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Discussions

Interactive comment on "Rapid Phase Transfer of DOC and DIC Transport in a Subtropical Small Mountainous River" *by* Yu-Ting Shih et al.

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General Comments This research makes a useful contribution to the understanding of the hydrologic controls on DOC and DIC streamwater export in a humid tropical region, and by quantifying the annual fluxes and DIC/DOC ratios, define these systems as end-members or 'hot spots' within the context of global measurements. While there has been evidence that sub-tropical regions were important with respect to both DOC and DIC fluxes due to high productivity and rainfall, the detailed long-term measurements of concentrations and evaluation of relationships with flow had not been previously studied in any detail. By consistently sampling during a range of flow conditions (including frequently during typhoons) over a relatively long period (2 1/2 years) and using the data in conjunction with measurements of flow, flow simulation and end-member

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Discussion paper

mixing analysis, they are able to evaluate the relationship between concentration and flow, estimate the relative contribution of different hydrologic flow paths to the DOC and DIC fluxes and quantify the importance of the typhoon events relative to non-event flow conditions. The research presented in this paper addresses a topic that is of interest to the carbon cycling and hydrologic community and while the presentation of concentrations, relationships to discharge and calculations of fluxes for flow components are useful and important, the description of methods needs considerably more clarity and completeness and the writing could be significantly improved in order to make this a more valuable contribution to the literature.

Reply:

We sincerely appreciate the reviewer's comment and acknowledgement of our efforts. In this revision, we addressed all the comments raised by the reviewer and fine-tuned the manuscript carefully, especially in the Method section. In the following, all comments are answered point-to-point

Specific Comments

Methods

The description of the calculation of DIC is confusing and the citations do not appear to be correct, I did not see an ion balance calculation method in either Lyons et al., 1992 or Zhong et al., 2017. DIC is/can be defined as CO2+H2CO3+HCO3- +CO3 2- . Are you estimating DIC as HCO3 which you are calculating by ion balance difference? Please clarify how you define and calculate DIC. With respect to the LOADEST and HBV, the models were run at a daily time-step, yet measurements during the typhoons were taken more frequently (3-hr interval). Indicate how the hourly data was incorporated into the flux and HBV models or did those models not use the hourly data? In reference to streamflow 'composition' (l 161), do you mean physical or chemical composition? I assume physical, meaning the model derives the relative flow in the 3 components of the total stream flow (rapid surface, subsurface and deep groundwater). Please clarify in the text as ‘composition’ is typically used to discuss chemical constituents. If correct, this would be the appropriate time to identify the names used to describe the 3 flow components. At the end of the streamflow simulation method description, it is stated that the streamflow composition was affirmed through 3-end member mixing using 3 different ions and electrical conductivity (l. 167- 169), but that requires knowledge of the end-member concentration of those analytes, not just streamwater concentrations? Did you measure or have estimates of surface, sub-surface and ground water concentrations for each of those analytes or am I not understanding how EMMA was used? Please explain how the EMMA analysis was conducted to verify the streamflow simulation. The description of the EMMA analysis (l. 171-184) to describe the three sources of DOC and DIC is unclear as written, specifically, 3 equations are referenced, only two are presented and ‘i’ is never defined. Is EMMA being used to calculate the concentration of DOC and DIC in each of the three flow components by using the calculated fractions of those flow components and the streamwater concentration of DOC and DIC for each timestep, ‘i’. I believe this is what was done but it should be more clearly stated. Is time invariance of the sources a valid assumption? I would think DOC would be variable in time, please provide a citation indicating that is a reasonable assumption. Results/Discussion Are reported concentrations flow-weighted? Since parameters are correlated with discharge, a flow-weighted estimate would be a more accurate representation of the data for comparisons to other systems (assuming those are also flow-weighted).

Reply:

Thanks for these comments, which help to improve our manuscript significantly. We separated this comment into 5 sub-comments for clarification. The sub-comments are: (1) Clarify the definition and calculation of DIC in this study. (2) Explain the time step in HBV model. (3) Clarify the so-called “streamflow composition” and explain how to verify the streamflow simulation. (4) Is time invariance of the sources a valid assumption? (5) Using flow-weighted concentration in results/discussion. Below are our point-to-point replies:

(1) DIC is defined as the sum of CO2+H2CO3+HCO3- +CO32-. These forms vary with temperature and pH. In strongly acidic or alkaline conditions, the CO2(aq) and CO32- would be the majority (over 95%) of DIC. In the neutral water (pH between 7.0-9.0), HCO3- would be the dominant one, also accounting for over 95%. The pH values in the sampling sites T1, T2, and M3 were 8.75, 9.0, and 8.57, respectively. Therefore, we used the ion balance method to estimate [HCO3-] and estimated DIC through [HCO3-] as the reviewer expected. To affirm the estimated DIC through [HCO3-], we also determined the DIC of some samples through NDIR method (OI Analitical® Aurora 1030W TOC). The high consistency (R2 =0.93) confirmed the estimated DIC through [HCO3-]. About the reference for DIC and ion balance method, we replaced Lyons et al. (1992) with Misra (2012). Chapter 7 in Misra's book gives a more straightforward description. In Zhong's paper, he mentioned: "The total cationic charge and total dissolved anions are well balanced, indicating that the unanalyzed ions play a minor role in charge balance." indicating the ion balance method is applied. We revised this paragraph in accordance with the above descriptions [Line: 153-158].

Misra, K. C.: Introduction to Geochemistry: Principles and Applications, Wiley, 2012. Chapter 7 page. 149. Eq 7.52.

(2) In HBV simulation, two simulations were conducted, one for a daily and the other for an hourly time step. The two simulations have their own parameter sets. For clarifying the streamflow simulation, we addressed the daily and hourly streamflow simulation in Line: 194-204 and added supplementary materials for describing the procedure and results of the simulations in more detail. In this supplementary material, the meaning of parameters, typhoon events, and the modeling performances were provided [supplementary].

(3) Re-considering the reviewer's suggestion, using "component" is better than the original one, we replaced "composition" with "component". For the issue of verifying the

streamflow simulation through end-member mixing, we added a section in the supplementary material to describe the end-member mixing. Note that "i" represents the time step which has been defined in this revision [Line: 243]. Basically, our procedure is like what the reviewer thinks. There are three unknown end-members and only the mixture in streamwater is known. With more than three observations in time series, the concentration of the end-members could be estimated. Therefore, we can estimate the concentrations of the 4 chemical tracers for each end-member. The satisfactory NSE values infer that the estimated end-member could be good. Meanwhile, we analyzed some samples of subsurface runoff and groundwater from a tunnel. The measured concentrations of the 4 chemical tracers were comparable to the estimated ones, although the sample size might not be representative enough due to the spatiotemporal heterogeneity. The above description was added in the supplementary material as well.

(4) We appreciate this comment, which is the key issue for the end-member mixing analysis. As the reviewer recognized, the end-member might be time-variant in most cases. However, the end-member, in most cases, is very difficult to obtain. In practice, Mills et al. (2014) argued that the slow turnover rate (large ratio of storage/flux) which results in continuous export of a substance could be a good indicator that time-invariance is a valid assumption. We provided two plots of the cumulative export/total export vs cumulative streamflow/total streamflow in the supplementary material, one for DOC and the other for DIC. The plots showed that the cumulative export linearly correlated with cumulative streamflow. It indicates that the continuous DOC and DIC export might justify the slow turnover rate and support the time-invariance assumption in this study.

Mills, R. T. E., Tipping, E., Bryant, C. L., and Emmett, B. A.: Long-term organic carbon turnover rates in natural and semi-natural topsoils, Biogeochemistry, 118, 257-272, 10.1007/s10533-013-9928-z, 2014.

(5) Yes, the values derived from our observations are flow-weighted.

Technical corrections

In the title, does "phase" refer to the transport of terrestrial carbon to the aqueous system? The word is never used within the paper. Change wording to illustrate the paper is focused on evaluating dynamics in relation to changing hydrology and flow paths.

Reply:

Thanks. We changed the title to: "Dynamic Responses of DOC and DIC Transport to Different Flow Regimes in a Subtropical Small Mountainous River".

(l. 31) Pluralize "model" Reply: Corrected.

(l. 41) Does "SMR" refer to sub-tropical mountain rivers or small mountain rivers. Please define and clarify in the abstract, figures and tables.

Reply:

The term "SMR" refers to small mountainous rivers. We used it in Line 31, but without the abbreviation. In this revision, we added the SMR in Line: 31. We also checked the term throughout the text, figures, and tables.

(l. 54) Extra period after (POM, DOM)

Reply: The term, "so that", was changed to " which". [Line: 59]

(l. 59-61) Check grammar, mismatch in "quantity" and "they"

Reply: Corrected. Use "it has" instead of "they". [Line: 65]

(l. 62/63) A citation is needed for the global river DOC and DIC statistics.

Reply: The citation, "Meybeck and Vörösmarty, 1999", was added [Line: 68]

(l. 68) As stated "an understanding of riverine C response in different regions is needed", but in response to what? Changing climate? Hydrology? Land use?

Reply:

We rephrased the sentence as: “an understanding of riverine C response to climatic and anthropogenic changes in different regions is needed.” [Line: 73]

(l. 78) The term “regular flow periods” is used to describe the biweekly sampling, but I believe either regularly sampled base flow or non-event flow would be more appropriate terms unless the biweekly sampling captured events. This is a term used throughout the paper.

Reply:

After rethinking about this, the term “non-event flow period” seems proper and was used in this revision.

(l. 110) It would be more useful to state the drainage area upstream of the sampling points, rather than the entire river watershed.

Reply: We added a sentence, “The drainage area for T1, T2 and M3 are 11.1, 40.1 and 274.1 km2, respectively” in Line: 127.

(l. 146) The phrase “then over the average” should be replaced by “divided by” or use a written equation.

Reply: Corrected [Line: 165].

(l. 165-166) Delete either the word “using” or “with”. Were the climate variables much different between T1, T2 and M3, they appear relatively close in proximity?

Reply:

The word, “with”, was removed. Yes, the three catchments are close in proximity. We tried our best to use all climatic variables we could collect and thus all observed climatic variables were included as much as possible.

(l. 191) Incomplete sentence, add “were observed” after “rapid increases”

Reply: Thanks for the correction. We added “were observed” after “rapid increases” [Line: 250].

(l. 229) Unsure of what is meant by “companying”. Also, the three end-member mixing model doesn’t note Chloride which was cited in the methods (l. 169).

Reply: The word “companying” is a typo of “accompanying” [Line: 296]. We added the result of Chloride in Line: 297.

(l. 243) Change “extreme” to “extremely”.

Reply: Corrected.

(l. 244) Sentence incomplete, “RSR is a predominant factor for transporting DOC due to the large amount”, I assume large amount of flow transported relative to the annual total.

Reply:

This sentence attempts to demonstrate the roles of sources and runoff in transporting DOC and DIC during typhoon period. The sentence was revised to “In sum, during typhoon period, the DOC is mainly transported by RSR due to the large amount of surface runoff coupled with large DOC storage on the land surface, whereas the DIC is predominantly transported by DG owing to the extremely high DIC concentration in groundwater storage, even though the DG flow is small.” in Line: 311-313.

(l. 264-265) “the abundant discharge has been well recognized” is incomplete/unclear. Are you referring to the positive relationship between DOC and discharge being strong, or that there is a lot of rainfall and/or runoff per unit area relative to other locations?

Reply:

We think that this sentence might be redundant, since we noted the abundant rainfall in Line: 350. Therefore, we removed this incomplete sentence.

(l. 273) “Incessant” is not the best word choice, perhaps consistent or invariable.

Reply: Rephrased “consistent”, instead of “incessant” [Line: 348].

(l. 300) Correct punctuation, extra period and capitalization

Reply: Corrected “The” by “the”. [Line: 380]

(l. 301) “subtle area” is not correct, perhaps minimal or small relative to global land mass?

Reply: Replaced “subtle area” with “minimal area relative to global land mass” as suggested. [Line: 381]

(l. 305) Correct capitalization

Reply: Corrected [Line: 385]

(l. 335) How would isotope techniques be used to clarify the importance of riparian and hillslope zones, please elaborate.

Reply:

DOC compounds which have different quality depend on the locality of their generation. On hillslopes, the humic-like DOC originating from litter tends to dominate while protein-like DOC can be found in riparian zones. The DOC quality can be determined by 13C isotope. On the other hand, although the flowpaths can be conceptually recognized by hydrological modeling and some geochemical analysis, the runoff ages (event water or pre-event water) in different flowpaths which are associated with different biogeochemical processes are still poorly understood. Therefore, using isotope techniques might improve our understanding in this topic. We added, “(e.g. 13C of DOM and 18O of different runoff pathways)” after isotope techniques for clarification [Line: 423].

(l. 338/339) Incomplete sentence. “Not only the change of DOC concentration but also DOC composition." Composition was never mentioned in the paper until this point and I don't think it is useful to include it in a single sentence unless the authors want to discuss the impact variability in DOC quality could have on their conclusions; how important may it be relative to quantity?

Reply:

Thanks for this comment. The term "composition" for DOC was replaced by DOC quality. We did not want to address this point too much, because of lacking solid evidence. We completed the sentence as follows: "Not only the change of DOC concentration, but also DOC quality was rapidly changed with the changing flow regimes through different sources." [Line: 427]

(l. 343) Add "per year" to the number of typhoons making landfall.

Reply: Thanks, we added "per year" in the sentence [Line: 432]

(l. 350/352) Elaborate on how changes in the DIC/DOC ratio would alter biogeochemical C processing in aquatic ecosystems.

Reply:

Global warming has been recognized to change precipitation patterns, making the dry season drier and wet season wetter. In this regard, the water residence time would be getting longer in the dry season, which might be favorable for autotrophic production and accumulation of DOC. The accumulated DOC would tend to change the heterotrophic microbes, potentially lower pH value by humic acid, and enhance the dissolution/precipitation of carbonate minerals (DIC). By contrast, the intensification of floods, the high flow velocity, would destroy the riverbed and reset the aquatic ecosystems which is unfavorable for heterotrophic microbes. We addressed the above descriptions in Line: 442-447.

Table 1. "Performance metrics" would be a better term to use in the title. Define and/or describe NSE.

Reply:

Thanks for the suggestion. “Performance metrics” is great and we used it in the title [Line: 504]. Also, we added calculation and description of NSE in Line: 161-164. The descriptions of NSE is as follows: “The NSE (Nash-Sutcliffe efficiency coefficient, Nash and Sutcliffe, 1970) calculates the explained variances and presents the performance as follows: Eq. (2) Where, Qo and Qs indicate the observed and simulated streamflow [m3 s-1] in time step, t, respectively, and (Q_o) ÌĚ represents the average of the observed streamflow [m3 s-1]. The NSE ranges from negative infinite to 1.0 and the unity presents the perfect match between estimations and observations.”

Table 2. Define dates for wet and dry season, respectively.

Reply:

We have mentioned the definition of dry season in the text, see Line: 193, “dry season (November to April of the following year)”. For this table, we added a footnote that “in Taiwan, wet and dry season are defined from May to October and November to April of the following year.” in Line: 513

Table 4. Is Meybeck and Vorosmarty, 1999 the correct reference for the global data? There is one table in that publication which only has flux in units of g C yr-1, there is no concentration data, perhaps it was another related reference, or state how calculations were made if it was derived from that citation. Should concentration be per liter? Are concentrations flow-weighted? Letters in footnotes are not consecutive.

Reply:

There were three sub-comments raised by the reviewer. The first one concerns the dataset from Meybeck and Vorosmarty (1999). The reviewer is right. In this report, only global average DOC and DIC flux were given. Huang et al. (2012) synthesized several studies and made their table 1 to show the DOC and DIC concentration. Not only Meybeck and Vorosmarty’s work, but also Ludwig’s works (1996 and 1998) was included. We added a footnote in this table. The second one is the unit of concentration. “uM” indicates 10-6 mole in a liter. The third one is to keep the footnotes consecutive. We checked the footnote to consecutive letters [Line: 620-630].

Huang, T.-H., Fu, Y.-H., Pan, P.-Y., and Chen, C.-T. A.: Fluvial carbon fluxes in tropical rivers, Current Opinion in Environmental Sustainability, 4, 162-169, 10.1016/j.cosust.2012.02.004, 2012.

Figure 1. Would be useful to outline the catchments defined by the 3 different sampling locations.

Reply: We delineated the catchment boundary of the three sampling sites in the revision [Figure. 1].

Figure 3-6. Nice job representing the data with different metrics that are uniquely useful.

Reply: Thank you. Glad to know that the reviewer like the figures as we do.

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