Review of Ran et al. "Riverine carbon export in the arid-semiarid Wuding River catchment on the Chinese Loess Plateau" (bg-2018-51)

Synopsis

The central focus of this manuscript is to investigate carbon cycling in the arid-semiarid Wuding River catchment using both campaign-style and time-series sampling approaches. The authors quantify dissolved carbon concentrations, both organic (DOC) and inorganic (DIC), as well as particulate organic carbon (POC) concentrations and CO_2 outgassing fluxes throughout the catchment over multiple seasons. In particular, the authors compare and contrast signals across a range of Strahler stream orders (1 to 6) from subcatchments underlain by sand and by loess and quantify differences in their respective carbon budgets.

As the authors point out, arid-semiarid river catchments are severely underrepresented in global riverine carbon-cycle budgets. By presenting a large dataset for the Wuding River catchment, this study begins to ameliorate this issue. I therefore find the goals and targets of the present study to be impactful, as they attempt to advance our collective understanding riverine carbon cycling. However, I do have some issues with the interpretation of these data, particularly related to a number of claims that seem unsubstantiated or somewhat contradictory. Additionally, I feel that there are some areas that warrant further clarification and detail. Overall, I feel that the authors should remove some of the weaker and highly speculative text that attempts to prescribe carbon sources and should instead focus on the strengths of this dataset – namely, carbon fluxes and budgets. If the authors can address these issues, which I think they can, then I believe that this manuscript could provide a valuable contribution to *Biogeosciences*.

I outline my larger concerns in detail below, followed by a list of smaller concerns and questions. Please do not hesitate to contact me for further discussion regarding this review.

Sincerely,

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Larger Comments

Methods details and measurement uncertainty

In general, I feel that more detail is required in describing the methodology and presenting data uncertainty. In particular, the paragraph beginning on L135 should be expanded considerably. For example, I would like to see more details related to:

i) Field titration methods. How was this done? Were any standards measured? Field titrations generally have quite high uncertainty associated with them (~5 – 10%), yet there is no uncertainty assessment presented here. What is the resulting propagated uncertainty for calculated DIC concentration values?

ii) DOC uncertainty. How was DOC uncertainty estimated? Was a standard calibration curve used? If so, how often was the calibration curve analyzed? Was each sample injected in triplicate? Duplicate? Single injection?

iii) Were solid samples fumigated with HCl at room temperature or at ≥60°C? I ask because dolomite will not be removed at temperatures below 60°C. If these samples are expected to contain dolomite, and if they were fumigated at room temperature, then I would expect resulting POC estimates to be biased upward.

iv) CO_2 $\delta^{13}C$ values. Were these analyzed by Beta Analytic using an IRMS on a separate gas split, or are these values generated by the AMS? I would expect these to be IRMS values, but this should be stated clearly.

v) Radiocarbon notation. Throughout the manuscript, the authors conflate ^{14}C age, $\Delta^{14}C$ (which is *always* reported in units of per mille!) and percent modern, or pMC. I would strongly suggest that the authors choose one notation and stick with it (my personal choice would be to use pMC). Still, if the authors choose to use ^{14}C age, this be reported in units of "^{14}C yr BP" rather than simply "years", as the latter is ambiguous and could refer to a calibrated age, which would not be appropriate here.

vi) Sediment accumulation rates. In Figure 10, a burial flux is presented in units of g C yr^{-1}, yet I find no reference to calculations for sediment accumulation rates (SAR). How was SAR calculated for each of these cores? This information is necessary in order to convert the measured %OC numbers into burial fluxes…

Additionally, all of the numbers reported in the "Results" section should include corresponding uncertainty, either analytical uncertainty (when reporting single values) or sample population uncertainty (when presenting averages). For averages, please be clear if reporting standard errors or standard deviations. Similarly, significant figures should be consistent throughout the manuscript!

Net Ecosystem Production

I am left somewhat confused by the assumptions and uncertainties related to NEP calculations. To convert S_R to R_h, the authors apply a "forested" and "non-forested" fraction heterotrophic derived from Hanson et al. (2000). However, the "non-forested" estimates from this reference are for pasture and grassland, not barren landscapes such as those presented in the current study. Presumably nearly 100% of soil respiration on barren landscapes is heterotrophic, no? Additionally, while the "non-forested" fraction heterotrophic in Hanson et al. averages 40%, they observe values ranging from 10% to 90% -- nearly the entire possible range!

I wonder if the authors have any way to estimate the uncertainty on NEP estimates presented here – if so, these should be discussed in detail. I would expect these uncertainties to be quite large, yet this is not mentioned or discussed in the manuscript. For example, how do the values here compare to those calculated by subtracting S_R from MODIS-derived GPP values? To me, this seems like a more straightforward method to estimate NEP that isn't subject to the uncertainties associated with converting S_R to R_h.

Interpretation of DIC, CO_2 $\delta^{13}C$, and $\Delta^{14}C$

In general, I am confused by the discussion on DIC sources, especially as they relate to measured CO_2 $\delta^{13}C$ and $\Delta^{14}C$ values – there seem to be a number claims that are either contradictory or are not explained in significant detail. Beginning in the abstract (L21) and repeated throughout the manuscript, the authors state that DIC is largely sourced from carbonate dissolution, especially in the loess subcatchment. Intuitively, this makes sense to me since loess contains a significant amount of carbonate, as the authors rightly state. However, this is incompatible with the $\delta^{13}C$ and $\Delta^{14}C$ values presented in this study, which suggest that remineralization of terrestrially derived OC is the main source of outgassed CO_2 behind check dams. What mechanisms could explain this discrepancy? I feel that there needs to be significantly more discussion and clarification here.

Furthermore, I find some of the claims related to CO_2 outgassing to be overstated. For example, the statement: "The evasion of old carbon [derived from pre-aged OC respiration as is seen here] is likely to be widespread in arid-semiarid catchments worldwide with similar hydrological regime and terrestrial ecosystems" (L477). This seems to be quite a stretch, especially given my confusion related to the lack of carbonate dissolution signature as stated above.

DOC sources and trends

Beginning on L204 and continuing throughout the manuscript, the authors refer to a "significant downward trend along the river course from headwater downstream… in both subcatchments." However, when I look at Figure 2, I am left puzzled and wondering if these trends are, in fact, significant. Given the large error bars for each stream order, my guess is that they are not. In my opinion, any subsequent discussion related to DOC sources and trends (e.g. L300-313; L306-309; L318-324) is highly speculative at best.

Additionally, I find some of these claims to be contradictory. For example, on L314, the authors state that "…there was no significant correlation between DOC and flow based on the spatial sampling results". However, for the high-frequency sampling the authors observe a "positive correlation between DOC export and hydrography [that] demonstrates the enhanced leaching of organic matter from surface vegetation and organic-rich top soil layers". Why would a positive correlation be expected during storm events yet not on a seasonal basis? What mechanism could explain this? This discrepancy is not addressed.

POC sources and trends

I find that a significant amount of discussion related to POC sources and sinks needs to be substantiated with more evidence or, at a minimum, alternate explanations need to be addressed. First, beginning on L326, the authors claim that low POC content (by which they mean % of suspended solids, a point that I address below) "reflects the ancient sedimentary OC origin of about 0.5% for fluvial sediments worldwide… [and is also] seen from the isotopic signature of the Yellow River sediment…" The authors go on to state that low %OC reflects "mobilization of subsurface soils that have a substantially lower OC content than surface soils" (L334). However, "ancient sedimentary OC" presumably refers to sedimentary rock derived material, which is *certainly* not the same as "subsurface soils". I'm left confused as to what the authors expect to be the major source of POC – sedimentary rocks or subsurface soils? I think that, with concentration measurements alone, one cannot make strong claims either way.

The well-known relationship between grain size and %OC is also not addressed. The observed POC concentration trends could easily be explained by variable hydrologic sorting – i.e. coarser, OC-poor sediments that are transported during high discharge periods – which would mask any POC source signal. In the absence of isotopic ($\delta^{13}C$, $\Delta^{14}C$) or grain-size-dependent measurements (e.g. %OC as a function of Al/Si ratios), I find it hard to believe that POC sources can be prescribed as is done here (also repeated beginning on L385).

Similarly, beginning on L408, %OC content behind check dams is compared to that on hillslopes and is used as evidence for burial efficiency. However, this "negligible OC loss after erosion" (L412) could be explained by alternative hypotheses. For example, deposited material could (likely does?) contain a different grain size distribution than that of hillslope soils, and thus a different %OC content. Also, any remineralization of terrestrially derived POC could be masked due to replacement by aquatic sources (as is discussed). Again, I find it hard to prescribe POC sources and burial efficiencies without additional measurements such as $\delta^{13}C$ and $\Delta^{14}C$. I also find the claim that this material "would have otherwise been mineralized to form CO_2 or CH_4 along fluvial delivery" (L418) to be somewhat speculative. Presumably some of this material would have been transported and buried in coastal marine sediments. Heuristically, it makes sense that burial efficiencies behind check dams are higher than for coastal marine sediments, as the authors imply, but I find a general lack of evidence supporting this claim.

Finally, I find that reporting "OC content" as %OC rather than a concentration (e.g. mg OC L^{-1}) or a flux (e.g. t OC km^{-2} d^{-1}) is ineffective and is somewhat misleading. For example, the authors state that "the substantially lower POC content in the wet season largely reflects the impact of gully erosion" (L385). However, one would expect that POC *concentration* and *flux* are actually significantly higher during the wet season! As described above, changes in %OC could reflect hydrologic sorting and are not necessarily indicative of source. I would strongly recommend discussing POC trends in the context of concentration and flux, rather than %OC. This would allow the authors to shift the focus away from attempting to prescribe POC sources (which I find to be a weakness overall) and toward OC flux and budget estimates, which I think is a strength of this manuscript.

Data availability

In my opinion, a major strength of data-rich manuscripts such as this is the ability for readers to incorporate these data into future studies – whether those be review articles or comparisons to other, similar catchments. Along those lines, I am left wondering why the authors do not make all of their raw data available as supplemental tables? I would strongly suggest do so or, at a minimum, including a "Data Availability" statement pointing the reader to a repository that includes these data.

Smaller Comments

L14: Remove dash between "terrestrially derived", change "represent" to "represents".

L15 (also L68): What is meant by "redistribution"? Do the authors mean "partitioning between DIC, DOC, and POC"? I would change this wording for clarity.

LL17: Change to "While DOC…"

L18: What is meant by "DOC concentration is spatially comparable within the catchment"? I'm confused by this statement. Don't you argue that DOC concentrations decrease with increasing stream order? (although I question this trend, as stated above).

L19: "This reflects the enhanced…" seems overly confident. I would say "This *likely* reflects…"

L21-22: I'm still confused by the DIC sources – carbonate dissolution seems incompatible with the measured CO_2 $\delta^{13}C$ and $\Delta^{14}C$ values.

L23: Please be clear that you mean %OC in sediments when stating that "[POC content] shows low values in the wet season." As stated, this implies that POC concentration or flux are lower in the wet season, which I presume is not true.
L27 (and throughout): Please update the ^{14}C notation, as described above. "Indicating the release of old carbon previously stored in soil horizons." Couldn't this also be described as a mixture of ^{14}C-free carbonate dissolution and respired young OC? I'm not sure that this claim is supported.

L32: Define "NEP". I don't follow the last sentence of the abstract. What is meant by "…has been significantly offset by riverine carbon export"?

L38: "Rivers play an exceptionally significant role by directly linking…" Role in what? The global carbon cycle?

L39: Remove dash between "terrestrially" and "derived".

L43: add "the" between "along" and "river".

L44: Remove comma after "processes".

L45: Change "in-situ" to "*in situ*" for consistency.

L46: How up-to-date is this 1.8 Pg C yr^{-1} number? See Drake et al. (2017) *L&O Letters* for an updated number.

L51: Has the number of studies on riverine carbon *really* been increasing *exponentially*? Change "recent" to "last".

L66: this should read "…through *the* drainage network to *the* catchment outlet…"

L67: Remove "in" before "northern".

L83: This should read "…and *is* located"

L85: Consider defining "loess" here.

L92: Citation for hydrologic regime description?

L94: I'm confused – is this sentence saying that one particular extreme event led to an erosion rate of 7000 t km^{-2} yr^{-1} for a particular year? If so, what is the average erosion rate? I feel like this would be more informative.

L102-103: "[The altered CO_2 exchange] remains to be quantified". Didn't you quantify this in Ran et al. (2017)? If so, how does this "remain to be quantified"?

L110: Change "was" to "is".

L124: Change "triple" to "triplicate".

L127: "radiocarbon $\Delta^{14}C$ samples" is somewhat redundant. Change to "collected samples for ^{14}C analysis" or similar.

L147 (and throughout): "The $\Delta^{14}C$ values were reported as percent modern carbon (pMC)". These are two separate units! (see above discussion).

L156: How reliable is this method for calculating carbon loads? This seems too simple. Why was something like LoadEst not used?

L160: "by multiplying annual sediment deposition rate…" How was deposition rate calculated? This is not described at all in the text.

L162: Change "was" to "were". Were these CO_2 flux data taken directly from Ran et al. (2017), or are these new data originally presented in this study? Overall, I would clearly state which data are new and which data are taken from previous studies (as these authors appear to have published multiple papers on this dataset…)

L172: Please provide the minimum catchment threshold area, as this will affect calculated Strahler stream order.

L177: How valid is the assumption that "each round of field sampling [is] representative of CO_2 emissions" for these four-month periods? What about for DIC, DOC, and POC concentrations – presumably you assume these are representative too?

L189: Heterotrophic soil respiration need not be due to bacteria – this could also be fungal or archaeal respiration. I would simply stick with "heterotrophs".

L216: Is this decline (insofar as it is statistically significant) really "remarkable"?

L225: I'm confused by the sentence beginning with "Because the flow regime in 2017 was significantly biased…" What is this saying? You applied the 2015 hydrological regime to the 2017 data?

L230: Fluxes should be in units of "g C yr^{-1}" (I'm assuming the "yr^{-1}" got dropped by accident).

L257: This should read "Assuming the water surface *area* remained constant…"

L265 (and throughout) Please add "VPDB" after "‰" when reporting $\delta^{13}C$ values.

L277: Should "soils" instead read "sediments"? How can sediment cores contain "soils"?

L300: How turbid are these rivers? If they are quite turbid, then I would expect that photochemical degradation is probably insignificant.

L301 (and throughout): Please change “labile” to “bioavailable” as this language is more consistent with our current understanding of OC decay dynamics.

L312: I’m confused by the statement “…and the mixture of carbon export from the two subcatchments.” I thought the “6th mainstem channels” *are* the two subcatchments, which combine to form the 7th order Wuding River? Or have I misinterpreted this? (It is hard to see on Figure 1).

L330: Similarly, please change “biogeochemically refractory” to “persistent” in order to be consistent with our current understanding of OC decay dynamics.

L358 & 362: Phytoplankton are not aquatic plants. Please clarify this language.

L426: I’m confused by the inclusion of this sentence – what does it add to the discussion?

L464: Is the correlation between $\delta^{13}C$ and $\Delta^{14}C$ statistically significant? Figure 9 does not report the regression slope equation nor any statistics, so I have no way of gauging the strength of this relationship (I’m not even sure if the line drawn in Figure 9 is a regression line…) Please clarify.

L470: “…which suggests the outgassing of ancient terrestrial OC after entering aquatic systems”. I’m confused here – OC itself cannot be outgassed. Does this refer to CO_2 generated from remineralization of old OC? If so, how do the authors know that this was remineralized *after entering* the aquatic system and not simply remineralized in soils and transported with soil pore waters?

L472: This claim (and others throughout the manuscript) isn’t necessarily supported – I would urge caution when making concrete statements such as this. Rather, I would phrase this along the lines of “These results are consistent with…”

L510: I’m confused by the statement “…this percentage (16%) falls into the range of global-scale estimates of 50-70%...” 16% is *not* in the range of 50-70%... am I missing something?

L514: In what way is the estimate of Cole et al. (2007) “conservative”?

L516-517 (and 531): Please remove “… it is worth noting that”.

L537: Remove the dash between “terrestrially” and “derived”.

L548: “CO_2 emissions represented an important pathway…” An important pathway for what? Carbon loss from the landscape? I would change this to “CO_2 emissions are quantitatively important…” or similar.

Figure 1: This figure is hard to read given the current color scheme and marker sizes. I would consider changing the color scheme for clarity and making the markers significantly larger. Also,

please provide a catchment outline for the “sandy” and “loess” subcatchments, as this delineation is currently unclear.

Figures 2-3: I would consider writing “Loess Subcatchment” and “Sandy Subcatchment” above panels (a) and (b) so that the reader does not have to dig through the caption to understand what is presented.

Figure 4: I’m confused by what the percentage numbers represent. This should be clarified in the figure caption.

Figure 5: Why has the nomenclature and color scheme changed for this figure? Why not use the colored bars from Figures 2-3 and the “spring”, “summer”, “autumn” notation that is used throughout the text? Also, what is meant by “conventional age”? Is this equivalent to ^{14}C yr BP?

Figure 7: Why is this figure showing NPP when the authors are interested in NEP? Why not show NEP directly? Also, please include the river network, subcatchment outlines, labels, etc. as in Figure 1.

Figure 9: Why are units of pMC (which is not the same as $\Delta^{14}C$!) used in this Figure but ^{14}C years used in Figure 5? Is this dashed line a regression line? If so, please include the regression equation and statistics. Technically, “young” and “old” only correspond to the *y*-axis and should point vertically, as the *x*-axis of this figure says nothing about age.

Figure 10: I’m confused by the inset pie chart – what does 100% represent? Is this all of the carbon in the river network? If so, at what time points, or does this represent the relative annual fluxes? Again, more detail in the caption would be very much appreciated.

Figure captions: In general, I would like to see significantly more description in this figure captions.