Review of "Environmental and hydrologic controls on sediment and organic carbon export from a subalpine catchment: insights from a time-series" by Melissa Schwab and co-authors.

## Summary:

This manuscript presents a large dataset from a long-term sampling campaign of river water and suspended sediment from a subalpine catchment in Switzerland. The authors generated a substantial amount of data, including a 40-month time-series of stable carbon isotopes and radiocarbon activity of dissolved and particulate organic carbon. Time-series data sets like this are incredibly valuable to the scientific community, particularly now as our field aims to mechanistically describe the feedbacks between climate change and the global carbon cycle. This manuscript addresses relevant scientific questions (i.e., what controls the magnitude and temporal variability of river organic carbon export?). The main dataset and introduction of statistical approaches are a great contribution to the field. The methods and statistical analyses used in this manuscript are state of the art, particularly the application of EA-IRMS for high throughput 14C measurements and the application of machine learning-based statistical analyses.

Overall, the manuscript is well-written, but there several points that need clarification and revision, as noted in the major points of concern and the detailed comments below. The authors do a nice job of presenting their data and using statistics to describe the distribution of the data, however, it seems that this manuscript is lacking robust interpretation of the statistical results. Based on the introduction of the paper, I expected their results to provide a mechanistic explanation linking geomorphic and hydrologic processes to organic carbon export from small headwater rivers. However, I was not able to take away any new ideas or significant conclusions from their data interpretation and discussion. Additionally, I find that some of the analyses are not entirely appropriate (i.e. the MixSIAR analysis) and should be either removed from the manuscript or redone to reflect appropriate endmember mixing. To make this manuscript of greater interest to the scientific community, the authors should also provide a framework for integrating their statistical results into Earth system models.

In summary, there are a number of issues that need to be addresses before this manuscript can be accepted for publication in *EGU Biogeosciences*. Major points of concern and suggestions for revising the manuscript are detailed below.

## Major points of concern:

The MixSiAR analysis is not applied appropriately here. Based on Figure 5a, two of the endmembers (soil and vegetation) are statistically indistinguishable such that they cannot be separate endmembers organic carbon sources. The authors constrain the soil endmember using samples from 0-40 cm soil depth, however, 0-10 cm soil typically contains a young organic horizon, such that its isotope composition will reflect modern vegetation. In lines 325-335, the authors explain that 14C-enriched bomb-derived OC can percolate through the soil column with DOC, causing homogenous isotopic composition with soil depth, however, the water-soluble phase of soil carbon should constitute only a minor portion of soil OC, such that it is unlikely for

this young OC pool to dominate the 14C activity of the soil profile. If the authors want to use soil as a distinct endmember in MixSIAR, I suggest they exclude soil data from <10 cm soil depth. Otherwise, they should perform a two end-member mixing model with biospheric and petrogenic OC as their end-member sources. Given that lake water/sediment samples are included in this study, perhaps an aquatic primary production endmember should be considered.

The authors do not discuss any underlying assumptions about the river system and its natural versus engineered state. I suspect that the response of suspended sediment and POC fluxes in the Sihl River will be dampened or altered by river engineering. The authors need to address the underlying assumptions of their study with respect to natural versus engineered rivers. They write in Line 88-90 that there are indeed weirs in the Sihl catchment that can trap 62-67% of the sediment, yet this effect is not addressed in the discussion.

The flow duration curve is an important aspect of this study, as it is used to define baseflow versus storm flow, however, I think this could be highlighted better in the main text and in a main figure. Figure C1 shows that the sample set covers nearly the entire range of discharge values, which is fantastic and shows how robust the statistical analyses can be. How does exceedance probability correlate to POC and DOC export and isotopic compositions? Instead of plotting run-off on the x-axis of Figure 7, would it be interesting to plot exceedance probability for the discharge recorded for each sample?

There are many details in the discussion section that are used to explain the data, but do not successfully build on the statistical results to make robust interpretations for how this analysis can be used to fill gaps in Earth system models. There are a lot of citations of previously published studies, although I feel that this is where new ideas should eb presented. This dataset and the statistical results can be used to predict carbon fluxes in Earth system models, something which we currently lack. I feel that the discussion and conclusions should be less focused on defending the data and more focused on developing a framework for including the predictive relationships in Earth system models.

## **Detailed comments:**

L19: What aspect of petrogenic OC decreases downstream? Concentration or relative abundance?

L20: Changes in the relative proportions of OC sources and "overprinting" of isotopic signatures does NOT illustrate rapid OC transformation. The term "transformation" implies a change in chemical composition of individual organic molecules or particles (e.g., oxidation to CO2). Here, the authors are describing a dilution of one organic carbon source with respect to the total organic carbon, which is not a transformation.

L22-23: This sentence should be re-organized. As it is written, it reads as though the authors are saying that storms trigger surface runoff and shallow landslides, which is an obvious process

and not what their data are testing. Rather, the sentence could be written as "Our data suggest that storms enhance mobilization of fresh leaf litter and shallow soils via increased surface runoff and shallow landslides.'

L24: "Diverging mobilization pathways" is quite unclear here. The following sentence suggests that suspended sediment and POC mobilization are both related to water stage. And 1-day antecedent precipitation and discharge are both related to runoff, so it is unclear how these reflect different mobilization pathways. Perhaps the authors could interpret their statistical results to provide a mechanistic explanation of how 1-day antecedent moisture conditions affect POC in a different way than suspended sediment, as well as why discharge and suspended sediment concentration are more strongly linked than discharge and POC content.

Given the amount of data included in this study, I would expect more robust interpretations of the data than what is highlighted here in the abstract. Are there any events captured in the dataset that can be analyzed to explain the effects of high runoff or landslides on POC export?

L113: It is better to report discharge in common units of m<sup>3</sup>/s

L115: I suggest writing "...while bedrock lithologies in the ... are predominantly calcareous sandstones" rather than "bedrocks"

L122: Why was this sampling location chosen? Based on the coordinates provided, this stretch of river is heavily engineered, which may be both good and bad for this study. The channelization of the river may lead to efficient export of sediment from the upper catchment, however, this site is downstream of several dam-like structures that can retain sediment. How are the collected samples influenced by river engineering? Is there a portion of POC that could be missing due to sediment retention behind dams? Is river discharge also regulated by these dams and weirs, such that storm pulses are dampened and the effects of storms on POC export not fully captured? These issues should be addressed either here in the sample collection section or in the discussion section.

L129-130: What is meant by identical replicates? Did the authors fill three separate sampling containers for each sample? Was each water sample filtered with three separate glass fiber filters? If there were three separate filters, how was it ensured that the sampled water was homogeneous with respect to sediment concentration? Please clarify what is meant by replicates.

L133: were the DOC samples stored at 4 degrees C? Clarify the term "cooled."

L140-143: Were there no process blanks run to correct for possible carbon contamination introduced through filtration and sample handling? It is good practice to run process blanks in geochemistry.

L147: How was the CO2 captured and stored? Were CO2 sample vessels evacuated sufficiently prior to collecting evolved CO2? Was there a process blank for the sodium persulfate addition and helium purging steps?

L145: Were DOC concentrations measured? If yes, add this procedure to the methods section. If not, how did the authors know how much carbon was in their aliquots?

L156: Start this paragraph by saying what MixSIAR was used for and why before defining what the model is and how it was parameterized.

L165: What outputs were used from the MixSIAR model and how? Did the authors use the full posterior distbrutions in the analysis, the median, the mean and standard deviations of the posterior distributions? Please clarify and explain how the model output was interpreted.

L169: What is meant by "discern" here? This sentence is unclear. Do the authors mean that particulate matter concentrations tend to correlate with water discharge? If so, please be more clear.

L169: Where does the discharge data come from?

L170: by "insufficient" do the authors mean too infrequent? Be more specific.

L175-177: Is there an equation for the bias correction factor? Is the correction factor a nonlinear least squares regression approach? The last sentence is not well-integrated with the previous sentence. How does the correction affect the results? Is underestimation reduced or completely eliminated?

L179: Introduce why machine learning techniques are applied here. It is unclear why fluvial loads need to be estimated when there is likely a gauging station with hydrologic data that can be paired with samples. Please provide an explanation of what the authors expect to achieve with the machine learning analyses and why different types of analyses need to be compared.

L187-189: Why were these predictor variables chosen? Are there other studies that have shown these to be statistically useful parameters for predicting river particulate matter fluxes? If yes, please cite these references here.

L320-324: Based on the data plotted in Figure 5, it appears that there is either an older soil OC source or aquatic biomass source. The authors need to propose a mechanism for producing the isotope values that do not plot between their vegetation, soil, and bedrock endmembers. If they are going to rule out autochthonous production, then they need to provide an alternate hypothesis.

L325-335: The authors should provide stronger evidence for combining all soil data from 0-40 cm, as water-soluble organic carbon is only a fraction of total soil organic carbon and likely does not have a large effect on soil carbon isotope values. I would expect larger isotopic differences

between mineral soil and the organic horizon, which should be mobilized under different hydrologic/erosion conditions.

L500-501: None of the figures in this manuscript demonstrate that the authors have found new insights into temporal variations in OC export from their study catchment. Discharge and precipitation time-series are plotted in Figure 2, but the other figures primarily show the distribution of data across seasons, or isotope mixing diagrams that show no statistically significant correlations. I question whether the data support the authors' conclusions.

L495-498: In Figure 2, there is surprisingly little variability in the POC concentration and 14C activity of the time-series samples. The authors should elaborate more on the potential role of dams, weirs, and other channel engineering methods in regulating POC export from rivers.

# Figures and Tables:

# Figure 2:

- It is unconventional to order the plots from bottom to top. I suggest re-labeling them with plot (a) at the top and (h) at the bottom. It was confusing to read the caption and see hydrograph listed first.
- Place the letter labels in the same position on each plot (e.g., upper left corner).
- The circles with sizes representing the discharge during sampling should be at the top of the plot, rather than the bottom. As it is now, the small legend seems to correspond only to the discharge plot, making it difficult to figure out what the circles represent.

**Figure 5a:** The soil and vegetation data are statistically indistinguishable, making the MixSIAR three end-member mixing model invalid for this dataset. It is clear that there are other endmember POC sources that have lower d13C values and lower F14C values than the swiss soil data plotted here. Based on the lake values, aquatic productivity may be an important organic carbon endmember in the Sihl.

**Figure 5b:** This figure only shows that DOC is younger than POC for nearly all samples, which is common across many river systems. It's not clear why this plot is significant because DOC and POC have different sources.

# Table 2:

- For the MixSIAR model input, there needs to be a number of samples (n) for each isotope tracer. In the table, n for F14C lists "est." The authors need to list what number was actually used, or put a note in the table footer.
- Need to insert table footer defining the variables (POC-d13C, POC-F14C, n, M, and SD).

**Figure 7:** There is not a clear purpose for including this figure in the main text. What are the gray arrows indicating on plots b and c? There are no statistics reported, yet it seems like the authors are proposing some sort of linear trend here.