

# 1 **Regional-scale lateral carbon transport and CO<sub>2</sub> evasion in** 2 **temperate stream catchments**

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9 **Abstract.** Inland waters play an important role in regional to global scale carbon cycling by transporting, processing  
10 and emitting substantial amounts of carbon, which originate mainly from their catchments. In this study, we  
11 analyzed the relationship between terrestrial net primary production (NPP) and the rate at which carbon is exported  
12 from the catchments in a temperate stream network. The analysis included more than 200 catchment areas in  
13 southwest Germany, ranging in size from 0.8 to 889 km<sup>2</sup> for which CO<sub>2</sub> evasion from stream surfaces and  
14 downstream transport with stream discharge were estimated from water quality monitoring data, while NPP in the  
15 catchments was obtained from a global data set based on remote sensing. We found that on average 2.7 % of  
16 terrestrial NPP (13.9 g C m<sup>-2</sup> yr<sup>-1</sup>) are exported from the catchments by streams and rivers, in which both CO<sub>2</sub>  
17 evasion and downstream transport contributed about equally to this flux. The average carbon fluxes in the  
18 catchments of the study area resembled global and large-scale zonal mean values in many respects, including NPP,  
19 stream evasion as well as the carbon export per catchment area in the fluvial network. A review of existing studies  
20 on aquatic-terrestrial coupling in the carbon cycle suggests that the carbon export per catchment area varies in a  
21 relatively narrow range, despite a broad range of different spatial scales and hydrological characteristics of the study  
22 regions.

## 23 **Keywords**

24 Regional carbon cycle, terrestrial-aquatic coupling, net primary production, CO<sub>2</sub> degassing from streams, land use

## 25 **1 Introduction**

26 Inland waters represent an important component of the global carbon cycle by transporting, storing and processing  
27 significant amounts of organic and inorganic carbon (C) and by emitting substantial amounts of carbon dioxide  
28 (CO<sub>2</sub>) to the atmosphere (Cole et al., 2007;Aufdenkampe et al., 2011). Globally about 0.32 to 0.8 Pg C is emitted per  
29 year as CO<sub>2</sub> from lakes and reservoirs (Raymond et al., 2013;Barros et al., 2011). For streams and rivers the global  
30 estimates range from 0.35 to 1.8 Pg C yr<sup>-1</sup> (Raymond et al., 2013;Cole et al., 2007), where the lower estimates can  
31 be considered as conservative because they omit CO<sub>2</sub> emissions from small headwater streams. In 2015 global CO<sub>2</sub>  
32 evasion from rivers and streams was estimated at 0.65 Pg C yr<sup>-1</sup> (Lauerwald et al., 2015). Comparable amounts of  
33 carbon are discharged into the oceans by the world's rivers (0.9 Pg C yr<sup>-1</sup>) and stored in aquatic sediments (0.6 Pg C  
34 yr<sup>-1</sup>) (Tranvik et al., 2009). In total, evasion, discharge and storage of C in inland waters have been estimated to  
35 account for about 4 % of global terrestrial net primary production (NPP) (Raymond et al., 2013) or 50-70 % of the  
36 total terrestrial net ecosystem production (NEP) (Cole et al., 2007). A recent continental-scale analysis, which  
37 combined terrestrial productivity estimates from a suite of biogeochemical models with estimates of the total aquatic  
38 C yield for the conterminous United States (Butman et al., 2015), resulted in mean C export rates from terrestrial  
39 into freshwater systems of 4 % of NPP and 27 % of NEP. These estimates varied by a factor of four across 18  
40 hydrological units with surface areas between 10<sup>5</sup> and 10<sup>6</sup> km<sup>2</sup>.

41 The substantial lateral and vertical transport of terrestrial-derived C in inland waters is currently not accounted for in  
42 most bottom-up estimates of the terrestrial uptake rate of atmospheric CO<sub>2</sub> (Battin et al., 2009) and results in high  
43 uncertainties in regional-scale C budgets and predictions of their response to climate change, land use and water  
44 management. Only few studies have quantified C fluxes and pools including inland waters at the regional-scale  
45 ( $O(10^3-10^4 \text{ km}^2)$ ) (Christensen et al., 2007;Buffam et al., 2011;Jonsson et al., 2007;Maberly et al., 2013) or for small  
46 ( $O(1-10 \text{ km}^2)$ ) catchments (Leach et al., 2016;Shibata et al., 2005;Billett et al., 2004). The majority of existing  
47 regional-scale studies on terrestrial-aquatic C fluxes are from the boreal zone and are characterized by a relatively  
48 large fractional surface area covered by inland waters, a high abundance of lakes and high fluvial loads of dissolved  
49 organic carbon (DOC). Landscapes in the temperate zone can differ in all these aspects, potentially resulting in  
50 differences in the relative importance of aquatic C-fluxes and flux paths (storage, evasion and discharge) in regional-  
51 scale C budgets. In this study, we analyzed the relationship between terrestrial NPP and CO<sub>2</sub> evasion and C  
52 discharge for more than 200 catchments in southwest Germany. The stream-dominated catchments range in size  
53 from 0.8 to 889 km<sup>2</sup> and are characterized by a relatively small fraction of surface water coverage (< 0.5 % of the  
54 land surface area). In contrast to studies from the boreal zone, the fluvial C load is dominated by dissolved inorganic  
55 carbon (DIC). Estimates of aquatic C export from the catchments were obtained from water quality and hydrological  
56 monitoring data and were related to terrestrial NPP derived from MODIS satellite data. The scale dependence of  
57 aquatic carbon fluxes in relation to NPP is analyzed by grouping the data according to Strahler stream order  
58 (Strahler, 1957). By comparing our results to a variety of published studies, we finally discuss the magnitude as well  
59 as the relative importance of different fluvial flux paths in regional-scale C budgets in different landscapes and  
60 climatic zones.

## 61 2 Materials and Methods

### 62 2.1 Study area and hydrological characteristics

63 The study area encompasses large parts of the federal state of Rhineland-Palatinate (RLP) in southwest Germany  
64 (Fig. 1). The average altitude is 323 m (48 m - 803 m) and the mean annual temperature and precipitation varied  
65 between 5.8 and 12.2 °C and 244 and 1576 mm during the time period between 1991 and 2011 at the 37  
66 meteorological stations operated by the state RLP (<http://www.wetter.rlp.de/>). The dominating land cover in the  
67 study area is woodland (41 %, mainly mixed and broad-leaved forest), tilled land (37 %, mainly arable land and  
68 vineyards) and grassland (13 %, mainly pastures) (Corine land cover (EEA, 2006)). The fraction of peatland in the  
69 study area is small (0.95 km<sup>2</sup>; 0.009% of the study area). 16 % of the study area contain carbonate bedrock.

70 Most of the rivers in RLP are part of the catchment area of the Rhine River. Other large rivers in the state are Mosel,  
71 Lahn, Saar and Nahe. The upland regions of RLP are sources to many small, steep and highly turbulent streams with  
72 gravel beds (MULEWF, 2015). Lakes in RLP are small with a total area of approximately 40 km<sup>2</sup> (Statistisches  
73 Landesamt Rheinland-Pfalz, 2014) and were omitted from the analysis. The river network has a total length of  
74 15800 km and consists of stream orders (Strahler, 1957) between 1 and 7. A catchment map of RLP, consisting of  
75 subcatchments of 7729 river segments was provided by the state ministry (MULEWF, 2013), where a river segment  
76 refers to the section between a source and the first junction with another river or between two junctions with other  
77 rivers. All subsequent analyses were conducted separately for each stream order and streams of Strahler order >4  
78 were omitted from the analysis because of the limited sample size with only few catchments available. Moreover,  
79 we omitted streams for which parts of the catchment area were outside of the study area. Overall, 3377, 1619, 861  
80 and 453 stream segments were retained for the analysis for Strahler order 1 to 4, respectively. Annual mean  
81 discharge and length of the river segments were obtained from digital maps provided by the state ministry  
82 (MULEWF, 2013).

### 83 2.2 Aquatic carbon concentrations

84 DIC concentrations and partial pressure of dissolved CO<sub>2</sub> (*p*CO<sub>2</sub>) in stream water were estimated from governmental  
85 water quality monitoring data which were acquired according to DIN EN ISO norms (DIN EN ISO 10523:2012-  
86 04;DIN EN ISO 9963-1:1996-02;DIN EN ISO 9963-2:1996-02).. The data include measurements of alkalinity, pH  
87 and temperature which were conducted between 1977 and 2011 (MULEWF, 2013). Sampling intervals differed  
88 between the sites and water sampling was conducted irregularly with respect to year and season. To exclude a  
89 potential bias resulting from the seasonality of DIC concentrations on the analysis, we only considered river  
90 segments for which at least one measurement was available for each season (spring, summer, autumn, winter). From  
91 these measurements, *p*CO<sub>2</sub> and DIC concentrations were estimated using chemical equilibrium calculations with the  
92 software PHREEQC (Version 2) (Parkhurst and Appelo, 1999). For 201 river segments with seasonally resolved  
93 measurements, we first computed seasonal mean *p*CO<sub>2</sub> and DIC concentrations, which subsequently were aggregated  
94 to annual mean values averaged over the entire sampling period:

95

$$\overline{pCO_{2annual}} = (\overline{pCO_{2spring}} + \overline{pCO_{2summer}} + \overline{pCO_{2autumn}} + \overline{pCO_{2winter}})/4 \quad (1)$$

97 Measurements of dissolved and total organic C (DOC, TOC) were available only for 64 of these sampling sites.

### 98 2.3 Estimation of lateral DIC export and catchment-scale CO<sub>2</sub> evasion

99 The lateral export of DIC and the total CO<sub>2</sub> evasion from the upstream located stream network was calculated for  
100 each of the 201 sampling sites with seasonally averaged concentration estimates. Lateral DIC export from the  
101 corresponding catchments was calculated as the product of the mean DIC concentration and discharge. CO<sub>2</sub> evasion  
102 from the stream network upstream of each sampling site was estimated by interpolating *p*CO<sub>2</sub> for all river segments  
103 without direct measurements by averaging the mean concentrations by stream order and assigning them to all stream  
104 segments of the river network (Butman and Raymond, 2011). Stream width (*w*, in m), depth (*d*, in m) and flow  
105 velocity (*v*, in m s<sup>-1</sup>) were estimated from the discharge (*Q*, in m<sup>3</sup> s<sup>-1</sup>) using the following empirical equations  
106 (Leopold and Maddock Jr, 1953):

$$w = a * Q^b \quad d = c * Q^d \quad v = e * Q^f, \quad (2)$$

108 For the hydraulic geometry exponents and coefficients, the values from Raymond et al. (2012) were used (*b*=0.42,  
109 *d*=0.29, *f*=0.29, *a*=12.88, *c*=0.4 and *e*=0.19).

110 The water surface area (*A*, in m<sup>2</sup>) was calculated as the product of length and width of the river segments. The  
111 average slope for each segment was estimated from a Digital Elevation Map (resolution 10 m) provided by the  
112 federal state of Rhineland-Palatinate (LVermGeoRP, 2012). Zhang and Montgomery (1994) investigated the effect  
113 of digital elevation model (DEM) resolution on slope calculation and performance in hydrological models for spatial  
114 resolutions between 2 and 90 m. They found that while a 10-m grid is a significant improvement over 30 m or  
115 coarser grid sizes, finer grid sizes provide relatively little additional resolution. Thus a 10-m grid size represents a  
116 reasonable tradeoff between increasing spatial resolution and data handling requirements for modeling surface  
117 processes in many landscapes. The gas transfer velocity of CO<sub>2</sub> at 20°C (*k*<sub>600</sub>, in m d<sup>-1</sup>) was calculated from slope (*S*)  
118 and flow velocity (*v*, in m s<sup>-1</sup>) (Raymond et al., 2012).

$$k_{600} = S * v * 2841.6 + 2.03 \quad (3)$$

120 This gas transfer velocity was adjusted to the in situ temperature (*k*<sub>*T*</sub>, in m d<sup>-1</sup>) using the following equation:

$$k_T = k_{600} * \left(\frac{Sc_T}{600}\right)^{-0.5}, \quad (4)$$

122 where *Sc<sub>T</sub>* is the Schmidt number (ratio of the kinematic viscosity of water and the diffusion coefficient of dissolved  
123 CO<sub>2</sub>) at the in situ temperature (Raymond et al., 2012). Finally the CO<sub>2</sub> flux (*F<sub>D</sub>*, in g C m<sup>-2</sup> yr<sup>-1</sup>) for each stream  
124 segment was calculated as:

$$F_D = k_T * K_H (pCO_2 - pCO_{2,a}) * M_C \quad (5)$$

126 The partial pressure of CO<sub>2</sub> in the atmosphere (*p*CO<sub>2,*a*</sub>) was considered as constant (390 ppm) and the Henry  
127 coefficient of CO<sub>2</sub> at in-situ temperature (*K<sub>H</sub>* in mol l<sup>-1</sup> atm<sup>-1</sup>) was estimated using the relationship provided in  
128 (Stumm and Morgan, 1996). *M<sub>C</sub>* is the molar mass of C (12 g mol<sup>-1</sup>). Finally, the total CO<sub>2</sub> evasion was estimated by

129 summing up the product of  $F_D$  with the corresponding water surface area for all stream segments located upstream  
130 of each individual sampling point.

## 131 **2.4 Estimation of the catchment NPP**

132 Average NPP in the catchment areas of the study sites were obtained from a global data set derived from moderate  
133 resolution imaging spectroradiometer (MODIS) observations of the earth observing system (EOS) satellites, which  
134 is available for the time period 2000 to 2013 with a spatial resolution of 30 arc seconds ( $\sim 1 \text{ km}^2$ ) (Zhao et al., 2005).  
135 In this data set, NPP was estimated based on remote sensing observations of spectral reflectance, land cover and  
136 surface meteorology as described in detail by Running et al. (2004). We used mean NPP data (2000-2013) averaged  
137 over the catchment areas of the individual sampling sites.

## 138 **2.5 Statistical analysis**

139 Linear regressions (F-test) were used to analyze the data. Group differences or correlations with  $p < 0.05$  were  
140 considered statistically significant. For the regression of total aquatic C export rate and annual catchment NPP, data  
141 were log-transformed to correct for normal distribution. All statistical analyses were performed with R (R  
142 Development Core Team, 2011).

## 143 **3 Results**

### 144 **3.1 Catchment characteristics and aquatic C load**

145 The size of the analyzed catchment areas varied over three orders of magnitude (0.8 to 889  $\text{km}^2$ ) and the mean size  
146 increased from 9  $\text{km}^2$  for 1<sup>st</sup> order streams to 243  $\text{km}^2$  for streams of the order 4 (Table 1). Mean discharge and  
147 catchment area were linearly correlated ( $r^2=0.74$ ,  $p < 0.001$ ). The runoff depth, i.e. the stream discharge divided by  
148 the catchment area, was relatively constant across stream orders with a mean value of 0.28  $\text{m y}^{-1}$ , corresponding to  
149 35 % of the annual mean precipitation rate in the study area. The mean discharge increased more than 30-fold from  
150 0.06 to 2.2  $\text{m}^3 \text{ s}^{-1}$  for 1<sup>st</sup> to 4<sup>th</sup> order streams, respectively. Similarly, the estimated water surface area increased with  
151 increasing stream order from 0.24 to 0.42 % of the corresponding catchment size (Table 1).

152 Individual estimates of the  $\text{CO}_2$  partial pressure at the sampling sites varied between 145 and 7759 ppm. Only 1 %  
153 of the  $p\text{CO}_2$  values were below the mean atmospheric value (390 ppm), indicating that the majority of the stream  
154 network was a source of atmospheric  $\text{CO}_2$  at all seasons. The  $p\text{CO}_2$  was higher in summer (mean $\pm$ sd: 2780 $\pm$ 2098  
155 ppm) and autumn (mean $\pm$ sd: 2848 $\pm$ 2019 ppm) than in winter (mean $\pm$ sd: 2287 $\pm$ 1716 ppm) and spring (mean $\pm$ sd:  
156 2172 $\pm$ 2343 ppm). The total mean value of  $p\text{CO}_2$  was 2083 ppm and  $p\text{CO}_2$  and DIC did not differ significantly  
157 among the different stream orders ( $p\text{CO}_2$ :  $p=0.35$ ; DIC:  $p=0.56$ ). On average, DIC in the stream water was  
158 composed of 91.2 % bicarbonate, 0.4 % carbonate and 8.4 %  $\text{CO}_2$ .

159

160 The few available samples of DOC and TOC indicate that the organic C concentration was about one order of  
161 magnitude smaller than the inorganic C concentration (Table 1). There were no pronounced regional or temporal  
162 differences of organic carbon. Only a small fraction of TOC was in particulate form (on average 8.6 %) and TOC  
163 was linearly related to DIC, indicating that the organic load made up only 4 % of the total carbon load at the  
164 sampling sites (Fig. 2). The data are provided as supplementary material.

### 165 3.2 Catchment NPP and C budget

166 NPP increased linearly with catchment size ( $r^2=0.98$ ,  $p<0.001$ ), but the specific NPP, i.e. the total NPP within a  
167 catchment divided by catchment area, did not differ significantly ( $p=0.24$ ) among catchments of different stream  
168 orders. The smallest mean value and the largest variability of specific NPP (mean $\pm$ sd:  $466\pm 127$  g C m<sup>-2</sup> yr<sup>-1</sup>, range:  
169 106 to 661 g C m<sup>-2</sup> yr<sup>-1</sup>) was observed among the small catchments of 1<sup>st</sup> order streams, while the variability was  
170 consistently smaller for higher stream orders (Table 2). The total average of terrestrial NPP in the study area was  
171  $515\pm 79$  g C m<sup>-2</sup> yr<sup>-1</sup> (mean $\pm$ sd).

172 In a simplified catchment-scale C balance, we consider the sum of the DIC discharge (DIC concentration multiplied  
173 by discharge) measured at each sampling site and the total CO<sub>2</sub> evasion from the upstream located stream network  
174 as the total amount of C that is exported from the catchment area through the aquatic conduit. The total evasion was  
175 estimated by interpolation with stream-order specific  $p\text{CO}_2$  values assigned to the complete stream network. Given  
176 the small number of available measurements, we neglect the fraction of organic C which is exported with stream  
177 discharge. As demonstrated above, TOC load is small in comparison to the DIC load (Fig. 2), resulting in a  
178 comparably small (< 4 %) error.

179 The resulting CO<sub>2</sub> evasion rates decreased slightly, but not significantly ( $p=0.26$ ) for increasing stream orders with a  
180 total mean evasion rate of  $2032$  g C m<sup>-2</sup> yr<sup>-1</sup> (expressed as per unit water surface area) (Table 2). The total aquatic  
181 evasion rate within catchments normalized by the size of the catchment increased significantly with stream order  
182 with a mean value of  $6.6$  g C m<sup>-2</sup> yr<sup>-1</sup>. (Table 2).

183 The total aquatic C export rate, i.e. the sum of evasion and DIC discharge, was strongly correlated with annual mean  
184 NPP averaged over the corresponding catchment area. Linear regression of the log-transformed data results in a  
185 power-law exponent of 1.06, indicating a nearly linear relationship (Fig. 3). As small streams of low stream order  
186 can be directly influenced by local peculiarities, the relationship is more variable for streams of Strahler order 1 and  
187 2, while larger streams represent more average conditions over larger spatial scales with less variability. Most of the  
188 correlation between the total aquatic C export rate and the annual mean NPP, however, can be attributed to their  
189 common linear scale-dependence.

190

191 After normalization with catchment area, the total aquatic C export rate increased slightly with stream order (Fig.  
192 4a). Also the fraction of NPP which was exported through the aquatic network, i.e. the sum of evasion and  
193 discharge, increased slightly, though not significantly ( $p=0.32$ ), from 2.18 % for first-order stream to 2.72 % for

194 stream order 4 (Fig. 4b). This increase was related to increasing rates of CO<sub>2</sub> evasion in streams of higher order and  
195 the contribution of evasion to the total C export rate increased from 39 to 53 % (Fig. 4c). The increasing evasion is  
196 mainly caused by the increasing fractional water surface area for increasing stream orders (Table 1), because the  
197 CO<sub>2</sub> fluxes per water surface showed a rather opposing trend with decreasing fluxes for increasing stream orders  
198 (Table 2). On average 1.31 % of the catchment NPP are emitted as CO<sub>2</sub> from the stream network and 1.49 % are  
199 discharged downstream (Table 2).

200

201 No regional (large-scale) pattern or gradients were observed in the spatial variation of catchment-scale NPP and  
202 aquatic C export (Fig. 5).

## 203 **4 Discussion**

### 204 **4.1 Uncertainty analysis**

205 Our estimates are subject to a number of uncertainties associated with sampling and interpolation and systematic  
206 errors including the neglect of carbon burial in sediments, carbon export and evasion as methane and unresolved  
207 spatial and temporal variability.

208 According to Abril et al. (2015), high uncertainties of pCO<sub>2</sub> estimates from pH and alkalinity measurements occur at  
209 pH values <7. In our study, only 7 % of the pH values were <7. For pH>7 the median and mean relative errors are  
210 1% and 15%, respectively (Abril et al., 2015). Raymond et al. (2013) estimated uncertainties from comparisons of  
211 estimates obtained using approaches comparable to the present study with direct measurements of CO<sub>2</sub>  
212 concentration on streams. For a density of sampling locations of 0.02 sites per km<sup>2</sup> (corresponding to this study)  
213 they derived an uncertainty of 30 %. Similarly, Butman and Raymond (2011) estimated uncertainties of overall flux  
214 estimates of 33 %, based on Monte Carlo simulation of similar data for hydrographic units in the United States.

215 While the riverine carbon concentrations were obtained from measurements that covered a time period from 1977 to  
216 2011, the NPP data were available for the time period from 2000 to 2013. In boreal and subtropical rivers a decadal  
217 increasing DIC export due to the climate change and anthropogenic activities has been observed (Walvoord and  
218 Striegl, 2007; Raymond et al., 2008), therefore the different time periods covered by the two data sets might pose a  
219 problem. Comparisons of DIC measurements in the study area between 1977-1999 and 2000-2011 however did not  
220 show significant changes. Furthermore, the sampling frequency for DIC increased so that the majority of DIC  
221 measurements originated from the same time period as the NPP data (Supplementary Material).

222 The hydraulic geometry exponents and coefficients used in this study were derived from various data sets obtained  
223 in North America, not for central Europe. Unfortunately, we are not aware of a comparably extensive data set of  
224 hydraulic geometry data derived for European rivers. The coefficients have been applied in global studies before,  
225 e.g. Raymond et al. (2013). A comparison of hydraulic geometry coefficients derived from various data sets,  
226 including data from England, Australia and New Zealand, is presented in Butman and Raymond (2011), who

227 estimated that the error associated with uncertainties of hydraulic geometry coefficients is rather small, compared to  
228 uncertainties derived for C-fluxes.

229 Carbon burial in sediments was neglected in this study but can make a significant contribution to catchment-scale C  
230 balances. Estimates vary between 22 % at a global scale (Aufdenkampe et al., 2011), 14 % for the Conterminous  
231 U.S. (Butman et al., 2015) and 39% for the Yellow River network (Ran et al., 2015). However, C storage in aquatic  
232 systems occurs mainly in lakes and reservoirs, which are virtually absent in the study area. Therefore we consider  
233 the bias caused by neglecting storage to be small in comparison to remaining uncertainties (30%).

234 Similarly, the transport of carbon as methane was neglected because measurements of methane concentration or  
235 fluxes were not available for the study area. According to a recent meta-analysis, the dissolved methane  
236 concentration in headwater streams varies mainly between 0.1 and 1  $\mu\text{mol L}^{-1}$ , with streams in temperate forests  
237 being at the lower end (Stanley et al., 2016). As the methane makes up only a small fraction of total carbon in  
238 comparison to the mean DIC concentration in the present study (500  $\mu\text{mol L}^{-1}$ ), it can be assumed that methane  
239 makes a rather small contribution to the catchment scale carbon balance.

240 Since no time-resolved discharge data were available for the sampling sites we cannot account for extreme events.  
241 Moreover, no information were available if the governmental monitoring included sampling during floods. Given  
242 the stochastic nature and short duration, we expect that such samples are at least underrepresented. Since it has been  
243 observed that high-discharge events can make a disproportionally high contribution to annual mean carbon export  
244 from catchments, we consider our estimates as a lower bound.

#### 245 **4. 2. An average study region**

246 The average carbon fluxes in the catchments of the study area resemble global and large-scale zonal mean estimates  
247 in many aspects. The mean atmospheric flux of  $\text{CO}_2$  from the stream network of  $2031 \pm 1527 \text{ g C m}^{-2} \text{ yr}^{-1}$  is in close  
248 agreement with bulk estimates for streams and rivers in the temperate zone of 2630 (Aufdenkampe et al., 2011) and  
249  $2370 \text{ g C m}^{-2} \text{ yr}^{-1}$  (Butman and Raymond, 2011). The fractional surface coverage of streams and rivers (0.42 % for  
250 stream order 4) corresponds to the global average of 0.47 % (Raymond et al., 2013) and also mean terrestrial NPP in  
251 the catchments ( $515 \text{ g C m}^{-2} \text{ yr}^{-1}$ ) was in close correspondence to recent global mean estimates ( $495 \text{ g C m}^{-2} \text{ yr}^{-1}$   
252 (Zhao et al., 2005)).

253 By combining  $\text{CO}_2$  evasion and downstream C-export by stream discharge, we estimated that 2.7 % of terrestrial  
254 NPP ( $13.9 \text{ g C m}^{-2} \text{ yr}^{-1}$ ) are exported from the catchments by streams and rivers, in which both evasion and  
255 discharge contributed equally to this flux. Also these findings are in close agreement with global and continental  
256 scale estimates, of 16 and  $13.5 \text{ g C m}^{-2} \text{ yr}^{-1}$ , respectively (Table 3).

#### 257 **4.3. Aquatic C export across spatial scales**

258 Though not exhaustive, Table 3 provides data from a large share of existing studies relating the aquatic C export to  
259 terrestrial production in the corresponding catchments which cover a broad range of spatial scales and different  
260 landscapes. Except for the tropical forest of the Amazon basin, the aquatic carbon export normalized to catchment



261 area estimated for temperate streams in our study, is surprisingly similar to those estimated at comparable and at  
262 larger spatial scale. In the Amazon, the fraction of terrestrial production that is exported by the fluvial network is  
263 more than twofold higher (nearly 7 % of NPP (Richey et al., 2002)). However, that a large fraction of the regional  
264 NPP in the Amazon is supported by aquatic primary production by macrophytes and carbon export is predominantly  
265 controlled by wetland connectivity, with wetlands covering up to 14 % of the land surface area (Abril et al., 2013).  
266 An additional peculiarity of the Amazon is, that in contrast to the remaining systems, the vast majority (87 %) of the  
267 total C export is governed by CO<sub>2</sub> evasion (Table 3), whereas lateral export constitutes a much smaller component.  
268 An exceptionally low fraction of NPP that is exported from aquatic systems at larger scale was estimated for the  
269 English Lake District (1.6 % (Maberly et al., 2013)), though only CO<sub>2</sub> evasion from lake surfaces was considered,  
270 i.e. downstream discharge by rivers was ignored. Their estimate agrees reasonably well with the fraction of  
271 catchment NPP that was emitted to the atmosphere from the stream network in the present study (1.3 %). If a similar  
272 share of catchment NPP was exported with river discharge also in the Lake District, the average mass of C exported  
273 from the aquatic systems per unit catchment area would be in close agreement with our and other larger-scale  
274 estimates (Table 3).  
275 In more detailed studies at smaller scales and for individual catchments, aquatic C export was exclusively related to  
276 net ecosystem exchange (NEE) measured by eddy covariance. Here the estimated fractions of aquatic export range  
277 between 2 % of NEE in a temperate forest catchment (only discharge, evasion not considered, (Shibata et al., 2005))  
278 and 160 % of NEE in a boreal peatland catchment (Billett et al., 2004). Analysis of inter-annual variations of stream  
279 export from a small peatland catchment in Sweden (Leach et al., 2016) resulted in estimates of C export by the  
280 fluvial network between 5.9 and 18.1 g Cm<sup>-2</sup> yr<sup>-1</sup> over 12 years. The total mean value of 12.2 g Cm<sup>-2</sup> yr<sup>-1</sup>, however,  
281 is in close agreement with the present and other larger-scale estimates (Table 3). In contrast to the present study, C  
282 export from the peatland catchments were dominated by stream discharge of dissolved organic carbon.

#### 283 **4.4 Controlling factors for aquatic C export**

284 We found a significant linear relationship between total catchment NPP and the C export from the catchment in the  
285 stream network across four Strahler orders. The relationship was mainly caused by a strong correlation between  
286 catchment size and water surface area. As expected for temperate zones, large streams and rivers with large surface  
287 area have larger catchments. A study analyzing aquatic carbon fluxes for 18 hydrological units in the conterminous  
288 U.S. (Butman et al., 2015) observed a significant correlation between catchment-specific aquatic C yield and  
289 specific catchment NEP, which in turn was linearly correlated to NPP. We did not observe such correlation at  
290 smaller scale, which could be related to the rather narrow range of variability in NPP among the considered  
291 catchments. Nevertheless, the linear correlation observed by (Butman et al., 2015) indicates that a constant fraction  
292 of terrestrial NPP is exported by aquatic systems if averaged over larger spatial scales.

293 The relatively narrow range of variability of C export per catchment area (between 9 and 18 g C m<sup>-2</sup> yr<sup>-1</sup>, with the  
294 two exceptions discussed above) in different landscapes (Table 3) is rather surprising. Although this range of  
295 variation is most likely within the uncertainty of the various estimates, the variability across different landscapes is

296 certainly small in comparison to the order of magnitude differences in potential controlling factors like catchment  
297 NPP, fractional water coverage as well as size and climatic zone of the study area. In lake-rich regions, evasion from  
298 inland waters was observed to be dominated by lakes (Buffam et al., 2011;Jonsson et al., 2007), which cover up to  
299 13 % of the surface area of these regions. In the present as well as in other studies on catchments where lakes are  
300 virtually absent (Wallin et al., 2013) and the fractional water coverage was smaller than 0.5 % of the terrestrial  
301 surface area, an almost identical catchment-specific C export and evasion rate has been observed (Table 3). CO<sub>2</sub>  
302 emissions from water surfaces depend on the partial pressure of CO<sub>2</sub> in water and are therefore related to DIC,  
303 which was the dominant form of dissolved C in the present study. Studies in the boreal zone, where dissolved C in  
304 the aquatic systems is mainly in the form of DOC, however, found comparable catchment-specific C export and  
305 evasion rates ((Leach et al., 2016;Jonsson et al., 2007;Wallin et al., 2013), cf. Table 3). The difference in the  
306 speciation of the exported C indicates that a larger fraction of the terrestrial NPP is respired by heterotrophic  
307 respiration in soils and exported to the stream network as DIC in the present study, in contrast to export as DOC and  
308 predominantly aquatic respiration. Observations and modeling of terrestrial-aquatic C fluxes across the U.S.  
309 suggested a transition of the source of aquatic CO<sub>2</sub> from direct terrestrial input to aquatic CO<sub>2</sub> production by  
310 degradation of terrestrial organic carbon with increasing stream size (Hotchkiss et al., 2015). Such transition was not  
311 observed in the present study, where organic carbon made a small contribution to the fluvial carbon load across all  
312 investigated stream orders. In addition to soil respiration, mineral weathering also contributes to DIC in stream  
313 water. The relative importance of soil respiration and weathering varies depending on geology and the presence of  
314 wetlands in the area (Hotchkiss et al., 2015;Lauerwald et al., 2013;Jones et al., 2003). In the present study, 16 % of  
315 the catchment areas contained carbonate bedrock. The DIC concentration in the water increased with the proportion  
316 of carbonate containing bedrock in the catchment ( $R^2=0.33, p<0.001$ ).

317 Despite the small number of observations in the meta-analysis, the narrow range of variability of C export per  
318 catchment area may indicate that neither water surface area nor the location of mineralization of terrestrial derived C  
319 (soil respiration and export of DIC versus export of DOC and mineralization in the aquatic environment), are  
320 important drivers for the total C export from catchments by inland waters at larger spatial scales. This rather  
321 unexpected finding deserves further attention, as it suggests that other, currently poorly explored, processes control  
322 the aquatic-terrestrial coupling and the role of inland waters in regional C cycling. Given the significant contribution  
323 of inland waters to regional and global scale greenhouse gas emissions, the mechanistic understanding of these  
324 processes is urgently required to assess their vulnerability to ongoing climatic and land use changes, as well to the  
325 extensive anthropogenic influences on freshwater ecosystems. Recent developments of process-based models, which  
326 are capable of resolving the boundless biogeochemical cycle in the terrestrial–aquatic continuum from catchment to  
327 continental scales (Nakayama, 2016), are certainly an important tool for these future studies.

328

329 **5 Conclusion:**

330 Our analysis of the carbon budget in a temperate stream network on regional scale revealed a relationship of aquatic  
331 carbon export and terrestrial NPP. On average 2.7 % of the terrestrial NPP were exported from the catchments by  
332 rivers and stream with CO<sub>2</sub> evasion and downstream transport contributing equally to the export. A comparison of  
333 our regional scale study with other studies from different scales and landscapes showed a relatively narrow range of  
334 variability of carbon export per catchment area. Future research is needed to understand the processes that control  
335 the aquatic-terrestrial coupling and the role of inland waters in regional carbon cycling.

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344 to in the reference list. The processed data, which were used to generate the figures and tables, are available upon  
345 request through the corresponding author.

- 347 Abril, G., Martinez, J.-M., Artigas, L. F., Moreira-Turcq, P., Benedetti, M. F., Vidal, L.,  
348 Meziane, T., Kim, J.-H., Bernardes, M. C., Savoye, N., Deborde, J., Souza, E. L., Alberic, P.,  
349 Landim de Souza, M. F., and Roland, F.: Amazon River carbon dioxide outgassing fuelled by  
350 wetlands, *Nature*, 505, 395-398, 10.1038/nature12797, 2013.
- 351 Abril, G., Bouillon, S., Darchambeau, F., Teodoru, C. R., Marwick, T. R., Tamooh, F., Omengo,  
352 F. O., Geeraert, N., Deirmendjian, L., and Polsenaere, P.: Technical Note: Large overestimation  
353 of pCO<sub>2</sub> calculated from pH and alkalinity in acidic, organic-rich freshwaters, *Biogeosciences*,  
354 12, 67, 2015.
- 355 Aufdenkampe, A. K., Mayorga, E., Raymond, P. A., Melack, J. M., Doney, S. C., Alin, S. R.,  
356 Aalto, R. E., and Yoo, K.: Riverine coupling of biogeochemical cycles between land, oceans, and  
357 atmosphere, *Front. Ecol. Environ.*, 9, 53-60, 10.1890/100014, 2011.
- 358 Barros, N., Cole, J. J., Tranvik, L. J., Prairie, Y. T., Bastviken, D., Huszar, V. L. M., del Giorgio,  
359 P., and Roland, F.: Carbon emission from hydroelectric reservoirs linked to reservoir age and  
360 latitude, *Nature Geosci.*, 4, 593-596, 10.1038/ngeo1211, 2011.
- 361 Battin, T. J., Luysaert, S., Kaplan, L. A., Aufdenkampe, A. K., Richter, A., and Tranvik, L. J.:  
362 The boundless carbon cycle, *Nature Geosci.*, 2, 598-600, 10.1038/ngeo618, 2009.
- 363 Billett, M. F., Palmer, S. M., Hope, D., Deacon, C., Storeton-West, R., Hargreaves, K. J.,  
364 Flechard, C., and Fowler, D.: Linking land-atmosphere-stream carbon fluxes in a lowland  
365 peatland system, *Global Biogeochem. Cycles*, 18, 10.1029/2003GB002058, 2004.
- 366 Buffam, I., Turner, M. G., Desai, A. R., Hanson, P. C., Rusak, J. A., Lottig, N. R., Stanley, E. H.,  
367 and Carpenter, S. R.: Integrating aquatic and terrestrial components to construct a complete  
368 carbon budget for a north temperate lake district, *Global Change Biol.*, 17, 1193-1211,  
369 10.1111/j.1365-2486.2010.02313.x, 2011.
- 370 Butman, D., and Raymond, P. A.: Significant efflux of carbon dioxide from streams and rivers in  
371 the United States, *Nature Geosci.*, 4, 839-842, 2011.
- 372 Butman, D., Stackpoole, S., Stets, E., McDonald, C. P., Clow, D. W., and Striegl, R. G.: Aquatic  
373 carbon cycling in the conterminous United States and implications for terrestrial carbon  
374 accounting, *Proceedings of the National Academy of Sciences*, 10.1073/pnas.1512651112, 2015.
- 375 Christensen, T. R., Johansson, T., Olsrud, M., Ström, L., Lindroth, A., Mastepanov, M., Malmer,  
376 N., Friborg, T., Crill, P., and Callaghan, T. V.: A catchment-scale carbon and greenhouse gas  
377 budget of a subarctic landscape, *Philosophical Transactions of the Royal Society of London A:*  
378 *Mathematical, Physical and Engineering Sciences*, 365, 1643-1656, 10.1098/rsta.2007.2035,  
379 2007.
- 380 Cole, J. J., Prairie, Y. T., Caraco, N. F., McDowell, W. H., Tranvik, L. J., Striegl, R. G., Duarte,  
381 C. M., Kortelainen, P., Downing, J. A., Middelburg, J. J., and Melack, J.: Plumbing the global  
382 carbon cycle: Integrating inland waters into the terrestrial carbon budget, *Ecosystems*, 10, 171-  
383 184, 10.1007/s10021-006-9013-8, 2007.
- 384 DIN EN ISO 9963-1:1996-02: Wasserbeschaffenheit - Bestimmung der Alkalinität - Teil 1:  
385 Bestimmung der gesamten und der zusammengesetzten Alkalinität (ISO 9963-1:1994); German  
386 version EN ISO 9963-1:1995,
- 387 DIN EN ISO 9963-2:1996-02: Wasserbeschaffenheit - Bestimmung der Alkalinität - Teil 2:  
388 Bestimmung der Carbonatalkalinität (ISO 9963-2:1994); German version EN ISO 9963-2:1995,

389 DIN EN ISO 10523:2012-04: Wasserbeschaffenheit - Bestimmung des pH-Werts (ISO  
390 10523:2008); German version EN ISO 10523:2012.

391 EEA: Corine Land Cover 2006 seamless vector data, European Environment Agency, 2006.

392 Hotchkiss, E. R., Hall Jr, R. O., Sponseller, R. A., Butman, D., Klaminder, J., Laudon, H.,  
393 Rosvall, M., and Karlsson, J.: Sources of and processes controlling CO<sub>2</sub> emissions change with  
394 the size of streams and rivers, *Nature Geosci.*, 8, 696-699, 10.1038/ngeo2507, 2015.

395 Jones, J. B., Stanley, E. H., and Mulholland, P. J.: Long-term decline in carbon dioxide  
396 supersaturation in rivers across the contiguous United States, *Geophysical Research Letters*, 30,  
397 2003.

398 Jonsson, A., Algesten, G., Bergström, A. K., Bishop, K., Sobek, S., Tranvik, L. J., and Jansson,  
399 M.: Integrating aquatic carbon fluxes in a boreal catchment carbon budget, *J. Hydrol.*, 334, 141-  
400 150, 10.1016/j.jhydrol.2006.10.003, 2007.

401 Lauerwald, R., Hartmann, J., Moosdorf, N., Kempe, S., and Raymond, P. A.: What controls the  
402 spatial patterns of the riverine carbonate system?—A case study for North America, *Chemical  
403 geology*, 337, 114-127, 2013.

404 Lauerwald, R., Laruelle, G. G., Hartmann, J., Ciais, P., and Regnier, P. A.: Spatial patterns in  
405 CO<sub>2</sub> evasion from the global river network, *Global Biogeochemical Cycles*, 29, 534-554, 2015.

406 Leach, J. A., Larsson, A., Wallin, M. B., Nilsson, M. B., and Laudon, H.: Twelve year  
407 interannual and seasonal variability of stream carbon export from a boreal peatland catchment, *J.  
408 Geophys. Res.-Biogeo.*, 121, 1851–1866, 10.1002/2016JG003357, 2016.

409 Leopold, L. B., and Maddock Jr, T.: The hydraulic geometry of stream channels and some  
410 physiographic implications 2330-7102, 1953.

411 LVermGeoRP: Vermessungs- und Katasterverwaltung Rheinland-Pfalz, Landesamt für  
412 Vermessung und Geobasisinformation Rheinland-Pfalz, 2012.

413 Maberly, S. C., Barker, P. A., Stott, A. W., and De Ville, M. M.: Catchment productivity  
414 controls CO<sub>2</sub> emissions from lakes, *Nat. Clim. Chang.*, 3, 391-394, 10.1038/nclimate1748, 2013.

415 MULEWF: GeoPortal Wasser, Ministerium für Umwelt, Landwirtschaft, Ernährung, Weinbau  
416 und Forsten Rheinland-Pfalz, 2013.

417 MULEWF: Wasserwirtschaftsverwaltung Rheinland-Pfalz, Ministerium für Umwelt,  
418 Landwirtschaft, Ernährung, Weinbau und Forsten Rheinland-Pfalz, 2015.

419 Nakayama, T.: New perspective for eco-hydrology model to constrain missing role of inland  
420 waters on boundless biogeochemical cycle in terrestrial–aquatic continuum, *Ecology &  
421 Hydrobiology*, 16, 138-148, 10.1016/j.ecohyd.2016.07.002, 2016.

422 Parkhurst, D. L., and Appelo, C.: User's guide to PHREEQC (Version 2): A computer program  
423 for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations,  
424 1999.

425 R Development Core Team: R: A language and environment for statistical computing. R  
426 Foundation for Statistical Computing, Vienna, Austria, 2011.

427 Ran, L., Lu, X. X., Yang, H., Li, L., Yu, R., Sun, H., and Han, J.: CO<sub>2</sub> outgassing from the  
428 Yellow River network and its implications for riverine carbon cycle, *J. Geophys. Res.-Biogeo.*,  
429 120, 1334-1347, 10.1002/2015JG002982, 2015.

430 Randerson, J. T., Chapin, F. S., Harden, J. W., Neff, J. C., and Harmon, M. E.: Net ecosystem  
431 production: a comprehensive measure of net carbon accumulation by ecosystems, *Ecol.  
432 Applications*, 12, 937-947, 10.1890/1051-0761(2002)012[0937:NEPACM]2.0.CO;2, 2002.

433 Raymond, P. A., Oh, N.-H., Turner, R. E., and Broussard, W.: Anthropogenically enhanced  
434 fluxes of water and carbon from the Mississippi River, *Nature*, 451, 449-452, 2008.

435 Raymond, P. A., Zappa, C. J., Butman, D., Bott, T. L., Potter, J., Mulholland, P., Laursen, A. E.,  
436 McDowell, W. H., and Newbold, D.: Scaling the gas transfer velocity and hydraulic geometry in  
437 streams and small rivers, *Limnology and Oceanography: Fluids and Environments*, 2, 41-53,  
438 2012.

439 Raymond, P. A., Hartmann, J., Lauerwald, R., Sobek, S., McDonald, C., Hoover, M., Butman,  
440 D., Striegl, R., Mayorga, E., Humborg, C., Kortelainen, P., Durr, H., Meybeck, M., Ciais, P., and  
441 Guth, P.: Global carbon dioxide emissions from inland waters, *Nature*, 503, 355-359,  
442 10.1038/nature12760, 2013.

443 Richey, J. E., Melack, J. M., Aufdenkampe, A. K., Ballester, V. M., and Hess, L. L.: Outgassing  
444 from Amazonian rivers and wetlands as a large tropical source of atmospheric CO<sub>2</sub>, *Nature*, 416,  
445 617-620, 10.1038/416617a, 2002.

446 Running, S. W., Nemani, R. R., Heinsch, F. A., Zhao, M., Reeves, M., and Hashimoto, H.: A  
447 Continuous Satellite-Derived Measure of Global Terrestrial Primary Production, *Bioscience*, 54,  
448 547-560, 10.1641/0006-3568(2004)054[0547:acsmog]2.0.co;2, 2004.

449 Sabine, C. L., Heimann, M., Artaxo, P., Bakker, D. C., Chen, C.-T. A., Field, C. B., Gruber, N.,  
450 Le Quéré, C., Prinn, R. G., and Richey, J. E.: Current status and past trends of the global carbon  
451 cycle, in: *The Global Carbon Cycle*, 2nd ed., edited by: Field, C. B., and Raupach, M. R.,  
452 Scientific Committee on Problems of the Environment (SCOPE) Series, Island Press, 17-44,  
453 2004.

454 Shibata, H., Hiura, T., Tanaka, Y., Takagi, K., and Koike, T.: Carbon cycling and budget in a  
455 forested basin of southwestern Hokkaido, northern Japan, *Ecological Research*, 20, 325-331,  
456 10.1007/s11284-005-0048-7, 2005.

457 Stanley, E. H., Casson, N. J., Christel, S. T., Crawford, J. T., Loken, L. C., and Oliver, S. K.: The  
458 ecology of methane in streams and rivers: patterns, controls, and global significance, *Ecological*  
459 *Monographs*, 2016.

460 Statistisches Landesamt Rheinland-Pfalz: Statistisches Jahrbuch 2014, 2014.

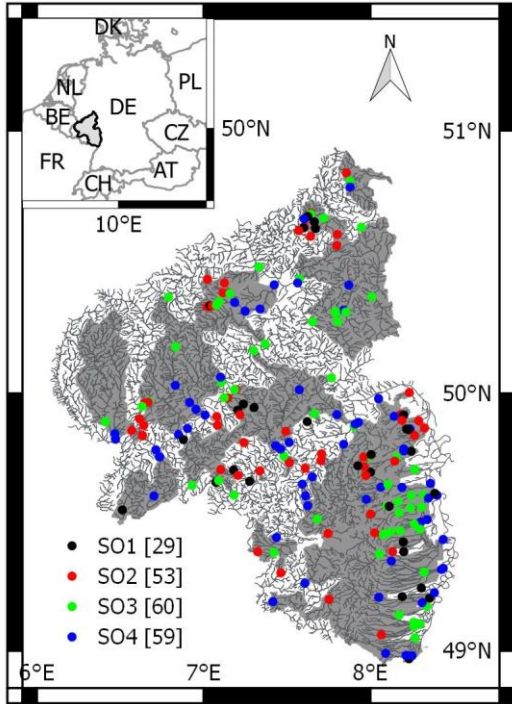
461 Strahler, A. N.: Quantitative analysis of watershed geomorphology, *Eos, Transactions American*  
462 *Geophysical Union*, 38, 913-920, 1957.

463 Stumm, W., and Morgan, J. J.: *Aquatic chemistry: chemical equilibria and rates in natural*  
464 *waters*, Wiley, 1996.

465 Tranvik, L. J., Downing, J. A., Cotner, J. B., Loiselle, S. A., Striegl, R. G., Ballatore, T. J.,  
466 Dillon, P., Finlay, K., Fortino, K., Knoll, L. B., Kortelainen, P. L., Kutser, T., Larsen, S.,  
467 Laurion, I., Leech, D. M., McCallister, S. L., McKnight, D. M., Melack, J. M., Overholt, E.,  
468 Porter, J. A., Prairie, Y., Renwick, W. H., Roland, F., Sherman, B. S., Schindler, D. W., Sobek,  
469 S., Tremblay, A., Vanni, M. J., Verschoor, A. M., von Wachenfeldt, E., and Weyhenmeyer, G.  
470 A.: Lakes and reservoirs as regulators of carbon cycling and climate, *Limnol. Oceanogr.*, 54,  
471 2298-2314, 10.4319/lo.2009.54.6\_part\_2.2298, 2009.

472 Wallin, M. B., Grabs, T., Buffam, I., Laudon, H., Ågren, A., Öquist, M. G., and Bishop, K.:  
473 Evasion of CO<sub>2</sub> from streams – The dominant component of the carbon export through the  
474 aquatic conduit in a boreal landscape, *Global Change Biol.*, 19, 785-797, 10.1111/gcb.12083,  
475 2013.

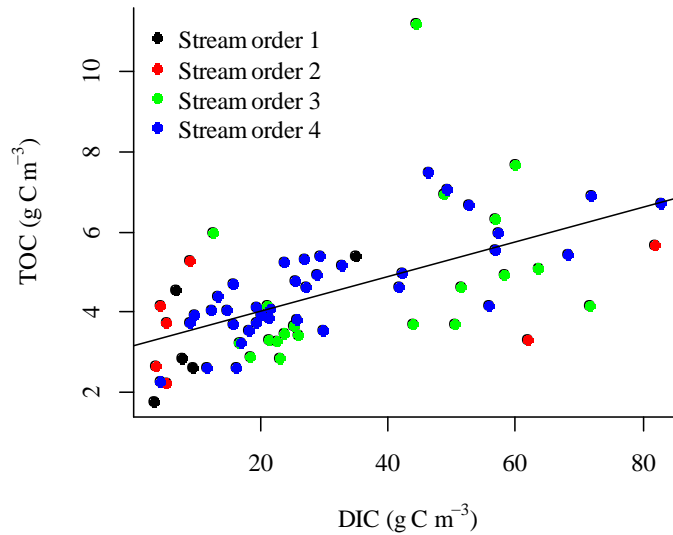
476 Walvoord, M. A., and Striegl, R. G.: Increased groundwater to stream discharge from permafrost  
477 thawing in the Yukon River basin: Potential impacts on lateral export of carbon and nitrogen,  
478 Geophysical Research Letters, 34, 2007.  
479 Zhang, W., and Montgomery, D. R.: Digital elevation model grid size, landscape representation,  
480 and hydrologic simulations, Water Resour. Res., 30, 1019-1028, 10.1029/93WR03553, 1994.  
481 Zhao, M., Heinsch, F. A., Nemani, R. R., and Running, S. W.: Improvements of the MODIS  
482 terrestrial gross and net primary production global data set, Remote Sensing of Environment, 95,  
483 164-176, 10.1016/j.rse.2004.12.011, 2005.



484

485 **Fig. 1:** Map of the stream network (black lines) within the state borders of Rhineland Palatinate in southwest Germany.  
486 The inset map in the upper left corner indicates the location of the study region in central Europe. Filled circles mark the  
487 position of sampling sites with color indicating stream order (SO1 – SO4; the numbers in brackets in the legend are the  
488 respective number of sampling sites). The catchment areas of the sampling sites are marked in grey color.

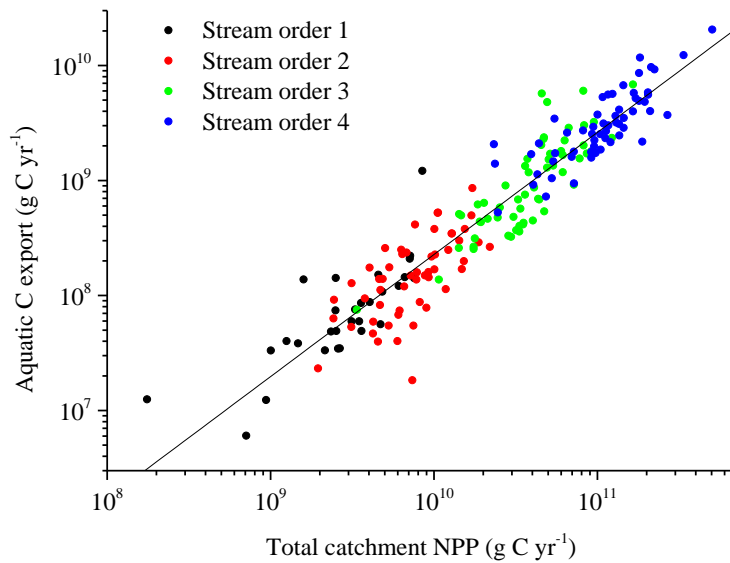
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490

491 **Fig. 2: TOC concentration versus DIC concentration. Different colors indicate sampling sites from different stream**  
 492 **orders. The solid line shows the fitted linear regression model with  $\text{TOC}=0.04 \cdot \text{DIC}$  ( $r^2=0.33, p<0.001$ ).**

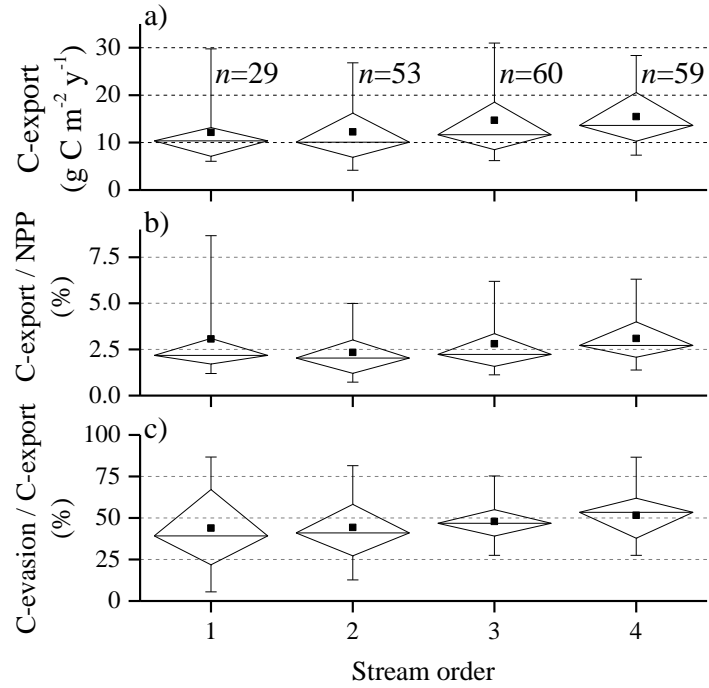
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495 **Fig. 3: Annual rate of C export through the stream network versus terrestrial NPP in the catchment area. Different colors**  
 496 **indicate sampling sites from different stream orders. The solid line shows the fitted linear regression model for the log-**  
 497 **transformed data with  $\text{C\_export}=0.005 \cdot \text{NPP}^{1.06}$  ( $r^2=0.89, p<0.001$ ).**

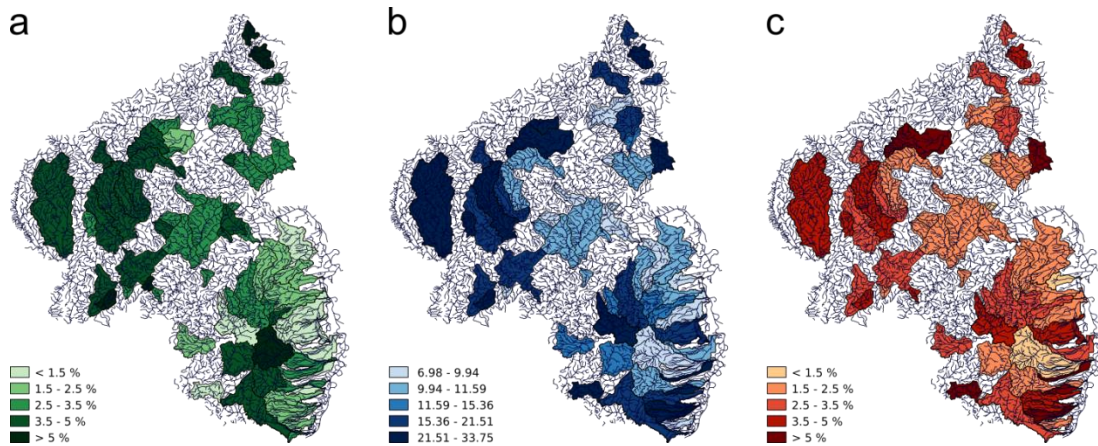




499

500 **Fig. 4:** a) Boxplots of C export (sum of evasion and discharge) normalized by catchment area. b) Boxplots of the ratio of  
 501 the total exported C and terrestrial NPP for different stream orders. c) Boxplots of the fraction of the total exported C  
 502 which is emitted to the atmosphere from the stream network for each stream order. The boxes demarcate the 25th and  
 503 75th percentiles, the whiskers demarcate the 95% confidence intervals. Median and mean values are marked as  
 504 horizontal lines and square symbols, respectively. The sample numbers (*n*) provided in a) apply to all panels.

505



506

507 **Fig. 5:** Map of 3rd and 4th order catchments showing a) Mean NPP (g C m<sup>-2</sup> yr<sup>-1</sup>), b) aquatic export (g C m<sup>-2</sup> yr<sup>-1</sup>), c) ratio  
 508 aquatic export/NPP (%).

509

510 **Table 1: Major hydrological characteristics,  $p\text{CO}_2$ , DIC and DOC concentrations averaged over stream orders (SO) and**  
 511 **for all sampling sites (total). All values are provided as mean $\pm$ sd (standard deviation) of the annual mean observations,**  
 512 **ranges are given in brackets,  $n$  is the number of observations.**

	SO 1	SO 2	SO 3	SO 4	Total
$n$	29	53	60	59	201
Catchment size ( $\text{km}^2$ )	9 $\pm$ 7 (1 – 35)	16 $\pm$ 9 (4 – 37)	87 $\pm$ 54 (9 – 298)	243 $\pm$ 140 (48 – 889)	103 $\pm$ 126 (1 – 889)
Water coverage (%)	0.24 $\pm$ 0.11 (0.05 – 0.43)	0.26 $\pm$ 0.09 (0.1 – 0.45)	0.36 $\pm$ 0.11 (0.09 – 0.6)	0.42 $\pm$ 0.13 (0.18 – 0.7)	0.33 $\pm$ 0.13 (0.05 – 0.7)
Discharge ( $\text{m}^3 \text{ s}^{-1}$ )	0.06 $\pm$ 0.05 (0.003 – 0.19)	0.15 $\pm$ 0.10 (0.01 – 0.36)	0.73 $\pm$ 0.63 (0.02 – 3.41)	2.20 $\pm$ 1.95 (0.22 – 12.22)	0.91 $\pm$ 1.41 (0.003 – 12.22)
Drainage rate ( $\text{m y}^{-1}$ )	0.26 $\pm$ 0.17 (0.05 – 0.67)	0.29 $\pm$ 0.16 (0.06 – 0.66)	0.27 $\pm$ 0.17 (0.05 – 0.74)	0.30 $\pm$ 0.21 (0.06 – 1.20)	0.28 $\pm$ 0.18 (0.05 – 1.20)
pH	7.58 $\pm$ 0.61 (6.20 – 8.97)	7.70 $\pm$ 0.46 (6.30 – 8.60)	7.81 $\pm$ 0.37 (6.60 – 8.30)	7.75 $\pm$ 0.29 (6.91 – 8.30)	7.73 $\pm$ 0.42 (6.20 – 8.97)
Alkalinity ( $\text{mmol L}^{-1}$ )	3.08 $\pm$ 2.50 (0.08 – 7.58)	2.74 $\pm$ 2.58 (0.08 – 8.55)	2.77 $\pm$ 1.85 (0.14 – 9.88)	2.58 $\pm$ 1.73 (0.32 – 7.22)	2.75 $\pm$ 2.12 (0.08 – 9.88)
$p\text{CO}_2$ (ppm)	2597 $\pm$ 1496 (145 – 6706)	1819 $\pm$ 1095 (681 – 5338)	1992 $\pm$ 1327 (573 – 7627)	2162 $\pm$ 1302 (366 – 7759)	2083 $\pm$ 1303 (145 – 7759)
DIC ( $\text{g m}^{-3}$ )	38.8 $\pm$ 30.3 (3.4 – 93.1)	34.2 $\pm$ 31.1 (3.5 – 104.5)	34.6 $\pm$ 22.4 (3.1 – 119.6)	32.4 $\pm$ 21.0 (4.1 – 89.3)	34.5 $\pm$ 25.7 (3.1 – 119.6)
DOC ( $\text{g m}^{-3}$ )	3.54 $\pm$ 1.86 (2.2 – 6.7) ( $n=5$ )	4.11 $\pm$ 0.73 (3.1 – 4.8) ( $n=4$ )	4.17 $\pm$ 1.08 (2.6 – 7.1) ( $n=22$ )	4.10 $\pm$ 1.24 (2.0 – 7.7) ( $n=33$ )	4.08 $\pm$ 1.20 (2.0 – 7.7) ( $n=64$ )

513

514 **Table 2: Aquatic C-fluxes and terrestrial NPP in catchments drained by streams of different stream orders (SO) and for**  
 515 **all sampling sites (total). All values are mean  $\pm$  standard deviation, ranges are given in brackets. The  $\text{CO}_2$  flux from the**  
 516 **water surface (first row) is expressed per square meter water surface area, while the remaining fluxes are expressed per**  
 517 **square meter catchment area.**

	SO 1	SO 2	SO 3	SO 4	Total
CO <sub>2</sub> flux from water surface (g C m <sup>-2</sup> yr <sup>-1</sup> )	2415±2335 (-335 – 12915)	1975±1364 (418 – 7143)	1998±1671 (704 – 11016)	1928±903 (851 – 5093)	2032±1528 (-335 – 12915)
Gas transfer velocity k <sub>600</sub> (m d <sup>-1</sup> )	7.04±4.52 (2.16 – 20.57)	7.74±3.78 (2.03 – 20.50)	5.86±2.81 (2.03 – 15.55)	4.23±0.96 (2.03 – 6.50)	6.05±3.32 (2.03 – 20.57)
CO <sub>2</sub> evasion per catchment area (g C m <sup>-2</sup> yr <sup>-1</sup> )	5.9±6.3 (-1.0 – 30.0)	5.2±4.1 (0.7 – 19.2)	7.0±6.6 (1.6 – 43.8)	8.0±4.6 (3.0 – 23.0)	6.6±5.5 (-1.0 – 43.8)
DIC discharge per catchment area (g C m <sup>-2</sup> yr <sup>-1</sup> )	6.2±4.5 (1.6 – 25.8)	7.1±6.1 (0.6 – 27.2)	7.7±5.7 (1.6 – 35.5)	7.5±4.7 (1.2 – 24.5)	7.3±5.4 (0.6 – 35.5)
Total aquatic C export per catchment area (g C m <sup>-2</sup> yr <sup>-1</sup> )	12.1±6.9 (4.7 – 34.5)	12.3±6.9 (1.5 – 29.6)	14.7±10.8 (5.3 – 66.8)	15.5±6.7 (7.0 – 33.8)	13.9±8.3 (1.5 – 66.8)
NPP (g C m <sup>-2</sup> yr <sup>-1</sup> )	466±127 (106 – 661)	536±66 (251 – 644)	527±57 (364 – 627)	508±69 (330 – 618)	515±79 (106 – 661)

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**Table 3: Summary of estimates of aquatic C export in relation to terrestrial production in the watershed across different spatial scales (spatial scale decreases from top to bottom). Aquatic C export is the sum of C-discharge and evasion (numbers in parentheses also include the change in C storage in the aquatic systems by sedimentation) normalized by the area of the terrestrial watershed. Aquatic C fate refers to the percentage of the total exported C which is emitted to the atmosphere (evasion) and transported downstream (discharge). The missing percentage is the fraction which is stored in the aquatic systems by sedimentation (if considered). Terrestrial production is expressed as NPP or as net ecosystem exchange (NEE). n.c. indicates that this compartment/flux was not considered in the respective study.**

Study area (Catchment size in km <sup>2</sup> )	Fractional water coverage (%) <u>R</u> ivers <u>L</u> akes	Aquatic C export (g C m <sup>-2</sup> yr <sup>-1</sup> )	Aquatic C fate (%): <u>E</u> vasion <u>D</u> ischarge	Aquatic C export / terrestrial production (%)		Reference
				NPP	NEE	
Global (1.3x10 <sup>8</sup> )	R: 0.2-0.3 L: 2.1-3.4	16 (20)	E: 44 D: 34	3.7 <sup>1</sup>	21-64 <sup>2</sup>	(Aufdenkampe et al., 2011)
Conterminous U.S. (7.8x10 <sup>6</sup> )	R: 0.52 L: 1.6	13.5 (18.8)	E: 58 D: 28	3.6	27 <sup>3</sup>	(Butman et al., 2015)
Central Amazon (1.8x10 <sup>6</sup> )	4-16	78	E: 87 D: 13	6.8 <sup>4</sup>	n.c.	(Richey et al., 2002)
Yellow River network (7.5x10 <sup>5</sup> )	R: 0.3-0.4 L: n.c.	18.5 (30)	E: 35 D: 26	n.c.	96 (62)	(Ran et al., 2015)
North temperate	R: 0.5	11.8	E: 33	n.c.	7	(Buffam et al.,

lake district (6400)	L: 13	(16)	D: 41			2011)
Northern Sweden (peat) (3025)	R: 0.33 L: 3.5	9	E: 50 (4.5) D: 50 (4.5)	n.c.	6	(Jonsson et al., 2007)
<b>Temperate streams (0.7- 1227)</b>	<b>R: 0.33 L: n.c.</b>	<b>13.9</b>	E: 47 D: 53	<b>2.7</b>	n.c.	<b>This study</b>
English Lake district (1 - 360)	R: n.c. L: 2.2	5.4	E: 100 D: n.c.	1.6	n.c.	(Maberly et al., 2013)
Forested stream catchments in Sweden (0.46 - 67)	R: 0.1-0.7 L:n.c. (<0.7)	9.4	E: 53 D: 47	n.c.	8-17	(Wallin et al., 2013)
Forest catchment in Japan (9.4)	R: - L: n.c.	4	E: n.c. D: 100	n.c.	2	(Shibata et al., 2005)
Peatland catchment (3.35)	R: 0.05 L: n.c.	30.4	E: 13 D: 87	n.c.	160	(Billett et al., 2004)
Peatland catchment (2.7)	R: n.c. L: 2.2	12.2	E: - D: -	n.c.	12-50	(Leach et al., 2016)

526 <sup>1</sup> For a value of 56 Pg C yr<sup>-1</sup> for global NPP (Zhao et al., 2005).

527 <sup>2</sup> Global mean NEE was estimated as the difference of GPP and ecosystem respiration, which was assumed to be 91-  
528 97 % of GPP (Randerson et al., 2002).

529 <sup>3</sup> This percentage refers to NEP instead of NEE.

530 <sup>4</sup> For a global mean value of NPP in tropical forests of 1148 g C m<sup>-2</sup> yr<sup>-1</sup> (Sabine et al., 2004).

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