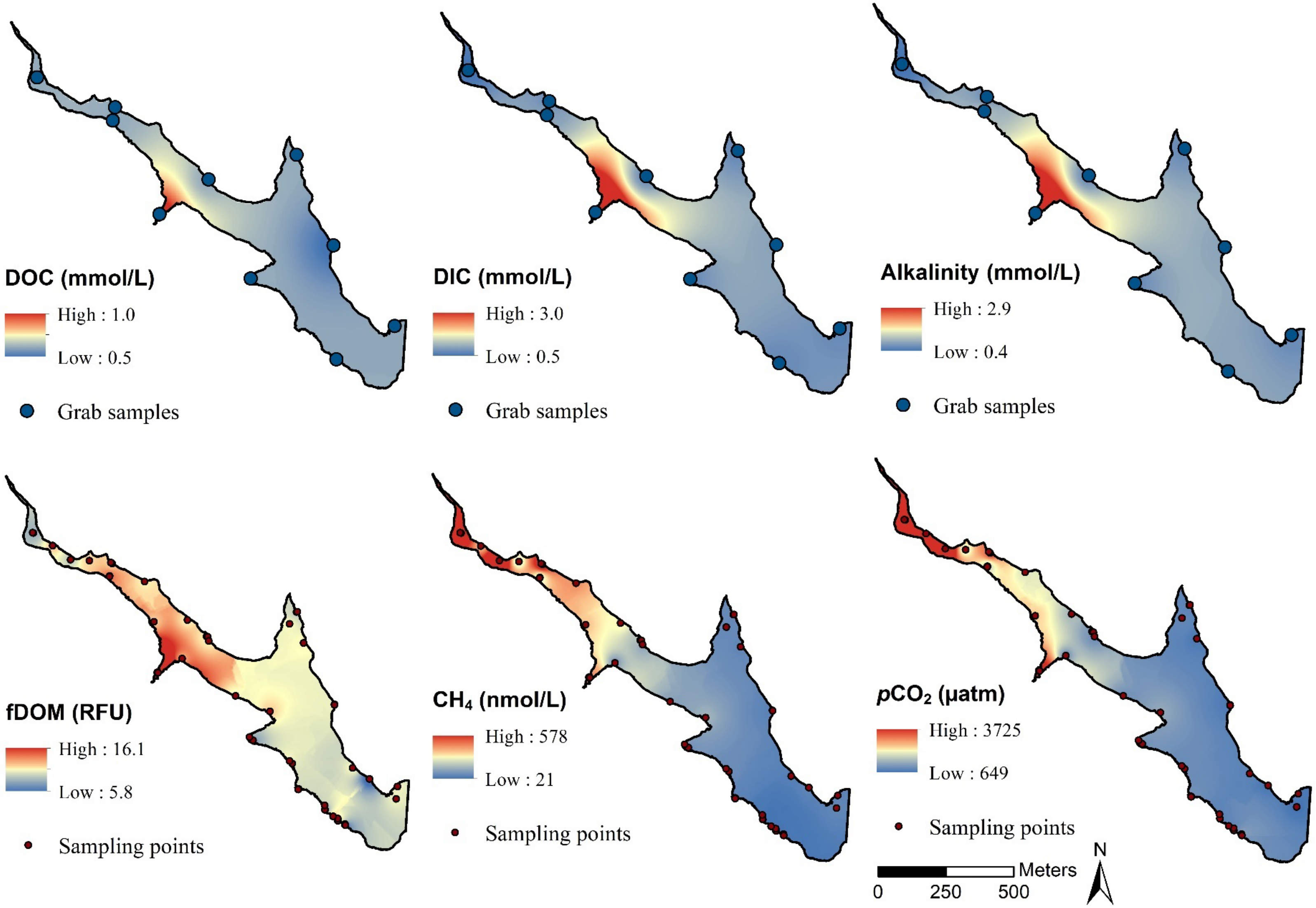

Figure 3. Spatial survey maps of fDOM, carbon species and greenhouse gases at the site. The creek on the north western side indicates a hotspot for carbon.

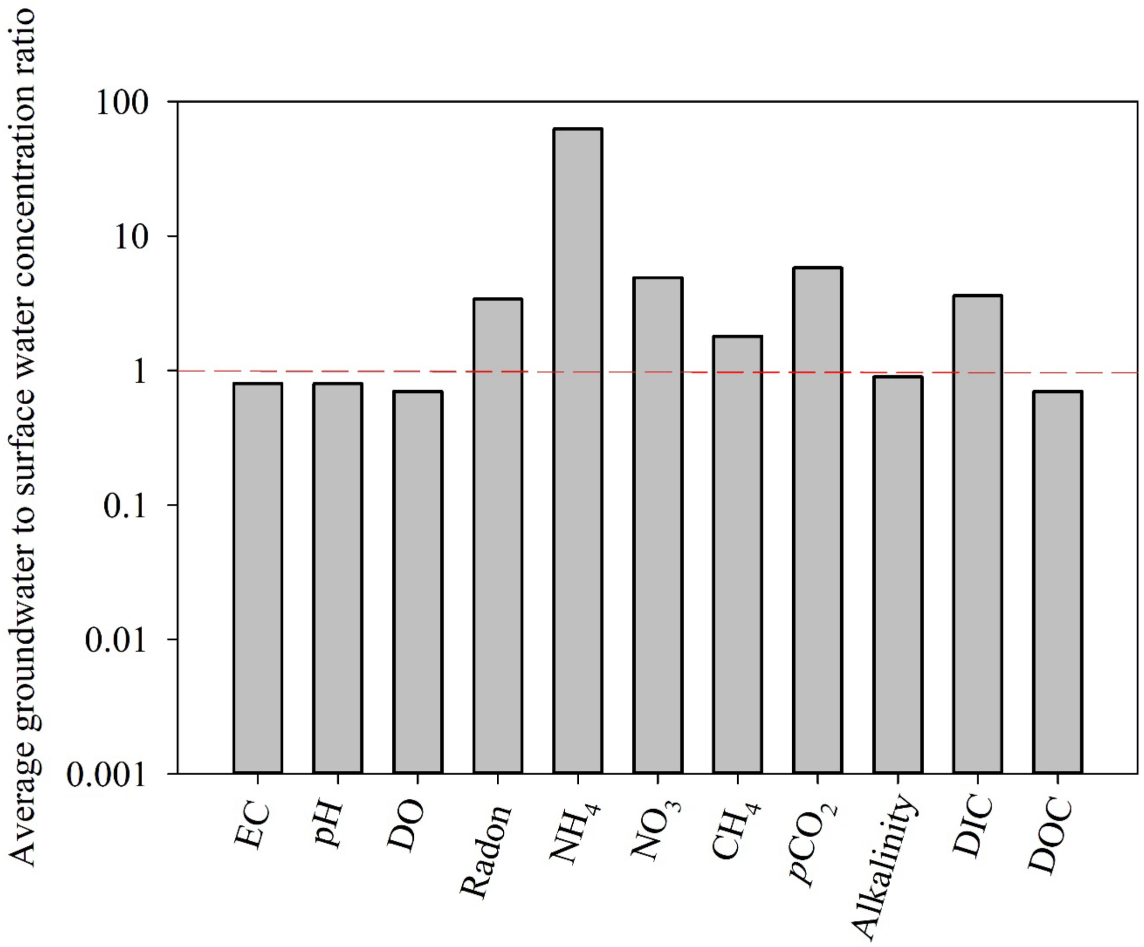

Figure 4. Plot illustrating the ratio of average concentration of measured parameters in groundwater to surface water. The red dashed line indicates 1:1 ratio.

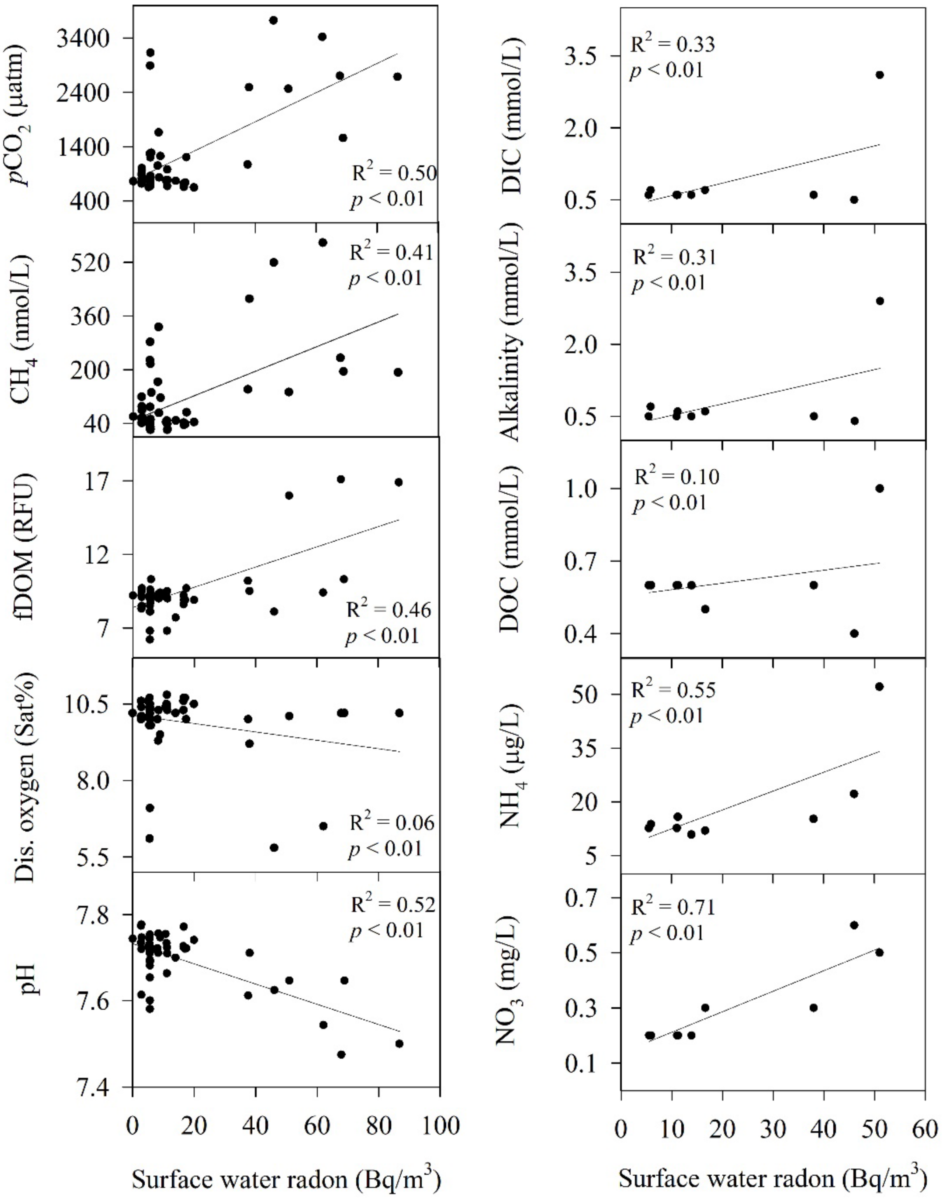

Figure 5. Correlation plots of surface water radon and physio-chemical parameters, nutrient, carbon and greenhouse gases collected by automated instruments (left column) and grab samples (right column). Correlations are all significant at $p < 0.01$.

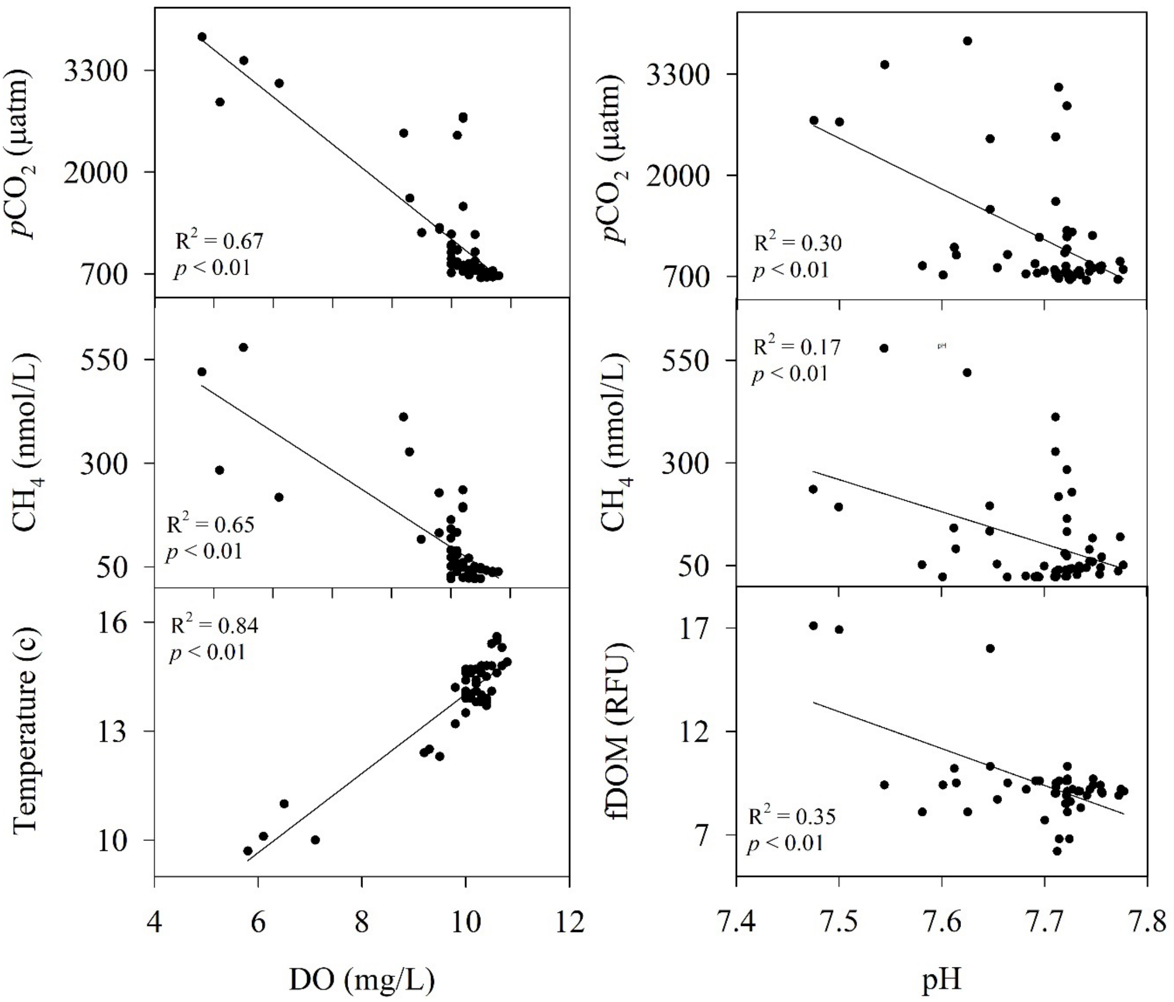

Figure 6. Scatter plots of surface water DO and pH versus temperature, fDOM and greenhouse gases.

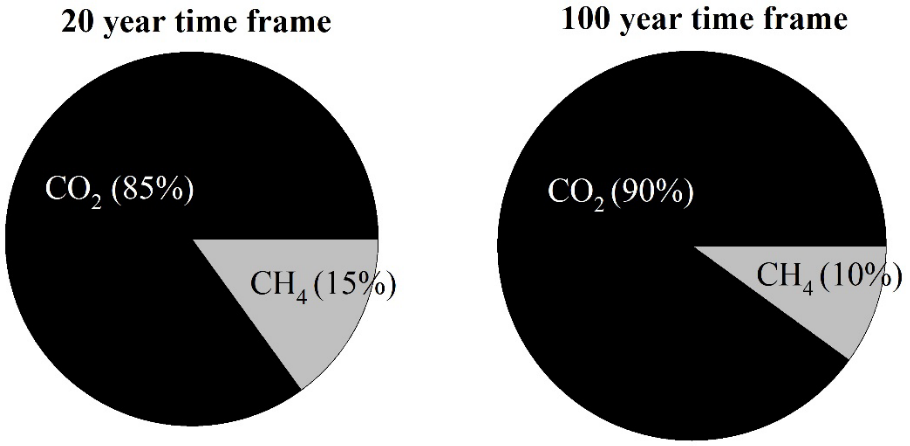

Figure 7. The contribution of greenhouse gases to global warming potential in CO_2 equivalents using the 20- and 100-year sustained-flux (Neubauer and Megonigal, 2015).

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