(1) Comments from referees

Anonymous Referee #1

Received and published: 8 March 2017

General Comments

Rivers and streams are an important link in the global C cycle and C export via aquatic systems has repeatedly been concluded to make a significant proportion of catchment C budgets at different spatial scales and in different climate zones. This is an interesting paper that will make a good contribution to the understanding of regional-scale carbon export via streams with stream order 1-4 in the temperate zone. The authors observed a narrow range of variability of C export per catchment area and conclude that other processes than water surface area or location of mineralization of terrestrial derived C control the aquatic-terrestrial coupling and the role of inland waters in regional C cycling. However, the final version of the paper would benefit from more details about lateral C export calculations. It is not clear if extreme runoff events are covered appropriately. The lack of extreme event data would of course lead to a much narrower range of variability of C export.

Specific Comments

Ln 20. Explain “catchment-specific”

Ln 53. Why is the fluvial C load dominated by DIC? Are there carbonates? Please also state why you neglected methane.

Ln 56. Strahler stream order?

Ln 61-66. What about the geology? Is there C-containing bedrock in the catchments?

Ln 70. “15 800” do not separate numbers

Ln 71. Delete “order”

Ln 82. How are pH values of investigated waters? The pCO2 calculation with alkalinity was found to high uncertainties for low pH values (Abril et al. 2014).

Ln 89. How exactly did you aggregate annual means? Did you calculate a (discharge) weighted average?

Ln 128. Name the program used for statistics

Ln 145-148. Discuss variance of organic C. How about peaty areas?

Ln 152. Specify which value is meant: mean NPP or mean specific NPP?

Ln 169. In Figure 3 some of the data points (mostly stream order 1 and one of stream order 2) scatter more. Please discuss reasons for these outliers.

Ln 186. You talk about average fluxes, but what happens during floods/ extreme events? Do measurement intervals cover extreme events?

Ln 205. “: : :wetlands covering up to 16 % of the land surface area.” Add a reference.

Ln 226. Expected for temperate zones? In dry regions such as deserts this can be different.

Ln 235. Discuss “uncertainty of the various estimates”

Ln 236. Name potential controlling factors

Ln 244-247. How do you know that? In regions with corresponding geology also weathering of C-bearing minerals can be a large source of stream DIC. Respiration in soils is more likely the dominant DIC source in catchments that lack carbonate rocks. Is that true for catchments in Rhineland-Palatinate? Can you give an example for cases with predominance of aquatic respiration? I would expect predominance of aquatic respiration in warmer climates where large DOC concentrations prevail.

Ln 249. How is the range of discharge? The study by Hotchkiss et al. covers values from 0.0001 to 10,000 m3 s-1. Can the lower range in your study be the reason that you do not observe findings in Hotchkiss et al.?

Ln 252. Does "small number of observations" relate to this study?

Ln 255-257. This section summarizes the paper well but it could go further. It might be speculative but can you say what these other, poorly explored processes could be?

Ln 267. I think it is preferable to provide data as supplement material.

Table 1 and Table 2 would be more informative if you could add ranges. Please also add calculated gas transfer velocity values to Table 2.

References:

Abril, G., S. Bouillon, F. Darchambeau, C. R. Teodoru, T. R. Marwick, F. Tamooh, F. O. Omengo, N. Geeraert, L. Deirmendjian, P. Polsenaere, and A. V. Borges (2015), Technical Note: Large overestimation of pCO2 calculated from pH and alkalinity in acidic, organic-rich freshwaters, Biogeosciences, 12(1), 67-78, doi:10.5194/Bg-12-67-2015.

Anonymous Referee #2

Received and published: 11 March 2017

Accurate estimation of aquatic carbon export is essential to understand the role of natural ecosystems and geochemical processes in global carbon cycles in the context of climate change and increasing anthropogenic activities. In this manuscript, the authors integrate the analysis of downstream export of riverine carbon and CO2 evasion to the atmosphere from more than 200 local catchments of variable sizes in temperate Europe along with the model estimation of ecosystem production. Based on this large dataset, the authors try to establish a carbon budget in a local scale and discuss the ecologic factors controlling the aquatic carbon export. Overall, the integration of the large dataset of riverine carbon concentrations spanning over last several decades is technically sound and strengthens the arguments in the manuscript.

My biggest concern arises from the estimation of the downstream export of riverine carbon. The riverine carbon concentrations adopted in this investigation were obtained during 1977-2011, which is significantly longer than NPP of 2000-2013. Investigations have already showed a decadal increasing DIC export in boreal and subtropical rivers due to the climate change and anthropogenic activities (Walvoord, M. A., and R. G. Striegl, 2007, Increased groundwater to stream discharge from permafrost thawing in the Yukon River basin: Potential impacts on lateral export of carbon and nitrogen, Geophys. Res. Lett., 34, L12402, doi:10.1029/2007GL030216; Raymond, P.A., Oh,

N.-H., Turner, R.E., Broussard, W., 2008. Anthropogenically enhanced fluxes of water and carbon from the Mississippi River. Nature 451, 449-452). Therefore, I would suggest using the environment monitoring dataset during the last 10 years or so, which is consistemt with NPP estimation, to estimate the riverine carbon export.

Secondly, it seems that the data points for the flux estimation is sparse as indicated in the section 2.2 (see Page 3 Line 83-86: ": : :: : :at least one measurement was available for each season: : :: : :"). Therefore, I will be happy to see the error or uncertainty analysis of the flux estimation with the method using the mean concentration and total river discharge (see Page 4 Line 94-95). Moreover, a comparison with other flux estimation methods, such as the one using flow-weighted mean concentration and discharge, the one based on the regression of instantaneous flux and discharge, and other methods (see Warnken, K.W., Santschi, P.H., 2004. Biogeochemical behavior of organic carbon in the Trinity River downstream of a large reservoir lake in Texas, USA. Sci. Total Environ. 329, 131-144), will be helpful to validate the flux estimation.

What do you mean "interpolating pCO2 for all river segments without direct measurement" (Page 4 Line 95-97)? Please clarify in the text.

For DOC, there are 64 observations (Table 1) in 54 sampling sites (Page 3 Line 90-91). On average, there are less than 2 observations in each site. Usually, DOC concentrations in rivers could vary seasonally with river discharge by couples of times. Therefore, the representativeness of the single DOC data in each catchment remains a critical question which may induce the great deviation of DOC flux estimation from the real value. Before resolving this issue, the statements that DOC load only made up 4% total carbon load (Page 5 Line 146-148) and that the error would be comparably small when neglecting the DOC term (Page 6 Line 159-162) seem arbitrary.

The authors extensively discuss the aquatic carbon export/NPP ratio in the manuscript (See Table 3 and text in Section 4.1s). They state in the manuscript:" By combining CO2 evasion and downstream C-export by stream discharge, we estimated that 2.7 % of terrestrial NPP (13.9 g C m2 yr-1) are exported from the catchments by streams and rivers, in which both evasion and discharge contributed equally to this flux (Page 7 Line 193-195)". Then they compare their results with some other studies of catchment ecosystems (see text in Section 4.2). However, what I understand is riverine DIC export flux is closely related to the weathering regimes and intensity in catchments (See Cai, W.-J., Guo, X., Chen, C.-T.A., Dai, M., Zhang, L., Zhai, W., Lohrenz, S.E., Yin, K., Harrison, P.J., Wang, Y., 2008. A comparative overview of weathering intensity and HCO3- flux in the world's major rivers with emphasis on the Changjiang, Huanghe, Zhujiang (Pearl) and Mississippi Rivers. Continental Shelf Research 28, 1538-1549; and Raymond, P.A., Bauer, J.E., Caraco, N.F., Cole, J.J., Longworth, B., Petsch, S.T., 2004. Controls on the variability of organic matter and dissolved inorganic carbon ages in northeast US rivers. Marine Chemistry 92, 353-366) although NPP could contribute part of DIC export flux through the respiration of DOM. Therefore, the aquatic carbon export/NPP ratio would be expected to be larger than the real contribution of NPP.

Anonymous Referee #1

Received and published: 20 March 2017

Please check equation 1. The exponents and coefficients between width and depth are switched. In "Stream Hydraulics" in Raymond et al. (2012) this can be checked. I think the correct formulas would be w=12.88*Qˆ0.42 and d=0.4*Qˆ0.29. This corresponds to width=c*Qˆd and depth=a*Qˆb. The coefficients and exponents of your equation lead to depth»width, which seems not realistic.

Anonymous Referee #3

Received and published: 21 March 2017

General comments:

Katrin Magin and colleagues presented a synthesis of >200 catchments examining the relationships between lateral carbon export and CO2 emissions and terrestrial net primary production (NPP) in southwest Germany. Inland waters have recently been recognized as important components in the global carbon cycle. While widespread studies have been conducted worldwide, most of these studies are based on individual catchments and a synthesis involving multiple catchments remains lacking. This manuscript is well-organized and quite timely, and will provide insights into the understanding of catchment carbon cycle (or budget) at regional scales.

My first major concern after reading this manuscript is the carbon storage term which has not yet been considered when the authors evaluated catchment-scale carbon budget. Caron burial associated with soil erosion and sediment deposition within catchments is a quite important component in carbon budget assessments (e.g., Smith et al., 2001). If the traditional sediment delivery ratio of 10% is assumed (Harden et al., 1999), 90% of the eroded POC from land may have been stored somewhere within the catchment and partly exposed to decomposition (thus evasion to the atmosphere). This missing term may affect the redistribution of carbon (downstream discharge vs. CO2 evasion) as well as the amount of total carbon input from land. Incorporating this term will thus refine the budget result.

My second concern is the estimation of CO2 evasion. What are the resulting k600 values? Are they comparable to those based on field direct measurements (e.g., floating chamber or eddy covariance)? Estimation of the total areal extent of water surface by means of the parameters derived from USA catchments is probably problematic (see my specific comment below). In addition, can the available dataset suggest any seasonal variability in CO2 evasion?

Specific comments:

Line 19: please clarify ‘catchment-specific total export rate’. Is it the normalized carbon export by catchment area?

Line 29-30: the latest CO2 evasion from global rivers and streams is 0.65 Pg C/yr by Lauerwald et al., (2015).

Line 50: remove ‘differ’.

Line 71: the reference ‘Strahler, 1957’ should move to line 56.

Line 77: remaining!retained

Line 81-83. What’s the data quality and what kinds of standards for water sampling and processing were used? Estimating pCO2 from alkalinity and pH has been criticized for causing biases due to noncarbonate impacts (Abril et al., 2015). An uncertainty analysis should be provided here. I also suggest to provide the range of pH and alkalinity, possibly into Table 1.

Line 95-97: how was the site-specific pCO2 interpolated to the upstream catchments? And which interpolation technique was used?

Line 102-103: These arbitrary parameters derived from American rivers may not necessarily be representative of German rivers. See Leopold and Maddock (1953).

Line 105: Is a resolution of 10m enough to estimate channel slope changes?

Line 125-126: Because the mean NPP for the period 2000-2013 is used here while the pCO2 data is for the period 1970-2011, it is better to explicitly indicate the distribution frequency of pCO2 data over the study period. For example, if the most of the pCO2 data were for the period 1970-1980, then using the NPP for 2000-2013 would be problematic.

Line 135: Based on the given definition, the 'drainage rate' term should be 'runoff depth' in a formal way.

Line 146: Please quantify 'only a small fraction'.

Line 158: For the total C input, how about the POC term and the carbon storage term? See my major comment.

Line 220-223: Are there peatlands within the studied catchments?

Line 229-230: Is the absence of the carbon yield and NPP correlation due to failure to measure pCO2 during flooding periods? The short-duration carbon export during flooding events usually accounts for disproportionately a large share of the annual total carbon export.

Line 238: please clarify the 'surface area'. The global surface area?

Line 244-247: Could it also be because of chemical weathering and groundwater inputs? Rock weathering in carbonate-dominated catchments can be a significant contributor to DIC. I would suggest the authors to make a brief introduction about the lithology and mineralogy in the study area section (2.1).

Line 262: please summarize the study and make a short conclusion.

Figure 2. It seems the top 2(?) data points far away from the majority are outliers. Please check and make the regression again, if necessary.

Table 1. pH could also be tabulated here. Is there any trend in pH from SO1 to SO4?

References

Abril, G., Bouillon, S., Darchambeau, F., Teodoru, C., Marwick, T., Tamooh, F., Omengo, F., Geeraert, N., Deirmendjian, L., Polsenaere, P., and Borges, A. V.: Technical Note: Large overestimation of pCO2 calculated from pH and alkalinity in acidic, organic-rich freshwaters, Biogeosciences, 12, 67-78, 2015.

Harden, J., Sharpe, J., Parton, W., Ojima, D., Fries, T., Huntington, T., and Dabney, S.: Dynamic replacement and loss of soil carbon on eroding cropland, Global Biogeochem. Cy., 13, 885–901, 1999.

Lauerwald, R., Laruelle, G. G., Hartmann, J., Ciais, P., and Regnier, P. A.: Spatial patterns in CO2 evasion from the global river network, Global Biogeochemical Cycles, 29, 534-554, 2015.

Leopold, L., and Maddock, T.: The hydraulic geometry of stream channels and some physiographic implications, USGS Professional Paper 252, USGS Professional Paper 252, 1953.

Smith, S. V., Renwick, W. H., Buddemeier, R. W., and Crossland, C. J.: Budgets of soil erosion and deposition for sediments and sedimentary organic carbon across the conterminous United States, Global Biogeochemical Cycles, 15, 697-707, 2001.

(2) Author's response

Anonymous Referee #1

Rivers and streams are an important link in the global C cycle and C export via aquatic systems has repeatedly been concluded to make a significant proportion of catchment C budgets at different spatial scales and in different climate zones. This is an interesting paper that will make a good contribution to the understanding of regional-scale carbon export via streams with stream order 1-4 in the temperate zone. The authors observed a narrow range of variability of C export per catchment area and conclude that other processes than water surface area or location of mineralization of terrestrial derived C control the aquatic-terrestrial coupling and the role of inland waters in regional C cycling. However, the final version of the paper would benefit from more details about lateral C export calculations. It is not clear if extreme runoff events are covered appropriately. The lack of extreme event data would of course lead to a much narrower range of variability of C export.

We would like to thank the reviewer for her/his positive evaluation and the very helpful comments and suggestions. Below we reply on each specific comment.

- Ln 20. Explain "catchment-specific"

Reply: Catchment-specific carbon export refers to the carbon export per catchment area. We explained this in the revised version of the manuscript.

- Ln 53. Why is the fluvial C load dominated by DIC? Are there carbonates? Please also state why you neglected methane.

Reply: 16% of the study area contain carbonate bedrock. The weathering of the carbonate rock can be an additional source of DIC in the streams. In our study area, the DIC concentration in the water increased with the proportion of carbonate containing bedrock in the catchment (R^2=0.33, $p<0.001$). We added the information on bedrock in the revised version of the manuscript.
On average, DIC in the stream water was composed of 91.2% bicarbonate, 0.4% carbonate and 8.4% CO_2. Alkalinity ranged between 0.02 – 13.5 mmol L^{-1} for the individual measurements and between 0.08 – 9.88 mmol L^{-1} for the averaged seasonal mean values.
Measurements of methane concentration or fluxes are not available for the present study. According to a recent meta-analysis, the dissolved methane concentration in headwater streams varies mainly between 0.1 and 1 µmol L^{-1}, with streams in temperate forests being at the lower end (Stanley et al., 2016). The methane makes up only a small fraction of total carbon (in comparison to the mean DIC concentration in the present study (500 µmol L^{-1})) and we assume that methane makes a rather small contribution to the catchment scale carbon balance.

We added these information, together with an upper bound of methane evasion (based on the published meta-analysis), to the revised manuscript.

- Ln 56. Strahler stream order?

Reply: Yes, Strahler stream order. We added this information to the revised manuscript.

- Ln 61-66. What about the geology? Is there C-containing bedrock in the catchments?

Reply: See our comment above - 16% of the study area contain carbonate bedrock. The weathering of the carbonate rock can be one additional source of DIC in the streams. In our study area, the DIC concentration in the water increased with the proportion of carbonate containing bedrock in the catchment (R^2=0.33, p<0.001). We added the information on the bedrock in the revised version of the manuscript.

- Ln 70. "15 800" do not separate numbers
- Ln 71. Delete "order"

Reply: We corrected this.

- Ln 82. How are pH values of investigated waters? The pCO2 calculation with alkalinity was found to high uncertainties for low pH values (Abril et al. 2014).

Reply: The range of pH values of the investigated waters is 6.2 – 8.97 with a mean of 7.73±0.42 (mean±sd). According to (Abril et al., 2015), high uncertainties of pCO2 estimates from pH and alkalinity measurements occur at pH values <7, while the median and mean relative errors were 1% and 15%, respectively for pH>7. Only 7% of the pH values in our study were <7. We added a discussion of the expected uncertainties to the revised manuscript.

- Ln 89. How exactly did you aggregate annual means? Did you calculate a (discharge) weighted average?

Reply: pCO2_annual=(pCO2_spring+pCO2_summer+pCO2_autumn+pCO2_winter)/4 (seasonal values are averaged over all available samples). Discharge was not measured during the water sampling and no time-resolved discharge data are available for the sampling sites. We used annual mean discharge data, which were derived from data-driven regionalization of discharges from 125 gauging station from the period of 1979-1998 for the entire fluvial network. Application of discharge-weighted averaging was therefore not possible.

- Ln 128. Name the program used for statistics

Reply: All statistical analyses were performed with R. We added this information to the revised manuscript.

- Ln 145-148. Discuss variance of organic C. How about peaty areas?

Reply: There are no pronounced regional or temporal differences of organic carbon. The fraction of peatland in the study area is small (0.95 km^2 ; 0.009% of the study area) and only seven of the investigated catchments contain peaty areas. As organic C was measured only in three of these catchments, an investigation of the influence of peat on organic C was not possible.
We added the information about the variance of organic C and the peatland in the study area in the revised version of the manuscript.

- Ln 152. Specify which value is meant: mean NPP or mean specific NPP?

Reply: Mean specific NPP is meant. We clarified this.

- Ln 169. In Figure 3 some of the data points (mostly stream order 1 and one of stream order 2) scatter more. Please discuss reasons for these outliers.

Reply: Small streams of low stream order can be directly influenced by local peculiarities which can increase the scatter of the data points while larger streams represent more average conditions over larger spatial scales. The scattering points in Figure 3 belong, e.g. to ditches or outflows from ponds which might differ in their characteristics to other rivers and streams. Based on the available data, however, there are no particular properties of all the scattering points, which would justify special treatment: the catchments are completely included, pH values are in the range of 7.1-8.3, and no urban areas around these catchments

Ln 186. You talk about average fluxes, but what happens during floods/ extreme events? Do measurement intervals cover extreme events?

Reply: Since we do not have time-resolved discharge data we cannot account for extreme events. Moreover, no information are available if the governmental monitoring included sampling during floods. Given the stochastic nature and short duration, we expect that such samples are at least underrepresented. Since it has been observed that high-discharge events can make a disproportionally high contribution to annual mean carbon export from catchments, we consider our estimates as a lower bound – in accordance with other uncertainty estimates, see below. We added this information to the discussion in the revised manuscript.

- Ln 205. ": : :wetlands covering up to 16 % of the land surface area." Add a reference.

Reply: The 16% was taken from (Richey et al., 2002). However, in the revised version we refer to a fraction of 14%, which was estimated in the study of (Abril et al., 2013). This reference cited earlier in that sentence was moved to the end of the sentence in our revisions.

- Ln 226. Expected for temperate zones? In dry regions such as deserts this can be different.

Reply: We changed the sentence as follows:
As expected for temperate zones, large streams and rivers with large surface area have larger catchments.

- Ln 235. Discuss “uncertainty of the various estimates”

Reply: For a comparable methodological approach, (Butman and Raymond, 2011), estimated the uncertainty in the calculation of the aquatic carbon flux to be 33% (based on Monte Carlo simulation). (Raymond et al., 2013) estimated uncertainties from comparisons of estimates obtained using similar approaches as we with direct measurements of CO2 concentration on streams. For a density of sampling locations of 0.02 sites per km^2 (corresponding to our study) they derived an uncertainty of 30%.
In addition to errors associated with sampling and interpolation, our estimates are subject to a number of systematic errors. The neglect of carbon burial in sediments, carbon export and evasion as methane and unresolved flood events can be expected to result in an underestimation of the carbon exported from the catchments in our study. We discussed these uncertainties at greater detail in the revised manuscript.

- Ln 236. Name potential controlling factors

Reply: Here we refer to the potentially controlling factors listed in Table 3, including catchment NPP, fractional water coverage as well as size and climatic zone of the study area. In the revised manuscript, we listed these factors in the text.

- Ln 244-247. How do you know that? In regions with corresponding geology also weathering of C-bearing minerals can be a large source of stream DIC. Respiration in soils is more likely the dominant DIC source in catchments that lack carbonate rocks. Is that true for catchments in Rhineland-Palatinate? Can you give an example for cases with predominance of aquatic respiration? I would expect predominance of aquatic respiration in warmer climates where large DOC concentrations prevail.

Reply: We agree. 16% of the study area contain carbonate bedrock and the observed association between DIC and the proportion of carbonate containing bedrock in the catchment (R^2=0.33, $p<0.001$) indicates, that weathering can be one additional source of DIC in the streams. We added these results and revised the discussion accordingly. We mentioned that both mineral weathering and soil respiration contribute to DIC in stream water and discussed the relative contributions of both sources observed in other studies (Hotchkiss et al., 2015;Lauerwald et al., 2013;Humborg et al., 2010;Jones et al., 2003).
Examples for cases with predominance of aquatic respiration can not only be found in the tropics, but also in the boreal zone and in peat-draining streams. We would refer to (Duarte and Prairie, 2005;Jonsson et al., 2007;Lynch et al., 2010;Richey et al., 2002) as examples.
(Hotchkiss et al., 2015) observed an increased CO2 emissions from internal production for increasing stream size.

- Ln 249. How is the range of discharge? The study by Hotchkiss et al. covers values from 0.0001 to 10,000 m3 s-1. Can the lower range in your study be the reason that you do not observe findings in Hotchkiss et al.?

Reply: The range of discharge in our study is 0.003 - 12.2 $m^3 s^{-1}$ which is indeed a lower range compared to the study by Hotchkiss et al. We added the range of discharge in the revised manuscript.

- Ln 252. Does "small number of observations" relate to this study?

Reply: No, at this point we refer to the meta-analysis presented in Table 3. We made this clearer in the revised manuscript.

- Ln 255-257. This section summarizes the paper well but it could go further. It might be speculative but can you say what these other, poorly explored processes could be?

Reply: We would speculate, that hydrology plays a major role for C-cycling at larger scale. Precipitation controls not only terrestrial NPP but also, drainage density, export of OM from land to water and retention time of OM in soil and in surface waters respectively. Since our hydrological data base is rather weak (annual discharge only, no precipitation), we think that these speculations would be not well supported by the presented results.

- Ln 267. I think it is preferable to provide data as supplement material.

Reply: We provide information about the investigated streams (stream order, water surface area, discharge, pH), catchment size and catchment NPP, DIC, DOC and TOC, pCO2 and the seasonality of pCO2, gas exchange velocity and total stream evasion as supplemental material.

- Table 1 and Table 2 would be more informative if you could add ranges. Please also add calculated gas transfer velocity values to Table 2.

Reply: We added the information to the tables.

References:

Abril, G., Martinez, J.-M., Artigas, L. F., Moreira-Turcq, P., Benedetti, M. F., Vidal, L., Meziane, T., Kim, J.-H., Bernardes, M. C., Savoye, N., Deborde, J., Souza, E. L., Alberic, P., Landim de Souza, M. F., and Roland, F.: Amazon River carbon dioxide outgassing fuelled by wetlands, Nature, 505, 395-398, 10.1038/nature12797, 2013.

Abril, G., Bouillon, S., Darchambeau, F., Teodoru, C. R., Marwick, T. R., Tamooh, F., Ochieng Omengo, F., Geeraert, N., Deirmendjian, L., Polsenaere, P., and Borges, A. V.: Technical Note: Large overestimation of pCO_2 calculated from pH and alkalinity in acidic, organic-rich freshwaters, Biogeosciences, 12, 67-78, 10.5194/bg-12-67-2015, 2015.

Butman, D., and Raymond, P. A.: Significant efflux of carbon dioxide from streams and rivers in the United States, Nature Geosci., 4, 839-842, 2011.

Duarte, C. M., and Prairie, Y. T.: Prevalence of Heterotrophy and Atmospheric CO2 Emissions from Aquatic Ecosystems, Ecosystems, 8, 862-870, 10.1007/s10021-005-0177-4, 2005.

Hotchkiss, E. R., Hall Jr, R. O., Sponseller, R. A., Butman, D., Klaminder, J., Laudon, H., Rosvall, M., and Karlsson, J.: Sources of and processes controlling CO_2 emissions change with the size of streams and rivers, Nature Geosci., 8, 696-699, 10.1038/ngeo2507, 2015.

Humborg, C., Mörth, C.-M., Sundbom, M., Borg, H., Blenckner, T., Giesler, R., and Ittekkot, V.: CO_2 supersaturation along the aquatic conduit in Swedish watersheds as constrained by terrestrial respiration, aquatic respiration and weathering, Global Change Biol., 16, 1966-1978, 10.1111/j.1365-2486.2009.02092.x, 2010.

Jones, J. B., Jr., Stanley, E. H., and Mulholland, P. J.: Long-term decline in carbon dioxide supersaturation in rivers across the contiguous United States, Geophys. Res. Lett., 30, 1495, 10.1029/2003gl017056, 2003.

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

Lauerwald, R., Hartmann, J., Moosdorf, N., Kempe, S., and Raymond, P. A.: What controls the spatial patterns of the riverine carbonate system? — A case study for North America, Chemical Geology, 337–338, 114-127, 10.1016/j.chemgeo.2012.11.011, 2013.

Lynch, J. K., Beatty, C. M., Seidel, M. P., Jungst, L. J., and DeGrandpre, M. D.: Controls of riverine CO_2 over an annual cycle determined using direct, high temporal resolution pCO_2 measurements, J. Geophys. Res., 115, G03016, 10.1029/2009jg001132, 2010.

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

Richey, J. E., Melack, J. M., Aufdenkampe, A. K., Ballester, V. M., and Hess, L. L.: Outgassing from Amazonian rivers and wetlands as a large tropical source of atmospheric CO_2, Nature, 416, 617-620, 10.1038/416617a, 2002.

Stanley, E. H., Casson, N. J., Christel, S. T., Crawford, J. T., Loken, L. C., and Oliver, S. K.: The ecology of methane in streams and rivers: patterns, controls, and global significance, Ecol. Monographs, 86, 146-171, 10.1890/15-1027, 2016.

Anonymous Referee #2

Accurate estimation of aquatic carbon export is essential to understand the role of natural ecosystems and geochemical processes in global carbon cycles in the context of climate change and increasing anthropogenic activities. In this manuscript, the authors integrate the analysis of downstream export of riverine carbon and CO2 evasion to the atmosphere from more than 200 local catchments of variable sizes in temperate Europe along with the model estimation of ecosystem production. Based on this large dataset, the authors try to establish a carbon budget in a local scale and discuss the ecologic factors controlling the aquatic carbon export. Overall, the integration of the large dataset of riverine carbon concentrations spanning over last several decades is technically sound and strengthens the arguments in the manuscript.

We would like to thank the reviewer for her/his positive evaluation and the very helpful comments and suggestions. Below we reply on each specific comment.

- My biggest concern arises from the estimation of the downstream export of riverine carbon. The riverine carbon concentrations adopted in this investigation were obtained during 1977-2011, which is significantly longer than NPP of 2000-2013. Investigations have already showed a decadal increasing DIC export in boreal and subtropical rivers due to the climate change and anthropogenic activities (Walvoord, M. A., and R. G. Striegl, 2007, Increased groundwater to stream discharge from permafrost thawing in the Yukon River basin: Potential impacts on lateral export of carbon and nitrogen, Geophys. Res. Lett., 34, L12402, doi:10.1029/2007GL030216; Raymond, P.A., Oh, N.-H., Turner, R.E., Broussard, W., 2008. Anthropogenically enhanced fluxes of water and carbon from the Mississippi River. Nature 451, 449-452). Therefore, I would suggest using the environment monitoring dataset during the last 10 years or so, which is consistemt with NPP estimation, to estimate the riverine carbon export.

Reply: Using only the monitoring data during the last 10 years would reduce the number of valid samples from currently 8020 to 5070. We compared DIC measured in the time periods 1977-1999 and 2000-2011 for all Strahler orders. The DIC did not change significantly. We provided this information in the revised version of the manuscript and also pointed towards the trends observed in other regions, as mentioned by the reviewer.

- Secondly, it seems that the data points for the flux estimation is sparse as indicated in the section 2.2 (see Page 3 Line 83-86: ": : :: : :at least one measurement was available for each season: : :: : :"). Therefore, I will be happy to see the error or uncertainty analysis of the flux estimation with the method using the mean concentration and total river discharge (see Page 4 Line 94-95). Moreover, a comparison with other flux estimation methods, such as the one using flow-weighted mean concentration and discharge, the one based on the regression of instantaneous flux and discharge, and other methods (see Warnken, K.W., Santschi, P.H., 2004. Biogeochemical behavior of organic carbon in the Trinity River downstream of a large reservoir lake in Texas, USA. Sci. Total Environ. 329, 131-144), will be helpful to validate the flux estimation.

Reply: Unfortunately, the only available discharge data are annual mean values derived using data-driven regionalization of discharges from 125 gauging station from the period of 1979-1998. Time-resolved discharge measurements or data for the sampling times and sites, which could be used for flow-weighted estimates of DIC export and CO2 evasion, are not available. For the uncertainty analysis, we used the more extensive analysis of (Raymond et al., 2013), where uncertainties were derived based on comparisons of estimates obtained using similar approaches as we used with direct measurements of CO2 concentration. For a density of sampling locations of 0.02 sites per km2 they derived an uncertainty of 30%. Similarly, (Butman and Raymond, 2011) estimated uncertainties of overall flux estimates of 33%, based on Monte Carlo simulation of similar data for hydrographic units in the United States.
In addition to errors associated with sampling and interpolation, our estimates are subject to a number of systematic errors. The neglect of carbon burial in sediments, carbon export and evasion as methane and under-sampling of high-discharge events, probably result in an

underestimation of the carbon exported from the catchments in our study. We discussed these uncertainties at greater detail in the revised manuscript.

- What do you mean "interpolating pCO2 for all river segments without direct measurement" (Page 4 Line 95-97)? Please clarify in the text.

Reply: The explanation is provided in the following sentence (Line 97-98):
For this, the mean concentrations were averaged by stream order and assigned to all stream segments of the river network (Butman and Raymond, 2011).
To clarify this, we joined the two sentences in the revised manuscript.

- For DOC, there are 64 observations (Table 1) in 54 sampling sites (Page 3 Line 90-91). On average, there are less than 2 observations in each site. Usually, DOC concentrations in rivers could vary seasonally with river discharge by couples of times. Therefore, the representativeness of the single DOC data in each catchment remains a critical question which may induce the great deviation of DOC flux estimation from the real value. Before resolving this issue, the statements that DOC load only made up 4% total carbon load (Page 5 Line 146-148) and that the error would be comparably small when neglecting the DOC term (Page 6 Line 159-162) seem arbitrary.

Reply: 54 is a mistake in writing, which we corrected. There are seasonally averaged DOC observations at 64 sampling sites; all values are averaged over several measurements covering all seasons.

The authors extensively discuss the aquatic carbon export/NPP ratio in the manuscript (See Table 3 and text in Section 4.1s). They state in the manuscript:" By combining CO2 evasion and downstream C-export by stream discharge, we estimated that 2.7 % of terrestrial NPP (13.9 g C m2 yr-1) are exported from the catchments by streams and rivers, in which both evasion and discharge contributed equally to this flux (Page 7 Line 193-195)". Then they compare their results with some other studies of catchment ecosystems (see text in Section 4.2). However, what I understand is riverine DIC export flux is closely related to the weathering regimes and intensity in catchments (See Cai, W.-J., Guo, X., Chen, C.-T.A., Dai, M., Zhang, L., Zhai, W., Lohrenz, S.E., Yin, K., Harrison, P.J., Wang, Y., 2008. A comparative overview of weathering intensity and HCO3- flux in the world's major rivers with emphasis on the Changjiang, Huanghe, Zhujiang (Pearl) and Mississippi Rivers. Continental Shelf Research 28, 1538-1549; and Raymond, P.A., Bauer, J.E., Caraco, N.F., Cole, J.J., Longworth, B., Petsch, S.T., 2004. Controls on the variability of organic matter and dissolved inorganic carbon ages in northeast US rivers. Marine Chemistry 92, 353-366) although NPP could contribute part of DIC export flux through the respiration of DOM. Therefore, the aquatic carbon export/NPP ratio would be expected to be larger than the real contribution of NPP.

Reply: Our analysis of aquatic C-export in relation to NPP was inspired by studies where correlations between aquatic C export and terrestrial NPP or NEP have been observed at different spatial scales and different landscapes (e.g., (Butman et al., 2015;Maberly et al., 2013); and other studies listed in Table 3). The reason for a lack of correlation in our study could be related to weathering, as pointed out by the reviewer. 16% of the study area contain carbonate bedrock. In our study area, the DIC concentration in the water increased with the proportion of carbonate containing bedrock in the catchment (R^2=0.33, p<0.001). In the discussion of the revised manuscript, we listed this as an uncertainty and added estimates of the contribution of weathering found in other studies.

References:

Butman, D., and Raymond, P. A.: Significant efflux of carbon dioxide from streams and rivers in the United States, Nature Geosci., 4, 839-842, 2011.

Butman, D., Stackpoole, S., Stets, E., McDonald, C. P., Clow, D. W., and Striegl, R. G.: Aquatic carbon cycling in the conterminous United States and implications for terrestrial carbon accounting, Proceedings of the National Academy of Sciences, 10.1073/pnas.1512651112, 2015.

Maberly, S. C., Barker, P. A., Stott, A. W., and De Ville, M. M.: Catchment productivity controls CO_2 emissions from lakes, Nat. Clim. Chang., 3, 391-394, 10.1038/nclimate1748, 2013.

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

Anonymous Referee #1

- Please check equation 1. The exponents and coefficients between width and depth are switched. In "Stream Hydraulics" in Raymond et al. (2012) this can be checked. I think the correct formulas would be w=12.88*Q^0.42 and d=0.4*Q^0.29. This corresponds to width=c*Q^d and depth=a*Q^b. The coefficients and exponents of your equation lead to depth>width, which seems not realistic.

Reply: Thank you for pointing this out. Indeed the numbers were swapped in the manuscript. All calculations were done with the correct equations. We corrected the coefficients in the revised manuscript.

Anonymous Referee #3

Katrin Magin and colleagues presented a synthesis of >200 catchments examining the relationships between lateral carbon export and CO2 emissions and terrestrial net primary production (NPP) in southwest Germany. Inland waters have recently been recognized as important components in the global carbon cycle. While widespread studies have been conducted worldwide, most of these studies are based on individual catchments and a synthesis involving multiple catchments remains lacking. This manuscript is well-organized and quite timely, and will provide insights into the understanding of catchment carbon cycle (or budget) at regional scales.

We would like to thank the reviewer for her/his positive evaluation and the very helpful comments and suggestions. Below we reply on each specific comment.

My first major concern after reading this manuscript is the carbon storage term which has not yet been considered when the authors evaluated catchment-scale carbon budget. Caron burial associated with soil erosion and sediment deposition within catchments is a quite important component in carbon budget assessments (e.g., Smith et al., 2001). If the traditional sediment delivery ratio of 10% is assumed (Harden et al.1999), 90% of the eroded POC from land may have been stored somewhere within the catchment and partly exposed to decomposition (thus evasion to the atmosphere). This missing term may affect the redistribution of carbon (downstream discharge vs. CO2 evasion) as well as the amount of total carbon input from land. Incorporating this term will thus refine the budget result.

Reply: See our response to your specific comment below.

My second concern is the estimation of CO2 evasion. What are the resulting k600 values? Are they comparable to those based on field direct measurements (e.g., floating chamber or eddy covariance)? Estimation of the total areal extent of water surface by means of the parameters derived from USA catchments is probably problematic (see my specific comment below). In addition, can the available dataset suggest any seasonal variability in CO2 evasion?

Reply: The k600 values in our study range from 2.0 m d-1 to 20.6 m d-1 with a mean of 6.0±3.3 m d-1. These transfer velocities are comparable to k600 values based on direct field measurements by floating chambers from small headwater streams in Alaska (Crawford et al., 2013) and also to some short chamber deployments within the study area (Lorke et al., 2015). The pCO2 is higher in summer (mean±sd: 2780±2098 ppm) and autumn (mean±sd: 2848±2019 ppm) than in winter (mean±sd: 2287±1716 ppm) and spring (mean±sd: 2172±2343 ppm). In contrast, the relationship of catchment NPP and CO2 evasion is not influenced by the season. We added the k600 values in Table 2 and discussed the seasonal variability of pCO2 in the revised version of the manuscript.

- Line 19: please clarify ‘catchment-specific total export rate’. Is it the normalized carbon export by catchment area?

Reply: Yes, the catchment-specific carbon export rate refers to the carbon export per catchment area. We clarified this in the revised version of the manuscript.

- Line 29-30: the latest CO2 evasion from global rivers and streams is 0.65 Pg C/yr by Lauerwald et al., (2015).

Reply: We included the reference in this section.

- Line 50: remove 'differ'.
- Line 71: the reference 'Strahler, 1957' should move to line 56.
- Line 77: remaining →retained

Reply: We applied these corrections.

- Line 81-83. What's the data quality and what kinds of standards for water sampling and processing were used? Estimating pCO2 from alkalinity and pH has been criticized for causing biases due to noncarbonate impacts (Abril et al., 2015). An uncertainty analysis should be provided here. I also suggest to provide the range of pH and alkalinity, possibly into Table 1.

Reply: The data are governmental monitoring data which are acquired according to DIN EN ISO norms ((DIN EN ISO 10523:2012-04;DIN EN ISO 9963-1:1996-02;DIN EN ISO 9963-2:1996-02)). The range of pH values of the investigated waters was 6.2 – 8.97 with a mean of 7.73±0.42 (mean±sd). The range of alkalinity is 0.08 – 9.88 mmol L^{-1} with a mean of 2.75±2.12 mmol L^{-1} (mean±sd). We added pH values and alkalinity in Table 1.
According to (Abril et al., 2015), high uncertainties of pCO2 estimates from pH and alkalinity measurements occur at pH values <7, while the median and mean relative errors were 1% and 15%, respectively for pH>7. Only 7 % of the pH values in our study were <7. We added a discussion of the expected uncertainties to the revised manuscript.

- Line 95-97: how was the site-specific pCO2 interpolated to the upstream catchments? And which interpolation technique was used?

Reply: The explanation is provided in the following sentence (Line 97-98):
For this, the mean concentrations were averaged by stream order and assigned to all stream segments of the river network (Butman and Raymond, 2011).
To clarify this, we joined the two sentences in the revised manuscript.

- Line 102-103: These arbitrary parameters derived from American rivers may not necessarily be representative of German rivers. See Leopold and Maddock (1953).

Reply: The coefficients we used were derived from various data sets obtained in North America, but have been applied also in global studies before, e.g. (Raymond et al., 2013). Unfortunately, we are not aware of a comparably extensive data set of hydraulic geometry data derived for European rivers. A comparison of hydraulic geometry coefficients derived from various data sets, including data from England, Australia and New Zealand, is presented in (Butman and Raymond, 2011), who estimated that the error associated with uncertainties of hydraulic geometry coefficients is rather small, compared to uncertainties derived for C-fluxes. We added these information to an extended discussion of uncertainties in the revised manuscript.

- Line 105: Is a resolution of 10 m enough to estimate channel slope changes?

Reply: (Zhang and Montgomery, 1994) investigated the effect of digital elevation model (DEM) resolution on slope calculation and performance in hydrological models for spatial resolutions between 2 and 90 m. They found that while a 10-m grid is a significant improvement over 30 m or coarser grid sizes, finer grid sizes provide relatively little additional resolution. Thus a 10-m grid size presents a reasonable compromise between increasing spatial resolution and data handling requirements for modeling surface processes in many landscapes. We justified the choice of DEM resolution in the revised manuscript.
It should be noted, that similar studies have derived slope information from coarser DEM resolution, e.g. SRTM 90m Digital Elevation Data in (Lauerwald et al., 2013), GMTED2010 with >250 m resolution in (Raymond et al., 2013), NHDPlus with 30 m ground resolution in (Butman et al., 2015).

- Line 125-126: Because the mean NPP for the period 2000-2013 is used here while the pCO2 data is for the period 1970-2011, it is better to explicitly indicate the distribution frequency of pCO2 data over the study period. For example, if the most of the pCO2 data were for the period 1970-1980, then using the NPP for 2000-2013 would be problematic.

Reply: The sampling frequency was increasing. There are nearly twice as much data from 2000-2011 than from 1977-1999. A comparison between DIC data from both sampling periods revealed no significant differences. We added the sampling frequency distribution as supplementary material.

- Line 135: Based on the given definition, the ‘drainage rate’ term should be ‘runoff depth’ in a formal way.

Reply: We corrected the term in our revisions.

- Line 146: Please quantify ‘only a small fraction’.

Reply: On average 8.6% of the TOC consist of POC. The highest percentage of POC found in a catchment is 28.2%.

- Line 158: For the total C input, how about the POC term and the carbon storage term? See my major comment.

Reply: POC as suspended load in the rivers was estimated along with DOC and was only 8.6% of the TOC load (0.8 % of the total C-load) at the sampling sites. We agree with the reviewer that storage can make a significant contribution to the catchment-scale C balance. Estimates vary between 22% at a global scale (Aufdenkampe et al., 2011), 14 % for the Conterminous U.S. (Butman et al., 2015) and 39% for the Yellow River network (Ran et al., 2015). However, C storage in aquatic systems occurs mainly in lakes and reservoirs, which are virtually absent in the catchments studied here. Therefore we consider the bias caused by neglecting storage to be comparable in magnitude to remaining uncertainties (30%). We added a more detailed discussion of the storage term and the associated uncertainty as part of a general uncertainty analysis (see comments above) in the revised discussion section. The neglect of storage, and potential high C loads during extreme discharge events, suggest that C-export from catchments estimated in the present study provides a lower bound of the aquatic C flux.

- Line 220-223: Are there peatlands within the studied catchments?

Reply: The fraction of peatlands in the area in really small (0.009%) and is restricted to 7 of the investigated catchments. For only 3 of these catchments DOC measurements were available and no influence of the peatland on the DOC was observable. We added the information about the peatland in the study area in the revised version of the manuscript.

- Line 229-230: Is the absence of the carbon yield and NPP correlation due to failure to measure pCO2 during flooding periods? The short-duration carbon export during flooding events usually accounts for disproportionately a large share of the annual total carbon export.

Reply: Since we do not have time-resolved discharge data we cannot account for extreme events. Moreover, no information are available if the governmental monitoring included sampling during floods. Given the stochastic nature and short duration, we expect that such samples are at least underrepresented. Since it has been observed that high-discharge events can make a disproportionally high contribution to annual mean carbon export from catchments, we consider our estimates as a lower bound – in accordance with other uncertainty estimates, see below. We added this information to the discussion in the revised manuscript.

- Line 238: please clarify the ‘surface area’. The global surface area?

Reply: No, this surface area refers to regions in the 2 studies cited in that sentence. We clarified this in our revisions.

- Line 244-247: Could it also be because of chemical weathering and groundwater inputs? Rock weathering in carbonate-dominated catchments can be a significant contributor to DIC. I would suggest the authors to make a brief introduction about the lithology and mineralogy in the study area section (2.1).

Reply: 16% of the area investigated in our study contain calcareous bedrock. The DIC concentration in the water increased with the proportion of carbonate bedrock in the catchments ($R^2=0.33$, $p<0.001$). We added the information about the bedrock in the study area section and included the influence of chemical weathering in our discussion.

- Line 262: please summarize the study and make a short conclusion.

Reply: We added the following conclusion to the revised version of the manuscript:
Our analysis of the carbon budget in a temperate stream network on regional scale revealed a relationship of aquatic carbon export and terrestrial NPP. On average 2.7% of the terrestrial NPP were exported from the catchments by rivers and streams with CO2 evasion and downstream transport contributing equally to the export. A comparison of our regional scale study with other studies from different scales and landscapes showed a relatively narrow range of variability of carbon export per catchment area. Future research is needed to understand the processes that control the aquatic-terrestrial coupling and the role of inland waters in regional carbon cycling.

- Figure 2. It seems the top 2(?) data points far away from the majority are outliers. Please check and make the regression again, if necessary.

Reply: The apparent outlier is only 1 data point. It does not influence the regression.

- Table 1. pH could also be tabulated here. Is there any trend in pH from SO1 to SO4?

Reply: We included pH in Table 1. There is no trend in pH from SO1 to SO4 but the variability of pH (e.g. standard deviation) is decreasing with increasing stream order.

References:

Abril, G., Bouillon, S., Darchambeau, F., Teodoru, C. R., Marwick, T. R., Tamooh, F., Ochieng Omengo, F., Geeraert, N., Deirmendjian, L., Polsenaere, P., and Borges, A. V.: Technical Note: Large overestimation of pCO2 calculated from pH and alkalinity in acidic, organic-rich freshwaters, Biogeosciences, 12, 67-78, 10.5194/bg-12-67-2015, 2015.

779 Aufdenkampe, A. K., Mayorga, E., Raymond, P. A., Melack, J. M., Doney, S. C., Alin, S. R.,
780 Aalto, R. E., and Yoo, K.: Riverine coupling of biogeochemical cycles between land,
781 oceans, and atmosphere, Front. Ecol. Environ., 9, 53-60, 10.1890/100014, 2011.
782 Butman, D., and Raymond, P. A.: Significant efflux of carbon dioxide from streams and rivers in
783 the United States, Nature Geosci., 4, 839-842, 2011.
784 Butman, D., Stackpoole, S., Stets, E., McDonald, C. P., Clow, D. W., and Striegl, R. G.: Aquatic
785 carbon cycling in the conterminous United States and implications for terrestrial carbon
786 accounting, Proceedings of the National Academy of Sciences, 10.1073/pnas.1512651112,
787 2015.
788 Crawford, J. T., Striegl, R. G., Wickland, K. P., Dornblaser, M. M., and Stanley, E. H.:
789 Emissions of carbon dioxide and methane from a headwater stream network of interior
790 Alaska, Journal of Geophysical Research: Biogeosciences, 118, 482-494, 2013.
791 DIN EN ISO 9963-1:1996-02: Wasserbeschaffenheit - Bestimmung der Alkalinität - Teil 1:
792 Bestimmung der gesamten und der zusammengesetzten Alkalinität (ISO 9963-1:1994);
793 German version EN ISO 9963-1:1995.
794 DIN EN ISO 9963-2:1996-02: Wasserbeschaffenheit - Bestimmung der Alkalinität - Teil 2:
795 Bestimmung der Carbonatalkalinität (ISO 9963-2:1994); German version EN ISO 9963-
796 2:1995.
797 DIN EN ISO 10523:2012-04: Wasserbeschaffenheit - Bestimmung des pH-Werts (ISO
798 10523:2008); German version EN ISO 10523:2012.
799 Lauerwald, R., Hartmann, J., Moosdorf, N., Kempe, S., and Raymond, P. A.: What controls the
800 spatial patterns of the riverine carbonate system? — A case study for North America,
801 Chemical Geology, 337–338, 114-127, 10.1016/j.chemgeo.2012.11.011, 2013.
802 Lorke, A., Bodmer, P., Noss, C., Alshboul, Z., Koschorreck, M., Somlai-Haase, C., Bastviken,
803 D., Flury, S., McGinnis, D. F., Maeck, A., Müller, D., and Premke, K.: Technical note:
804 drifting versus anchored flux chambers for measuring greenhouse gas emissions from
805 running waters, Biogeosciences, 12, 7013-7024, 10.5194/bg-12-7013-2015, 2015.
806 Ran, L., Lu, X. X., Yang, H., Li, L., Yu, R., Sun, H., and Han, J.: CO2 outgassing from the
807 Yellow River network and its implications for riverine carbon cycle, J. Geophys. Res.-
808 Biogeo., 120, 1334-1347, 10.1002/2015JG002982, 2015.
809 Raymond, P. A., Hartmann, J., Lauerwald, R., Sobek, S., McDonald, C., Hoover, M., Butman,
810 D., Striegl, R., Mayorga, E., Humborg, C., Kortelainen, P., Durr, H., Meybeck, M., Ciais, P.,
811 and Guth, P.: Global carbon dioxide emissions from inland waters, Nature, 503, 355-359,
812 10.1038/nature12760, 2013.
813 Zhang, W., and Montgomery, D. R.: Digital elevation model grid size, landscape representation,
814 and hydrologic simulations, Water Resour. Res., 30, 1019-1028, 10.1029/93WR03553,
815 1994.
816
817

(3) Author's changes in the manuscript

Regional-scale lateral carbon transport and CO_2 evasion in temperate stream catchments

Katrin Magin[1], Celia Somlai-Haase[1], Ralf B. Schäfer[1] and Andreas Lorke[1]

[1]Institute for Environmental Sciences, University of Koblenz-Landau, Fortstr. 7, D-76829 Landau, Germany

Correspondence to: Katrin Magin (magi6618@uni-landau.de)

Abstract. Inland waters play an important role in regional to global scale carbon cycling by transporting, processing and emitting substantial amounts of carbon, which originate mainly from their catchments. In this study, we analyzed the relationship between terrestrial net primary production (NPP) and the rate at which carbon is exported from the catchments in a temperate stream network. The analysis included more than 200 catchment areas in southwest Germany, ranging in size from 0.8 to 889 km^2 for which CO_2 evasion from stream surfaces and downstream transport with stream discharge were estimated from water quality monitoring data, while NPP in the catchments was obtained from a global data set based on remote sensing. We found that on average 2.7 % of terrestrial NPP (13.9 g C m^{-2} yr^{-1}) are exported from the catchments by streams and rivers, in which both CO_2 evasion and downstream transport contributed about equally to this flux. The average carbon fluxes in the catchments of the study area resembled global and large-scale zonal mean values in many respects, including NPP, stream evasion as well as the ~~catchment-specific total export rate of carbon~~carbon export per catchment area in the fluvial network. A review of existing studies on aquatic-terrestrial coupling in the carbon cycle suggests that the ~~catchment-specific carbon export~~carbon export per catchment area varies in a relatively narrow range, despite a broad range of different spatial scales and hydrological characteristics of the study regions.

Keywords

Regional carbon cycle, terrestrial-aquatic coupling, net primary production, CO_2 degassing from streams, land use

1 Introduction

Inland waters represent an important component of the global carbon cycle by transporting, storing and processing significant amounts of organic and inorganic carbon (C) and by emitting substantial amounts of carbon dioxide (CO_2) to the atmosphere (Cole et al., 2007;Aufdenkampe et al., 2011). Globally about 0.32 to 0.8 Pg C is emitted per year as CO_2 from lakes and reservoirs (Raymond et al., 2013;Barros et al., 2011). For streams and rivers the global estimates range from 0.35 to 1.8 Pg C yr^{-1} (Raymond et al., 2013;Cole et al., 2007), where the lower estimates can be considered as conservative because they omit CO_2 emissions from small headwater streams. In 2015 global CO_2 evasion from rivers and streams was estimated at 0.65 Pg C yr^{-1} (Lauerwald et al., 2015). Comparable amounts of carbon are discharged into the oceans by the world's rivers (0.9 Pg C yr^{-1}) and stored in aquatic sediments (0.6 Pg C yr^{-1}) (Tranvik et al., 2009). In total, evasion, discharge and storage of C in inland waters have been estimated to account for about 4 % of global terrestrial net primary production (NPP) (Raymond et al., 2013) or 50-70 % of the total terrestrial net ecosystem production (NEP) (Cole et al., 2007). A recent continental-scale analysis, which combined terrestrial productivity estimates from a suite of biogeochemical models with estimates of the total aquatic C yield for the conterminous United States (Butman et al., 2015), resulted in mean C export rates from terrestrial into freshwater systems of 4 % of NPP and 27 % of NEP. These estimates varied by a factor of four across 18 hydrological units with surface areas between 10^5 and 10^6 km^2.

The substantial lateral and vertical transport of terrestrial-derived C in inland waters is currently not accounted for in most bottom-up estimates of the terrestrial uptake rate of atmospheric CO_2 (Battin et al., 2009) and results in high uncertainties in regional-scale C budgets and predictions of their response to climate change, land use and water management. Only few studies have quantified C fluxes and pools including inland waters at the regional-scale ($O(10^3\text{-}10^4$ $km^2)$) (Christensen et al., 2007;Buffam et al., 2011;Jonsson et al., 2007;Maberly et al., 2013) or for small (O(1-10 km^2)) catchments (Leach et al., 2016;Shibata et al., 2005;Billett et al., 2004). The majority of existing regional-scale studies on terrestrial-aquatic C fluxes are from the boreal zone and are characterized by a relatively large fractional surface area covered by inland waters, a high abundance of lakes and high fluvial loads of dissolved organic carbon (DOC). Landscapes in the temperate zone can differ in all these aspects, potentially resulting in differences in the relative importance of aquatic C-fluxes and flux paths (storage, evasion and discharge) in regional-scale C budgets ~~differ~~. In this study, we analyzed the relationship between terrestrial NPP and CO_2 evasion and C discharge for more than 200 catchments in southwest Germany. The stream-dominated catchments range in size from 0.8 to 889 km^2 and are characterized by a relatively small fraction of surface water coverage (< 0.5 % of the land surface area). In contrast to studies from the boreal zone, the fluvial C load is dominated by dissolved inorganic carbon (DIC). Estimates of aquatic C export from the catchments were obtained from water quality and hydrological monitoring data and were related to terrestrial NPP derived from MODIS satellite data. The scale dependence of aquatic carbon fluxes in relation to NPP is analyzed by grouping the data according to Strahler stream order (Strahler, 1957). By comparing our results to a variety of published studies, we finally discuss the magnitude as well as the relative importance of different fluvial flux paths in regional-scale C budgets in different landscapes and climatic zones.

2 Materials and Methods

2.1 Study area and hydrological characteristics

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

Most of the rivers in RLP are part of the catchment area of the Rhine River. Other large rivers in the state are Mosel, Lahn, Saar and Nahe. The upland regions of RLP are sources to many small, steep and highly turbulent streams with gravel beds (MULEWF, 2015). Lakes in RLP are small with a total area of approximately 40 km^2 (Statistisches Landesamt Rheinland-Pfalz, 2014) and were omitted from the analysis. The river network has a total length of 15 800 km and consists of stream orders (Strahler, 1957) between 1 and 7 ~~order~~. A catchment map of RLP, consisting of subcatchments of 7729 river segments was provided by the state ministry (MULEWF, 2013), where a river segment refers to the section between a source and the first junction with another river or between two junctions with other rivers. All subsequent analyses were conducted separately for each stream order and streams of Strahler order >4 were omitted from the analysis because of the limited sample size with only few catchments available. Moreover, we omitted streams for which parts of the catchment area were outside of the study area. Overall, 3377, 1619, 861 and 453 stream segments were ~~remaining~~ retained for the analysis for Strahler order 1 to 4, respectively. Annual mean discharge and length of the river segments were obtained from digital maps provided by the state ministry (MULEWF, 2013).

2.2 Aquatic carbon concentrations

DIC concentrations and partial pressure of dissolved CO_2 (pCO_2) in stream water were estimated from governmental water quality monitoring data which were acquired according to DIN EN ISO norms (DIN EN ISO 10523:2012-04;DIN EN ISO 9963-1:1996-02;DIN EN ISO 9963-2:1996-02).. The data include measurements of alkalinity, pH and temperature which were conducted between 1977 and 2011 (MULEWF, 2013). Sampling intervals differed between the sites and water sampling was conducted irregularly with respect to year and season. To exclude a potential bias resulting from the seasonality of DIC concentrations on the analysis, we only considered river segments for which at least one measurement was available for each season (spring, summer, autumn, winter). From these measurements, pCO_2 and DIC concentrations were estimated using chemical equilibrium calculations with the software PHREEQC (Version 2) (Parkhurst and Appelo, 1999). For 201 river segments with seasonally resolved measurements, we first computed seasonal mean pCO_2 and DIC concentrations, which subsequently were aggregated to annual mean values averaged over the entire sampling period ~~.~~ :

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

Measurements of dissolved and total organic C (DOC, TOC) were available only for ~~54~~ 64 of these sampling sites.

2.3 Estimation of lateral DIC export and catchment-scale CO_2 evasion

The lateral export of DIC and the total CO_2 evasion from the upstream located stream network was calculated for each of the 201 sampling sites with seasonally averaged concentration estimates. Lateral DIC export from the corresponding catchments was calculated as the product of the mean DIC concentration and discharge. CO_2 evasion from the stream network upstream of each sampling site was estimated by interpolating pCO_2 for all river segments without direct measurements~~. For this,~~ by averaging the mean concentrations ~~were averaged~~ by stream order and ~~assigned~~ assigning them to all stream segments of the river network (Butman and Raymond, 2011). Stream width (w, in m), depth (d, in m) and flow velocity (v, in m s^{-1}) were estimated from the discharge (Q, in m^3 s^{-1}) using the following empirical equations (Leopold and Maddock Jr, 1953):

$$w = a * Q^b \qquad d = c * Q^d \qquad v = e * Q^f, \quad (~~1~~2)$$

For the hydraulic geometry exponents and coefficients, the values from Raymond et al. (2012) were used (b=0.~~29~~42, d=0.~~42~~29, f=0.29, a=~~0.4~~12.88, c=~~12.88~~0.4 and e=0.19).

The water surface area (A, in m^2) was calculated as the product of length and width of the river segments. The average slope for each segment was estimated from a Digital Elevation Map (resolution 10 m) provided by the federal state of Rhineland-Palatinate (LVermGeoRP, 2012). Zhang and Montgomery (1994) investigated the effect of digital elevation model (DEM) resolution on slope calculation and performance in hydrological models for spatial resolutions between 2 and 90 m. They found that while a 10-m grid is a significant improvement over 30 m or coarser grid sizes, finer grid sizes provide relatively little additional resolution. Thus a 10-m grid size represents a reasonable tradeoff between increasing spatial resolution and data handling requirements for modeling surface processes in many landscapes. The gas transfer velocity of CO_2 at 20°C (k_{600}, in m d^{-1}) was calculated from slope (S) and flow velocity (v, in m s^{-1}) (Raymond et al., 2012).

$$k_{600} = S * v * 2841.6 + 2.03 \quad (~~2~~3)$$

This gas transfer velocity was adjusted to the in situ temperature (k_T, in m d^{-1}) using the following equation:

$$k_T = k_{600} * \left(\frac{Sc_T}{600}\right)^{-0.5}, \quad (~~3~~4)$$

where Sc_T is the Schmidt number (ratio of the kinematic viscosity of water and the diffusion coefficient of dissolved CO_2) at the in situ temperature (Raymond et al., 2012). Finally the CO_2 flux (F_D, in g C m^{-2} yr^{-1}) for each stream segment was calculated as:

$$F_D = k_T \cdot K_H\left(pCO_2 - pCO_{2,a}\right) \cdot M_C \quad (~~4~~5)$$

The partial pressure of CO_2 in the atmosphere ($pCO_{2,a}$) was considered as constant (390 ppm) and the Henry coefficient of CO_2 at in-situ temperature (K_H in mol l^{-1} atm^{-1}) was estimated using the relationship provided in (Stumm and Morgan, 1996). M_C is the molar mass of C (12 g mol^{-1}). Finally, the total CO_2 evasion was estimated by

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

2.4 Estimation of the catchment NPP

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

2.5 Statistical analysis

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

3 Results

3.1 Catchment characteristics and aquatic C load

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

Individual estimates of the CO_2 partial pressure at the sampling sites varied between 145 and 7759 ppm. Only 1 % of the pCO_2 values were below the mean atmospheric value (390 ppm), indicating that the majority of the stream network was a source of atmospheric CO_2 at all seasons. The pCO_2 was higher in summer (mean±sd: 2780±2098 ppm) and autumn (mean±sd: 2848±2019 ppm) than in winter (mean±sd: 2287±1716 ppm) and spring (mean±sd: 2172±2343 ppm). The total mean value of pCO_2 was 2083 ppm and pCO_2 and DIC did not differ significantly among the different stream orders (pCO_2: $p=0.35$; DIC: $p=0.56$). On average, DIC in the stream water was composed of 91.2 % bicarbonate, 0.4 % carbonate and 8.4 % CO_2.

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

The data are provided as supplementary material.

3.2 Catchment NPP and C budget

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

In a simplified catchment-scale C balance, we consider the sum of the DIC discharge (DIC concentration multiplied by discharge) measured at each sampling site and the total CO_2 evasion from the upstream located stream network as the total amount of C that is exported from the catchment area through the aquatic conduit. The total evasion was estimated by interpolation with stream-order specific pCO_2 values assigned to the complete stream network. Given the small number of available measurements, we neglect the fraction of organic C which is exported with stream discharge. As demonstrated above, TOC load is small in comparison to the DIC load (Fig. 2), resulting in a comparably small (< 4 %) error.

The resulting CO_2 evasion rates decreased slightly, but not significantly (p=0.26) for increasing stream orders with a total mean evasion rate of 2032 g C m^{-2} yr^{-1} (expressed as per unit water surface area) (Table 2). The total aquatic evasion rate within catchments normalized by the size of the catchment increased significantly with stream order with a mean value of 6.6 g C m^{-2} yr^{-1}. (Table 2).

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

After normalization with catchment area, the total aquatic C export rate increased slightly with stream order (Fig. 4a). Also the fraction of NPP which was exported through the aquatic network, i.e. the sum of evasion and discharge, increased slightly, though not significantly (p=0.32), from 2.18 % for first-order stream to 2.72 % for stream order 4 (Fig. 4b). This increase was related to increasing rates of CO_2 evasion in streams of higher order and the contribution of evasion to the total C export rate increased from 39 to 53 % (Fig. 4c). The increasing evasion is mainly caused by the increasing fractional water surface area for increasing stream orders (Table 1), because the CO_2 fluxes per water surface showed a rather opposing trend with decreasing fluxes for increasing stream orders (Table 2). On average 1.31 % of the catchment NPP are emitted as CO_2 from the stream network and 1.49 % are discharged downstream (Table 2).

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

4 Discussion

4.1 Uncertainty analysis

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

According to Abril et al. (2015), high uncertainties of pCO_2 estimates from pH and alkalinity measurements occur at pH values <7. In our study, only 7 % of the pH values were <7. For pH>7 the median and mean relative errors are 1% and 15%, respectively (Abril et al., 2015). Raymond et al. (2013) estimated uncertainties from comparisons of estimates obtained using approaches comparable to the present study with direct measurements of CO_2 concentration on streams. For a density of sampling locations of 0.02 sites per km^2 (corresponding to this study) they derived an uncertainty of 30 %. Similarly, Butman and Raymond (2011) estimated uncertainties of overall flux estimates of 33 %, based on Monte Carlo simulation of similar data for hydrographic units in the United States.

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

The hydraulic geometry exponents and coefficients used in this study were derived from various data sets obtained in North America, not for central Europe. Unfortunately, we are not aware of a comparably extensive data set of

hydraulic geometry data derived for European rivers. The coefficients have been applied in global studies before, e.g. Raymond et al. (2013). A comparison of hydraulic geometry coefficients derived from various data sets, including data from England, Australia and New Zealand, is presented in Butman and Raymond (2011), who estimated that the error associated with uncertainties of hydraulic geometry coefficients is rather small, compared to uncertainties derived for C-fluxes.

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

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

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

4. ~~1~~2. An average study region

The average carbon fluxes in the catchments of the study area resemble global and large-scale zonal mean estimates in many aspects. The mean atmospheric flux of CO_2 from the stream network of 2031±1527 g C m^{-2} yr^{-1} is in close agreement with bulk estimates for streams and rivers in the temperate zone of 2630 (Aufdenkampe et al., 2011) and 2370 g C m^{-2} yr^{-1} (Butman and Raymond, 2011). The fractional surface coverage of streams and rivers (0.42 % for stream order 4) corresponds to the global average of 0.47 % (Raymond et al., 2013) and also mean terrestrial NPP in the catchments (515 g C m^{-2} yr^{-1}) was in close correspondence to recent global mean estimates (495 g C m^{-2} yr^{-1} (Zhao et al., 2005)).

By combining CO_2 evasion and downstream C-export by stream discharge, we estimated that 2.7 % of terrestrial NPP (13.9 g C m^{-2} yr^{-1}) are exported from the catchments by streams and rivers, in which both evasion and discharge contributed equally to this flux. Also these findings are in close agreement with global and continental scale estimates, of 16 and 13.5 g C m^{-2} yr^{-1}, respectively (Table 3).

4.~~1~~3. Aquatic C export across spatial scales

Though not exhaustive, Table 3 provides data from a large share of existing studies relating the aquatic C export to terrestrial production in the corresponding catchments which cover a broad range of spatial scales and different landscapes. Except for the tropical forest of the Amazon basin, the aquatic carbon export normalized to catchment area estimated for temperate streams in our study, is surprisingly similar to those estimated at comparable and at larger spatial scale. In the Amazon, the fraction of terrestrial production that is exported by the fluvial network is more than twofold higher (nearly 7 % of NPP (Richey et al., 2002)). However, that a large fraction of the regional NPP in the Amazon is supported by aquatic primary production by macrophytes and carbon export is predominantly controlled by wetland connectivity ~~(Abril et al., 2013)~~, with wetlands covering up to ~~16~~ 14 % of the land surface area (Abril et al., 2013). An additional peculiarity of the Amazon is, that in contrast to the remaining systems, the vast majority (87 %) of the total C export is governed by CO_2 evasion (Table 3), whereas lateral export constitutes a much smaller component. An exceptionally low fraction of NPP that is exported from aquatic systems at larger scale was estimated for the English Lake District (1.6 % (Maberly et al., 2013)), though only CO_2 evasion from lake surfaces was considered, i.e. downstream discharge by rivers was ignored. Their estimate agrees reasonably well with the fraction of catchment NPP that was emitted to the atmosphere from the stream network in the present study (1.3 %). If a similar share of catchment NPP was exported with river discharge also in the Lake District, the average mass of C exported from the aquatic systems per unit catchment area would be in close agreement with our and other larger-scale estimates (Table 3).

In more detailed studies at smaller scales and for individual catchments, aquatic C export was exclusively related to net ecosystem exchange (NEE) measured by eddy covariance. Here the estimated fractions of aquatic export range between 2 % of NEE in a temperate forest catchment (only discharge, evasion not considered, (Shibata et al., 2005)) and 160 % of NEE in a boreal peatland catchment (Billett et al., 2004). Analysis of inter-annual variations of stream export from a small peatland catchment in Sweden (Leach et al., 2016) resulted in estimates of C export by the fluvial network between 5.9 and 18.1 g Cm^{-2} yr^{-1} over 12 years. The total mean value of 12.2 g Cm^{-2} yr^{-1}, however, is in close agreement with the present and other larger-scale estimates (Table 3). In contrast to the present study, C export from the peatland catchments were dominated by stream discharge of dissolved organic carbon.

4.~~2~~ 4 Controlling factors for aquatic C export

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

catchments. Nevertheless, the linear correlation observed by (Butman et al., 2015) indicates that a constant fraction of terrestrial NPP is exported by aquatic systems if averaged over larger spatial scales.

The relatively narrow range of variability of C export per catchment area (between 9 and 18 g C m^{-2} yr^{-1}, with the two exceptions discussed above) in different landscapes (Table 3) is rather surprising. Although this range of variation is most likely within the uncertainty of the various estimates, the variability across different landscapes is certainly small in comparison to the order of magnitude differences in potential controlling factors like catchment NPP, fractional water coverage as well as size and climatic zone of the study area. In lake-rich regions, evasion from inland waters was observed to be dominated by lakes (Buffam et al., 2011;Jonsson et al., 2007), which cover up to 13 % of the surface area of these regions. In the present as well as in other studies on catchments where lakes are virtually absent (Wallin et al., 2013) and the fractional water coverage was smaller than 0.5 % of the terrestrial surface area, an almost identical catchment-specific C export and evasion rate has been observed (Table 3). CO_2 emissions from water surfaces depend on the partial pressure of CO_2 in water and are therefore related to DIC, which was the dominant form of dissolved C in the present study. Studies in the boreal zone, where dissolved C in the aquatic systems is mainly in the form of DOC, however, found comparable catchment-specific C export and evasion rates ((Leach et al., 2016;Jonsson et al., 2007;Wallin et al., 2013), cf. Table 3). The difference in the speciation of the exported C indicates that a larger fraction of the terrestrial NPP is respired by heterotrophic respiration in soils and exported to the stream network as DIC in the present study, in contrast to export as DOC and predominantly aquatic respiration. Observations and modeling of terrestrial-aquatic C fluxes across the U.S. suggested a transition of the source of aquatic CO_2 from direct terrestrial input to aquatic CO_2 production by degradation of terrestrial organic carbon with increasing stream size (Hotchkiss et al., 2015). Such transition was not observed in the present study, where organic carbon made a small contribution to the fluvial carbon load across all investigated stream orders. In addition to soil respiration, mineral weathering also contributes to DIC in stream water. The relative importance of soil respiration and weathering varies depending on geology and the presence of wetlands in the area (Hotchkiss et al., 2015;Lauerwald et al., 2013;Jones et al., 2003). In the present study, 16 % of the catchment areas contained carbonate bedrock. The DIC concentration in the water increased with the proportion of carbonate containing bedrock in the catchment (R^2=0.33, p<0.001).

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

are capable of resolving the boundless biogeochemical cycle in the terrestrial–aquatic continuum from catchment to continental scales (Nakayama, 2016), are certainly an important tool for these future studies.

5 Conclusion:

Our analysis of the carbon budget in a temperate stream network on regional scale revealed a relationship of aquatic carbon export and terrestrial NPP. On average 2.7 % of the terrestrial NPP were exported from the catchments by rivers and stream with CO_2 evasion and downstream transport contributing equally to the export. A comparison of our regional scale study with other studies from different scales and landscapes showed a relatively narrow range of variability of carbon export per catchment area. Future research is needed to understand the processes that control the aquatic-terrestrial coupling and the role of inland waters in regional carbon cycling.

Acknowledgments

This study was financially supported by the German Research Foundation (grant no. LO 1150/9-1). We thank Miriam Tenhaken for contributing to a preliminary analysis. All raw data for this paper is properly cited and referred to in the reference list. The processed data, which were used to generate the figures and tables, are available upon request through the corresponding author.

References

Abril, G., Martinez, J.-M., Artigas, L. F., Moreira-Turcq, P., Benedetti, M. F., Vidal, L., Meziane, T., Kim, J.-H., Bernardes, M. C., Savoye, N., Deborde, J., Souza, E. L., Alberic, P., Landim de Souza, M. F., and Roland, F.: Amazon River carbon dioxide outgassing fuelled by wetlands, Nature, 505, 395-398, 10.1038/nature12797, 2013.

Abril, G., Bouillon, S., Darchambeau, F., Teodoru, C. R., Marwick, T. R., Tamooh, F., Omengo, F. O., Geeraert, N., Deirmendjian, L., and Polsenaere, P.: Technical Note: Large overestimation of pCO2 calculated from pH and alkalinity in acidic, organic-rich freshwaters, Biogeosciences, 12, 67, 2015.

Aufdenkampe, A. K., Mayorga, E., Raymond, P. A., Melack, J. M., Doney, S. C., Alin, S. R., Aalto, R. E., and Yoo, K.: Riverine coupling of biogeochemical cycles between land, oceans, and atmosphere, Front. Ecol. Environ., 9, 53-60, 10.1890/100014, 2011.

Barros, N., Cole, J. J., Tranvik, L. J., Prairie, Y. T., Bastviken, D., Huszar, V. L. M., del Giorgio, P., and Roland, F.: Carbon emission from hydroelectric reservoirs linked to reservoir age and latitude, Nature Geosci., 4, 593-596, 10.1038/ngeo1211, 2011.

Battin, T. J., Luyssaert, S., Kaplan, L. A., Aufdenkampe, A. K., Richter, A., and Tranvik, L. J.: The boundless carbon cycle, Nature Geosci., 2, 598-600, 10.1038/ngeo618, 2009.

Billett, M. F., Palmer, S. M., Hope, D., Deacon, C., Storeton-West, R., Hargreaves, K. J., Flechard, C., and Fowler, D.: Linking land-atmosphere-stream carbon fluxes in a lowland peatland system, Global Biogeochem. Cycles, 18, 10.1029/2003GB002058, 2004.

Buffam, I., Turner, M. G., Desai, A. R., Hanson, P. C., Rusak, J. A., Lottig, N. R., Stanley, E. H., and Carpenter, S. R.: Integrating aquatic and terrestrial components to construct a complete carbon budget for a north temperate lake district, Global Change Biol., 17, 1193-1211, 10.1111/j.1365-2486.2010.02313.x, 2011.

Butman, D., and Raymond, P. A.: Significant efflux of carbon dioxide from streams and rivers in the United States, Nature Geosci., 4, 839-842, 2011.

Butman, D., Stackpoole, S., Stets, E., McDonald, C. P., Clow, D. W., and Striegl, R. G.: Aquatic carbon cycling in the conterminous United States and implications for terrestrial carbon accounting, Proceedings of the National Academy of Sciences, 10.1073/pnas.1512651112, 2015.

Christensen, T. R., Johansson, T., Olsrud, M., Ström, L., Lindroth, A., Mastepanov, M., Malmer, N., Friborg, T., Crill, P., and Callaghan, T. V.: A catchment-scale carbon and greenhouse gas budget of a subarctic landscape, Philosophical Transactions of the Royal Society of London A: Mathematical, Physical and Engineering Sciences, 365, 1643-1656, 10.1098/rsta.2007.2035, 2007.

Cole, J. J., Prairie, Y. T., Caraco, N. F., McDowell, W. H., Tranvik, L. J., Striegl, R. G., Duarte, C. M., Kortelainen, P., Downing, J. A., Middelburg, J. J., and Melack, J.: Plumbing the global carbon cycle: Integrating inland waters into the terrestrial carbon budget, Ecosystems, 10, 171-184, 10.1007/s10021-006-9013-8, 2007.

DIN EN ISO 9963-1:1996-02: Wasserbeschaffenheit - Bestimmung der Alkalinität - Teil 1: Bestimmung der gesamten und der zusammengesetzten Alkalinität (ISO 9963-1:1994); German version EN ISO 9963-1:1995,

DIN EN ISO 9963-2:1996-02: Wasserbeschaffenheit - Bestimmung der Alkalinität - Teil 2: Bestimmung der Carbonatalkalinität (ISO 9963-2:1994); German version EN ISO 9963-2:1995,

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

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

Hotchkiss, E. R., Hall Jr, R. O., Sponseller, R. A., Butman, D., Klaminder, J., Laudon, H., Rosvall, M., and Karlsson, J.: Sources of and processes controlling CO_2 emissions change with the size of streams and rivers, Nature Geosci., 8, 696-699, 10.1038/ngeo2507, 2015.

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

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

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

Lauerwald, R., Laruelle, G. G., Hartmann, J., Ciais, P., and Regnier, P. A.: Spatial patterns in CO2 evasion from the global river network, Global Biogeochemical Cycles, 29, 534-554, 2015.

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

Leopold, L. B., and Maddock Jr, T.: The hydraulic geometry of stream channels and some physiographic implications2330-7102, 1953.

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

Maberly, S. C., Barker, P. A., Stott, A. W., and De Ville, M. M.: Catchment productivity controls CO_2 emissions from lakes, Nat. Clim. Chang., 3, 391-394, 10.1038/nclimate1748, 2013.

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

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

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

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

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

Ran, L., Lu, X. X., Yang, H., Li, L., Yu, R., Sun, H., and Han, J.: CO_2 outgassing from the Yellow River network and its implications for riverine carbon cycle, J. Geophys. Res.-Biogeo., 120, 1334-1347, 10.1002/2015JG002982, 2015.

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

Raymond, P. A., Oh, N.-H., Turner, R. E., and Broussard, W.: Anthropogenically enhanced fluxes of water and carbon from the Mississippi River, Nature, 451, 449-452, 2008.
Raymond, P. A., Zappa, C. J., Butman, D., Bott, T. L., Potter, J., Mulholland, P., Laursen, A. E., McDowell, W. H., and Newbold, D.: Scaling the gas transfer velocity and hydraulic geometry in streams and small rivers, Limnology and Oceanography: Fluids and Environments, 2, 41-53, 2012.
Raymond, P. A., Hartmann, J., Lauerwald, R., Sobek, S., McDonald, C., Hoover, M., Butman, D., Striegl, R., Mayorga, E., Humborg, C., Kortelainen, P., Durr, H., Meybeck, M., Ciais, P., and Guth, P.: Global carbon dioxide emissions from inland waters, Nature, 503, 355-359, 10.1038/nature12760, 2013.
Richey, J. E., Melack, J. M., Aufdenkampe, A. K., Ballester, V. M., and Hess, L. L.: Outgassing from Amazonian rivers and wetlands as a large tropical source of atmospheric CO_2, Nature, 416, 617-620, 10.1038/416617a, 2002.
Running, S. W., Nemani, R. R., Heinsch, F. A., Zhao, M., Reeves, M., and Hashimoto, H.: A Continuous Satellite-Derived Measure of Global Terrestrial Primary Production, Bioscience, 54, 547-560, 10.1641/0006-3568(2004)054[0547:acsmog]2.0.co;2, 2004.
Sabine, C. L., Heimann, M., Artaxo, P., Bakker, D. C., Chen, C.-T. A., Field, C. B., Gruber, N., Le Quéré, C., Prinn, R. G., and Richey, J. E.: Current status and past trends of the global carbon cycle, in: The Global Carbon Cycle, 2nd ed., edited by: Field, C. B., and Raupach, M. R., Scientific Committee on Problems of the Environment (SCOPE) Series, Island Press, 17-44, 2004.
Shibata, H., Hiura, T., Tanaka, Y., Takagi, K., and Koike, T.: Carbon cycling and budget in a forested basin of southwestern Hokkaido, northern Japan, Ecological Research, 20, 325-331, 10.1007/s11284-005-0048-7, 2005.
Stanley, E. H., Casson, N. J., Christel, S. T., Crawford, J. T., Loken, L. C., and Oliver, S. K.: The ecology of methane in streams and rivers: patterns, controls, and global significance, Ecological Monographs, 2016.
Statistisches Landesamt Rheinland-Pfalz: Statistisches Jahrbuch 2014, 2014.
Strahler, A. N.: Quantitative analysis of watershed geomorphology, Eos, Transactions American Geophysical Union, 38, 913-920, 1957.
Stumm, W., and Morgan, J. J.: Aquatic chemistry: chemical equilibria and rates in natural waters, Wiley, 1996.
Tranvik, L. J., Downing, J. A., Cotner, J. B., Loiselle, S. A., Striegl, R. G., Ballatore, T. J., Dillon, P., Finlay, K., Fortino, K., Knoll, L. B., Kortelainen, P. L., Kutser, T., Larsen, S., Laurion, I., Leech, D. M., McCallister, S. L., McKnight, D. M., Melack, J. M., Overholt, E., Porter, J. A., Prairie, Y., Renwick, W. H., Roland, F., Sherman, B. S., Schindler, D. W., Sobek, S., Tremblay, A., Vanni, M. J., Verschoor, A. M., von Wachenfeldt, E., and Weyhenmeyer, G. A.: Lakes and reservoirs as regulators of carbon cycling and climate, Limnol. Oceanogr., 54, 2298-2314, 10.4319/lo.2009.54.6_part_2.2298, 2009.
Wallin, M. B., Grabs, T., Buffam, I., Laudon, H., Ågren, A., Öquist, M. G., and Bishop, K.: Evasion of CO_2 from streams – The dominant component of the carbon export through the aquatic conduit in a boreal landscape, Global Change Biol., 19, 785-797, 10.1111/gcb.12083, 2013.

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

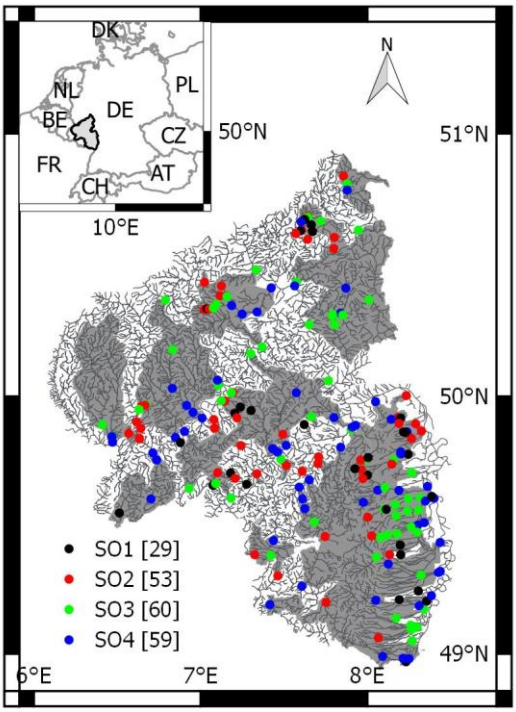
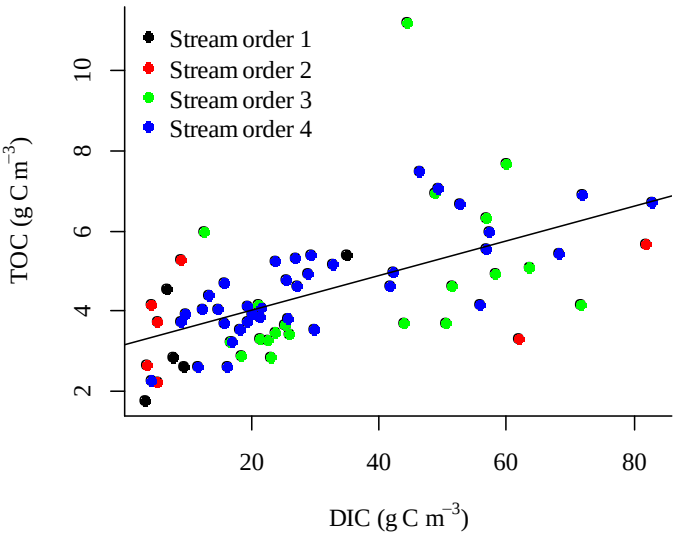


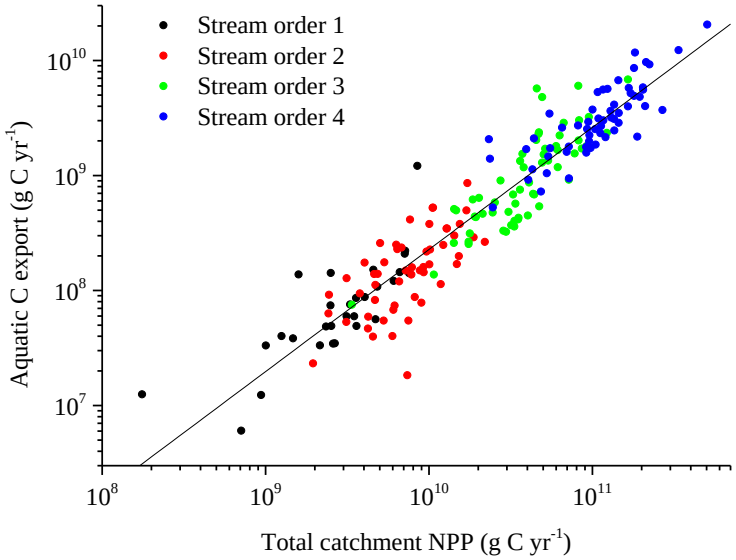
Fig. 1: Map of the stream network (black lines) within the state borders of Rhineland Palatinate in southwest Germany. The inset map in the upper left corner indicates the location of the study region in central Europe. Filled circles mark the position of sampling sites with color indicating stream order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



1313

1314 **Fig. 2: TOC concentration versus DIC concentration. Different colors indicate sampling sites from different stream**
1315 **orders. The solid line shows the fitted linear regression model with TOC=0.04·DIC (r^2=0.33, p<0.001).**

1316



1317

1318 **Fig. 3: Annual rate of C export through the stream network versus terrestrial NPP in the catchment area. Different colors**
1319 **indicate sampling sites from different stream orders. The solid line shows the fitted linear regression model for the log-**
1320 **transformed data with C_export=0.005·NPP$^{1.06}$ (r^2=0.89, p<0.001).**

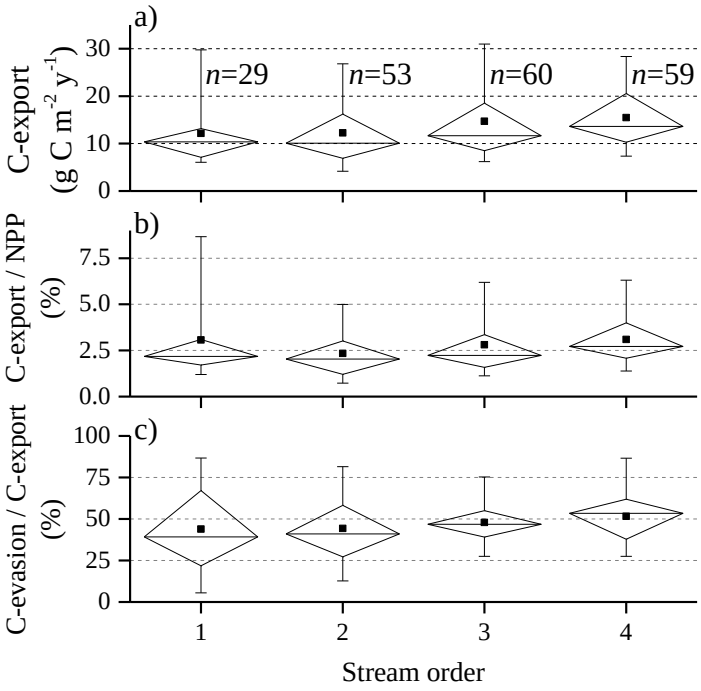


Fig. 4: a) Boxplots of C export (sum of evasion and discharge) normalized by catchment area. b) Boxplots of the ratio of the total exported C and terrestrial NPP for different stream orders. c) Boxplots of the fraction of the total exported C which is emitted to the atmosphere from the stream network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

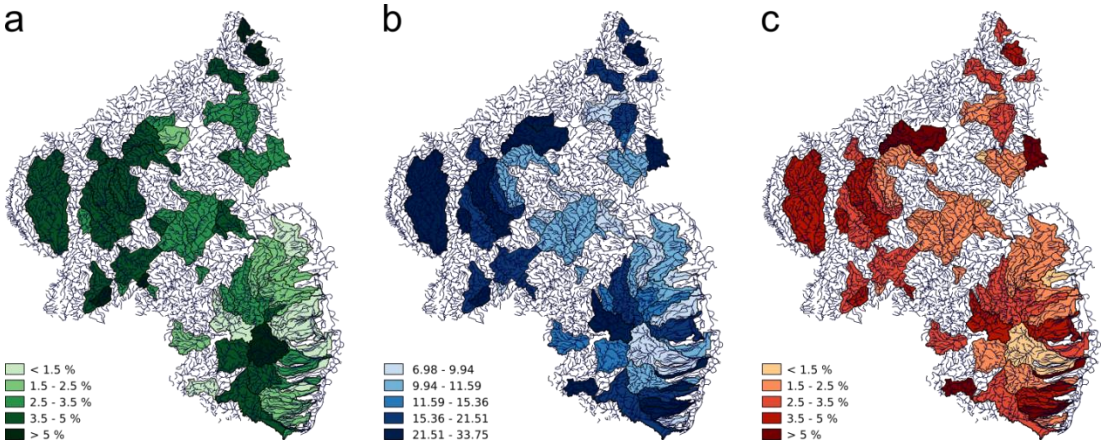


Fig. 5: Map of 3rd and 4th order catchments showing a) Mean NPP (g C m^{-2} yr^{-1}), b) aquatic export (g C m^{-2} yr^{-1}), c) ratio aquatic export/NPP (%).

Table 1: Major hydrological characteristics, pCO_2, DIC and DOC concentrations averaged over stream orders (SO) and for all sampling sites (total). All values are provided as mean±sd (standard deviation) of the annual mean observations, 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 (km^2)	9±7 (1 – 35)	16±9 (4 – 37)	87±54 (9 – 298)	243±140 (48 – 889)	103±126 (1 – 889)
Water coverage (%)	0.24±0.11 (0.05 – 0.43)	0.26±0.09 (0.1 – 0.45)	0.36±0.11 (0.09 – 0.6)	0.42±0.13 (0.18 – 0.7)	0.33±0.13 (0.05 – 0.7)
Discharge ($m^3\ s^{-1}$)	0.06±0.05 (0.003 – 0.19)	0.15±0.10 (0.01 – 0.36)	0.73±0.63 (0.02 – 3.41)	2.20±1.95 (0.22 – 12.22)	0.91±1.41 (0.003 – 12.22)
Drainage rate ($m\ y^{-1}$)	0.26±0.17 (0.05 – 0.67)	0.29±0.16 (0.06 – 0.66)	0.27±0.17 (0.05 – 0.74)	0.30±0.21 (0.06 – 1.20)	0.28±0.18 (0.05 – 1.20)
pH	7.58±0.61 (6.20 – 8.97)	7.70±0.46 (6.30 – 8.60)	7.81±0.37 (6.60 – 8.30)	7.75±0.29 (6.91 – 8.30)	7.73±0.42 (6.20 – 8.97)
Alkalinity ($mmol\ L^{-1}$)	3.08±2.50 (0.08 – 7.58)	2.74±2.58 (0.08 – 8.55)	2.77±1.85 (0.14 – 9.88)	2.58±1.73 (0.32 – 7.22)	2.75±2.12 (0.08 – 9.88)
pCO_2 (ppm)	2597±1496 (145 – 6706)	1819±1095 (681 – 5338)	1992±1327 (573 – 7627)	2162±1302 (366 – 7759)	2083±1303 (145 – 7759)
DIC ($g\ m^{-3}$)	38.8±30.3 (3.4 – 93.1)	34.2±31.1 (3.5 – 104.5)	34.6±22.4 (3.1 – 119.6)	32.4±21.0 (4.1 – 89.3)	34.5±25.7 (3.1 – 119.6)
DOC ($g\ m^{-3}$)	3.54±1.86 (2.2 – 6.7) (*n*=5)	4.11±0.73 (3.1 – 4.8) (*n*=4)	4.17±1.08 (2.6 – 7.1) (*n*=22)	4.10±1.24 (2.0 – 7.7) (*n*=33)	4.08±1.20 (2.0 – 7.7) (*n*=64)

Table 2: Aquatic C-fluxes and terrestrial NPP in catchments drained by streams of different stream orders (SO) and for all sampling sites (total). All values are mean ± standard deviation, ranges are given in brackets. The CO_2 flux from the water surface (first row) is expressed per square meter water surface area, while the remaining fluxes are expressed per square meter catchment area.

	SO 1	SO 2	SO 3	SO 4	Total
CO_2 flux from water surface ($g\ C\ m^{-2}\ yr^{-1}$)	2415±2335 (-335 – 12915)	1975±1364 (418 – 7143)	1998±1671 (704 – 11016)	1928±903 (851 – 5093)	2032±1528 (-335 – 12915)
Gas transfer velocity k600 ($m\ d^{-1}$)	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_2 evasion per catchment area ($g\ C\ m^{-2}\ yr^{-1}$)	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 ($g\ C\ m^{-2}\ yr^{-1}$)	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 ($g\ C\ m^{-2}\ yr^{-1}$)	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 ($g\ C\ m^{-2}\ yr^{-1}$)	466±127 (106 – 661)	536±66 (251 – 644)	527±57 (364 – 627)	508±69 (330 – 618)	515±79 (106 – 661)

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^2)	Fractional water coverage (%) Rivers Lakes	Aquatic C export ($g\ C\ m^{-2}\ yr^{-1}$)	Aquatic C fate (%): Evasion Discharge	Aquatic C export / terrestrial production (%)		Reference
				NPP	NEE	
Global ($1.3x10^8$)	R: 0.2-0.3 L: 2.1-3.4	16 (20)	E: 44 D: 34	3.7 [1]	21-64 [2]	(Aufdenkampe et al., 2011)
Conterminous U.S. ($7.8x10^6$)	R: 0.52 L: 1.6	13.5 (18.8)	E: 58 D: 28	3.6	27 [3]	(Butman et al., 2015)
Central Amazon ($1.8x10^6$)	4-16	78	E: 87 D: 13	6.8 [4]	n.c.	(Richey et al., 2002)
Yellow River network ($7.5x10^5$)	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)
Temperate streams (0.7- 1227)	**R: 0.33** **L: n.c.**	**13.9**	E: 47 D: 53	**2.7**	n.c.	**This study**
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)

[1] For a value of 56 Pg C yr^{-1} for global NPP (Zhao et al., 2005).

[2] Global mean NEE was estimated as the difference of GPP and ecosystem respiration, which was assumed to be 91-97 % of GPP (Randerson et al., 2002).

[3] This percentage refers to NEP instead of NEE.

[4] For a global mean value of NPP in tropical forests of 1148 g C m^{-2} yr^{-1} (Sabine et al., 2004).