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1 **Catchment productivity controls CO₂ emissions from lakes**

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17 Most lakes are oversaturated with CO₂ and are net CO₂-sources to the atmosphere, yet their
18 contribution to the global carbon-cycle is poorly constrained¹⁻⁴. Their CO₂-excess is widely
19 attributed to in-lake oxidation of terrestrially-produced dissolved organic carbon (DOC)⁵.
20 Here we use data collected over 26 years to show that the CO₂ in 20 lakes is primarily
21 delivered directly via inflowing streams rather than being produced *in situ* by degradation of
22 terrestrial carbon. This implies that high CO₂ concentrations and atmospheric emissions are
23 not necessarily symptoms of heterotrophic lake ecosystems. Instead, the annual mean CO₂
24 concentration increased with lake productivity and was proportional to the estimated net
25 primary productivity of the catchment. Overall, about 1.6% of net primary productivity (range
26 1.2 to 2.2%) was lost to the atmosphere. Extrapolating globally this is equivalent to CO₂
27 losses of ~0.9 Pg C yr⁻¹ (range 0.7 to 1.3), consistent with existing estimates. These data and
28 our catchment productivity hypothesis re-enforce the high connectivity found between lakes,
29 their catchment and the global C-cycle⁶. They indicate that future concentrations of CO₂ in
30 lakes, and losses to the atmosphere, will be highly sensitive to altered catchment management
31 and concomitant effects of climate change that modify catchment productivity.

32

33 The generally elevated concentration of CO₂ in lakes has led to the belief that they are
34 heterotrophic systems that oxidise terrestrially-produced DOC⁵. While this is undoubtedly
35 true at some locations, it is less likely in relatively clear-water lakes. An additional
36 hypothesis, that we examine here, is that high CO₂ concentrations can also result from direct
37 inputs of CO₂, fixed and broken-down in the terrestrial catchment and delivered via
38 hydrological pathways. Moreover, we hypothesise that CO₂ concentrations in lakes are a
39 consequence of the catchment carbon cycle implying that catchment processes, driven by land
40 use, will regulate the contribution of lakes to the global carbon cycle^{6,7}.

41

42 Twenty lakes in the English Lake District were sampled quarterly (January/February, April,
43 July and October) in 1984, 1991, 1995, 2000, 2005 and 2010. The average rainfall on these
44 catchments (2.34 m yr⁻¹) and catchment slope (277 m km⁻¹) are high and the geology largely
45 comprises impermeable slates, shales and igneous rocks that do not support major
46 groundwater aquifers (See Supplementary Fig. 1) so inflow of water is dominated by surface-
47 flow and potentially soil throughflow and interflow. The lakes have a low alkalinity (mean
48 0.21 equiv m⁻³, range 0.05 to 0.54 equiv m⁻³ in 2010) and relatively low concentrations of
49 DOC (mean 0.13 mol m⁻³, range 0.06 to 0.22 mol C m⁻³⁸ Supplementary Table 1) and hence
50 have relatively clear-water. Their productivity is largely controlled by the availability of
51 phosphorus⁹. The concentration of CO₂ varied significantly with lake trophic status, as
52 expressed using measured total P (Fig. 1) and verified by the morpho-edaphic index¹⁰ that
53 excludes point-sources of P (See Supplementary Information). There was little variability in
54 the concentration of CO₂ in unproductive, oligotrophic lakes, where concentrations of total P
55 were less than about 10 mg m⁻³. In contrast, there was a large dynamic range of CO₂
56 concentration in the more productive lakes, with minima in summer when productivity was
57 high² and maxima in the autumn when CO₂ produced by mineralisation of organic carbon at

58 depth¹¹ is mixed into the surface waters on breakdown of stratification. On average, these
59 lakes were about 2-fold oversaturated with CO₂, in broad agreement with previous
60 surveys^{1,3,4}.

61

62 Paradoxically however, the annual mean concentration of CO₂ increased with lake
63 productivity, despite summer CO₂-depletion and high productivity indicated by elevated
64 concentrations of chlorophyll and oxygen in the surface waters during the growing season.

65 We hypothesise that the large CO₂-excess in the more productive lakes results from them
66 receiving large subsidies of carbon from productive terrestrial ecosystems. This hypothesis
67 was tested using the ratio of ¹³C to ¹²C ($\delta^{13}\text{C}$) to trace inputs of terrestrial carbon fixed by C₃
68 photosynthesis which is depleted in ¹³C. Our spot-sample data from 2005 show that the $\delta^{13}\text{C}$
69 value of dissolved inorganic carbon (DIC, $\delta^{13}\text{C}_{\text{DIC}}$) decreased with increasing concentration of
70 total P (Fig. 2a) consistent with an increasing contribution of terrestrially-fixed carbon to the
71 inorganic carbon pool in productive lakes. Moreover, a time-integrated estimate of $\delta^{13}\text{C}$ based
72 on analysis of proteins within the silica frustules of epilithic lake diatoms ($\delta^{13}\text{C}_{\text{diatom}}$),
73 confirmed the strong negative relationships between $\delta^{13}\text{C}_{\text{diatom}}$ and lake P concentration (Fig.
74 2a). The lake $\delta^{13}\text{C}_{\text{DIC}}$ and $\delta^{13}\text{C}_{\text{diatom}}$ values were also strongly correlated with other measures
75 of lake productivity: the mean concentration of phytoplankton chlorophyll *a* (Pearson
76 correlation coefficient: $r = -0.70$ for DIC and -0.92 for diatoms, $P < 0.001$ for both) and Secchi
77 depth (Pearson correlation coefficient: $r = 0.46$, $P < 0.05$ for DIC and $r = 0.88$, $P < 0.001$ for
78 diatoms) (See Supplementary Fig. 2).

79

80 These carbon isotope data are consistent with our hypothesis that aquatic systems within
81 productive catchments receive more allochthonous biogenic carbon, relatively depleted in ¹³C,
82 than those in unproductive catchments. Furthermore, in each month and overall, high

83 concentrations of CO₂ are associated with the most negative values of δ¹³C_{DIC} (Fig. 2b) which
84 suggests that high concentrations of CO₂ are linked to input from terrestrial C₃-fixed carbon.
85 A similar relationship has been found for lakes in the North America and Finland sampled
86 prior to ice-melt¹².

87

88 The conventional explanation for excess CO₂ in a lake is *in situ* mineralisation of organic
89 carbon produced in the catchment¹³. This is unlikely in lakes where the concentration of DOC
90 is low such as in the lakes studied here and an alternative hypothesis is that the CO₂ is
91 produced in the catchment and brought in directly via water transfer^{14 15}. Hydrological
92 pathways that link the terrestrial and aquatic components of a catchment often contain high
93 concentrations of CO₂^{14 15 16} which our hypothesis would predict. In other regions where
94 aquifers contribute significantly to the water budget of a lake, CO₂ can be delivered by
95 groundwater and emitted from the lake^{17,18}.

96

97 The source of CO₂ in these lakes was determined by a survey of the 33 streams entering 19 of
98 lakes (excluding Thirlmere reservoir with many small inflowing streams). The δ¹³C_{DIC} values
99 of the inflowing streams (Fig. 2a) also decreased in proportion to the P concentration in a
100 nearly identical way to that of the lakes. These spot water samples were extended temporally
101 by analysing the δ¹³C of stream bryophytes, which lack roots and are unable to use HCO₃⁻ as
102 a carbon source¹⁹ requiring them to derive their inorganic carbon from CO₂ in water.

103 Bryophyte δ¹³C also declined with total P (Fig. 2a) and the relationship between bryophyte
104 δ¹³C and stream δ¹³CO₂ (See Supplementary Information for method of calculation) was close
105 to 1:1 with an average discrimination of 14.3 ‰ against CO₂ (linear regression with standard
106 errors in parenthesis, Bryophyte δ¹³C‰ = -14.3 (4.75) + 1.09 (0.26) stream δ¹³CO₂‰;
107 adjusted R² = 0.45, P<0.001). These data support the direct input of CO₂ to lakes from

108 inflowing streams because the retention time in these short (typically less than 10 km), high-
109 slope streams is too little for substantial oxidation of DOC. Furthermore, the mean stream
110 concentration of DIC (0.37, SD = 0.24 mol m⁻³) is nearly three times greater than the mean
111 concentration of DOC (0.13, SD = 0.06 mol m⁻³).

112

113 These data strongly suggest that the source of the excess CO₂ lies in the terrestrial catchment.

114 There was a strong positive relationship between the CO₂ concentration in each lake and
115 terrestrial Net Primary Productivity (NPP) i.e., lakes with higher mean concentrations of CO₂

116 lie in more productive catchments (Fig. 3a). To estimate the proportion of carbon fixed by

117 catchment NPP that is lost at the lake surface, CO₂ efflux was estimated from the measured

118 CO₂ concentrations for each lake using a gas transfer velocity of 5.43 cm hr⁻¹ based on annual

119 mean wind speed measured at five of the lakes (see Supplementary Information for more

120 detail on derivation). Excluding four lakes with a major lake upstream, there was a significant

121 relationship between lake CO₂-efflux and NPP in the lake's catchment (Fig. 3b). In contrast,

122 stepwise regression showed that other possible explanatory variables including mean

123 catchment slope, rainfall, discharge, stream length, residence time and concentration of DOC

124 did not contribute significantly to explaining the variation in CO₂-efflux among lakes

125 (Supplementary Information Table 4a). On average, 1.6% of the carbon fixed in the

126 catchment is lost at the lake surface (linear regression with standard errors in parenthesis: net

127 CO₂ efflux = -0.85 10⁻² (3.29 10⁻²) + 1.56 10⁻² (0.19 10⁻²) * total catchment NPP; adjusted R²

128 = 0.84, P<0.001; units are Gg C yr⁻¹). Using the minimum and maximum mean gas transfer

129 coefficients in Supplementary Table 3, this ranged between 1.2 and 2.2% of catchment NPP.

130 The mean loss of CO₂ to the atmosphere is about 16-times larger from lakes than the loss of

131 CO₂ in the outflow river (Fig. 3b) assuming that the CO₂ exiting the lake reaches atmospheric

132 equilibrium during the passage downstream.

133 The global CO₂-efflux from lakes has been estimated previously from the product of the
134 average CO₂ concentration (converted to an efflux using a gas transfer velocity as above) and
135 an estimate of the global number of lakes and their size-distribution which is poorly
136 constrained²⁰. This approach produces an estimate of 0.53 Pg C yr⁻¹⁴. If the hypothesised link
137 between catchment productivity and CO₂ losses from lakes is broadly correct and applicable
138 globally, the product of global terrestrial NPP and our estimates of proportionate losses
139 should produce a similar value. Using a value of CO₂-losses from lakes of 1.6% of NPP and
140 an estimated global terrestrial NPP of 56.4 Pg C yr⁻¹²¹, global CO₂-losses from lakes are
141 about 0.9 Pg C yr⁻¹. The similar magnitude of the two estimates is consistent with the
142 hypothesis that there is a broad link between catchment productivity and CO₂-losses from
143 lakes. Work on CO₂-concentration in streams and rivers in the USA which found a strong
144 positive, but likely indirect, correlation between CO₂ evasion and annual precipitation¹⁶ could
145 also be explained by this hypothesis since precipitation and NPP are generally positively
146 correlated over larger spatial scales²².

147

148 Our results reinforce the established link between lakes, their catchment and the global
149 carbon-cycle^{6,7}. While the focus hitherto has been on the *in situ* oxidation of terrestrially-
150 produced DOC as the cause of high concentrations of CO₂ in lakes, the results presented here
151 demonstrate that high concentrations of CO₂ can also derive from terrestrially-fixed carbon
152 broken down in the soil²³ and entering lakes directly. The lakes analysed in the present work
153 had a maximum DOC concentration of 0.22 mol m⁻³ and lie in the lower quartile of a dataset
154 of 7500 lakes where the median DOC concentration was 0.48 mol m⁻³²⁴. It is likely that in
155 lakes where the DOC concentration is low the direct input of CO₂ will be important and *vice*
156 *versa*, but further research is needed to define the relative importance of these two routes of
157 carbon entry in different types of lakes.

158

159 Understanding these contrasting routes to CO₂ excess is critical in understanding the role of
160 lakes in the global carbon cycle. The strong coupling of lakes to their terrestrial catchment
161 mean that large scale factors that increase terrestrial productivity, such as increasing regional
162 temperature and nitrogen deposition, plus local change in land use and management, will
163 potentially increase the supply of CO₂ to lakes. This will consequently increase aquatic
164 emissions of CO₂ to the atmosphere, potentially reducing gains in carbon sequestration made
165 by enhanced terrestrial productivity. The concentration of CO₂ in lakes is much more likely to
166 be controlled by land use than by rising atmospheric CO₂ concentrations, or temperatures²⁵.
167 Increasing atmospheric CO₂ will consequently have little direct ecological impact on all but
168 the most unproductive systems. At the largest scale, our hypothesis is highly relevant to
169 global carbon-cycling models by providing a quantitative explanation of the link between
170 terrestrial productivity and CO₂ losses from lakes. Recent studies²⁶ have concluded that
171 experimental observations cannot quantify the impacts of land-cover changes on the global
172 carbon cycle, so studies such as this are essential to understand processes delivering carbon
173 through lake catchments and back to the atmosphere.

174

175 **Methods**

176 Depth-integrated lake water samples were collected with a 5 or 7 m tube. Alkalinity was
177 measured by Gran titration and pH with a combination electrode. Total P was measured
178 following²⁷. Carbon species were calculated following², using an estimate of ionic strength
179 from the cation and anion analysis made in 2005. As a result of the low concentrations of
180 DOC in these lakes⁸, DOC anions are estimated to have contributed on average 5.5% of
181 alkalinity²⁸ which will not have had a major effect on the calculations of carbon speciation.

182

183 In 2005, water for stable isotope analysis was collected sub-surface in the 20 lakes on four
184 occasions and for the 33 major inflowing streams in July. The carbon isotope ratio $\delta^{13}\text{C}/\delta^{12}\text{C}$ (δ
185 ^{13}C) was analysed on the dissolved inorganic carbon (DIC)²⁹. Submerged mosses or
186 liverworts were collected in July 2005 from inflowing streams where present (22 of the 33
187 streams). Lacustrine diatoms were collected from five randomly selected stones at
188 approximately 30 cm water depth in fourteen of the lakes in July 2005. The cleaned samples
189 of diatom frustules were dried at 40°C for 24 h. Stable isotope analysis of proteins within the
190 silica frustule was undertaken by high temperature combustion in an elemental analyser
191 coupled to a ‘continuous flow’ isotope ratio mass spectrometer.

192

193 The land cover of each catchment was allocated to one of nineteen categories using the CEH
194 satellite-based land cover map LCM2000³⁰. Net primary productivity (NPP) of the different
195 land cover types is given in Supplementary Table 2 and catchment NPP was calculated as the
196 product of cover and NPP, summed for each land cover category. Further details are available
197 in the Supplementary Information.

198

199 Concentrations of CO₂ were converted to rates of CO₂ exchange estimated from hourly wind
200 speed measurements at five of the lakes and four different relationships between wind speed
201 and gas transfer (Supplementary Table 3).

202

203 Further details of all the methods are available in the Supplementary Information.

204

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284
285

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292 1991, 1995, 2000 and 2005. We thank three anonymous reviewers whose comments helped us
293 to improve the manuscript.

294

295 **Author contributions**

296 S.C.M. conceived the work, led the analysis and co-wrote the manuscript. P.A.B. undertook
297 the diatom isotope work and analysis and co-wrote the manuscript. A.W.S. undertook the
298 remainder of the isotope measurements. M.M.D.V. led the field work.

299

300 **Competing Financial Interests**

301 There are no competing financial interests

302

303 **Figure legends**

304 **Figure 1 Effect of lake productivity on concentration of CO₂.** Mean (●), maximum (▲)
305 and minimum (■) concentrations of free CO₂ and approximate CO₂-excess for 20 lakes
306 sampled four times a year in 1984, 1991, 1995, 2000, 2005 and 2010 vs mean concentration
307 of total P between 1984 and 2010. The horizontal grey-line represents the mean air-
308 equilibrium concentration (CO₂-excess equals 1) calculated from lake temperature and annual
309 mean atmospheric partial pressure of CO₂ from
310 ftp://ftp.cmdl.noaa.gov/ccg/co2/trends/co2_annmean_mlo.txt. The error bars represent one
311 standard deviation. The regression lines relate the concentration of CO₂ to total P. The
312 regression for mean CO₂ is (standard errors in parentheses): CO₂ (mol m⁻³) = 0.0216 (0.0021)
313 + 0.0012 (0.0001) total P (mg m⁻³), adjusted R² = 0.87, P<0.001.

314
315 **Figure 2 Relationship between inorganic and organic δ¹³C values in lakes and streams**
316 **and productivity and CO₂ concentration.** a) Relationship between δ¹³C of dissolved
317 inorganic and organic carbon and mean concentration of Total P in lakes and streams and b)
318 relationship between δ¹³C of dissolved inorganic carbon and lake concentration of CO₂.
319 Values of δ¹³C for lake dissolved inorganic carbon for January (●), April (●), July (●) and
320 October (●); solid regression line average for all months (all individual months also
321 significant P<0.05 in July and P<0.001 in the other months). Results from July for stream
322 dissolved inorganic carbon (▲, dashed regression line), organic carbon from lake epilithic
323 diatom frustules (◆, solid regression line) and organic carbon from stream bryophytes (■,
324 dashed regression line). All data from 2005.
325

326 **Figure 3 Links between lake CO₂ concentration, CO₂-efflux and catchment productivity.**
327 a) Relationship between mean CO₂ concentration measured four times a year in 1984, 1991,
328 1995, 2000, 2005 and 2010 and mean NPP estimated from area of different land cover
329 categories in the catchment; b) estimated CO₂-efflux from the lake surface (●) and loss of

330 CO₂ to the downstream river (○) for lakes without another major lake upstream. The grey
331 horizontal line in a) is the approximate mean air-equilibrium concentration.

332

333

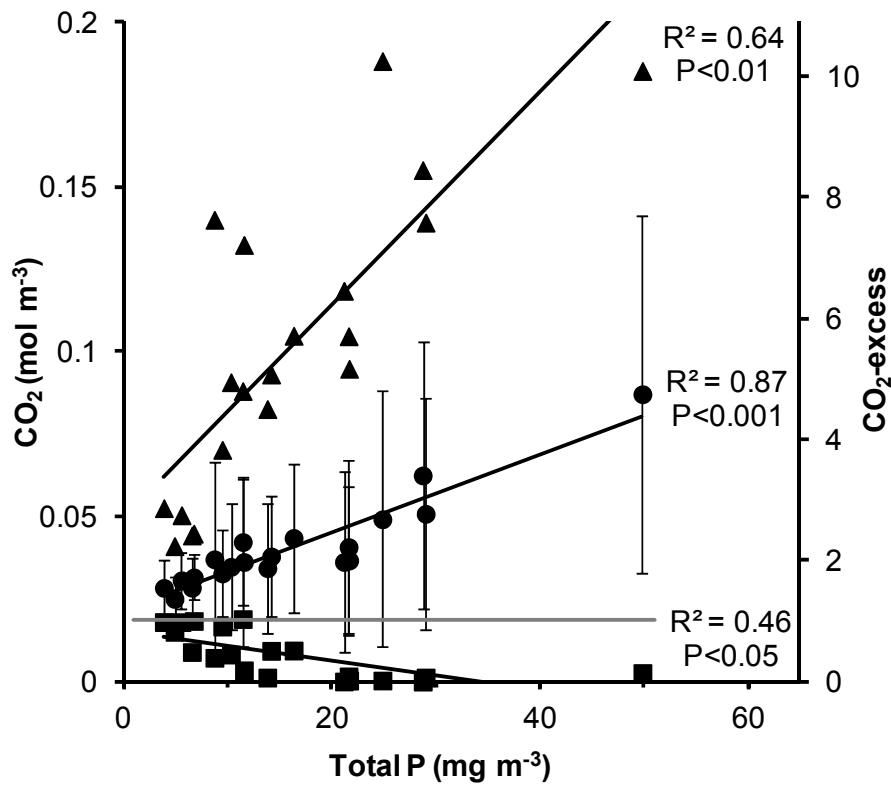


Figure 1

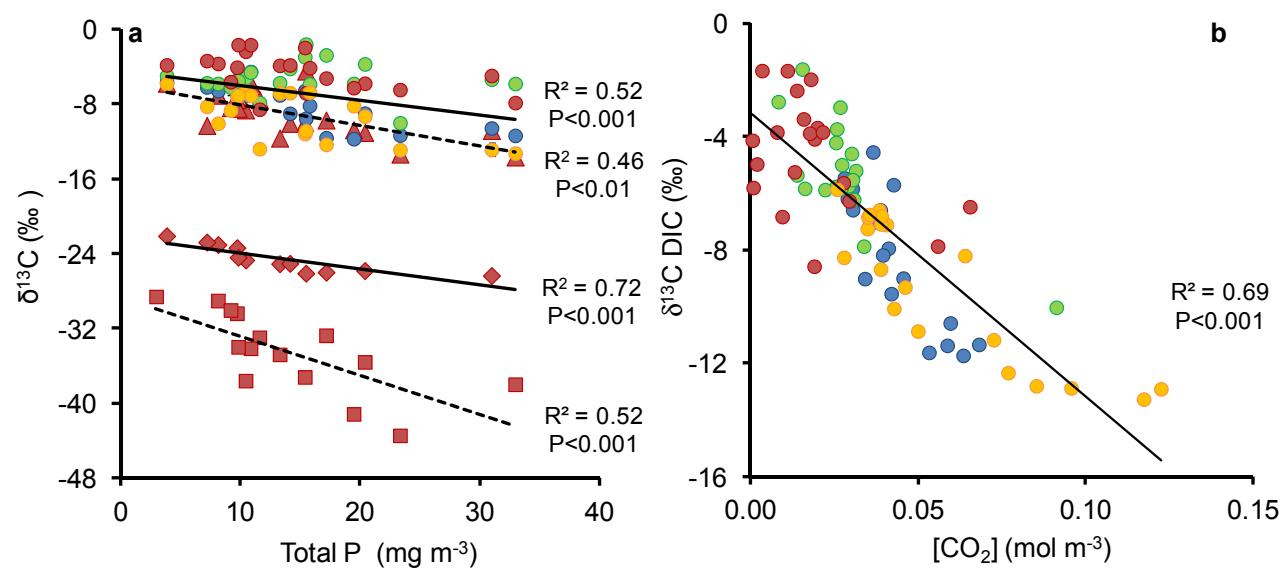


Figure 2.

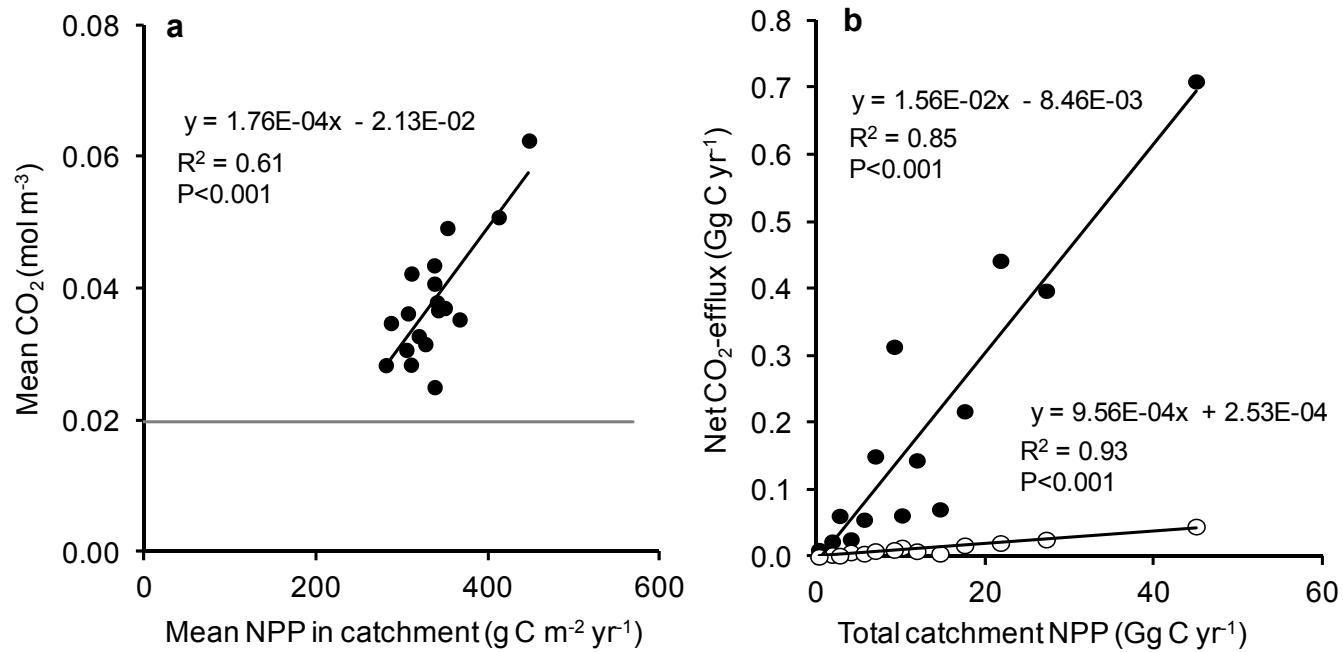


Figure 3.