

1 **Carbon dioxide emissions and sediment organic carbon burials across a**  
2 **gradient of trophic state in eleven New Zealand lakes**

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8 **Abstract**

9 Lakes are known to be important to the global carbon balance as they are both CO<sub>2</sub> sources to the  
10 atmosphere and also accumulate large amounts of carbon in their sediment. CO<sub>2</sub> flux dynamics  
11 across air-water interface in 11 lakes of varying trophic state in the Rotorua region, New Zealand,  
12 derived from measured alkalinity, pH and wind speed at given temperature showed that lakes may  
13 shift from being atmospheric CO<sub>2</sub> sources to sinks due to seasonal changes in phytoplankton  
14 productivity and lake mixing dynamics. Decreases in trophic state (i.e., improved water quality) in  
15 some of the lakes over the eight-year monitoring period were associated with increased surface  
16 water CO<sub>2</sub> concentrations and as a consequence, increasing CO<sub>2</sub> flux to the atmosphere. Organic  
17 carbon content analysis collected from bottom sediments revealed that lakes with high  
18 phytoplankton productivity, indicated by high chlorophyll *a* biomass, generally had high rates of  
19 carbon deposition to the sediments, but not all deposited carbon was permanently buried.  
20 Remineralization of the organic carbon accrual in productive lakes may potentially generate CO<sub>2</sub>, as  
21 well as CH<sub>4</sub>, in which this promotes lakes to act as greenhouse gas emitters.

22 Keywords: CO<sub>2</sub> flux, sediment carbon accumulation, seasonal variation, lake restoration, carbon  
23 balance.

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## 25 **Introduction**

26 Inland waters (including ponds, lakes, wetlands, reservoirs, streams and rivers) cover approximately  
27 3% of the Earth's surface (Downing et al., 2006) and have been estimated to be a sink for 0.23 – 0.6  
28 Pg y<sup>-1</sup> of carbon (Cole et al., 2007; Tranvik et al., 2009; Regnier et al., 2013). This estimate is the same  
29 order of magnitude as the global oceanic carbon sink (0.29 Pg y<sup>-1</sup>, Le Quéré et al., 2015). This shows  
30 that, although there is some degree of uncertainty in the estimates, lakes are important in regulating  
31 the global carbon cycle.

32 Lakes process organic carbon (OC) derived from their catchments and within the waterbody itself  
33 (i.e., allochthonous and autochthonous production, respectively). This carbon is either stored in lake  
34 sediments, exported through streams, or released as carbon dioxide (CO<sub>2</sub>) and methane (CH<sub>4</sub>) to the  
35 atmosphere (Cole et al., 2007; Tranvik et al., 2009). The majority of world's lakes are considered to  
36 be CO<sub>2</sub> sources to the atmosphere (Cole et al., 1994), largely due to respiration of OC derived from  
37 terrestrial sources, which subsidises lake community respiration (Hanson *et al.* 2003; Sobek *et al.*  
38 2005), and inputs of dissolved inorganic carbon derived from carbonate weathering in the watershed  
39 (Marcé *et al.* 2015). Carbon dioxide fluxes vary seasonally (López Bellido et al., 2009), and as a result  
40 lakes may alternate between net sources of CO<sub>2</sub> to the atmosphere and net sinks of CO<sub>2</sub> (Trolle et al.,  
41 2012). Physical processes associated with water column mixing and overturn (Striegl &  
42 Michmerhuizen, 1998), storm loads of organic and inorganic carbon (Ojala et al., 2011; Vachon & del  
43 Giorgio, 2014), as well as seasonal variations in phytoplankton productivity and community  
44 respiration (Del Giorgio et al., 1999) influence the concentration of dissolved CO<sub>2</sub>, and thereby alter  
45 the magnitude of CO<sub>2</sub> lake-atmosphere exchanges. Nutrient availability (Hanson et al., 2003; Trolle  
46 et al., 2012) also plays a role in regulating CO<sub>2</sub> in lakes, as it is an important determinant of  
47 autochthonous production. The highest rates of lake CO<sub>2</sub> influx tend to occur in eutrophic lakes, but  
48 can vary with the structure of the food web, which in turn regulates primary production (Cole et al.,

49 2000; Marotta et al., 2012). In contrast, oligotrophication can lead to an increase in CO<sub>2</sub> emissions  
50 from lakes (Trolle et al., 2012).

51 The progression of eutrophication is characterised by rates of OC burial in lake sediments that  
52 exceed rates of carbon emission from the water surface (Hanson et al., 2004). However, the burial  
53 efficiency of OC (i.e., the ratio of burial to mineralization rate) in eutrophic lakes can be low, as  
54 sedimentary OC sourced from phytoplankton is readily decomposed. High decomposition rates  
55 result in less accumulated carbon in the sediment (Burdige, 2007), often despite relatively high  
56 sedimentation rates (Downing et al., 2008). Less productive lakes receive a higher relative load of  
57 allochthonous refractory carbon, leading to higher carbon burial efficiency (Sobek et al., 2009).

58 In this study, a combined analysis of CO<sub>2</sub> flux dynamics and sediment carbon deposition from 11  
59 lakes of varying trophic state (oligotrophic to eutrophic) and mixing regime (monomictic to  
60 polymictic) in Rotorua, New Zealand, was used to determine the fate of carbon. Action Plans  
61 developed by the regional council have been put in place to remediate a number of the Rotorua  
62 lakes from excess of nutrient loading leading to decreases in chlorophyll *a* concentration (Burns et  
63 al., 2009; Abell et al., 2011) thus it was hypothesized that this would increase CO<sub>2</sub> concentrations in  
64 surface waters and as a consequence would also increase CO<sub>2</sub> evasion from the lakes. We too  
65 hypothesized that as a sink for atmospheric CO<sub>2</sub> due to high autotrophic activity eutrophic lakes  
66 would also have higher rates of net carbon deposition than oligotrophic lakes.

## 67 **Methods**

### 68 **Study sites and parameter of interest**

69 The Rotorua lakes (Fig. 1) lie in the Central Volcanic Plateau of the North Island and were formed  
70 around 140,000 years BP by a series of volcanic eruptions (Lowe & Green, 1987). Several of the lakes  
71 are influenced by surface geothermal inflows (Vincent and Forsyth 1987). (Mazot et al., 2014)  
72 identified that Lake Rotomahana has been an active hydrothermal area since Tarawera eruption in  
73 1886 and might massively release 29.5 mol CO<sub>2</sub> m<sup>-2</sup> d<sup>-1</sup> through ebullition. Anthropogenic activities,

74 i.e. urbanisation and agriculture (McColl, 1972; Hamilton, 2005), also threaten lakes in this area  
75 while others remain largely unaffected by human influence, resulting in variation in trophic state  
76 from oligotrophic to highly eutrophic (Table 1).

77 Water column variables used in this study were compiled from monthly measurements taken by Bay  
78 of Plenty Regional Council (BOPRC) at a deep-water station of each lake during the period of 2002 to  
79 2010. Measurements included chlorophyll *a* (Chl), total nitrogen (TN) and total phosphorus (TP) at  
80 the surface (1 m depth) and pH at both surface and bottom water (~1 m above the sediment).

81 Vertical profiles of temperature and dissolved oxygen were also measured from CTD casts (SBE 19  
82 plus, Seabird Electronics). Alkalinity was measured from the surface water at least twice a year by  
83 BOPRC. All water quality parameters (Chl, TN, TP and alkalinity) were analysed using standard  
84 methods based on APHA, (1998) and described by (Burns et al., 2000). Relevant morphological and  
85 water quality parameters for each lake are given in Table 1. Sediment carbon content data were  
86 sourced from Pickett (2008) for Lake Rotorua and from Trolle et al. (2008) for the remaining lakes.

87 Intact sediment cores were taken between 2006 and 2007 from the deepest basin of the lakes using  
88 a piston corer for Lake Rotorua Pickett (2008) or a cylindrical gravity corer for the other lakes (Trolle  
89 et al., 2008). McColl (1977) reported that sediments of Rotorua lakes are mostly non-calcareous with  
90 total carbon (TC) content contributed mostly in organic form. The cores were sliced at 1-2 cm  
91 intervals and the slices were dried and analysed for percentage OC content using a LECO TruSpec CN  
92 Determinator. The Mt Tarawera eruption of 1886 provided a distinctive tephra layer in the core  
93 which was used to calculate annual mean sedimentation rate for the period of 1886 – 2006 (see  
94 Trolle et al., 2008).

### 95 **Thermal stratification**

96 The depth of thermocline was defined as greatest rate of density change with depth, determined  
97 from vertical variations in temperature from CTD casts. The rLakeAnalyzer software (Winslow et al.,  
98 2015) was used to assist with calculations of thermocline depth (see theoretical basis given by Read  
99 et al., 2011).

100 **Dissolved CO<sub>2</sub> calculation**

101 Concentrations of CO<sub>2</sub> (μmol C L<sup>-1</sup>) in the water column were calculated from the dissociation of  
102 dissolved inorganic carbon in freshwater according to pH and alkalinity values at a given  
103 temperature (Stumm & Morgan, 1996). Due to the limited number of alkalinity measurements, CO<sub>2</sub>  
104 was calculated by varying the alkalinity value by 20% from the measured data to give a range of  
105 possible of CO<sub>2</sub> concentrations. This range corresponds to the variations of alkalinity values in  
106 Rotorua lakes reported by Timperley & Vigor-Brown (1986) and McColl (1972).

107 **CO<sub>2</sub> air-water exchange estimation**

108 Air-water exchange of CO<sub>2</sub> was computed using Fick's law of gas diffusion:

109 
$$F_{CO_2} = k_{CO_2} (CO_{2aq} - CO_{2sat}) \quad (1)$$

110 where  $F_{CO_2}$  is the CO<sub>2</sub> flux across the air-water interface (mmol C m<sup>-2</sup> d<sup>-1</sup>),  $CO_{2aq}$  is the  
111 concentration of dissolved CO<sub>2</sub> atmosphere in the surface water (μmol C L<sup>-1</sup>),  $k_{CO_2}$  is the gas exchange  
112 coefficient (cm d<sup>-1</sup>) and  $CO_{2sat}$  is the CO<sub>2</sub> saturation concentration (μmol C L<sup>-1</sup>) for a given  
113 temperature and atmospheric CO<sub>2</sub> mole fraction in dry air (Weiss & Price, 1980). A monthly average  
114 atmospheric CO<sub>2</sub> dataset from 2001 to 2010 was obtained from Baring House Station, Wellington,  
115 New Zealand (Dlugokencky *et al.* 2013). Values of  $k_{gas}$  were determined from  $k_{600}$  standardized to a  
116 Schmidt number of 600 (Jähne *et al.*, 1987):

117 
$$k_{CO_2} = k_{600} (SC_{CO_2} / 600)^{-n} \quad (2)$$

118 where  $SC_{CO_2}$  is the Schmidt number for CO<sub>2</sub> at given water temperature (Wanninkhof, 1992). A value  
119 of  $n$  of 0.67 and 0.5 was assigned for a wind speed below and above 3 m s<sup>-1</sup>, respectively (Crusius &  
120 Wanninkhof, 2003). Values of  $k_{600}$  were derived from a wind-based model that accounts for lake size  
121 (Vachon & Prairie, 2013):

122 
$$k_{600} = 2.51 + 1.14U_{10} + 0.39U_{10}\log_{10}LA \quad (3)$$

123 where  $U_{10}$  is the wind speed (m s<sup>-1</sup>) at 10 m elevation and  $LA$  is lake area in km<sup>2</sup>.

124 **Sediment deposition and burial**

125 Sediment carbon deposition and burial were calculated based on a first-order diagenesis model for  
126 labile organic matter (Berner, 1980; Klump et al., 2009). The composition of OC deposited on the  
127 sediment surface was assumed to initially consist of two fractions: permanently buried and  
128 metabolizable material. The latter is remineralized and released back to the hypolimnetic layer. The  
129 model calculates percentage of OC content in the dry mass of sediment:

130 
$$G_z = G_m \exp[(-k_m \omega^{-1})/z] + G_{inf} \quad (4)$$

131 where  $G_z$  is OC content (%) at depth  $z$  (cm) in the sediment column,  $G_m$  is the metabolizable carbon  
132 (%) in the initially deposited carbon in the sediments,  $G_{inf}$  is the non-metabolizable residual (%), and  
133  $k_m$  and  $\omega$  are the first-order rate constant ( $\text{y}^{-1}$ ) and mass accumulation rate ( $\text{kg m}^{-2} \text{y}^{-1}$ ), respectively.  
134 Published values of  $\omega$  were used for each lake from (Trolle et al., 2008). This value was based on an  
135 assumption that deposition rates were constant after the Tarawera eruption in 1886. The model was  
136 fitted with the measured carbon profile in the sediment using a Nelder-Mead optimization algorithm  
137 to estimate the values of  $G_m$ ,  $k_m$  and  $G_{inf}$ , minimizing negative log-likelihood errors and maximizing  
138 the Pearson correlation coefficient ( $r$ ). The carbon fluxes ( $\text{mol m}^{-2} \text{y}^{-1}$ ) for carbon deposition ( $J_{in}$ ),  
139 burial ( $J_{bur}$ ) and remineralization ( $J_{rec}$ ) were calculated by multiplying the %C of the estimated  
140 sedimentary matter fractions with  $\omega$ :

141 
$$J_{in} = \omega (G_m + G_{inf}) \quad (5)$$

142 
$$J_{bur} = \omega (G_{inf}) \quad (6)$$

143 
$$J_{rec} = \omega (G_m) \quad (7)$$

144 Using the observed tephra depth, the recent areal OC stock (from 1886 to 2006) in the lake sediment  
145 was estimated by summing the OC content down to the tephra layer. The total %C concentration in  
146 that layer was multiplied by the annual mass accumulation rate ( $\omega$ ) and the age of the tephra (120  
147 years). Knowing that lake sediments do not accumulate uniformly over the lake's surface but are

148 influenced by sediment focusing, we then calculated the mean thickness of the sediment above the  
149 tephra layer and spread it over the entire lake basin based on Ferland et al. (2014) as:

$$150 \quad Z_{\text{mean\_sed}} = Z_{\text{max\_sed}} / (q + 1) \quad (8)$$

151 where  $Z_{\text{mean\_sed}}$  is mean depth at which tephra was located,  $Z_{\text{max\_sed}}$  is the maximum depth of the  
152 tephra layer and  $q$  is exponent value describing the shape of the lake. Following Ferland et al. (2014)  
153  $q$  was estimated based on the hypsometric relationship between surface area and water depth  
154 (Imboden, 1973) as:

$$155 \quad A_z = A_0 (1 - Z / Z_{\text{max}})^q \quad (9)$$

156 where  $A_z$  is the planar area at depth  $Z$ ,  $A_0$  is the surface area of lake and  $Z_{\text{max}}$  is the maximum lake  
157 depth. The value  $q$  was solved using a Nelder-Mead optimization algorithm by minimizing negative  
158 log-likelihood errors between  $A_z$  and the lake's planar area from the hypsometric curve.

## 159 **Data analysis**

160 Monthly patterns for dissolved CO<sub>2</sub> concentration, fluxes and other measured variables in each lake  
161 were developed using a bootstrapping and decomposition technique to examine seasonal and long-  
162 term dynamics in water column variables. The extracted median and 95% confidence interval of the  
163 bootstrapped data were then plotted to depict seasonal patterns. Pearson's correlation coefficient  
164 was used to examine the relationship between CO<sub>2</sub> flux and water quality variables (Chl, TP and TN).  
165 A seasonal Mann-Kendall test was used to determine the trend of change (units y<sup>-1</sup>) in each variable  
166 over the entire period of study (Jassby and Cloern 2014). To calculate cumulative annual CO<sub>2</sub> flux, we  
167 calculated the areas under the curve of the median bootstrapped flux using the trapezoidal rule (R  
168 package Hmisc: Harrell, 2015). All computations and analyses were performed in the R statistical  
169 package (R Core Team 2014; Version 3.1.2).

## 170 **Results**



171 Atmospheric CO<sub>2</sub> flux and surface water quality parameters (Chl, TP and TN) in the 11 Rotorua lakes  
172 ranged widely but there was a strong seasonal pattern in water temperature and mixing regimes,  
173 which were either monomictic or dimictic. In addition, the pattern of carbon deposition to the  
174 sediment was distinguishable by lake trophic state. To further illustrate seasonal variations in CO<sub>2</sub>  
175 flux and water quality variables, as well as sediment carbon profiles, three examples (Tarawera,  
176 Okaro and Rotoehu) representing different mixing regimes and trophic states are presented below.  
177 Lakes Tarawera and Okaro are oligotrophic and eutrophic, respectively, and both are monomictic,  
178 while Lake Rotoehu is eutrophic and polymictic.

### 179 **Seasonal variation of CO<sub>2</sub> flux**

180 There were strong seasonal variations in CO<sub>2</sub> concentrations among the lakes in association with  
181 thermal stratification dynamics (Fig. 2). In the monomictic lakes (see Table 1), surface water CO<sub>2</sub>  
182 concentrations increased as the thermocline started to deepen in autumn (around May) and  
183 reached maximum levels during the winter mixing period. As this group of lakes stratified, surface  
184 CO<sub>2</sub> concentrations decreased. Concentrations varied from under- to over-saturation seasonally (Fig.  
185 2) apart from Lakes Rotomahana, Tarawera and Rotoiti, which were usually supersaturated and  
186 therefore released CO<sub>2</sub> to the atmosphere (Fig. 3). Bottom water CO<sub>2</sub> concentrations showed an  
187 inverse pattern to the surface concentrations in the monomictic lakes, with concentrations highest  
188 in late summer. In the polymictic lakes (Table 1), thermal stratification only occurs in 2 – 3 months  
189 during summer (January to February), hence, CO<sub>2</sub> concentrations in surface and bottom waters were  
190 relatively similar throughout the year (Fig. 2).

191 Apart from highly eutrophic Lake Okaro, the Rotorua lakes were calculated to be annual net CO<sub>2</sub>  
192 emitters to the atmosphere (Fig. 3). However, there was no distinct pattern of net annual CO<sub>2</sub>  
193 emission with regard to trophic state. Eutrophic (Lake Rotorua) and mesotrophic lakes (Lakes Rotoiti  
194 and Rotomahana) were calculated to emit more CO<sub>2</sub> annually than the oligotrophic lakes.

### 195 **Correlations and long-term trends of CO<sub>2</sub> and water quality variables**

196 Influences of Chl, TP and TN concentrations on CO<sub>2</sub> fluxes in the lakes were examined using annual  
197 average values. Lake Rotomahana was excluded from the analysis because of its extreme CO<sub>2</sub> fluxes  
198 associated with geothermal emissions (see Fig. 3). Fluxes of CO<sub>2</sub> were significantly negatively  
199 correlated with Chl, TP and TN (Table 2). Chlorophyll *a* showed a significant positive correlation with  
200 nutrients (TP and TN). Therefore, lakes with higher concentrations of Chl and nutrients tended to  
201 have low surface water CO<sub>2</sub> concentrations. However, while lakes undergoing restoration  
202 programmes showed declining trends of Chl (~2 – 6% per year) and nutrients, this was not always  
203 reflected in increasing CO<sub>2</sub> emissions (Table 3). Only Lakes Okaro and Rotoma showed a significantly  
204 increasing (12 and 19% per year, respectively) CO<sub>2</sub> emissions following a decrease in Chl  
205 concentrations.

#### 206 **Sediment organic carbon**

207 A diagenetic model was used to reconstruct the observed sediment carbon profile in the 11 Rotorua  
208 lakes based on the accumulated sediment between 1886 and 2006. The model reproduced sediment  
209 carbon profiles based on an exponential decrease of carbon involving deposition, remineralization,  
210 and burial (Table 4). There was an exponential pattern of decay of total carbon (TC) through the  
211 profile in the core, as visualized by the three example lakes (Tarawera, Okaro, Rotoehu; Fig. 4).  
212 Deposition rates ( $J_{in}$ ) of carbon ranged from 0.31 to 2.82 mol C m<sup>-2</sup> y<sup>-1</sup>, with meso- to eutrophic lakes  
213 having higher deposition fluxes than the oligotrophic lakes (Table 4). However, the lowest carbon  
214 burial rate ( $J_{bur}$ ) was calculated to be in the most eutrophic lake, Okaro (0.8 x 10<sup>-3</sup> mol C m<sup>-2</sup> y<sup>-1</sup>),  
215 while the highest was in eutrophic Lake Rotorua (0.19 mol C m<sup>-2</sup> y<sup>-1</sup>) (Table 4). By using the  
216 diagenetic model to sum the carbon content to the tephra layer in the sediment core, the recent  
217 areal carbon stock (1886 to 2006) was determined for the lake sediment. Eutrophic lakes were  
218 calculated to have higher areal carbon stock (e.g., Lake Okaro: 3.65 x 10<sup>3</sup> mol C mol<sup>-2</sup>) while  
219 oligotrophic lakes stored less carbon (e.g., Lake Tikitapu: 0.29 x 10<sup>3</sup> mol C mol<sup>-2</sup>) (Table 4).

#### 220 **Discussion**

221 Lake hydrodynamics are known to control the seasonal patterns of CO<sub>2</sub> concentrations in lakes  
222 (Striegl & Michmerhuizen, 1998; Riera et al., 1999; López Bellido et al., 2009). In mono- and dimictic  
223 lakes, CO<sub>2</sub> produced by decomposition accumulates in the hypolimnion during summer stratification  
224 while surface water CO<sub>2</sub> concentrations become depleted due to photosynthetic uptake. Under these  
225 later conditions CO<sub>2</sub> fluxes are from the atmosphere into the surface water of lakes (del Giorgio et  
226 al., 1999). Once in the water column, the dissolved CO<sub>2</sub> is assimilated by phytoplankton and  
227 converted into biomass, although 50 – 95% of phytoplankton production is respired back to the  
228 water column (Quay & Emerson, 1986; Cole et al., 2002). When monomictic lakes become fully  
229 mixed in winter, the accumulated hypolimnetic CO<sub>2</sub> is released, causing supersaturation and CO<sub>2</sub>  
230 emissions to the atmosphere. This pattern was observed in all 11 Rotorua lakes, including those that  
231 are polymictic (Rotorua, Rotoehu and Rerewhakaaitu), however, large hypolimnetic accumulations  
232 of CO<sub>2</sub> were not observed in polymictic lakes as they frequently mix. Thus the timing of mixing and  
233 stratification events play an important role in the extent, timing and duration of pulses of  
234 greenhouse gases release to the atmosphere (e.g. Fig. 2).

235 In addition to the hydrodynamics and internal carbon processing discussed above lake CO<sub>2</sub>  
236 concentrations are influenced by other two processes including: 1) external carbon inputs (Maberly  
237 et al., 2013; Marcé et al., 2015) and 2) dissociation with carbonate species which is controlled by pH  
238 and alkalinity (Stets et al., 2009). High OC mineralization, supported by allochthonous (OC) inputs,  
239 may yield CO<sub>2</sub> supersaturation (Sobek et al., 2005) when respiration dominates over primary  
240 production (del Giorgio et al., 1999). With a relatively low range of dissolved organic carbon (DOC) in  
241 the water column (1.2 – 5.2 mg L<sup>-1</sup>: BOPRC unpublished data), it is possible that the contribution of  
242 water column OC mineralization to CO<sub>2</sub> supersaturation in Rotorua lakes is minimal, as also found in  
243 other studies (e.g., Stets et al., 2009). Geothermal activity, on the other hand, may influence CO<sub>2</sub>  
244 concentrations in some of the study lakes knowing that Rotorua lakes lie in an active volcanic zone  
245 and many were formed by volcanic eruptions (Lowe & Green, 1987). The volcanic geology may  
246 influence lake CO<sub>2</sub> concentrations as bicarbonate is the predominant salt for lakes in this region

247 (McColl, 1972; Timperley & Vigor-Brown, 1986) and a decrease in pH due to the influence of  
248 geothermal inputs strongly modulates the carbonate equilibrium towards high CO<sub>2</sub> concentrations  
249 (Stumm & Morgan, 1996). Surface waters at times became highly supersaturated in CO<sub>2</sub> in Lakes  
250 Rotomahana, Rotoiti, Rotorua and Tarawera; each subject to varying levels of geothermal influence  
251 (Timperley & Vigor-Brown, 1986). A special case is Lake Rotomahana, which emits a large amount of  
252 CO<sub>2</sub> (Fig. 3). Mazot et al. (2014) reported that Lake Rotomahana is an active hydrothermal area, even  
253 prior to the eruption of Mt Tarawera in 1886. Substantial CO<sub>2</sub> emissions were related to eruption  
254 craters observed in their study.

255 Marcé et al. (2015) synthesized that above an alkalinity threshold of 1 meq L<sup>-1</sup> supersaturation of  
256 CO<sub>2</sub> can be attributed to carbonate weathering in the watershed in which in situ net ecosystem  
257 productivity, and dissolution and precipitation of carbonate minerals, e.g. calcite, complicate this  
258 process. Carbon dioxide removal in the epilimnion due to photosynthesis increases pH which in turn  
259 strengthens calcite oversaturation and lowering the alkalinity (Müller et al., 2016). Further, studies  
260 have identified that algal metabolisms could be linked to calcite precipitation (Stabel, 1986; Dittrich  
261 et al., 2004). With the limited data set in alkalinity and calcium carbonate concentration we lack  
262 direct evidence of calcite precipitation and its controlling factors. However, knowing that (i)  
263 dissolved oxygen supersaturations and low CO<sub>2</sub> in the surface water coincides (data not shown) and  
264 (ii) calcium concentrations in the high alkalinity lakes is in moderate range (5 – 18 mg L<sup>-1</sup>: Timperley  
265 & Vigor-Brown, 1986), it is likely that calcite precipitation may occur. The proportion of CO<sub>2</sub> fractions  
266 that lost to the atmosphere and assimilated by algae productivity is therefore still a puzzle.

267 The recent synthesis of CO<sub>2</sub> emission from global lake and reservoirs is 0.3 – 0.6 Pg C y<sup>-1</sup> (Raymond et  
268 al., 2013; Holgerson & Raymond, 2016). For natural lakes alone, Cole et al. (2007) estimated a mid-  
269 range emission value of 0.1 Pg C y<sup>-1</sup>. This value yields an estimate of ~23.8 g C m<sup>-2</sup> y<sup>-1</sup> (~2.0 x 10<sup>3</sup> mmol  
270 C m<sup>-2</sup> y<sup>-1</sup>, Fig. 3) based on the total surface area of world's natural lakes of 4.2 x 10<sup>12</sup> m<sup>2</sup> (Downing et  
271 al., 2006). This estimate rate is within the mid-range emissions in Rotorua lakes of -0.3 x 10<sup>3</sup> – 5.4 x

272  $10^3 \text{ mmol C m}^{-2} \text{ y}^{-1}$  (Fig 3), excluding Lake Rotomahana ( $57.2 \times 10^3 \text{ mmol C m}^{-2} \text{ y}^{-1}$ ) due to its active  
273 hydrothermal area (Mazot et al., 2014). These results show that geothermal influence may contribute  
274 significant source for  $\text{CO}_2$  emission from lakes in addition to internal carbon reworking (e.g. Cole et al.,  
275 2002) and external carbon inputs (e.g. Maberly et al., 2013; Marcé et al., 2015). However,  
276 combinations of those controls over carbon cycle complicate the analysis of  $\text{CO}_2$  source in lakes as in  
277 this study geothermal influence is dominant in regulating  $\text{CO}_2$  emission in Lake Rotomahana.

278 Eutrophication and oligotrophication processes have also shown to influence surface water  $\text{CO}_2$  by  
279 reducing and increasing the concentration, respectively (Schindler, 1997; Cole et al., 2000; Marotta  
280 et al., 2012; Trolle et al., 2012; Pacheco et al., 2013). In this study, apart from Lake Rotomahana, the  
281 negative correlation between surface water  $\text{CO}_2$  and TN and TP across all lakes (Table 2) is in  
282 agreement with previous findings. However, in response to decreasing Chl concentrations through  
283 the period of this study, only Lakes Okaro and Rotoma exhibited significant increases in  $\text{CO}_2$   
284 emissions (Table 2). Primary production either in the watershed or in the water body itself is the  
285 ultimate route for OC production, therefore, it follows that more productive systems accumulate  
286 more carbon in the sediment. Such accumulation represents short- to long-term sequestration of  
287 atmospheric  $\text{CO}_2$  in lake sediment (Tranvik et al., 2009). The sediment carbon analysis for the  
288 Rotorua lakes showed that Chl has a significant positive relationship with areal storage of carbon in  
289 sediment for the period 1886 to 2006 (Fig. 5A). This result indicates that phytoplankton productivity  
290 is the dominant process contributing to carbon deposition in the sediment. It is also in agreement  
291 with a recent study by Trolle et al. (2008) showing that the carbon to nitrogen ratio (C/N: 4.8 – 10.1)  
292 of the surficial sediment organic matter in these lakes is sourced from an autochthonous base (C/N  
293 <10: Meyers, 1994).

294 Downing et al. (2008) estimated that eutrophic lakes with fertile agricultural catchments accumulate  
295 more organic carbon than those in undeveloped catchments. Thus, due to the high lake primary  
296 production fed by high nutrient concentrations, as well as high rates of terrestrial carbon input

297 through erosion, eutrophic lakes might act as active organic carbon sinks. Moreover, the study by  
298 Sobek et al. (2009) showed that sediment receiving high inputs of autochthonous material (more  
299 labile organic carbon) would have a lower burial efficiency (low buried OC: deposited OC) than that  
300 of allochthonous material (high buried OC: deposited OC). Although not showing a strong statistical  
301 fit, the organic carbon burial efficiency of the Rotorua lakes was negatively correlated with Chl (Fig.  
302 5B). This result agrees with the study by Sobek et al. (2009) and confirms that although productive  
303 lakes store more carbon in the sediment (Fig. 5A), only a small proportion of the deposited carbon is  
304 permanently buried. The remainder is remineralized, producing dissolved organic and inorganic  
305 carbon as well as CO<sub>2</sub> and CH<sub>4</sub> to re-enter water column in which this process can be associated with  
306 atmospheric carbon emission (Klump et al., 2009). Thus, in this study, except for the geothermally  
307 influenced lakes, carbon mineralization rate was of the same magnitude as CO<sub>2</sub> atmospheric  
308 emissions (Fig. 3). Our results, therefore, confirm the synthesis that eutrophication in lakes does  
309 increase carbon accumulation in the sediment, and is likely to increase the release of carbon gases,  
310 hence contributes to global warming (Moss et al., 2011).

### 311 **Conclusion**

312 This study demonstrated that CO<sub>2</sub> fluxes in lakes are driven by an interplay between chlorophyll *a*,  
313 nutrient availability and hydrodynamic processes. Geothermal activity may also directly contribute  
314 to elevated CO<sub>2</sub> concentrations and supersaturation in lakes. Surface water CO<sub>2</sub> concentrations were  
315 low during the summer and high in winter in all 11 study lakes. These seasonal variations, except in  
316 geothermally influenced lakes, result in atmospheric CO<sub>2</sub> uptake in the summer and CO<sub>2</sub> emissions in  
317 the winter. Nutrient concentrations and chlorophyll *a* were negatively correlated with CO<sub>2</sub>  
318 atmospheric fluxes. However, reductions in chlorophyll *a* and nutrient concentrations in lakes  
319 undergoing restoration were not necessarily matched by increasing CO<sub>2</sub> emissions.

320 Results of this study confirm that productive lakes, indicated by chlorophyll *a* concentrations,  
321 accumulate more carbon in sediment than less productive lakes. However, the burial efficiency in

322 productive lakes is low. Knowing that productive lakes remineralize more carbon in the sediment  
323 than less productive lakes, and that remineralization can be associated with the emission of CO<sub>2</sub> (as  
324 well as CH<sub>4</sub>), this study underlines that eutrophication may promote increased rates of greenhouse  
325 gas emissions and, therefore, global warming.

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Table 1. Physical and chemical properties of the study lakes. Values in water quality parameters are the mean of long term measurements and numbers in parentheses indicate the range of values. Trophic state categories are oligotrophic (oligo), mesotrophic (meso) and eutrophic (eu). Mixing regimes are monomictic (mono) and polymictic (poly).

Lake	Max depth (m)	Mean depth (m)	Surface area (km <sup>2</sup> )	Chl (µg L <sup>-1</sup> )	TN (µg L <sup>-1</sup> )	TP (µg L <sup>-1</sup> )	pH	Alkalinity (meq L <sup>-1</sup> )	Trophic state (-trophic)	Mixing regime (-mictic)
Okareka	33.5	20	3.3	3.8 (1.3-9.2)	206.6 (48.5-323.5)	7.7 (0.5 - 24)	7.6 (6.7-8.6)	0.64 (0.58-0.69)	meso	mono
Okaro	18	12.5	0.3	29.3 (0.9-283)	875.3 (202-2940.5)	65.3 (11 - 161)	8.5 (6.5-10.5)	0.67 (0.64-0.74)	eu	mono
Okataina	78.5	39.4	10.8	2.4 (0.3-7.2)	134.7 (40.5-438)	8.3 (0.5 - 49)	7.6 (6.66-8)	0.67 (0.59-0.79)	oligo	mono
Rerewhakaaitu	15.8	7	5.8	3.5 (1-9.8)	389.3 (65-708)	9 (1 - 21)	7.5 (6.6-8.1)	0.49 (0.43-0.58)	meso	poly
Rotoehu	13.5	8.2	8.1	10.6 (2.8-28.7)	400.1 (120-809)	37.2 (10 - 118)	8.0 (7.5-8.7)	1.38 (1.26-1.68)	eu	poly



Table 1. Continued

Lake	Max depth (m)	Mean depth (m)	Surface area (km <sup>2</sup> )	Chl (µg L <sup>-1</sup> )	TN (µg L <sup>-1</sup> )	TP (µg L <sup>-1</sup> )	pH	Alkalinity (meq L <sup>-1</sup> )	Trophic state (-trophic)	Mixing regime (-mictic)
Rotoiti	124	31.5	34.6	9.7 (2.4-38.6)	298.3 (82-573)	24.1 (4 - 51)	7.1 (6.32-8.5)	0.45 (0.39-0.58)	meso	mono
Rotoma	83	36.9	11.2	1.3 (0.3-3.5)	151.2 (36.5-425)	4.7 (0.5 - 13)	7.4 (6.5-8.12)	0.45 (0.30-0.57)	oligo	mono
Rotomahana	125	60	9	4.3 (1.3-13.7)	215.9 (72.5-366)	33.3 (6 - 98)	7.3 (6.6-7.9)	3.85 (3.58-4.62)	meso	mono
Rotorua	44.8	11	80.8	21.2 (0.1-78.1)	452.6 (215-1810.5)	35.9 (9 - 70)	6.9 (6.4-8.5)	0.2 (0.15-0.25)	eu	poly
Tarawera	87.5	50	41.7	1.5 (0.4-3.6)	127.4 (18-657.5)	9.5 (2 - 25)	7.8 (6.8-8.2)	2.35 (2.22-2.72)	oligo	mono
Tikitapu	27.5	18	1.5	2 (0.3-5.6)	206.7 (53-483)	5.9 (0.5 - 27)	6.7 (5.6-8.4)	0.08 (0.05-0.11)	oligo	mono

Table 2. Pearson correlation matrix of surface water CO<sub>2</sub> and water quality parameters for Rotorua lakes.

	Chlorophyll <i>a</i>	Total phosphorus	Total nitrogen
Total phosphorus	0.87***		
Total nitrogen	0.89***	0.85***	
CO <sub>2</sub> flux	-0.29**	-0.34**	-0.37***

Lake Rotomahana was excluded in the analysis due to its extreme CO<sub>2</sub> concentration compared with the other lakes (See Table 4.1) and log transformation did not yield a substantial improvement in strength of the correlation. n = 90, \*\* significant at  $p < 0.01$ , \*\*\* significant at  $p < 0.001$ .

Table 3. Trends in eight-year (2002 – 2010) of CO<sub>2</sub> flux and water quality in selected Rotorua lakes calculated by seasonal Mann-Kendall tests where there is active management to reduce nutrient loads. Numbers in parentheses indicate percentage change calculated from the long term mean concentration.

Lake	CO <sub>2</sub> flux (mmol m <sup>-2</sup> y <sup>-1</sup> )	TP (µg L <sup>-1</sup> y <sup>-1</sup> )	TN (µg L <sup>-1</sup> y <sup>-1</sup> )	Chl (µg L <sup>-1</sup> y <sup>-1</sup> )
Okareka	0.56 (-18.75)	0 (0)	-0.1 (-0.05)	0.06 -1.48
Okaro	0.38* (19.40)*	-4.38*** (-6.71)	-18.24*** (-2.08)	-1.00*** (-3.40)
Rotoehu	-0.79 (-41.45)	1 (-2.69)	-17.05*** (-4.26)	-0.34 (-3.18)
Rotoiti	-0.28 (-0.52)	-0.69 (-3.52)	-20.37*** (-6.83)	-0.57*** (-5.95)
Rotoma	1.72* (12.68)*	-0.16 (-3.52)	-1.5 (-0.99)	-0.03* (-2.16)*
Rotorua	2.04 (10.44)	-2.45*** (-6.82)	-8.19 (-1.81)	-1.34*** (-6.29)

\* significant at  $p < 0.05$ , \*\* significant at  $p < 0.01$ , \*\*\* significant at  $p < 0.001$

Table 4. Sediment accumulation rates and organic carbon diagenesis model outputs for 11 Rotorua lakes for the period 1886 -2016.

Lake	Mass accumulation rate $\omega$ (kg m <sup>-2</sup> y <sup>-1</sup> )	First order rate constant $k_m$ (y <sup>-1</sup> )	Mineralizable organic carbon $G_m$ (%C)	Non-mineralizable organic carbon $G_{inf}$ (%C)	Organic carbon deposition rate $J_{in}$ (mol m <sup>-2</sup> y <sup>-1</sup> )	Organic carbon remineralization rate $J_{rec}$ (mol m <sup>-2</sup> y <sup>-1</sup> )	Organic carbon burial rate $J_{bur}$ (mol m <sup>-2</sup> y <sup>-1</sup> )	Organic carbon stock (mol m <sup>-2</sup> )	Fitness of the model: Pearson correlation coefficient
Okareka	0.26	0.03	5.54	0.70	1.35	1.20	0.15	1030	0.989***
Okaro	0.21	0.01	13.26	0.01	2.32	2.32	<0.01	3650	0.960***
Okataina	0.21	0.02	3.61	0.64	0.74	0.63	0.11	580	0.936**
Rerewhakaaitu	0.21	0.03	15.59	0.51	2.82	2.73	0.09	1350	0.960**
Rotoehu	0.36	0.01	5.92	0.62	1.96	1.78	0.18	3360	0.943***
Rotoiti	0.2	0.03	7.72	0.69	1.40	1.29	0.12	670	0.982**
Rotoma	0.27	0.03	5.17	0.78	1.34	1.16	0.18	1130	0.956*

\* significant at  $p < 0.05$ , \*\* significant at  $p < 0.01$ , \*\*\* significant at  $p < 0.001$ .

Table 4. Continued

Lake	Mass accumulation rate $\omega$ (kg m <sup>-2</sup> y <sup>-1</sup> )	First order rate constant $k_m$ (y <sup>-1</sup> )	Mineralizable organic carbon $G_m$ (%C)	Non-mineralizable organic carbon $G_{inf}$ (%C)	Organic carbon deposition rate $J_{in}$ (mol m <sup>-2</sup> y <sup>-1</sup> )	Organic carbon remineralization rate $J_{rec}$ (mol m <sup>-2</sup> y <sup>-1</sup> )	Organic carbon burial rate $J_{bur}$ (mol m <sup>-2</sup> y <sup>-1</sup> )	Organic carbon stock (mol m <sup>-2</sup> )	Fitness of the model: Pearson correlation coefficient
Rotomahana	0.08	0.02	3.83	0.78	0.31	0.25	0.05	140	0.860*
Rotorua	0.35	0.04	4.51	0.66	1.51	1.31	0.19	1500	0.894***
Tarawera	0.21	0.01	4.31	0.76	0.89	0.75	0.13	1220	0.914**
Tikitapu	0.11	0.01	4.06	0.57	0.42	0.37	0.05	290	0.973**

\* significant at  $p < 0.05$ , \*\* significant at  $p < 0.01$ , \*\*\* significant at  $p < 0.001$ .

## Figure headings

Fig. 1. Location of the 11 Rotorua lakes in the North Island of New Zealand.

Fig. 2. Seasonal variation of thermocline depth and CO<sub>2</sub> concentration in Lakes Tarawera, Okaro and Rotoehu. Dashed lines and dotted lines indicate the median of the bootstrapped monthly data over the period of 2002 – 2010 and the 95% confidence interval, respectively. Solid gray lines indicate CO<sub>2</sub> saturation concentrations.

Fig. 3. Atmospheric carbon flux (FCO<sub>2</sub>) and sediment carbon diagenesis rate in 11 Rotorua lakes. Negative values of atmospheric flux represent flux into the lake. Sediment carbon remineralization (J<sub>rec</sub>) is presented as positive values to indicate release of carbon from the sediment. Permanent burial of carbon in the sediment (J<sub>bur</sub>) is presented by negative value to indicate sink of carbon in the sediment. Horizontal dashed line indicates the average of carbon emission from global lakes.

Fig. 4 Organic carbon profile in the sediment of Lakes Tarawera, Okaro and Rotoehu. Open circles-lines indicate field measurements, dashed lines indicate model output, horizontal dashed lines indicate the depth of the 1886 Tarawera tephra.

Fig. 5. Phytoplankton productivity and sedimentary organic carbon where solid lines indicate linear regression relationships. (A) Relationship between phytoplankton biomass and sediment organic carbon stock to the 1886 tephra layer ( $R^2 = 0.485$ ,  $p < 0.05$ ). (B) Relationship between phytoplankton biomass and organic carbon burial efficiency ( $R^2 = 0.332$ ,  $p < 0.1$ ).

Fig. 1.

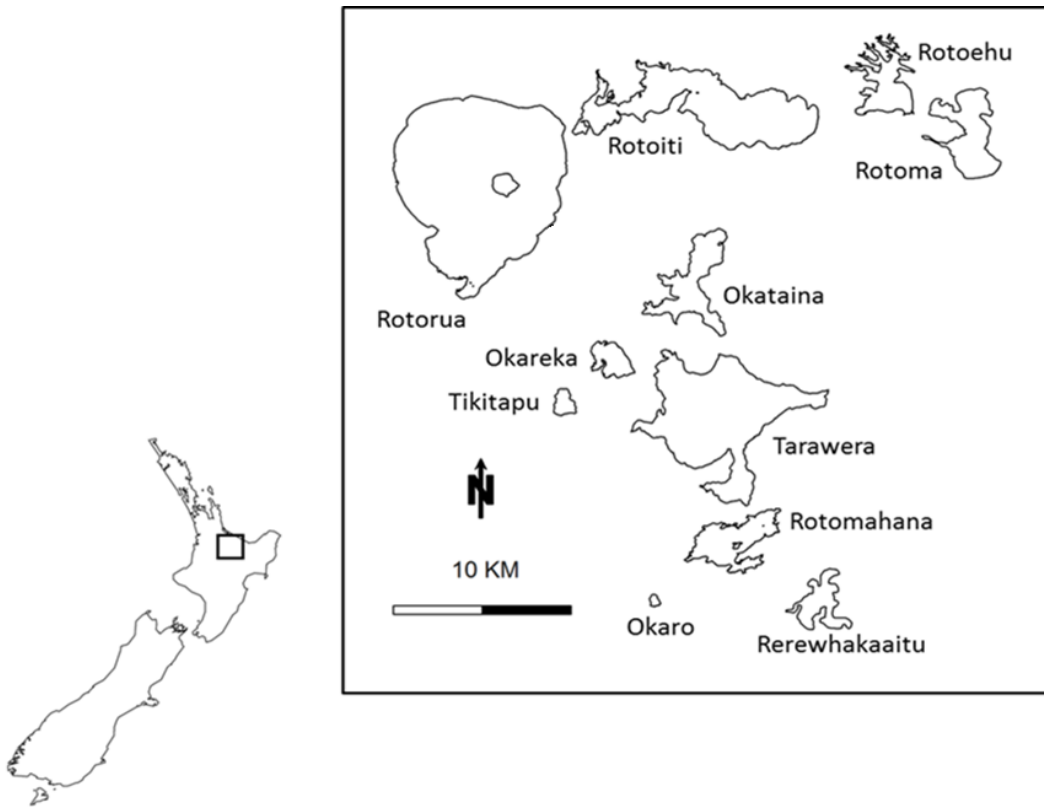


Fig. 2.

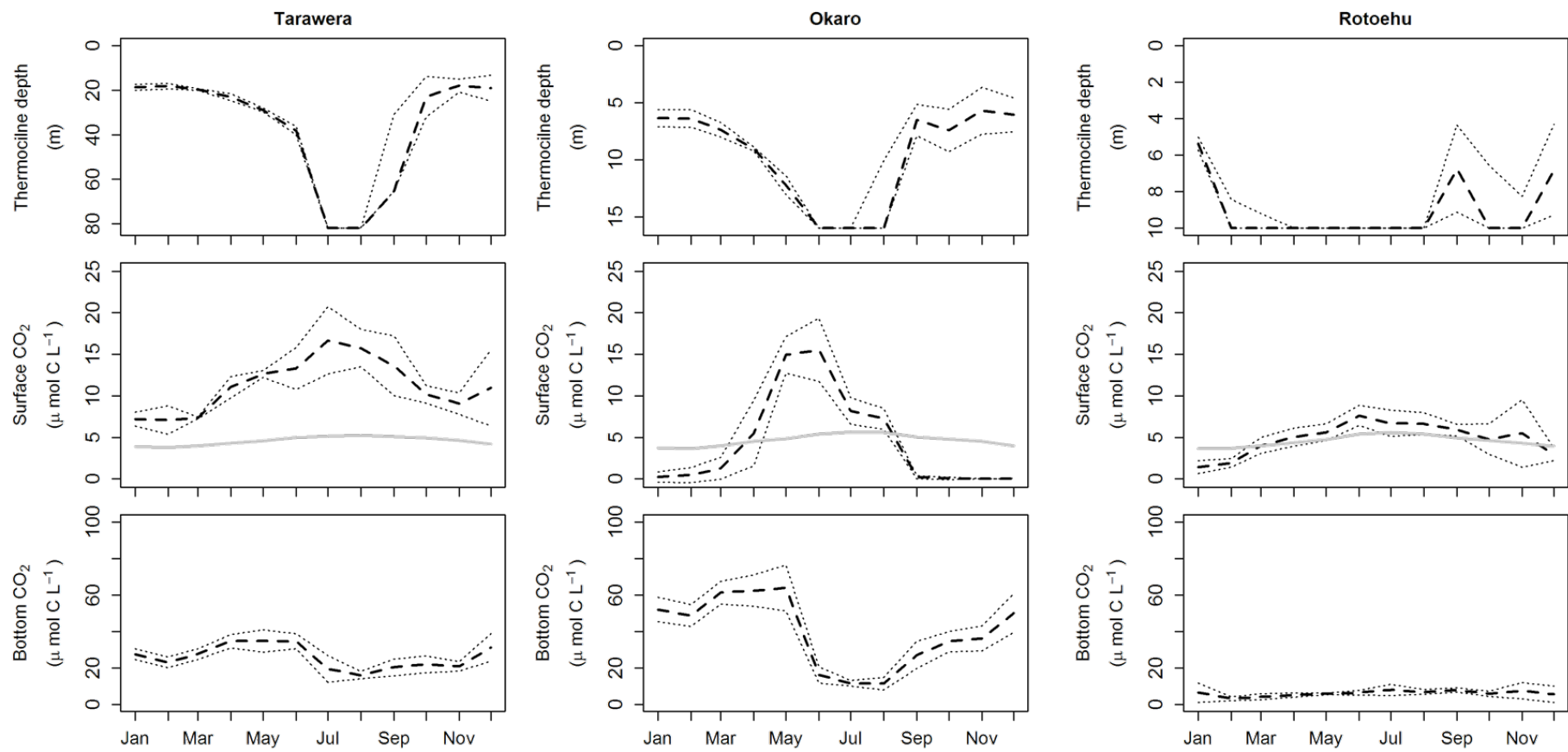




Fig. 3.

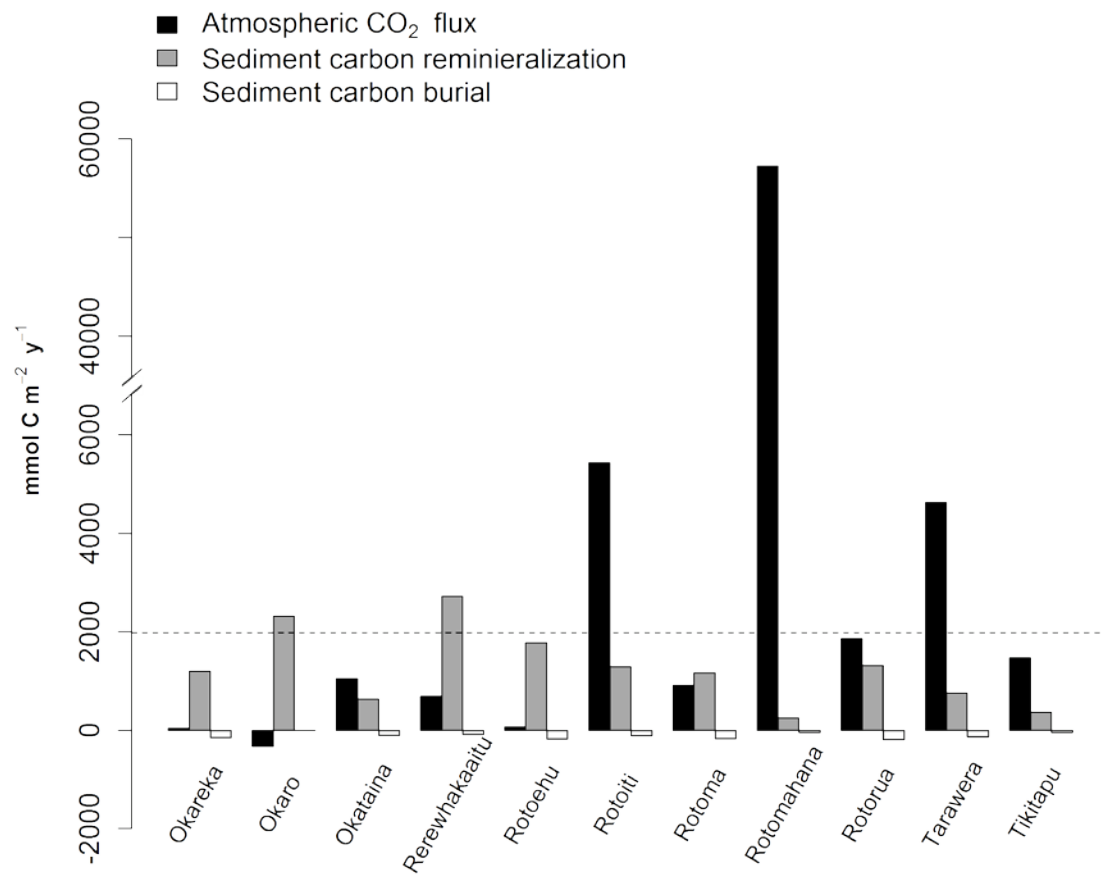


Fig. 4.

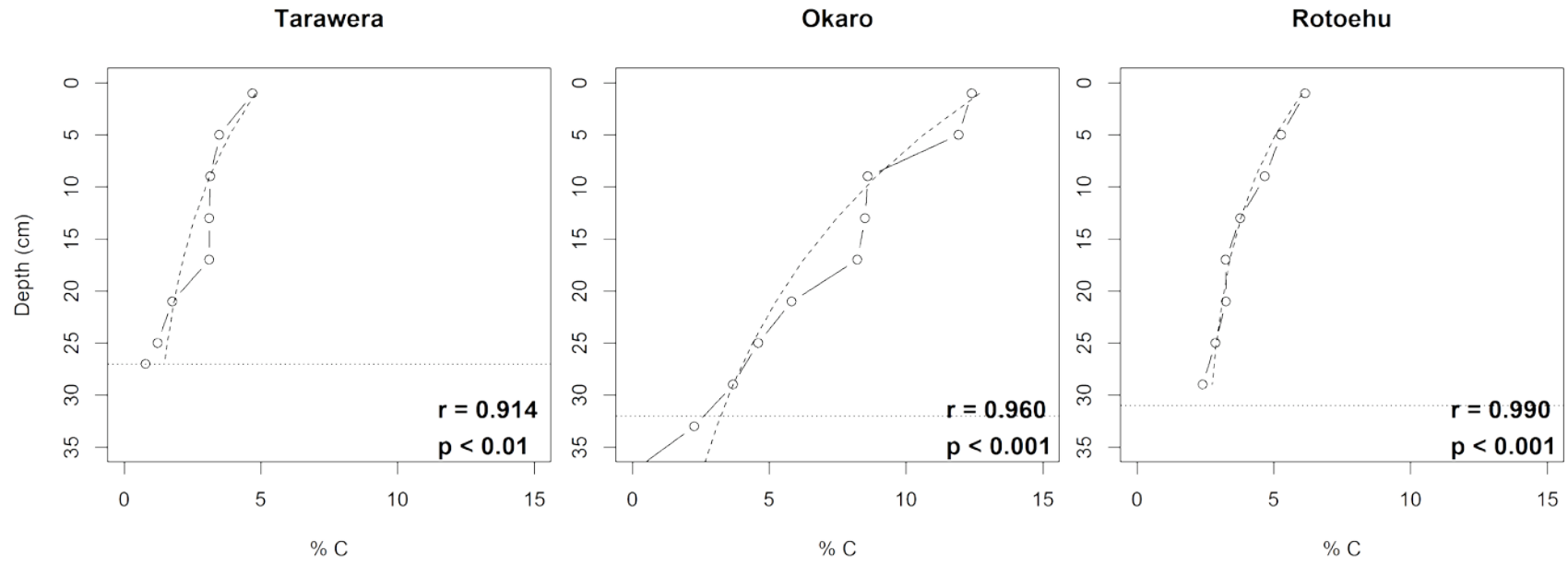


Fig. 5.

