Reply to Reviewer 1

General impression

Botter et al. examines in the resubmitted manuscript "Anthropogenic and catchment characteristic signatures in the water quality of Swiss rivers: a quantitative assessment" the dataset of the Swiss National River and Survey Program (NADUF). The revised version gained clarity on some aspects but also still contains some points to improve.
We thank the reviewer for the positive comment to the revised version of the manuscript and for highlighting points where the manuscript can be improved.

Different inconsistencies and errors in referring to figures or findings exist and confuse when reading the manuscript (e.g. L391 but also others).
We thank the reviewer for pointing out these inconsistencies and we refers him/her to the specific comments for the corrections.

As mentioned in the comments to the first version of the manuscript, a geological map is necessary and would help to link observations and catchment characteristics. L148 mentions "crystalline silicic rocks are dominant" but it seems that the HA or DI catchments have mainly sedimentary rock. Including this in the results and discussion would certainly help.
We added to Figure 1 the geological map and we referred to it throughout the manuscript. Please see also the specific comments.

A methodologically concern is how the parameter *a* was treated. This was never explained and it is therefore not clear whether this parameter was fixed or variable and could potentially affect conclusions concerning the temporal variable parameter *b*. Please clarify this point in the manuscript.
The *a* parameter is a coefficient with units of concentration resulting from the linear interpolation of discharge (Q) and concentration (C) data. It is computed together with *b* but it does not affect *b*. Being our analysis focused on the solute behaviours, which, according to the wide literature, is determined by the *b* exponent, the *a* coefficient is unimportant. However, we agree that we should mention in the manuscript how it is computed. We added a statement in Paragraph 3.2 (L214-216).

The comment to the definition of "hybrid catchments" was previously made to stimulate the thinking of the authors about the reason why these catchments are hybrid. My interpretation about the meaning is that they are defined "hybrid" because they contain one or multiple lakes, which could cause a dampened run off, residence of water particles and in or decrease of certain solute concentrations. This is also visible in the different figures. Please discuss the effect of lakes in your study.
We agree and we explain that the catchments we define "hybrid" are characterised by extended surface. They all include lakes in their domain, but also other catchments that we classified as Alpine or in the Swiss Plateau area have comparable percentage of lakes in their domain, e.g., BR and WM have the same fraction of lake surface in their domain. The subdivision per macro-geological areas is more functional to the analysis we carried out. However, we agree with the Reviewer that discussing the issue of lakes in the manuscript is necessary. We therefore added some statements at L180-185.

The discussion is long and contains a lot of information. One would expect that the analysis of water collected in a human influenced catchment would show an anthropogenic signal. However with the rich dataset and analysis already performed, it is possible to link the different results in a logic way and will allow the reader to understand which are the effects of the climatological forcing (temporal variable signal), catchment characteristics (difference between plateau, alpine and "damped" catchments with lakes) and human influence (specific solutes and their temporal variably). Subsequently it is possible to see different catchment with different runoff regimes and temporal solute behaviour in relation to each and allows highlighting differences and why certain observations or patterns were observed or not. By ending each discussion section with a short summary could help to make stronger statements and highlight the main findings. A summarizing paragraph at the end of the discussion would also help to go beyond a statement that solutes are human induced and write a more specific abstract and conclusion.
We thank the Reviewer for the useful suggestion and we modified the discussion. Specifically, we focused on the first part of the discussion, which contains a large amount of information and we introduced a final outlook to sections 5.1 and 5.2 to summarise the take-home messages. Section 5.3 was better structured and the take-home messages are already specified in the conclusion, so that an outlook would have been redundant. Please

note that key messages are summarized in a short conclusion section, repeating those a few lines earlier in the discussion would be excessively redundant in our opinion.

These modifications are of minor type. Incorporating the general and specific comments will improve the manuscript and better highlight the specific novel aspects of the manuscript.
We thank the Reviewer for the general positive impression about our work and for the suggestions that contributed to improving the manuscript.

Specific comments referring to line

Sometimes basins were used while other times 11 catchments. Please use consistent wording for all definitions throughout the manuscript.
In the revised version of the manuscript we use consistently the term "catchments".

L23 "certain solutes" add which ones.
We explicitly point out the solutes in the revised version of the manuscript.

L25 Which variability temporal or spatial is meant here? Which one is higher, the natural or the anthropogenic? The conclusion L587-590 is much clearer.
In this case we refer to the variability in time, which we tackle in the seasonality analysis. We modified with the explicit expression "The variability in time..". We also underlined the stronger variability due to anthropogenic factors adding the statement "..and the most significant trends in time are due to the variation of the anthropogenic forcing in the long-term".

L106 The Erlenbach and Lumpernenbach seem not really river basins. Please classify them differently!
We adjusted the definition of case studies at L107-108 as follows: "The resulting case studies include 5 catchments (Thur - AN, Aare - BR, Rhine – WM, Rhone – PO and Inn - SA), 3 sub-catchments (Rhone – PO, Rhine – RE and Rhine – DI) and 2 small headwater catchments (Erlenbach and Lümpenenbach)."

L107 Which are the subcatchments? Please specify.
Please, see comment above.

L129 Please specify which are the detection threshold and accuracy of the different instruments are. This will help to better understand the signal. I.e. if the instrument accuracy in solute X is ±0.1 and the signal variability as well as, there is not a significant difference between the different catchments (Figure 2). This example is valid for all other figures. Please take this into account and modify accordingly.
We added a short paragraph in the Supplementary Information (Paragraph S1) focused on the detection thresholds issue and we commented on this in relation to the results.

L148 Please include a geological map similar to map made by v. Freyberg 2018.
We thank the reviewer for the suggestion and we included it in Figure 1.

L156 What is a low intensity fertilization, please specify the tons ha-1.
We thank the reviewer for this comment because we realised the previous version of the definition of "low intensity fertilization" was incorrect. We rectified the definition of extensive agriculture in the revised version of the manuscript at L157-158.

L161 Please add after "south-north gradient" and within the alpine valleys.
We added this information to the revised version of the manuscript (L163-164).

L164-166 Move to introduction
We agree with the Reviewer that this statement is not in the correct section and we removed it from the manuscript, since in the introduction it was redundant.

L177 Maybe you could use a classification: basin (Biggest scale - dampened), catchment ("meso scale"10-... km2) and subcatchment (Small scale <10km2)
We adjusted the catchments definition in L107-108. Here, instead, we keep the morphology-based classification because, we think it is more functional to the following analyses.

L178 What do these extremes relate to, magnitude or timing. Please be specific and use hydrological terms.

We thank the reviewer for this observation and we added a more precise hydrological description at L178-179.

L184-192 How the index of variability was calculated and presented was confusing. Especially the caption of Figure 4 confuses "*Bar plot of the index of variability. Each bar represents the monthly variability of average concentration 900 relatively to discharge variability per catchment class.*" However, which month was presented in Figure 4, or where different average or spatial average presented here? It's not clear. Please clarify and rewrite this section.

We clarified in the caption of Figure 4 that the bar plot refers to the average monthly deviation and not to the deviation of a specific month. To enhance clarity, we added to the manuscript a non-symbolic formulation of the expression of the index of variability (L194).

L394-399 S2a and S2b do not correspond with text and makes this section difficult to read. Please modify.

We apologise for the inconsistency and we corrected the reference to the figure from Figures S2a and S2b to Figures S3a and S3b.

L427 Which analysis and figure support this statement?

The analysis of trends is supporting this result. In the revised version of the manuscript we are more precise referring explicitly to the analysis and to the Figure showing the result.

L434 Not only fertilizer application but also manure can dissolve calcite and affect Mg/Ca ratios. Please discuss this in the manuscript with appropriate references.

Manure can be somehow considered a fertilizer. Nonetheless, we thank the reviewer for the suggestion. We integrated this aspect in the discussion with appropriate references (L443-444)

L449 Here the geological map of Switzerland would help. Please also perform a multiple comparison to show significant differences between the different catchments which will help to relate H4SiO4 to geology.

We now referred to the new geological map introduced in Figure 1.

L460 Is there a reference available to support this statement? Not all Alpine catchments do have high sediment loads (Figure S5).

Accordingly to the catchment classification in L111-112, in the revised version of the manuscript we explicitly say that the results are supported by the analysis for all the Alpine catchments except for the two small headwater catchments, because, with their small size, they are peculiar.

L463 For clarity refer to the respective figure.

We added the reference to Figure 4.

L483 Precipitation amount but also annual distribution are important. When describing precipitation e.g. table 1 it is not clear how this was calculated and also if spatial variability was incorporated e.g. max and min mm y-1.

All the description data come from the information included in the NADUF database, which provides a satisfactory description of each catchment. The data source was not clear from the caption of Table 1 so we modified the caption to make it clearer.

L491-493 By using residence time runoff flow paths are inferred and not demonstrated. Please modify.

We apologise for the incorrect citation and modified accordingly.

L506 "Removal" and entrain are rather similar. Is the word "removal" linked to biological reduction e.g. nitrification? Please specify in the manuscript.

Yes, we meant exactly this kind of removal processes. We modified to enhance clarity.

L518-520 This sentence confuses since earlier H4SiO4 was linked to weathering and geology (L303) while now to bioactive processes. Please clearly state which is the dominant process.

We thank the reviewer for pointing out the inconsistency. We clarified this point.

L526 Please specify here which catchments are mentioned here.

We specified the catchments.

L528 But fast response is followed by fast recession, are alpine and sub-alpine rather affected by dilution caused by the high precipitation?

A high precipitation is definitely an important reason for the fast hydrological response (e.g., fast peak flows, fast recession). We mentioned explicitly this point in the text. However, high-precipitation alone would not be a sufficient reason, and dilution should be also related to the fact that water already in the catchment and the new water may not mix properly. As a matter of fact, in a groundwater dominated system, with large groundwater volumes, the chemical composition of discharge is expected to be more similar and to show little dilution regardless of the amount of precipitation.

L532 This statement is not fully clear. Isn't it that the water "picks" up a certain composition due to its flow-path?

It depends from which perspective one looks at the problem, if from the perspective of a parcel of water entering the catchment and following a certain flow-path (in this case, yes, it "picks" a certain composition). If we look at the problem from the perspective of some water leaving the catchment from an outlet. In this case, the chemical composition is a combination of the chemistry originated by the multiple flowpaths reaching the outlet at that time. This second case is what is measured by water-quality observations and it is what we refer to in the discussion. We acknowledged the fact that complex watershed in the Alpine region may have multiple flowpaths, including very long ones, but we state that given the widespread observed dilution behaviour those flowpaths are unlikely dominant in the composition of the outlet discharge.

L567 Statement concerning subsurface flow is not clear. Is subsurface flow only occurring with natural conditions while human activity influences overland flow? Please modify this sentence

We rephrased the sentence to improve clarity. Subsurface flow is occurring regardless of the fact the catchment is natural or affected by human activities, it is the effect on DOC, which can be seen only if the catchment is natural, because in catchments affected by human activities the DOC signature is not anymore due only to natural processes.

L588 All or only certain solutes?

> **What is the anthropogenic signal, one solute or a series? What is the influence of the catchment characteristics? Do small catchments with high agriculture % behave different solutes compared to large catchments with lakes? Although statistically it is difficult to show relations between observations and catchment characteristics, a quantitative statement can be made to explain certain observations. Also, explain what caused the temporal variability in Figure 5, 6 and 8. Clearly highlight in your take home message e.g. there is a variability due to climate but anthropogenic can be noticed in region 1 while less in catchments in region 2 because of ...**

We agree with the Reviewer that the conclusion was general and sometimes vague. In the revised version of the manuscript we integrated some more detailed messages referring to the explanation of results pointed out by the Reviewer.

L594 What is a "macro-pattern"? Please explain or remove.

We removed the sentence.

L604 Important findings are missing e.g. a non-seasonal behaviour of "anthropic" induced solutes as e.g. discussed in L395 and differences between different catchments are missing.

We thank the reviewer for the suggestion and added some statements to the conclusion.

L606-608 This statement is too general and not fully clear.

We rephrased this part.

L614 A clear take home message of how the different regions or catchment types are missing and would be valuable to include.

We are not sure to fully understand what the reviewer meant with this comment, however, we prefer to conclude the manuscript with what we can clearly state rather than what is missing from the analysis.

Figure 1 catchment boundaries are difficult to see. From the stream network it seems that the hybrid catchments containing lakes, are dampened. Maybe just call them dampened catchment. This would also be agreement of Figure S2. Also add letters a-... to facilitate connecting the text and different panels.

We modified Figure 1 as suggested. Particularly:
- The map with the morphological regions was substituted with the maps of macro-geological classes because it is more informative;
- Borders of catchments were highlighted;
- The letters a, b (upper panel) and c, d, e (bottom panel) were added

For comments to the definition "dampened catchments" please refer to the answer above.

Figure 5 &S2 The variability in time is interesting. Is it possible to relate this temporal pattern to climate variability, i.e. wetter and drier decades? In addition is it possible to state that in wetter years the anthropogenic signal is
higher or lower (e.g. Mg, No3 or …) ? Please include in manuscript.

In the first round of Review, Referee 1 raised this point, therefore we considered the natural variability of climate as a potential driver for the long-term trends that we observe in the concentration data. The results are shown in the reply to the Referee, but the conclusion are already stated in L200-207. Consistently with this statement, we did not investigate the relationship between the climatic and the anthropogenic forcing.

Figure 8b Really interesting to see changes but which variable do I see…? Continue to label the different panels as letters or add as new figure.

We adjusted Figure 8 adding the name of the solute in the capture and adding the label to the left panel.