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1   **Catchment productivity controls CO$_2$ emissions from lakes**

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17   Most lakes are oversaturated with CO_2 and are net CO_2-sources to the atmosphere, yet their

18   contribution to the global carbon-cycle is poorly constrained[1-4]. Their CO_2-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 CO_2 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 CO_2 concentrations and atmospheric emissions are

23   not necessarily symptoms of heterotrophic lake ecosystems. Instead, the annual mean CO_2

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 CO_2

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-cycle[6]. They indicate that future concentrations of CO_2 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 CO_2 in lakes has led to the belief that they are

34   heterotrophic systems that oxidise terrestrially-produced DOC[5]. 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 CO_2 concentrations can also result from direct

37   inputs of CO_2, fixed and broken-down in the terrestrial catchment and delivered via

38   hydrological pathways. Moreover, we hypothesise that CO_2 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^{-3} [8] Supplementary Table 1) and hence

50   have relatively clear-water. Their productivity is largely controlled by the availability of

51   phosphorus[9]. The concentration of CO_2 varied significantly with lake trophic status, as

52   expressed using measured total P (Fig. 1) and verified by the morpho-edaphic index[10] that

53   excludes point-sources of P (See Supplementary Information). There was little variability in

54   the concentration of CO_2 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 CO_2

56   concentration in the more productive lakes, with minima in summer when productivity was

57   high[2] and maxima in the autumn when CO_2 produced by mineralisation of organic carbon at

58 depth[11] is mixed into the surface waters on breakdown of stratification. On average, these

59 lakes were about 2-fold oversaturated with CO_2, in broad agreement with previous

60 surveys[1,3,4].

61

62 Paradoxically however, the annual mean concentration of CO_2 increased with lake

63 productivity, despite summer CO_2-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 CO_2-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 ^{13}C to ^{12}C ($\delta^{13}C$) to trace inputs of terrestrial carbon fixed by C_3

68 photosynthesis which is depleted in ^{13}C. Our spot-sample data from 2005 show that the $\delta^{13}C$

69 value of dissolved inorganic carbon (DIC, $\delta^{13}C_{DIC}$) 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 $\delta^{13}C$ based

72 on analysis of proteins within the silica frustules of epilithic lake diatoms ($\delta^{13}C_{diatom}$),

73 confirmed the strong negative relationships between $\delta^{13}C_{diatom}$ and lake P concentration (Fig.

74 2a). The lake $\delta^{13}C_{DIC}$ and $\delta^{13}C_{diatom}$ 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 ^{13}C,

82 than those in unproductive catchments. Furthermore, in each month and overall, high

4

83   concentrations of CO_2 are associated with the most negative values of $\delta^{13}C_{DIC}$ (Fig. 2b) which

84   suggests that high concentrations of CO_2 are linked to input from terrestrial C_3-fixed carbon.

85   A similar relationship has been found for lakes in the North America and Finland sampled

86   prior to ice-melt[12].

87

88   The conventional explanation for excess CO_2 in a lake is *in situ* mineralisation of organic

89   carbon produced in the catchment[13]. 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 CO_2 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 CO_2 [14] [15] [16] which our hypothesis would predict. In other regions where

94   aquifers contribute significantly to the water budget of a lake, CO_2 can be delivered by

95   groundwater and emitted from the lake [17,18].

96

97   The source of CO_2 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 $\delta^{13}C_{DIC}$ 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 $\delta^{13}C$ of stream bryophytes, which lack roots and are unable to use HCO_3^- as

102   a carbon source[19] requiring them to derive their inorganic carbon from CO_2 in water.

103   Bryophyte $\delta^{13}C$ also declined with total P (Fig. 2a) and the relationship between bryophyte

104     $\delta^{13}C$ and stream $\delta^{13}CO_2$ (See Supplementary Information for method of calculation) was close

105   to 1:1 with an average discrimination of 14.3 ‰ against CO_2 (linear regression with standard

106   errors in parenthesis, Bryophyte $\delta^{13}C$‰ = -14.3 (4.75) + 1.09 (0.26) stream $\delta^{13}CO_2$‰;

107   adjusted R^2 = 0.45, P<0.001). These data support the direct input of CO_2 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 CO_2 lies in the terrestrial catchment.

114   There was a strong positive relationship between the CO_2 concentration in each lake and

115   terrestrial Net Primary Productivity (NPP) i.e., lakes with higher mean concentrations of CO_2

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, CO_2 efflux was estimated from the measured

118   CO_2 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 CO_2-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 CO_2-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   CO_2 efflux = -0.85 10^{-2} (3.29 10^{-2}) + 1.56 10^{-2} (0.19 10^{-2}) * total catchment NPP; adjusted R^2

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 CO_2 to the atmosphere is about 16-times larger from lakes than the loss of

131   CO_2 in the outflow river (Fig. 3b) assuming that the CO_2 exiting the lake reaches atmospheric

132   equilibrium during the passage downstream.

133 The global CO_2-efflux from lakes has been estimated previously from the product of the

134 average CO_2 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 constrained[20]. This approach produces an estimate of 0.53 Pg C yr^{-1} [4]. If the hypothesised link

137 between catchment productivity and CO_2 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 CO_2-losses from lakes of 1.6% of NPP and

140 an estimated global terrestrial NPP of 56.4 Pg C yr^{-1} [21], global CO_2-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 CO_2-losses from

143 lakes. Work on CO_2-concentration in streams and rivers in the USA which found a strong

144 positive, but likely indirect, correlation between CO_2 evasion and annual precipitation[16] could

145 also be explained by this hypothesis since precipitation and NPP are generally positively

146 correlated over larger spatial scales[22].

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 CO_2 in lakes, the results presented here

151 demonstrate that high concentrations of CO_2 can also derive from terrestrially-fixed carbon

152 broken down in the soil [23] 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^{-3} [24]. It is likely that in

155 lakes where the DOC concentration is low the direct input of CO_2 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 CO_2 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 CO_2 to lakes. This will consequently increase aquatic

164 emissions of CO_2 to the atmosphere, potentially reducing gains in carbon sequestration made

165 by enhanced terrestrial productivity. The concentration of CO_2 in lakes is much more likely to

166 be controlled by land use than by rising atmospheric CO_2 concentrations, or temperatures[25].

167 Increasing atmospheric CO_2 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 CO_2 losses from lakes. Recent studies[26] 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 following [27]. Carbon species were calculated following[2], 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 lakes[8], DOC anions are estimated to have contributed on average 5.5% of

181 alkalinity[28] 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 $^{13}C/^{12}C$ (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 LCM2000[30]. 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 CO_2 were converted to rates of CO_2 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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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 CO_2.** Mean (●), maximum (▲)

305 and minimum (■) concentrations of free CO_2 and approximate CO_2-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 (CO_2-excess equals 1) calculated from lake temperature and annual

309 mean atmospheric partial pressure of CO_2 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 CO_2 to total P. The

312 regression for mean CO_2 is (standard errors in parentheses): CO_2 (mol m^{-3}) = 0.0216 (0.0021)

313 + 0.0012 (0.0001) total P (mg m^{-3}), adjusted R^2 = 0.87, P<0.001.

314
315 **Figure 2 Relationship between inorganic and organic $\delta^{13}C$ values in lakes and streams**

316 **and productivity and CO_2 concentration.** a) Relationship between $\delta^{13}C$ of dissolved

317 inorganic and organic carbon and mean concentration of Total P in lakes and streams and b)

318 relationship between $\delta^{13}C$ of dissolved inorganic carbon and lake concentration of CO_2.

319 Values of $\delta^{13}C$ 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 CO_2 concentration, CO_2-efflux and catchment productivity**.

327 a) Relationship between mean CO_2 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 CO_2-efflux from the lake surface (●) and loss of

330 CO_2 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.
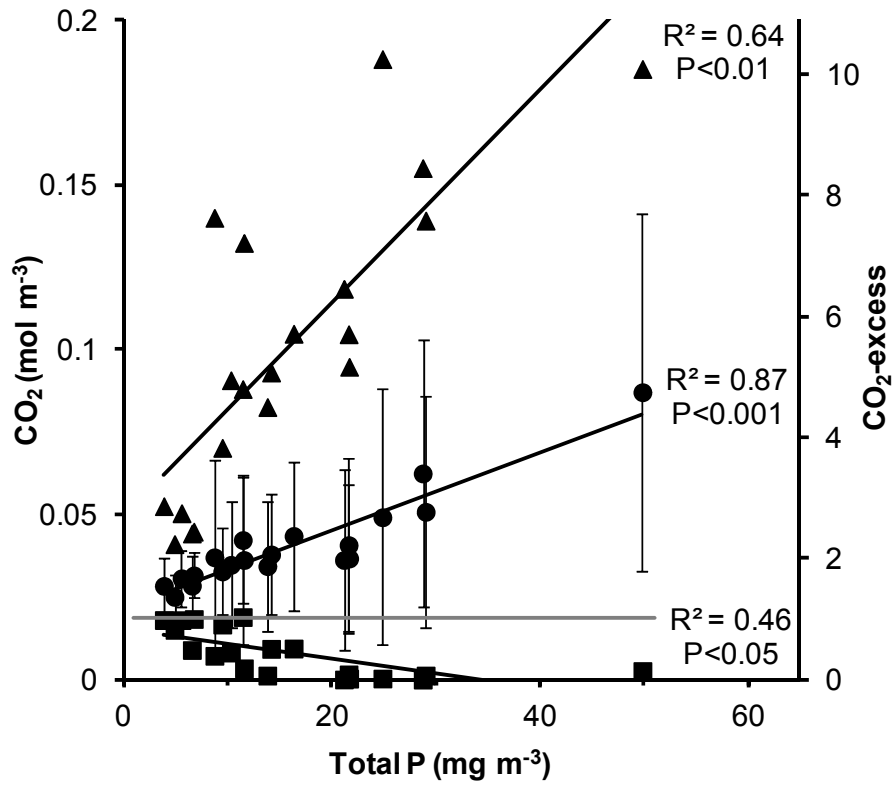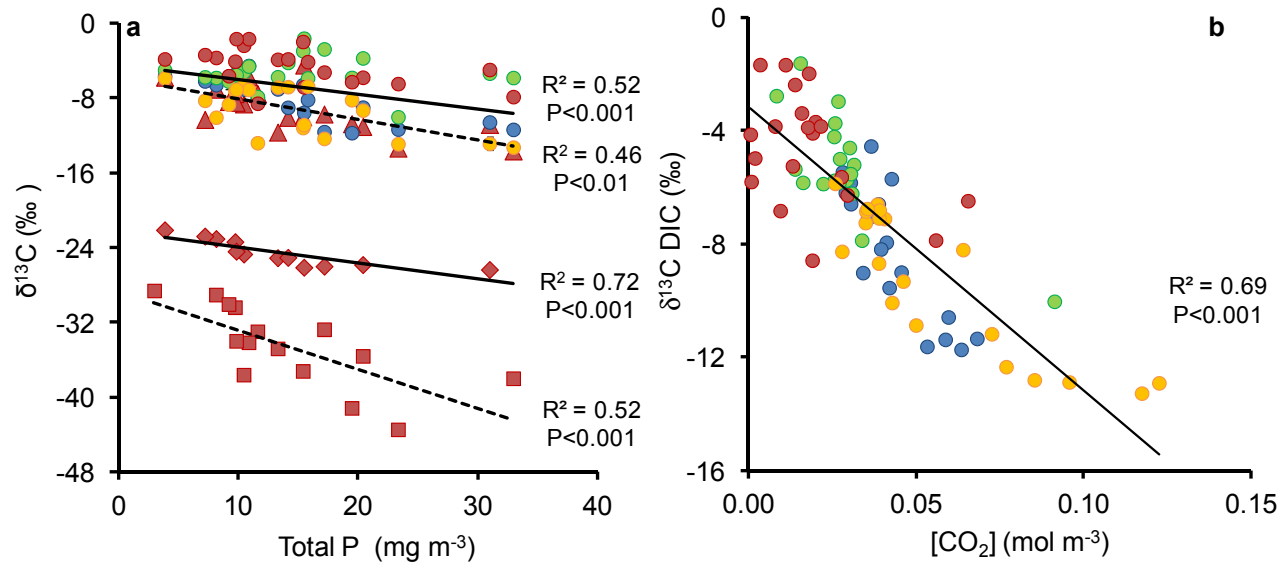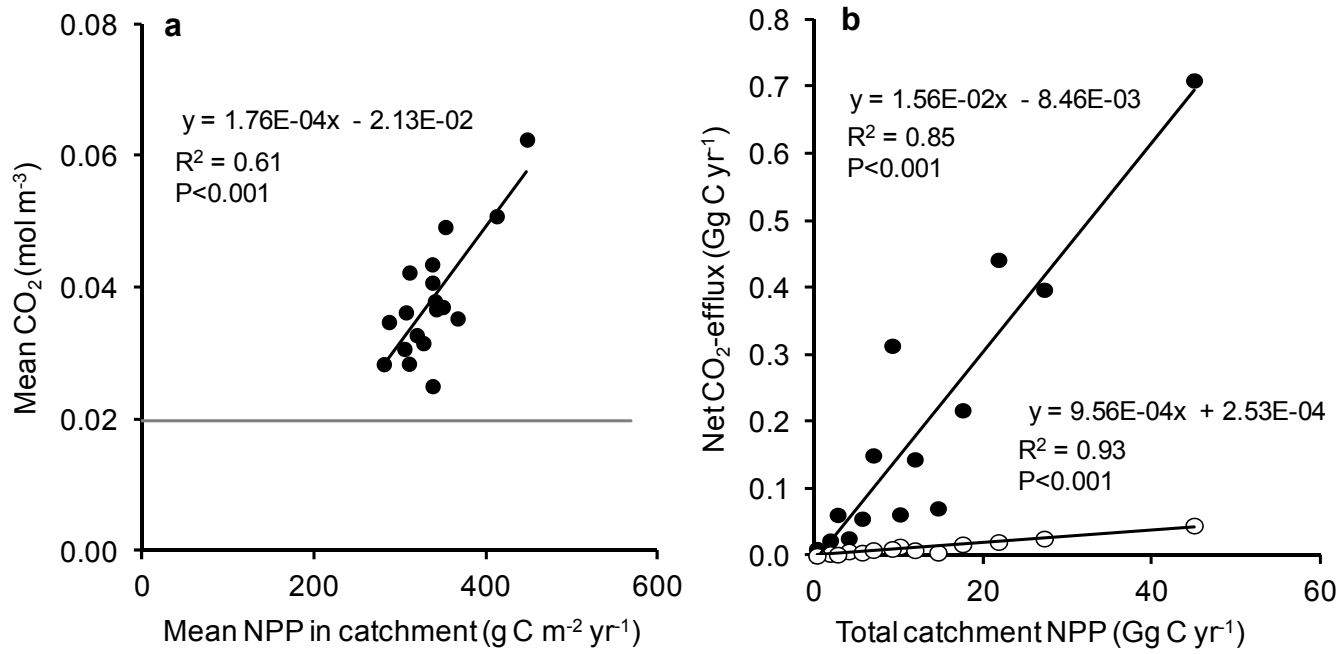
332

333

Figure 1

Figure 2.

a

$y = 1.76\text{E-}04x - 2.13\text{E-}02$

$R^2 = 0.61$

$P < 0.001$

Mean CO_2 (mol m^{-3})

Mean NPP in catchment (g C m^{-2} yr^{-1})

b

$y = 1.56\text{E-}02x - 8.46\text{E-}03$

$R^2 = 0.85$

$P < 0.001$

$y = 9.56\text{E-}04x + 2.53\text{E-}04$

$R^2 = 0.93$

$P < 0.001$

Net CO_2-efflux (Gg C yr^{-1})

Total catchment NPP (Gg C yr^{-1})

Figure 3.