Reply to Referee 1

Botter et al. examines in the 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 dataset consisting of biweekly water samples collected in different catchments throughout Switzerland, which were analysed on wide range of different chemical variables. The authors represented the different variables of eleven catchments as boxplots, regime type, variability index, temporal representation and concentration-discharge relations to infer and generalize the impact of catchment characteristics and human activities. The separation of the data into low and high flows gives a new view on the data.

The manuscript is structured but contains some inconsistencies, is sometime not clear or confusing.

We thank the reviewer for the interest in the paper and of the constructive criticism of our study. We will work on the first version for enhancing the clarity and consistency.

Definitions need to be better explained, e.g. anthropogenic, human influence and intensive and extensive agriculture in the introduction.

The definition of these terms is fundamental for a straightforward understanding of the analysis and of the results. We thank the reviewer for pointing out the inaccuracy in the explanations. We will give clearer definitions in the next version of the manuscript.

Findings need to be reported consistently, e.g. section 4.1 phosphorous or silica L250 is coming from fertilizers/humans while section 5.1 and L283 reports that it might be also due erosion or geology. Related to this, chose the appropriate data and analysis to answer the research question.

We thank the reviewer for pointing out this inconsistency, which occurred due to an improper or inconsistent use of the term "input" across the manuscript. The sources of nutrients (e.g., phosphorus, nitrate,..) intended as input into the catchment system are often fertilisers. Once in the catchment, these solutes are transported and can be transformed in the different compartments of the catchments. Considering phosphorus, as an example, consolidated knowledge in literature states that it tends to accumulate in the soil where it can sorb, desorb, be mineralised or immobilised, and only a minimal fraction leaches into the groundwater. When soil is eroded, phosphorus-rich soil particles are taken by flowing water and therefore soil erosion is one of the main contributor to the phosphorus load into the rivers. The two processes are strictly connected and the contribution of one does not exclude the other. This point will be better explained in the manuscript.

Not coming from Switzerland, it is hard to understand where the metropolitan areas are, which kind of land use and land cover or geology the different catchments have and how this affects the water quality. Therefore adding such information in Figure 1 will help to interpret the data, e.g. why certain catchment have higher Ca, NO3 or DOC concentrations compared to others.

We agree with the reviewer that the case study description was lacking of some fundamental information and that Table 1 and Figure 1 do not explain exhaustively the catchments. We will add a more extensive description including land use, land cover, and geology information in section 2 and we will find a more suitable graphical representation of Figure 1.

In addition to the defined objectives, it might help to phrase a clear research question and state which the different hypothesis are. This will allow to distinguish between different processes and the complex interaction of climate, catchment characteristics (land use and land cover, geology, topography, shape…) and humans affecting stream chemistry.

We will re-phrase the research questions in the introduction to clearly state what we are investigating, concerning hypothesis, being this a "data-driven" analysis and not a numerical or field experiment we prefer to refrain from formulating a posteriori hypotheses, given also the challenge to test them with 11 catchments only.

The influence of climate forcing on chemical variables was only vaguely discussed and not supported through any analysis, but it is required in the next version.

We thank the Reviewer for this observation. In the manuscript there is not a specific analysis dedicated to the influence of climate on stream biogeochemistry, because the sample does not suit the requirements of size and independence necessary for a formal statistical analysis of climatic effects. The study is indeed based on only 11 catchments across Switzerland, often nested catchments. Table 1 gives an overview of the catchments including mean annual rainfall, which could represent the major source of climatic variability across the catchments being other variables as temperature, humidity and solar radiation rather similar at catchment scale. However, the mean annual rainfall across the catchments vary in a limited range 1063 – 1506 mm/y; the only exceptions are Lümpenenbach (LU, 2127 mm/y) and Erlenbach (ER, 2182 mm/y) catchments, situated in the Alptal valley. These two catchments are also the two smallest catchments considered in the study, with an area at least three orders of magnitude smaller than the others and therefore some observed behaviours might be due to the wetter conditions but also due to the smaller size. The effects of the two factors cannot discerned with such a small sample size and any dedicated analysis to partition climatic effects is not meaningful given the similarity in climate of all the other basins.

The number of figures in the main article and supplementary material is overwhelming. By refereeing to both main article and supplementary material, results in that the reader get lost and forgets about the main findings.

The number of figures will be reduced and some figures will be moved from the main article to the supplementary material and vice versa. Some of these modifications include moving Figure S4 from supplementary information to the main manuscript, removing Figure 3 and merging Figure 2 with Figure 10.

Figures contain lots of information, but the results are not equally explained for every figure.

We will be more precise in referring results to the figures and we will reduce the information content of each figure so that it matches only the one required for the discussion. For example, Figure 3 is not crucial for the discussion and Figure 7 contains much more information than the one discussed in the article. The reviewer's suggestion of combining figures 5 and 7 will be taken into account.

With regard to the figures, I suggest moving important figures into the main article and leaving "less" important ones in the supplementary material.

As explained above, we will take into consideration the suggestion of moving Figure S4 to the main article and leave Figure 3 either out of the article or in the supplementary material.

To decrease the number of figures and focus on the main findings different figures could be combined, e.g. Figure 2 and 10, leave out Figure 3 (almost similar information as Figure 4?) and combine Figure 5 and 7.

We thank the Reviewer for these suggestions. Please see our replies above.

In the presented work, a subset with consistent temporal data was used. However, it would be unfortunate to exclude how the stream chemistry changes in space. The full data set could be used to perform an additional spatial analysis to infer at which scale the effects of climatological forcing, catchment characteristics and human influence can be detected.

The objective of our study is to analyse long-term water quality data in order to investigate the possible signature of anthropic activity and of catchment characteristics. The focus of this article is on purpose on the temporal analysis more than on the spatial variability and on time-series of a length that is deemed sufficient to filter short-term variability and average long-term behaviours. An exhaustive spatial analysis would require different criteria for station selection, different type of analysis, in other words a very different study with another database, which we consider to be out of the scope of our study. The eleven selected catchments, meaning water quality samples in eleven points across the entire Switzerland provide some information about spatial variability that is included in the narrative of the article, but are not sufficient for an extensive and statistically robust analysis of spatial variability.

It is necessary to correlate the chemistry with other variables than agricultural land use as land cover, geology, urban area etc. To strengthen the findings it is necessary to perform a comparison between variables and catchments and test whether the findings of Figure 4, 6, 7 and 9 are significant different.

The study will be modified to benefit of the integration of other variables like land cover, geology and urban areas. We thank the reviewer for the suggestion of testing the correlation between these variables and the catchment behaviours. Other studies (e.g., *Godsey et al.*, 2009; *Moatar at al.*, 2017) apply the Spearman's non parametric test (*Spearman*, 1904) to this purpose. This test quantifies the correlation between the b exponent, representing the biogeochemical response of the catchment, and the variables, representing the different catchment characteristics. We are planning to integrate this analysis in our work, thus supporting the discussion with more quantitative results. However, please note that we are considering 11 catchments only.

In addition, to be able to judge the validity of the results and limitations of the dataset, it is necessary to consider measurement errors and detection limits of chemical variables.

We agree with the reviewer that the manuscript is lacking comments concerning measurement errors and detection limits of chemical values. Concerning the detection limits, we considered them during the preliminary data elaborations, when the database was pre-processed to clean outliers due to issues in detection limits. This was not mentioned in the manuscript and it must be integrated in the revised version.

The discussion and conclusion sections are wordy, without highlighting the new findings.

In the revised manuscript, the discussion and conclusion sections will be more essential and the main findings will be pointed out clearly.

To explain the data, different streamflow generation and runoff processes were hypothesized to occur. However, the discussion section lacks debating the temporal sampling interval and its ability describe potential occurring processes at shorter time scales.

This is an important observation and we agree that the discussion should include statements on the ability of the temporal sampling interval to describe potential occurring processes at the shorter time scale. The sampling method of the NADUF database is flow-proportional and it is characterised by a 14-days frequency. The low sampling frequency does not allow recognising short-time scale signals in the biogeochemical signature of rivers, even though these are integrated in the 14-days frequency, being the sampling "flow-proportional". Water quality programmes established in many catchments around the world record data at quarterly, monthly, 14-days or weekly frequency because of time and financial constraints. Despite this low sampling frequency, we think that these data have a high information content if used in the proper way. The representation of short time scales processes cannot be the goal of this kind of database, but the description of long-term patterns of water quality parameters in relation to external forcings (i.e., anthropic activities and catchment characteristics) can. Studies addressing the comparison between information at different time resolutions are cited in the manuscript as alternative to our approach (*Butturini et al.*, 2008; *Duncan et al.*, 2017; *Minaudo et al.*, 2017; *Wade et al.*, 2012).

In addition, it is necessary to refer to the current understanding of streamflow generation, runoff processes and stream network connectivity observed around the world. But also studies from Switzerland, which is known as a country to have a long, history and good knowledge of detailed small-scale catchment processes understanding (from lowlands to Alpine regions), needs to be included. The authors need to revise this section and including these points to be able to put findings into a spatial and temporal perspective.

We thank the reviewer for the suggestion and we will enrich the discussion with examples from literature focused on the hydrological processes understanding whenever it is suited.

The manuscript will benefit by streamlining the discussion and conclusion with focus on the effects of climatological forcing, catchment characteristics and human influence on the spatial and temporal variability of chemical variables.

Concerning climatological forcing effects and spatial variability please refer to our comments above. The discussion and conclusion sections will be modified to streamline the research objectives of the work. The discussion section is structured already in paragraphs referring to each one of the research objectives, but it can be improved making it more essential and focused on the most important results only.

It would be also valuable to add a discussion section, from a hydrologist – scientific point of view with an outlook for potential next steps or a critical note on the data collection and what could / should be done differently to address certain future questions.

We thank the reviewer for these suggestions. Since the data issue is widely discussed in water quality studies (e.g., *Stelzer and Likens*, 2006) we will just add a short note on data collection. A brief outlook with potential next steps will be also included in the conclusion.

Reply to Referee 2

Several recent papers studied long-term series of water quality and discharge aiming to generalize behaviors of selected solutes across catchments in order to infer anthropogenic and catchment characteristic influences. This study provides some more results on Alpine streams. The authors analyzed geogenic solutes, chloride, nitrogen, phosphorus and organic carbon species, monitored by the Swiss National River and Survey Program for 11 Swiss rivers with a temporal resolution of 14 days as composite sampling (sampling represent an integration of the preceding 14 days) for more than 10 years. The analysis of basic statistics, seasonality, temporal trends and concentration-discharge behavior revealed impacts of human activities for some catchments. However, the influence of catchment characteristics is much less evident. This is probably due to the small number of analyzed catchments and to their area range which is very bi-modal (one group with catchment area around 5 000 to 30 000 km2 vs. 2 small catchments with area < 1km2) which do not help having a more quantitative spatial analysis.

We agree with the reviewer that the sample of catchments is not wide enough for an exhausting representation of the spatial variability and variety of Swiss river biogeochemistry. Indeed, the main focus of our analysis is on the long-term temporal trends.

The manuscript needs to better explain the relation between temporal metrics and spatial characteristics.

The manuscript will be modified to include a clearer presentation of the spatial characteristics of catchments. A more exhaustive description will be integrated in Section 2. Moreover, also Figure 1 will be modified so that it can be more effective in illustrating the spatial characteristics of the catchments (e.g., urban areas, land use, geology)

Another way of analyzing the results could be to consider the variation of these relationships along nested catchments (Rhein, Rhone, Aare).

We thank the reviewer for the suggestion. In theory, this is a good idea, but the sample of nested catchment is limited to 3. Therefore, we are sceptical about the possibility to obtain any robust pattern or generalization originated by these three nested catchments. A detailed spatial analysis would require a different database, or better different criteria of selection of the catchments from the NADUF database favouring a higher number of stations with a much more limited number of years. Here we selected the catchments with at least 15 consecutive years of measurements for the investigation of long-term trends. For an exhaustive spatial analysis, a different selection would be necessary. However, this would require a very different methodology and it is considered to be out of the scope of our study.

The manuscript has a relatively good structure, but the results could be presented in a more factual way, in order to better distinguish them from the discussion.

We thank the reviewer for the positive comment and for the constructive criticism. We will present results in a more factual way. Specifically we plan to:

- Streamline the discussion section,
- Better link the results and observations in the figure,
- Eliminate the redundant or excessive information in the figures,

The conclusion needs to highlight the new findings of this work.

We thank the reviewer for this comment and we agree that new findings need to be clearly summarised in the conclusions because they are only mentioned throughout the manuscript.

Database and study sites
The authors do not present very well the database (numbers of data/years for each site and element, screening, discussion about the difference between composite sampling and grab sampling, representativeness of metrics calculated from composite sampling, especially for small catchments).

We agree that the database can be presented more accurately. We will integrate additional information following the suggestion of the reviewer.

It is not clear either whether all the calculated temporal metrics are based on mean bi-monthly concentration and discharge data time series. If this is the case, the authors need to discuss how this

sampling design impacts the analysis of the temporal metrics (especially concentration-discharge relationships).

Yes, all the calculated temporal metrics are based on mean bi-monthly concentration and discharge. However, please note that concentration is a “flow-averaged quantity” and not a snapshot every two weeks. The only statistic computed from hourly discharge data is the median daily discharge used in the C-Q relations and this is pointed out at lines 177-181. We will introduce a sentence on how the sampling design impacts the analysis of the temporal metrics, referring to literature (e.g., *Stelzer and Likens*, 2006).

Catchment characteristics are not very well presented. Figure 1 could be reworked to present land use/land cover. Colors for catchment could be replaced by contour lines.

We plan to integrate section 2 with additional and more detailed information concerning the characteristics of the catchments. Specifically we will be more precise in describing the geological zones, the land use, the land cover and the urban areas. We will replace colours of catchments in Figure 1 with contour lines and, if the final result will be easier to read we will substitute the current one.

For example, authors defined three categories of catchments according to their morphology and geographical locations (lines 148) but it is not clear why only these criteria. It seems that these regions are homogenous also for land use, lithology and climate? Hence, do they belong to the same hydro-ecoregion? It might help to see on figure 1 or in table 1 theses three categories (how many catchments for each category) to link them to geology, landuse/land cover.

The three categories of catchments are defined for the analysis of the seasonality and the categories are based on the catchment morphology and geographical locations. Since we analyse the seasonality of in-stream concentrations in relation to the seasonality of discharge, we retain important to differentiate hydrological regimes of the catchments, which have different seasonalities. Switzerland is characterised by basically two main geographical zones, the Swiss Plateau a lowland in the north and the mountainous Alpine area in the centre and south. The two different zones have substantially different hydrological regimes (Figure 5, upper and bottom panels). However, some of the selected catchments extend in both areas and are therefore defined as “hybrid catchments”. They are characterised by a seasonality, which is intermediate between the two extremes (Figure 5, central panel) and they have to be treated separately from the other two classes. The geographical sub-division of these areas is used to distinguish different hydrological regimes. It does not imply that these regions are homogeneous in terms of land use or geology. We will present more clearly the catchments characteristics in Figure 1 and we will be provide further explanations for the analysis of seasonality, pointing out that the classification is done based on the different hydrological regimes and highlighting the main conclusions:

- the seasonality of Ca^{2+}, Na^{2+}, K^+ and Cl^- is dictated by the seasonality of discharge,
- the seasonality of Mg^{2+}, TP, DOC and TOC overwhelms the seasonality of discharge due to natural controls,
- the seasonality of H_4SiO_4, NO_3, TN and DRP overwhelms the seasonality of discharge due to anthropic factors (e.g., input of fertilisers).

Table 1. Please use km2 as unit for catchment size, and specific discharge (l s-1 km-2) for discharge, also in figures (ex. Figure S5), in order to allow catchment comparisons.

We thank the reviewer for the suggestion and we will adjust the unit in Table 1 and plot the C-Q relation with Q as specific discharge instead of discharge, however we will use “mm” rather than “l/km2”, since it is a much more intuitive metric from a hydrological perspective.

ID=VW on table 1 but ID=WM on figure 1. Is it the same catchment? Temporal metrics: it is not very clear what is the aim of each indicator, especially for the seasonality and C-Q relationship.

Yes, this is the same catchment but the station in the original database changed the name during the monitoring period. The error originates from this inconsistency; we will use a single name throughout the manuscript so that it is going to be consistent.

Index of “seasonal” variability: the numerator of the equation could be reformulated to take into account that it performs a sum of deviations for different catchments belonging to the specific “topographic” class. It is consistent for all “topographic” classes with only 3 to 4 catchments in a category ?

The equation was not properly formulated since it should simply represent the average of the index of seasonal variability over catchments belonging to the same category. It will be corrected.

Figure 5. How hydrological regimes were defined? The method is not presented in chapter 3.

We defined the hydrological regimes based on *Weingartner and Aschwanden,* 1992. We will mention this in the manuscript.

What is the link with Figure 6 (index of seasonal concentration variability), and with figure S2?

The link between the classes of hydrological regime and Figure 6 is explained above. The link with Figure S2, instead, refers to one of the result we can observe in Figure 6, i.e., the seasonality of H_4SiO_4, NO_3, TN and DRP overwhelms the seasonality of discharge because of anthropic factors (e.g., input of fertilisers). Indeed, these nutrients have their own seasonality, as Figure S2 shows. In the case of Ca^{2+} (bottom panel of Figure S2), instead, the pattern of the load along the year follows quite well the pattern of the discharge, also in the most human-impacted catchments indicating that external forcings is not larger than natural variability. We will emphasize this point in the revised manuscript.

Concentration-discharge relationship. Please define why you calculate integral "b" exponent and truncated "b" exponent, b50sup, b50inf.

We compute the truncated b exponent (i.e., b_{50sup} and b_{50inf}) for the classification of the solute behaviours, because, as explained in lines 182-184, this allows a finer classification of their behaviours. The integral b, instead was computed to analyse how the anthropic activity influence the solute behaviours (Figure 9) beyond influencing its magnitude. The objectives of these two parts of the study are different. While the first one aims at the understanding the processes that potentially are at the basis of the observed behavior, the second one aims at detecting possible long-term trends in solute behaviour.

Figure 2 and Figure 10 can be merged, indicating that you use the conceptual diagram of C-Q relationships proposed by Moatar et al, 2017 and test it for Swiss rivers (mean altitudes > 1000 m, mean rainfall 1000 - 2000 mm/y).

We thank the reviewer for the suggestion and we plan to merge Figure 2 and Figure 10.

You can also compare with other recent papers (ex. Diamond, Cohen, 2017 for coastal Plain Rivers in Florida).

We thank the reviewer for the suggestion and we will integrate more references in the manuscript.

In the split-hydrograph method, separate concentration-discharge relationships are described for below and above median discharge, Q50 is the median of daily discharge. Are your C-Q diagrams (Figure 9, 10) realized from mean bi-monthly concentration with mean bi-monthly discharge? It would be the reason why only 29% of the catchment-solute combinations have different behaviors between low- and highflow conditions.

Yes, the C-Q diagrams are computed from bi-monthly concentration with bi-monthly discharge. Concentrations are flow-proportional, while the discharge is averaged on a 14-days period. The reviewer raises a very interesting point. The answer to the question is challenging since it is not possible to have a precise evaluation of which is the main factor determining different behaviours of solutes between low- and high-flows in 29% of the cases. The low sampling frequency may play a role in this. As *Stelzer and Likens* (2006) point out, sampling frequency has different effects depending on the response that concentration has to discharge, so the uncertainty related to the sampling frequency might be different from solute to solute and it is impossible to quantify it with the data available in this study. We will add a statement about the influence of sampling frequency in the discussion section.

Or perhaps, it is a characteristic of alpine rivers where dilutions and exports of elements are the major behaviors while biogeochemical and retention removal processes at low flows are not very significant. Or perhaps, Q50 is not the appropriate discharge percentile break-point?

We did not investigate the effects of using other metrics than Q50 as break-point. However, we think that the characteristic of alpine rivers dampen biological retention and removal processes at low flow, which are therefore not very significant.

Figure 8. What site? Figure 6. A, B, C not defined in section 3.2

The site is not mentioned because this is an example of the most common patterns across all of the catchments and we intentionally did not want to refer to any specific catchments. We will add in the caption the sites, the patterns are referred to, but we do not think it is an important information for the subsequent discussion.

Figure 10. define grey areas

We thank the reviewer for the observation and we will complete the caption of Figure 10 with the definition of the grey areas.

References

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