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Discussions

Anthropogenic and catchment characteristic signatures in the water quality of Swiss rivers: a quantitative assessment

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Abstract

The hydrological and biogeochemical response of rivers carries information about solute sources, pathways, and transformations in the catchment. We investigate long-term water quality data of eleven Swiss catchments with the objective to discern the influence of catchment characteristics and anthropogenic activities on delivery of solutes in stream water. Magnitude, trends and seasonality of water quality samplings of different solutes are evaluated and compared across catchments. Subsequently, the empirical dependence between concentration and discharge is used to classify different solute behaviors.

Although the influence of catchment geology, morphology and size is sometime visible on in-stream solute concentrations, anthropogenic impacts are much more evident. Solute variability is generally smaller than discharge variability. The majority of solutes shows dilution with increasing discharge, especially geogenic species, while sediment-related solutes (e.g. Total Phosphorous and Organic Carbon species) show higher concentrations with increasing discharge. Both natural and anthropogenic factors impact the biogeochemical response of streams and, while the majority of solutes show identifiable behaviors in individual catchments, only a minority of behaviors can be generalized across catchments that exhibit different natural, climatic and anthropogenic features.

Keywords: water quality, catchment biogeochemistry, stream chemistry, concentration-discharge relations.

1. Introduction

Hydrological and biogeochemical responses of catchments are essential for understanding the dynamics and fate of solutes within the catchment, as material transported with water carries information about water sources, residence time, and biogeochemical transformations [*Abbott et al.*, 2016]. A quantitative description of water quality trends can also shed light on the consequences of watershed changes as well as on the possibilities for preventive or remedial actions [*Turner and Rabalais*, 1991]. Concerning changes in watershed land use or management practices, for example, the United States Geological Survey (USGS) established the Hydrologic Benchmark Network (HBN) [*Leopold*, 1962], a long-term monitoring system of dissolved concentrations in 59 differently impacted sites across the United States with the goal of quantifying the human impacts on the ecosystems [*Beisecker and Leifeste*, 1975]. Water quality monitoring and assessment are also crucial for stream and catchment restoration, which has been widely practiced in the USA and Europe for several decades and still represent an important challenge of river basin management. However, the system responses to restoration often contradicts a priori expectations, and the lack of adequate monitoring and assessment of basin functioning before the application of restoration measures is considered to be one of the main reasons [*Hamilton*, 2011].

The relationship between observed in-stream solute concentrations and discharge has been explored in various catchments and with different methods in the last decades [*Langbein and Dawdy*, 1964; *Johnson et al.*, 1969; *Hall*, 1970; *Hall*, 1971; *White and Blum*, 1995; *Evans and Davies*, 1998; *Calmels et al.*, 2011]. One emerging postulate is that concentration (C)-discharge (Q) relations represent the quantitative expression of the interaction between the catchment structure, hydrological dynamics and the solute releases, thus reflecting the mixing process taking place along flow paths of variable lengths and residence time [*Chorover et al.*, 2017]. Therefore, C-Q relations have been studied with reference to hydrological variables, e.g., hydrologic connectivity and residence time [*Herndon et al.*, 2015; *Baronas et al.*, 2017; *Duncan et al.*, 2017a; *Gwenzi et al.*, 2017; *Torres et al.*, 2017], biological processes [*Duncan et al.*, 2017a], catchment characteristics, e.g., catchment topography, land use, vegetation, size, and lithological properties [*Musolff et al.*, 2015; *Baronas et al.*, 2017; *Hunsaker and Johnson*, 2017; *Moatar et al.*, 2017; *Wymore et al.*, 2017], and anthropogenic activities [*Basu et al.*, 2010; *Thompson et al.*, 2011; *Musolff et al.*, 2015; *Baronas et al.*, 2017].

In a log(C)-log(Q) space, C-Q relations have been observed to be usually linear [*Godsey et al.*, 2009], so that the empirical relations can be well approximated by a power-law, $C = aQ^b$, where a and b are fitting parameters [*Godsey et al.*, 2009; *Basu et al.*, 2010; *Thompson et al.*, 2011; *Moquet et al.*, 2015; *Moatar et al.*, 2017; *Musolff et al.*, 2017]. A very common metric, relevant also for this study, is based on the value of the b exponent, the slope of the regression in the log(C)-log(Q) plot, because it is related to the concept of "chemostasis" [*Godsey* *et al.*, 2009] or "biogeochemical stationarity" [*Basu et al.*, 2010]. A catchment shows "chemostatic" behavior when despite a sensible variation in discharge, solute concentrations show a negligible variability, i.e., $b \cong 0$. Conversely, positive slopes (i.e., increasing concentrations with increasing discharge) would support an enrichment behavior where the solute amount grows with discharge and negative slopes (i.e., decreasing concentrations with increasing discharge) support a dilution behavior with solute mass that does not increase proportionally to the growing discharge. A solute is typically defined transport-limited if it is characterized by enrichment, while it is called source-limited in case it dilutes [*Duncan et al.*, 2017a].

The exact mechanisms leading to C-Q relations are, to a large extent, an open question, but these relations are anyway providing insights on solute and/or catchment behavior [*Godsey et al.*, 2009; *Moatar et al.*, 2017]. The concept of chemostasis emerged in studies that explored the C-Q power-law with the aim of demonstrating the similarities in the export behavior of nutrients [*Basu et al.*, 2010; *Basu et al.*, 2011] and geogenic solutes [*Godsey et al.*, 2009] exist across a range of catchments [*Musolff et al.* 2015]. These studies were mostly carried out in agricultural catchments, where a "legacy storage" was supposed to exist due to antecedent intensive agricultural fertilization practices [*Basu et al.*, 2010; *Basu et al.*, 2011; *Hamilton*, 2012; *Sharpley et al.*, 2013; *van Meter and Basu*, 2015; *van Meter et al.*, 2016a; *van Meter et al.*, 2016b]. This storage of nutrients might have long-memory effects and it was considered to buffer the variability of concentrations in streams, leading to the emergence of biogeochemical stationarity [*Basu et al.*, 2011]. However, biogeochemical stationarity has been questioned outside of agriculturally impacted catchments [*Thompson et al.*, 2011] and a unifying theory explaining catchment-specific C-Q behavior is not available yet, considering that solutes can show different behaviors in relation to landscape heterogeneity [*Herndon et al.*, 2015] and to the spatial and temporal scales of measurement [*Gwenzi et al.*, 2017]. Therefore, approaching the study of solute export and C-Q relations requires the separate analysis of several solutes in as many catchments as possible with the possibility to find, at least, some general behavior that can be characteristic of a given region or solute. The recent literature is moving toward this direction [*Herndon et al.*, 2015; *Wymore et al.*, 2017] with the aim to sort out the relative influence of climatic forcing, solute properties, and catchment characteristics on solute behavior in search for generalizations across different river basins.

This study contributes to this line of research investigating a unique dataset of long-term water quality data in eleven catchments in Switzerland, where multiple solutes were observed at the bi-weekly scale with limited gaps. Specifically, we focus on the following research objectives: (i) exploring the magnitude and temporal trends of solute concentrations in the discharge and their dependence on catchment characteristics; (ii)

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investigating to which extent the solute concentrations are influenced by human activities; (iii) generalizing the behaviors of selected solutes across different catchments by means of the slope in the C-Q relations.

2. Study sites

Observations used in this study are obtained from the Swiss National River and Survey Program (NADUF[1]), which represents the Swiss long-term surface water quality monitoring program. This database includes in total 26 monitoring stations located in different catchments. To ensure representativity and robustness of the analysis we focus only on those stations with at least 10 consecutive years of water quality measurements. This restricts the database to eleven catchments, the corresponding locations of which are shown in Figure 1. The resulting case studies include 6 main river basins (Thur, Aare, Rhine, Rhone, Inn, Erlenbach and Lümpenenbach) and respective sub-catchments.

Measurements have a temporal resolution of 14 days, which is similar to the resolution of other studies that analyzed long-term water quality data. The temporal resolution of observations ranges namely from weekly [*Duncan et al.*, 2017a; *Duncan et al.*, 2017b; *Gwenzi et al.*, 2017; *Moatar et al.*, 2017; *Wymore et al.*, 2017] to 14-days [*Hunsaker and Johnson*, 2017] to monthly [*Basu et al.*, 2010; *Thompson et al.*, 2011; *Musolff et al.*, 2015; *Mora et al.*, 2016; *Moatar et al.*, 2017] or even coarser resolution [*Godsey et al.*, 2009]. In fact, only, very rarely higher-frequency databases are collected and analyzed (e.g., *Neal et al.*, 2012; *Neal et al.*, 2013; *von Freyberg et al.*, 2017a).

The analyzed catchments cover most of Swiss territory, and they are characterized by different climatic forcing, geologies and anthropogenic pressures across catchments, all features that support the choice of the NADUF database as suitable for the objectives of this work. Despite the relative small dimension of Switzerland, there are climatic differences across the selected catchments, i.e., precipitation ranges from about 1000 mm/y in the Swiss Plateau to more than the double in the Alptal valley. Catchments in the geomorphological zone of Swiss Plateau (northern Switzerland) experience higher intensive agriculture pressure, which decreases moving toward the Alpine zone (southern Switzerland). Northern catchments also host a larger number of inhabitants compared to the southern Switzerland, so that the anthropogenic pressure generally follows a south to north gradient.

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[1] https://www.bafu.admin.ch/bafu/en/home/topics/water/state/water--monitoring-networks/national-surface-water-quality-monitoring-programme--nawa-/national-river-monitoring-and-survey-programme--naduf-.html

Stream water is analyzed only twice per month, but is collected continuously thus providing samples that represent an integral of the preceding 14 days. River water is lifted continuously by a submersible pump into a closed overflow container (25L) in the station, at a flow rate of 25-75 L min^{-1}. From the container, samples are transferred in 1 mL portions to sampling bottles. The frequency for the transfer of 1 mL samples is proportional to the discharge monitored continuously by the gauging device in the same station. The discharge-proportional sampling device is designed to collect 1-3 L of sample per bottle in each period. The sampling mechanism also allows the simultaneous collection of up to four integrated samples.

The concentrations reported in the database concern the following solute types: (i) geogenic solutes, originating mainly form rocks weathering, such as calcium (Ca^{2+}), magnesium (Mg^{2+}), sodium (Na^{+}), silicic acid (H_4SiO_4) and potassium (K^{+}); (ii) deposition derived solutes, as chloride (Cl^{-}); (iii) nitrogen species (nitrate (NO_3) and total nitrogen (TN)); (iv) phosphorus species (dissolved reactive phosphorus (DRP) and total phosphorus (TP)); and (v) organic carbon species (dissolved organic carbon (DOC) and total organic carbon (TOC)). The time series of these concentrations are used in the analyses carried out in this study. Furthermore, the dataset includes also the average discharge, computed as the mean value over the period between two water quality analyses, as well as other parameters such as water temperature, hardness (Ca^{2+} + Mg^{2+}), alkalinity (H^{+}) and pH.

3. Methods

3.1 Magnitude, seasonality and trends

The solute time series are first investigated to characterize magnitude, seasonality and trends of concentrations across the considered Swiss rivers.

The magnitude of a solute is evaluated through basic statistics (i.e., median, 25th and 75th percentiles, minimum and maximum values). These are computed for each solute grouping together all the catchments as well as for each solute in each catchment. The first set of statistics aims at quantifying the variability of each solute in the Swiss rivers, while the second one highlights differences across catchments, which are the result of catchment heterogeneities with respect to natural and anthropogenic factors affecting the quantity of a given solute.

The seasonality of discharge and of solute concentrations is analyzed and cross-compared to highlight difference and similarities of controls that are related to the seasonality of the natural dynamics and man-induced forcing. For this analysis, catchments are subdivided according to their morphology and geographical locations in three categories: Swiss Plateau, Alpine, and hybrid catchments. The last category includes catchments spanning both of the two major morphologic zones (Alps and Swiss Plateau). The partition into morphologic classes helps highlighting not only the effects of different catchments characteristics, but also the impact of climatic gradients and, especially, of human activities on some solutes, given the presence of an increasing gradient of anthropogenic pressure from the Alpine to the Swiss Plateau catchments. The comparison between the two variables is made through an "index of variability" defined as the ratio between the deviations from the mean of solute concentration and discharge respectively, where the "deviation" is determined as the average difference between the monthly mean and the annual average value, resulting in the following equation:

$$Index\ of\ variability = \frac{\frac{\frac{\sum_{i=1}^{12}|C_i-\overline{C}|}{12}}{\frac{\sum_{i=1}^{12}|Q_i-\overline{Q}|}{12}}}{n},$$

where *i* represents the month of the year, from 1 to 12, and *n* is the number of the catchments belonging to the specific topographic class for which the index of variability is computed. In other words, an index of variability larger the one suggests that the seasonality of the solute is more pronounced than that of discharge, and vice-versa for an index of variability smaller than one.

Finally, we evaluated the occurrence of trends in the long-term concentration time series at monthly and annual scale using the monthly average concentration of each solute in each catchment and each year for the entire period. The statistical significance of trends was tested with the Mann-Kendall test modified to account for the effect of autocorrelation [*Hamed and Rao,* 1998; *Kendall,* 1975; *Mann,* 1945], fixing a significance level of 0.05. Trends are investigated and compared across catchments, in order to understand if they are consistent across Switzerland, thus suggesting the presence of clear drivers inducing the trend, or if they are just occurring in a sub-set of catchments.

3.2 Concentration-Discharge relations

The empirical relation between solute concentration and discharge $C = aQ^b$ was explored separately for each solute and for each catchment. The two variables are expected to exhibit in a log-log scale a linear relation, the slope of which is given by the b exponent. The Student's t test was applied to verify the statistical significance of having a b exponent different from zero. The level of significance α was set at 0.05. When the p value was lower than α, the slope identifying the log-linear C-Q relation was considered significant and characterized by the computed value of b, otherwise the slope was considered indistinguishable from zero, thus suggesting no evidence of a dependence of concentration on discharge.

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In each catchment, the time series of discharge were divided into two subsets using the median daily discharge q_{50} to separate flow below the median (low-flows) and flows above the median (high-flows). Hourly discharge time series were available from the Swiss Federal Office for the Environment (FOEN) at the same river sections and for the same period of the time series of water quality provided by the NADUF monitoring program. The median daily discharge was computed from the hourly series, which were aggregated to obtain daily resolution. Determining the C-Q relations separately for high and low-flows allows a finer classification of the solute behavior into different categories (*Moatar et al.* 2017), than when considering only the dependence on the mean discharge. The three main behaviors – "enrichment" (i.e., positive slope), "chemostatic" (i.e., near-zero slope) and "dilution" (i.e., negative slope) – can indeed be the result of specific streamflow conditions, which are in turn the result of mechanisms controlling the runoff formation and, thus, the transport mechanism. Accordingly, we have in total 9 different combinations characterizing the C-Q relation across high and low flow regimes, which allow assigning distinct behaviors to a given solute (Figure 2).

For solutes that showed long-term trends over the monitoring period, we also investigated the evolution of the b exponent in time. In this case, the concentration and discharge time series were divided into decades and the C-Q relations were computed separately for each decade.

4. Results

4.1 Magnitude

The variability of the long-term average concentrations in the 11 catchments is shown as boxplots in Figure 3. Among the geogenic solutes, Ca^{2+} is the most abundant, most likely due to the composition of the bedrock present in most of the catchments (calcite, dolomite and anhydrite/gypsum [*Rodriguez-Murillo et al.*, 2014]). In absolute terms, geogenic solutes and Cl^- have the highest concentrations (≈10-50 mg/L), while phosphorus species concentrations (≈0.01-0.1 mg/L) are on average one to two order of magnitude less abundant than nitrogen species (≈0.5-1.5 mg/L) and organic carbon (≈1.5-5 mg/L).

Some solutes are constituents of other species: NO_3 of TN, DRP of TP and DOC of TOC. NO_3 is the major constituent of TN, since it is about 60% of TN, DOC is about 70% of TOC, while DRP contributes much less to TP, being only its 20%. We computed the ratio between the solute and its component for the three couples (NO_3/TN, DRP/TP and DOC/TOC) and showed their patterns across catchments (Figure S1). Only DRP/TP has an evident decreasing pattern with decreasing catchment anthropogenic disturbances, while fractions of nitrogen and organic carbon on the total N and C do not show any clear trend.

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Effects of catchment characteristics and human activities on the observed stream solute concentrations can be seen for certain solutes as shown by Figure 4, where each box shows the measured concentrations in the 11 catchments and the last box on the right refers to all the catchments grouped together. The catchments, expressed by the corresponding acronym (see Table 1), are ordered from the most impacted by human activity - i.e., higher percentage of catchment area used for intensive agriculture - to the least impacted, which is almost equivalent to considering a south-to-north gradient. The most evident effect of catchment characteristics refers to the presence of Ca^{2+} and H_4SiO_4 in the stream water (Figure 4a). Only the southern Alpine catchments of Inn (SA), Rhine (DI) and Rhône (PO) rivers show H_4SiO_4 concentrations higher than the median value. The bedrock of northern and central Switzerland, in fact, is mainly composed of calcareous rocks, while in the Alpine area silicic rocks are dominant. The impact of human activities, instead, is more evident in Na^+ and Cl^- concentrations. These are showing, basically, the same pattern across catchments (Figure 4b), indicating that they are most likely influenced by the same driver, which is the spreading of salt on roads during winter months for deicing purposes. DOC and TOC concentrations are very high in Lümpenenbach (LU) and Erlenbach (ER) catchments (Figure 4c). This should not be surprising, as they are the smallest catchments, with the highest average yearly precipitation rate and very low anthropogenic presence. Also Thur (AN) and Aare (BR) catchments show DOC and TOC concentrations higher than the average, but in these catchments the presence of wastewater treatment plants can influence TOC concentrations. Finally, some nutrients, such as nitrogen species, phosphorus species, and potassium, which are connected with anthropic activities (fertilization, wastewater treatment plants) show decreasing median concentrations from the most to the least impacted catchment (Figure 4d).

4.2 Seasonality

Different catchment topographies and climates determine various hydrological responses, as we can observe in Figure 5 from the analysis of discharge seasonality across the eleven catchments, expressed through the monthly average streamflow normalized by its long-term average. We divided the catchments into 3 groups depending on the morphological zone they belong to and on the streamflow pattern. The seasonality of streamflow in Swiss Plateau catchments is determined by a combination of precipitation and snowmelt. The peak flow is typically observed in spring and is not much higher than the average in the other months. Alpine catchments, instead, show stronger seasonality induced by snow and ice-melt in spring and summer, which generate higher streamflows than in the other months. Hybrid catchments exhibit flow peaks in June-August similarly to the Alpine ones, but the deviation from the average value is less pronounced.

The deviations of discharge and concentration are compared using the index of variability (Section 3.1) for each morphological class of catchments (Figure 6). Only few solutes show a value of the index higher than 1, thus indicating that seasonality of solute concentrations is generally lower or much lower than the seasonality of streamflow. This is especially true for the Alpine catchments, where the marked seasonality of streamflow seems to dominate on the variability of concentrations. For TP this index is higher than one in Alpine catchments, and also the highest compared to the other two types of morphology. In Swiss Plateau and hybrid catchments, instead, only solutes impacted by human activity (Na^+, Cl^-, nitrogen species and DRP) show a ratio close or even higher than 1.

DOC and TOC concentrations are characterized by low indexes of variability, especially in the hybrid catchments.

The patterns of the index of variability across different morphologies can be classified into three categories, represented by the symbols A, B and C in Figure 6. The monotonic A line type refers to those solutes the variability index of which changes across morphologies solely as a result of the seasonality of streamflow (Ca^{2+}, Na^{2+}, K^+ and Cl^-). Type B solute (Mg^{2+}, TP, DOC and TOC) response shows a higher variability index in Alpine catchments compared to types A and C, thus indicating that, among the factors controlling the seasonality of biogeochemical response, there are factors that are specific to the Alpine environment. The type C pattern, instead, mostly refers to human-related solutes (H_4SiO_4, NO_3, TN and DRP). These solutes are characterized by a much lower variability index in Alpine catchments than in hybrid and Swiss Plateau catchments. Difference in their regime are further discussed in Section 4.

The analyzed solutes show different intra-annual dynamics. Despite the quite pronounced streamflow seasonality of the Rhine River at Rekingen (hybrid catchment used as a representative example), solute concentration patterns shows different seasonal cycles (Figure 7). Ca^{2+}, Mg^{2+}, Na^+, K^+, Cl^-, NO_3 and TN concentrations peak in February-March and have lower values during spring-summer period, showing a pattern opposite to that of streamflow. H_4SiO_4, instead, has a shifted seasonality compared to the other solutes, peaking in December-January. Phosphorus species together with organic carbon species do not show any consistent seasonality over the year.

4.3 Trends

Long-term trends in the concentration time series are investigated with respect to the seasonal cycle for each year separately (Figure 7**)**. One catchment (Rhine-Rekingen) is taken as an example for illustration purposes but generality of trend results is discussed in the following.

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Focusing on the long-term horizon, different dynamics can be observed across the different solutes. Some of them show visible trends: for instance Cl^- has increased from 1970s to 2015, while phosphorus species have decreased considerably. Some solutes have different trends across different catchments. A generalization of long-term patterns is shown in Figure 8 for the three main detected behaviors. The upper panel represents the occurrence of an evident trend, either increasing (as in the example) or decreasing. Na^+, Cl^-, DRP and TP belong to this category. While Na^+, Cl^- have increased in time, DRP and TP have decreased in the monitoring period, as the monthly trends in Table S1a shows.

The middle panel shows a non-monotonic trend. This is typical of Mg^{2+}, which first increased in most catchments (1970s-1990s) and then decreased (1990s-2015). K^+, TN and TOC also show this type of trend in most catchments. Finally, the lower panel of Figure 8 shows a number of solutes (Ca^{2+}, H_4SiO_4, NO_3 and DOC) that do not exhibit any long-term trend, although the monthly analysis revealed some significant trends (Table S1c).

4.4 C-Q relations

Concentration-discharge relations were computed for all the solutes across all the catchments as summarized in Table 2. For each selected solute, we computed the number of catchments showing a given specific behavior, which we denoted with the combination of the symbols "+" (i.e. enrichment), "-" (i.e. dilution) and "=" (i.e. chemostatic behavior) for discharge above and below the median, as explained in Figure 2.

Geogenic solutes are mostly characterized by dilution. The only exception is H_4SiO_4, which shows 6 different behaviors across the 11 catchments, making impossible to identify the most representative behavior for this solute. This is the case also of other species (nitrogen species, TP and organic carbon species), which show at least three different behaviors across catchments. Silicium is mainly generated through rock weathering, but it is also involved in biological processes, which might influence its behavior across catchments.

Overall, dilution is dominant for all solutes in both low- and high-flow conditions, as it occurs respectively in 65% and 57% of the catchments. Therefore, even in low-flow conditions, the solute transport is mainly source limited across catchments. Only sediment-related solutes (i.e., TP, TOC), show a marked transport limited behavior. Indeed, we investigated also C-Q relations for suspended sediment concentrations and they show increasing slope across all the catchments, indicating, as expected, higher erosion rates in presence of high flow conditions. Only 29% of the catchment-solute combinations have different behaviors between low- and high-flow conditions and therefore the C-Q relations are represented by bended lines, having different slopes between low- and high-flow conditions.

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NO_3 and DOC represent a conspicuous component of TN and TOC respectively, but NO_3 shows almost the same behaviors of TN, in spite of a different distribution across catchments, while DOC and TOC behave completely differently. Phosphorus species also show different behaviors, consistently with the fact that DRP represents only a small fraction of TP.

Since in the trend analysis we identified four species (Na^{2+}, Cl^-, DRP and TP) that are characterized by remarkable long-term trends, we investigated if such a significant change in magnitude has an effect on the C-Q relation analyzing the temporal changes of the b exponent. The changes in b across all catchments with record length longer than 30 years during different decades is shown in Figure 9a, whereas Figure 9b shows an example of variation of the TP C-Q relations across decades for the catchment Rhine–Rekingen. Although the observed concentrations of all four solutes - Na^{2+}, Cl^-, DRP and TP - are characterized by the presence of evident trends in time, the behaviors in the C-Q relation differ. Na^+ and Cl^- have barely constant b exponent across decades, while phosphorous species show increasing b, which, in some catchments, leads to a switch from a dilution to an enrichment behavior.

5 Discussion

5.1 Influences of human activities on solute concentrations

Solute export across catchments seems to be mostly controlled by anthropogenic factors rather than by catchment characteristics. The impact of human activities on solutes concentrations in stream water is already evident from the analysis of the magnitudes (Figure 4). Phosphorus and nitrogen are the main nutrients applied for agricultural fertilization and, following the stoichiometric composition of plants, nitrogen species concentrations are one order of magnitude higher than phosphorus species concentrations (Figure 3). Nitrogen is the main nutrient required for crop growth [*Addiscott*, 2005; *Bothe*, 2007, *Galloway et al*., 2004; *Zhang*, 2017] and indeed NO_3 is one of the main components of fertilizers applied in agriculture. NO_3 represents a large fraction of TN (Figure 3). The ratio between average NO_3 and TN concentrations exhibits a more limited variability across the different catchments (Figure S1), than that estimated by *Zobrist and Reichert* (2006), who observed a variation from 55% in Alpine rivers to 90% for rivers in the Swiss Plateau. This difference might be due to the analysis of different Swiss catchments. For example, *Zobrist and Reichert* (2006) did not analyze the Inn River data, a rather natural and Alpine catchment with little agriculture, which has a ratio of NO_3:TN comparable to that of Thur River, although the latter is the catchment with the highest fraction of intensive agricultural land (Figure S1). This result may suggest that nitrogen transformations as nitrification and denitrification in the river could partially mask the effect of exogenous introduction of NO_3 quantities. In the case of phosphorus, instead, the ratio between average DRP and average TP concentration is decreasing from more to less anthropogenic catchments (from about 0.5 in Thur

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river to about 0.2 in Inn River). This can be explained as the result of the cumulative effect of two main factors: the lower DRP input due to lower intensive agricultural activity in the Alpine zone and the higher share of phosphorus sourced by suspended sediments contributing to TP in Alpine catchments due to higher erosion rates.

Other clues of human impacts on in-stream concentrations emerge from the analysis of seasonality. In Figure 6, we assigned the pattern "C" to those solutes characterized by a much lower variability index in Alpine catchments than in hybrid and Swiss Plateau catchments. For those solute concentrations, variability in Swiss Plateau and hybrid basins are comparable or higher than streamflow variability, while in Alpine catchments streamflow seasonality is much stronger than solute seasonality. A non-negligible fraction of these solutes is introduced through agricultural practices or by means of other human activities. This input is characterized by its own seasonality, which influences the solute dynamics and makes it comparable or larger than the discharge seasonality, a behavior non-observable for most geogenic solutes (Figure 6). An additional evidence supporting this result is represented by the patterns of the average monthly discharge and solute load (computed as the product between concentration and discharge) for Ca^{2+}, originated by rocks weathering, and NO_3, mainly of anthropogenic origin (Figures S2a and S2b). The plot, inspired by the analysis of *Hari and Zobrist* (2003), shows how the seasonality of Ca^{2+} load follows the seasonality of discharge across all catchments, while NO_3 load has its own seasonality in the catchments with the largest agriculture extent, especially in the first part of the year.

Anthropic activities do not only influence the average solute concentrations and the seasonality, but also the long-term dynamics. Na^+ and Cl^- show clear positive trend in time (Table S1a), largely because of the increasing application of deicing salt (NaCl) [*Gianini et al.*, 2012**;** *Novotny et al.*, 2008; *Zobrist and Reichert*, 2006]. A clue of the cause-effect relation between deicing salt application and increased Na^+ and Cl^- concentrations in stream water comes from stoichiometry. The molar ratio between Na^+ and Cl^- in salt is 1:1, therefore, the closer to 1 is the ratio computed on observed in-stream concentrations, the more likely deicing salt may be the driver. Figure S3 shows the boxplot of the Na:Cl molar ratio across catchments and it is clear that catchments with higher population density show values closer to one. However, the Erlenbach (ER) and Lümpenenbach (LU) catchments, which do not show any increasing long-term trend neither in Na^+ nor in Cl^- concentrations, show, consistently with catchments with the lowest inhabitants density (i.e., Rhône (PO), Rhine (DI) and Inn (SA)), Na:Cl values higher than one. In this respect, *Müller and Gächter* (2011) analyzed the phenomenon of increasing Cl^- concentrations in Lake Geneva basing their analysis on the NADUF data at the Rhine-Diepoldsau (DI) station. The concentrations detected by the water quality monitoring station are much lower than the amount of the input of salt declared by the cantonal authorities and the increasing trend characterizes the whole year and not only the winter months. These two factors suggest that an accumulation effect with a long-memory in the system might exist. The salt

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could be stored somewhere in the soil or in the groundwater and could be progressively delivered to the streams over years. However, this is difficult to assert conclusively since the dependence of observed trends on the salt input is uncertain because of the input uncertainty. Indeed, estimating the input of salt used for deicing purposes is not trivial, due to the lack of reliable data [*Müller and Gächter*, 2011]. Official sources [*EAWAG*, 2011] state that improved technologies have enabled a sensible decrease of the specific amount of spread salt (from 40 g/m^2 in 1960s to 10-15 g/m^2 of today), but the total amount of salt still shows increasing trend, because it is spread more often and on wider surfaces.

Phosphorus species, instead, decreased consistently since 1986, when the phosphate ban was introduced in Switzerland [*Jakob et al.*, 2002; *Rodriguez-Murillo et al.*, 2014; *Prasuhn and Sieber*, 2005; *Zobrist and Reichert*, 2006; *Zobrist*, 2010]. From 1986, an evident decrease in TP concentrations can be observed, especially in the catchments with higher anthropogenic pressures (Figure S4). This pattern highlights the positive cause-effect relation between the applied phosphorus management policies and the in-stream phosphorus concentration reduction.

A non-monotonic trend emerged from the analysis for Mg^{2+}, K^+, TN and TOC. This might reflect secondary effects of anthropogenic nature. In the case of K^+ and Mg^{2+}, such trend could be "*coming from soils brought in by applied fertilizers containing* Mg^{2+} *as a minor ingredient*" [*Zobrist*, 2010]. In this respect, the analysis of monthly trends gives further information about possible drivers of the dynamics of solutes (Table S1b). Mg^{2+} might be indeed related to the application of fertilizer, as suggested by Zobrist (2010), because agricultural catchments show more evident increasing trends than non-agricultural catchments. For K^+ the difference across the gradient of agricultural pressure is not as remarkable as for Mg^{2+}. Monthly trends of TN and DOC revealed increasing tendency in the first months of the year (January-April) and decreasing ones in the last part of the year (August-December), thus suggesting that they are induced either by streamflow trends (*Birsan et al*., 2005) or by biogeochemical processes, which have a pronounced seasonality related to temperature and moisture controls rather than to human activities.

5.2 Influence of catchment characteristics on magnitude and trends of solute concentrations

Although the signature of human activities on solute concentrations in rivers is more evident than the influence of catchment characteristics, the latter still play a role for certain solutes. Concentration magnitudes are rather uniform across catchments and only a few tangible effects of catchment characteristics emerge from the analysis. First, the geological composition of the bedrock influences considerably the weathering products, increasing Ca^{2+} concentrations in mostly calcareous catchments (northern and central Switzerland) and of H_4SiO_4 in silicic catchments (Alpine catchments in southern Switzerland). The influence of lithology was identified before in literature, with, for instance, high Ca^{2+} concentrations in one of the tributaries of the Amazon River attributed to the presence of carbonate-richer lithology in the corresponding catchment (*Baronas et al.*, 2017; *Rue et al.*, 2017; *Torres et al.*, 2017).

The seasonality analysis suggests, moreover, that also topography plays a role. In the Alpine catchments, discharge seasonality generally dominates the seasonality of solute concentrations, except for TP, which is related to erosion and the presence of suspended sediments in the stream flow [*Haggard and Sharpley*, 2007]. Being erosion in Alpine catchments higher than in catchments characterized by less pronounced topography, the presence of suspended sediments and TP is enhanced. Furthermore, eroded soil, which partially becomes suspended sediments in stream water, represents a source also for DOC and TOC [*Schlesinger and Melack*, 1981]. TP, DOC and TOC together with Mg^{2+} have been classified as solutes belonging to "B" class, i.e. their concentration patterns show higher variability in Alpine catchments than across other morphologies. The driver of Mg^{2+} variability is, however, less clear than for the others. The higher variability of its concentrations in Alpine catchments in comparison to other catchments might be due to the presence of glaciers. Mg^{2+} concentrations are significantly higher during low-flow periods than during high-flow periods, and this is consistent with the observations of *Ward et al.* (1998), who explained that the increased concentration is a sign of the shift from an icemelt-dominated system in summer to a groundwater-dominated system in autumn and winter with larger Mg^{2+} concentrations. Another possible explanation might be the incongruent dissolution of bedrock [*Kober et al.*, 2007], which is likely to take place also in presence of carbonate-poor glacial sediments [*McGillen and Fairchild*, 2005]. Carbonate rocks might dissolve with preferential release of Mg^{2+}, which therefore contributes strongly to solute fluxes in rivers. This phenomenon has been observed also in the Swiss Alps (Haut Glacier d'Arolla), where carbonate contents of sediments are of the order of 1% [*Brown et al.*, 1996**;** *Fairchild et al.*, 1999], but their contribution to solute fluxes is much higher [*McGillen and Fairchild*, 2005].

Catchment size or precipitation might also influence river solute concentrations. This is evident from the behavior of the Lümpenenbach (LU) and Erlenbach (ER) catchments, which are at least three orders of magnitude smaller than the other catchments considered in the study and show median concentrations lower than those of the other catchments. This is true for all solutes, except DOC and TOC, the concentrations of which are the highest in Erlenbach (ER) and Lümpenenbach (LU) rivers. These catchments are situated in Alptal valley, which is characterized by more humid climate (double annual precipitation), compared to other catchments. This leads to higher soil moisture conditions and baseflow, which are likely driving lower geogenic solute concentration and higher organic carbon concentrations in stream water [*Evans et al.*, 2005, *von Freyberg et al.*, 2017b], thus offering a possible explanation for the higher concentration of DOC and TOC.

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5.3 Consistency of solute behaviors across catchments.

This study showed that concentration-discharge relations reveal nearly chemostatic behavior for most of the considered solutes across catchments, i.e. analyzed solute concentrations vary a few order of magnitude less than discharge (Figure S5). This outcome agrees with other studies (e.g., *Godsey et al.*, 2009; *Kim et al.*, 2017; *McIntosh et al.*, 2017). However, we are aware of the fact that the presence of lakes within the domain of the selected catchments (Table 1) might contribute to the dampening of the chemical signal of rivers. Indeed, lakes represent discontinuities in the river network, so that the fraction of the stream network and catchment area effectively contributing to the observed solute dynamics is limited to the contributing area from the lake to the gauging station, and therefore smaller than the entire basin area. Aware of the influence of this factor to our results, we found that the in-stream biogeochemical signal is highly dampened, coherently with other studies [*Kirchner et al.*, 2000; *Kirchner and Neal*, 2013], but different solute behaviors could be nonetheless detected in the log(C)-log(Q) space, thus allowing a partition of possible behaviors into four categories, as suggested by *Moatar et al.* (2017). A representation of such positions is offered in Figure 10, where the space between the negative-slope line and the near-horizontal line represents the dilution behavior, and the space delimited by the positive-slope line and the near-horizontal line represents the enrichment behavior. Enrichment for low-flow conditions (i.e. $q<q_{50}$) is typically associated with biogeochemical processes of solute retention or removal, while for high-flow conditions (i.e. $q>q_{50}$) it is generally associated with the capacity of the flow to entrain particles containing the solute, thus leading to the so-called “hydrological export”. In search for generalizations, we assigned a solute to each specific class if the same behavior was observed in at least 60% of the analyzed catchments. Geogenic solutes are grouped in a single circle since almost all of them show a dilution behavior. Only H_4SiO_4 does not show a clear dilution signal, probably because it is a bioactive compound and, therefore, it is involved in complex dynamics related to biological processes [*Tubaña and Heckman*, 2015]. The diluting behavior of geogenic solutes is a quite well consolidated fact in the literature [*Godsey et al.*, 2009; *Thompson et al.*, 2011; *Baronas et al.*, 2017; *Hunsaker and Johnson*, 2017; *Kim et al.*, 2017; *Moatar et al.*, 2017; *Winnick et al.*, 2017; *Wymore et al.*, 2017] and this study contributes to this body of knowledge confirming this behavior. Only recently, *Hoagland et al.* (2017), observed enrichment for Ca^{2+} and Na^{2+} in Shaver’s Creek watershed (central Pennsylvania), but this is described as an anomaly, probably due to the contribution of spring water rich in these elements, and to the additional inputs from stocks of Ca^{2+} laying in the hyporheic zone, which actively contribute during high-flows. Therefore, there is quite high confidence in claiming that geogenic solutes are characterized by a dilution behavior.

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The Cl^- solute is also clearly characterized by dilution and our results are in agreement with other studies [*Thompson et al.*, 2011; *Hoagland et al.*, 2017; *Hunsaker and Johnson*, 2017].

NO_3 relations with discharge are less clear [*Aguilera and Melack*, 2018; *Butturini et al.*, 2008; *Hunsaker and Johnson*, 2017], but this study highlighted a dilution behavior also for NO_3 in the majority of catchments for both low-flow and high-flow conditions. This result partially agrees with the observations of *Wymore et al.* (2017), who claimed that NO_3 shows variable responses to increasing discharge. In fact, we observed that while dilution is evident in 80% of the catchments for low-flow conditions, this percentage drops to 63% for high-flow conditions. Although NO_3 is one of the main components of TN (Figure S1), TN does not show the same behavior. For low-flows, TN is also characterized by dilution, but for high flows TN shows chemostatic behavior in about 70% of catchments.

The behavior of phosphorus and its compounds is neither clear. For low-flows, DRP behaves chemostatically in about 40% of catchments, but dilutes in about 60% of catchments. TP behavior could not be classified due to its heterogeneity across catchments for low-flows, whereas, for high-flows, it clearly shows hydrological export in 90% of catchments, as a result of increased suspended sediments concentration. In-stream sediments can be, however, both source and sink for phosphorus [*Haggard and Sharpley*, 2007], as high suspended sediment concentrations in rivers favor the sorption of phosphorus to particles thus lowering DRP concentrations [*Zobrist et al.*, 2010]. For high-flow conditions, we observed various DRP behaviors across catchments (about 45% of dilution, 45% chemostatic and 10% enrichment), so that a clear behavior classification is not possible. The weak correlation between DRP and suspended sediments concentration suggests that the sorption of phosphorus to particles is not the only and most influencing factor of DRP dynamic.

TOC is the only solute characterized by enrichment in both low-flow and high-flow conditions. DOC was proved by a set of studies to exhibit an enrichment behavior (e.g., *Boyer et al.*, 1996; *Boyer et al.*, 1997; *Butturini et al.*, 2008; *Hornberger et al.*, 1994; *McGlynn and McDonnell*, 2003; *Perdrial et al.*, 2014; *Wymore et al.* (2017)), but our results are in this respect highly uncertain for low-flows and suggest a chemostatic behavior for high-flows. *Wymore et al.* (2017), for instance, analyzed the biogeochemical response in the Luquillo catchment in Puerto Rico and detected an enrichment behavior. This catchment is mainly covered by the tropical forest, where net primary production is higher than in Swiss catchments. The occurrence of abundant net primary production and wet conditions due to tropical climatic forcing is the likely reason leading to higher DOC concentration with increasing streamflow. The underlying mechanism could be that of a larger share of streamflow coming in wet conditions from shallower soil pathways [*von Freyberg et al.*, 2017b], which are generally organic-richer than the deeper horizons hosting lower DOC quantities [*Evans et al.*, 2005]. Our study seems to confirm this hypothesis, as the wettest catchments analyzed in this study (Erlenbach (ER) and Lümpenenbach (LU)) show enrichment of DOC for low-flows. These are likely mainly dominated by sub-surface flow, thus confirming the impact of soil wetness in the unsaturated zone on DOC behavior for catchments where natural conditions dominate.

The results of this study also showed that the variability of solute magnitude in the long-term can play a role in the definition of a solute behavior. Na^+ and Cl^- show dilution during the entire monitoring period, despite the increasing concentrations through time. DRP and TP switch from highly negative b exponent of the C-Q power-law relation to even positive b, after the time when the measures to reduce the phosphate input were introduced (Figure 9). Such measures [*Zobrist and Reichert*, 2006] lead to a conspicuous decrease of DRP concentration and partially also of TP. Therefore, the fraction of DRP in TP decreased in time (Figure S6) and the other TP components became more important than DRP in the definition of TP behavior. Among these, the component carried with sediments might be responsible for the switch, which took place in all the analyzed catchments, from dilution to enrichment across the last four decades. DRP also shows increasing trend of the b exponent of the C-Q relations across decades, but only in one catchment the behavior switches from dilution to enrichment. This means that when DRP inputs were higher, the transport was not source limited, while decreasing the input forced DRP to have a more chemostatic behavior, probably because the input became so low that the phosphorus transport is likely controlled by a legacy of phosphorus storage in the soil, which was accumulated during the years of undisciplined agricultural practices [*Sharpley et al.*, 2013; *Powers et al.*, 2016; *van Meter et al.*, 2016a].

6 Conclusion

The long-term water quality data analysis of this study was designed for understanding the influence of catchment characteristics and of anthropic activities on solutes concentrations observed in Swiss rivers. The analysis of magnitude, seasonality, and temporal trends revealed clear cause-effect relation between human activities and solute concentrations, while the influence of catchment characteristics is much less evident. Although the solute export is the result of multiple complex processes, catchment topography, geology and size are expected to have a role in determining solute concentrations, especially of weathering solutes and sediment-binding substances (i.e., TP, TOC and DOC). However, these influences are mostly undetectable in our analysis, probably because of the small sample of catchments. Few exceptions are the macro-pattern in the Ca^{2+} and H_4SiO_4 concentrations and the DOC response in small wet catchments.

The analysis of the empirical C-Q power-laws was used to investigate and possibly obtain a general classification of solute behaviors. The variability of solute concentration is generally much smaller than that of streamflow,

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which, in first instance, would support a chemostatic behavior. However, when C-Q relations are partitioned between high and low-flows and are analyzed for significant trends, the overall dominant behavior across solutes and catchments is dilution. For many solutes, this result is consistent with other studies (i.e., geogenic solutes and Cl^-). Sediment-binding substances (TP, DOC and TOC) show, however, a clear enrichment during high-flow events, while for other solutes it is not possible to define a clear behavior (e.g., DRP).

Finally, we observed that anthropic activities affect not only the magnitude of concentrations of solutes in rivers, but also their seasonality and long-term dynamics. Remarkable variation in long-term dynamics, moreover, might also determine changes of solutes behavior in time, as we demonstrated for DRP and TP. This and the above results reinforce and extend the current knowledge, demonstrating that quantitative observations allow not only to identify the effects of anthropic activities on the solute inputs into rivers, but also to characterize the biogeochemical responses of rivers.

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List of tables

Table 1: Description of the catchments included in the NADUF database. The selected catchments are characterized by different size, altitude and average yearly precipitation. Four catchments are entirely Alpine (ER, PO, DI, SA), while the others encompass different morphologies (mainly Swiss Plateau and pre-Alpine zone). A south-north gradient of intensive agriculture and inhabitants density exist, as the colors blue and orange highlight.

Catchment	ID	Area (10^3 m^2)	Mean altitude (m a.s.l.)	Mean rainfall (mm/y)	Mean discharge (m^3/s)	Lake area (%)	Morphology			Agriculture		Inhabitants density (inhab*km^{-2})
							Swiss Plateau (%)	Alps (%)	Other (%)	Intensive (%)	Extensive (%)	
Thur – Andelfingen	AN	1.7	770	1'429	47.3	0.1	50	23	20	51.9	10.6	222.9
Aare – Brugg	BR	11.73	1'010	1'352	315	3.6	38	23	30	35.8	17.7	181.1
Rhein – Village Neuf/Weil	VW	36.47	1'100	1'353	1'057	3.6	30	43	11	31.5	20.6	207.5
Rhein - Rekingen	RE	14.72	1'260	1'262	442	3.9	27	60	-	30.1	24.9	188.1
Aare – Hagneck	HA	5.1	1'370	1'506	179	2.1	25	52	23	23.9	29.2	147.3
Lümpenenbach – Alpthal	LU	0.94 *10^{-3}	1'300	2'127	0.067	0	-	100	-	21.3	55.8	0
Rhône – Chancy	CH	10.32	1'580	1'335	341	5.8	-	77	10	14.4	23.9	167.9
Rhein - Diepoldsau	DI	6.12	1'800	1'319	256	0.4	-	100	-	8	46.9	54.9
Rhône - Porte du Scex	PO	5.24	2'130	1'372	183	0.4	-	100	-	6.1	31.7	58.5
Inn - S Chanf	SA	0.62	2'466	1'063	20.3	1.6	-	100	-	3.3	43	27.5
Erlenbach – Alpthal	ER	0.76 *10^{-3}	1'300	2'182	0.04	0	-	100	-	2.9	52.5	0

>30 %	>100
10÷30 %	50÷100
<10%	<50

Table 2: Results of the C-Q relations analysis. The symbols ″+″,″–″ and ″=″ refer to the possible behavior combinations described in Figure 2, while the numbers indicate how many catchments exhibit a specific behavior for each solute. The solutes are classified as reported in the first column.

Solute class	**Solute**	**Behavior**								
		+/+	+/=	+/-	=/+	=/=	=/-	-/+	-/=	-/-
Geogenic solutes	Ca^{2+}	0	0	0	0	1	1	0	1	8
	Mg^{2+}	0	0	0	0	0	0	0	0	11
	Na^+	0	0	0	0	0	0	0	0	11
	H_4SiO_4	1	1	0	1	1	2	0	0	5
	K^+	0	0	0	0	0	0	0	0	11
Deposition derived	Cl^-	0	0	0	0	0	0	0	1	10
Nitrogen species	NO_3	0	0	0	0	2	0	0	2	7
	TN	0	1	0	0	2	0	0	5	3
Phosphorus species	DRP	0	0	0	1	2	1	0	3	4
	TP	2	1	0	5	0	0	3	0	0
Organic Carbon species	DOC	0	3	0	1	5	0	0	0	2
	TOC	6	1	0	4	0	0	0	0	0
	Total (%)	6.8	5.3	0	9.1	9.8	3.0	2.3	9.1	54.5

Figures

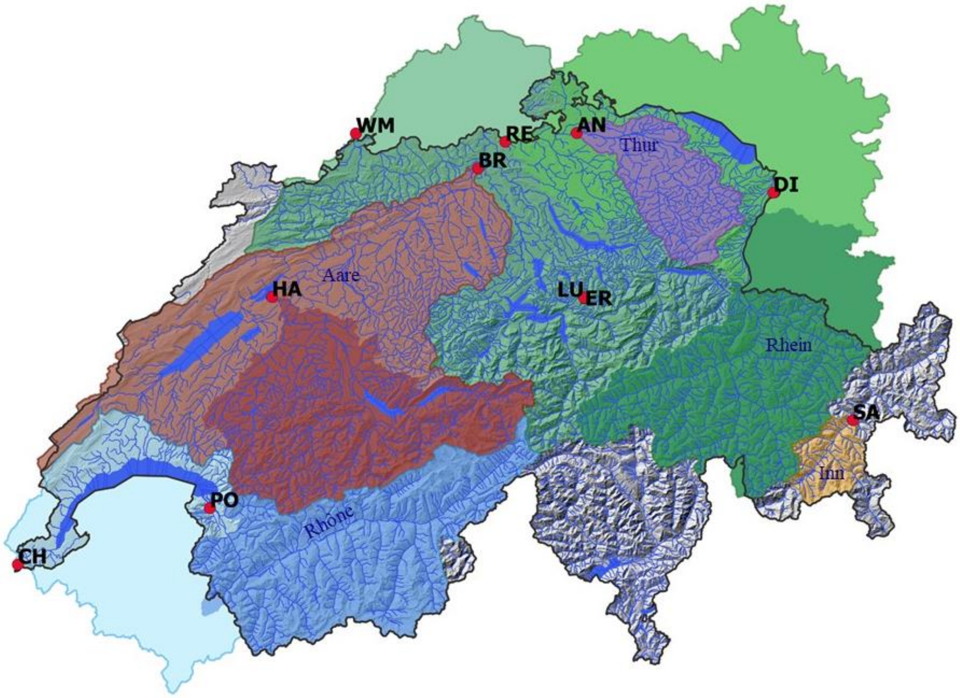

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Figure 1: Map of NADUF monitoring stations. Catchments and sub-catchments that refer to the same river are represented in different hues of the same color (blue, red and green).

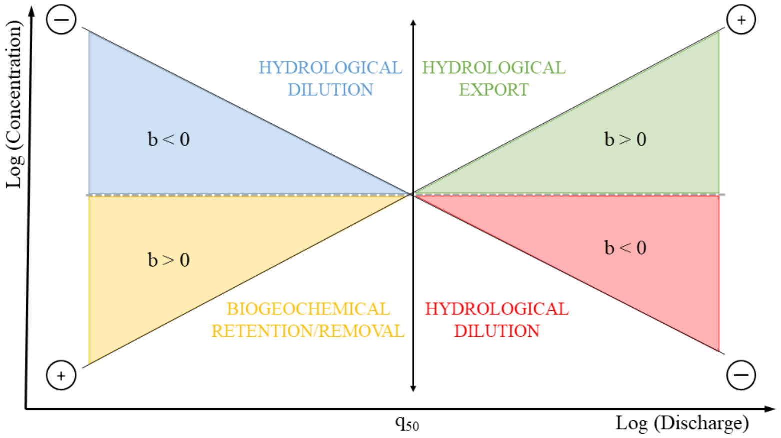

Figure 2: Conceptual representation in the log(C)-log(Q) space of possible solute behaviors. The definitions are derived from the classification of *Moatar et al.*, 2017.

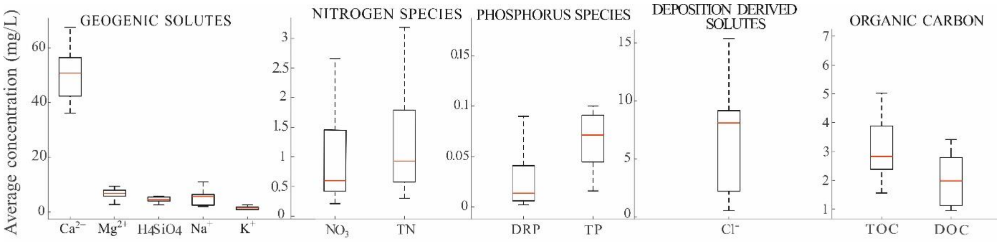

Figure 3: Boxplot of solutes magnitude. The statistics refer to the average concentrations across all the analyzed catchments.

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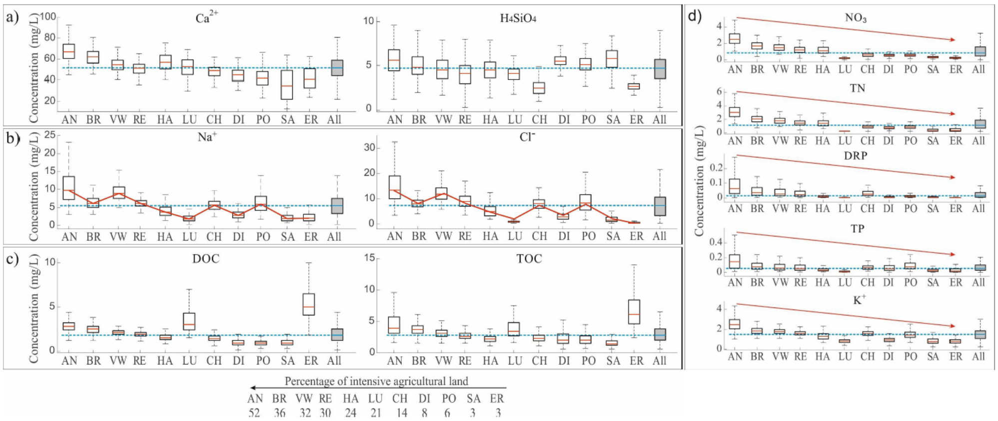

Figure 4: Boxplot of measured concentrations across catchments. The grey box on the right of each subplot refers to the concentrations computed from all the observations of all the catchments. The light blue horizontal line represents the median of all the measurements across all the catchments. Panel a) shows the effect of bedrock geological composition on Ca^{2+} and H_4SiO_4 concentrations. Panel b) shows the pattern of Na^+ and Cl^- concentrations across catchments. Panel c) shows the DOC and TOC concentrations. Panel d) shows the decreasing trend of nutrients median concentrations. The catchments are ordered by increasing percentage of land used for intensive agriculture, as shown in the bottom table.

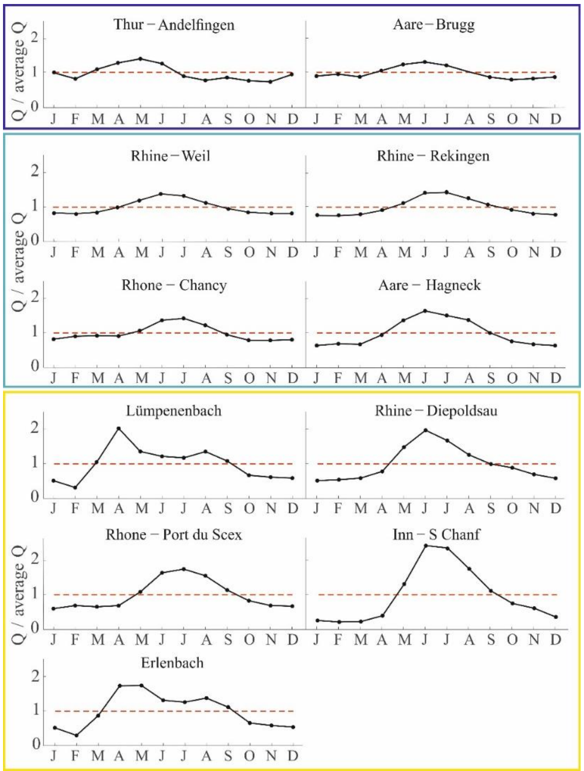

Figure 5: Discharge seasonality. Each point represents the monthly average discharge, while the red dashed line is the average discharge over the entire monitoring period. Blue upper box: Swiss Plateau catchments. Light blue middle box: hybrid catchments. Yellow bottom box: Alpine catchments.

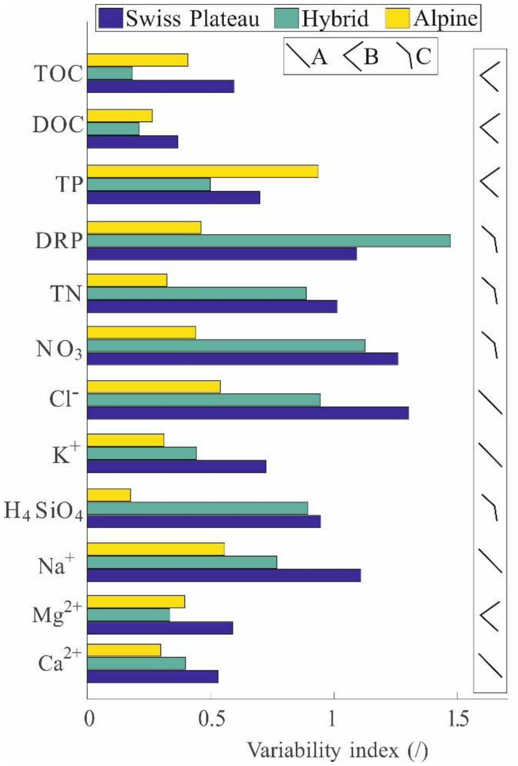

Figure 6: Bar plot of the index of variability. Each bar represents the monthly variability of average concentration relatively to discharge variability per catchment. The colors of the bars differentiate catchment morphologies: blue for Swiss Plateau, aqua-green for hybrid and yellow for Alpine catchments. The A, B and C represent the observable patterns of the variability index across the three morphologies (Section 3.2).

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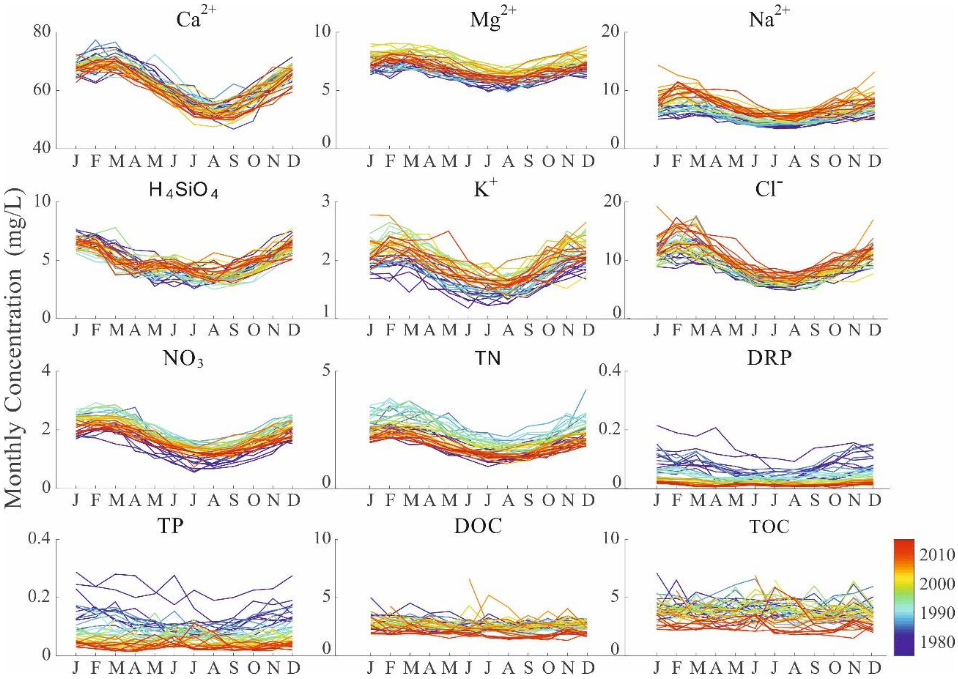

***Figure 7*:** Long-term solutes trends. Each line represents the monthly average concentration of each solute. The color bar indicates the years of the monitoring period, from the first year (blue) to the last year (red). The presented figure refers to the Rhine catchment at the monitoring section of Rekingen.

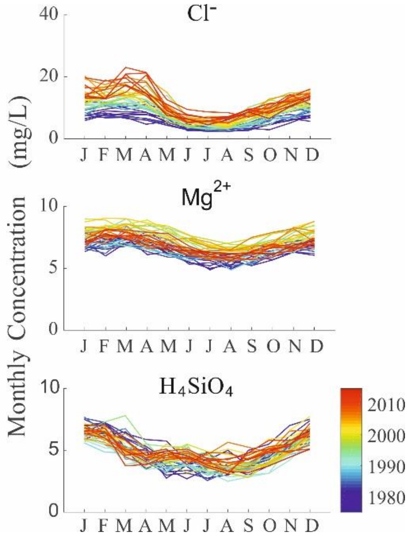

Figure 8: Three exemplary long-term patterns of solute concentrations. The upper box represent a clear increasing trend, the middle box a non-monotonic trend (firstly increasing and then decreasing), while the bottom box shows the absence of any trend.

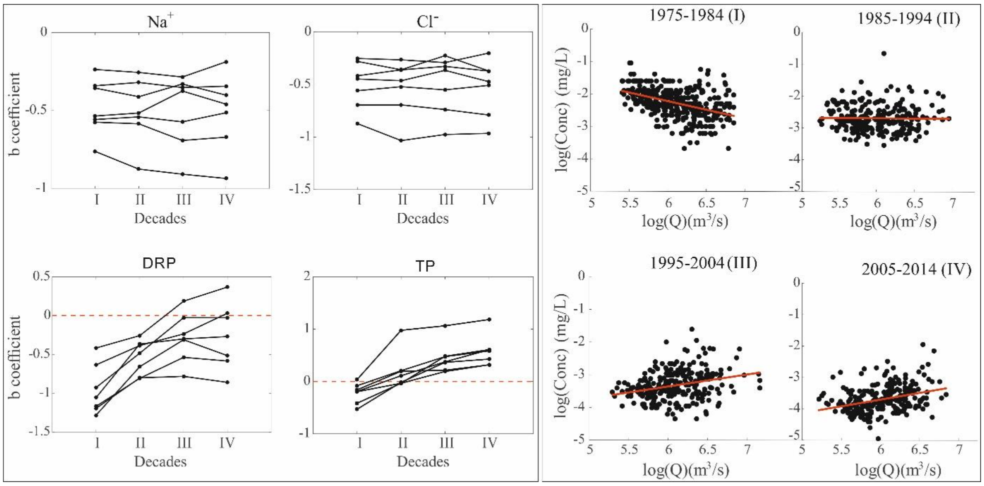

Figure 9: Analysis of b exponent variation in time. The left plots represent the values of b exponent of the C-Q empirical relation ($C = aQ^b$) across four decades, from 1975 to 2015 across all the catchments with monitoring period longer than 30 years. The dashed red line represents the zero threshold (i.e. chemostatic behavior). The right plots are an example of the C-Q relation across the four decades for TP in the Rhine-Rekingen catchment.

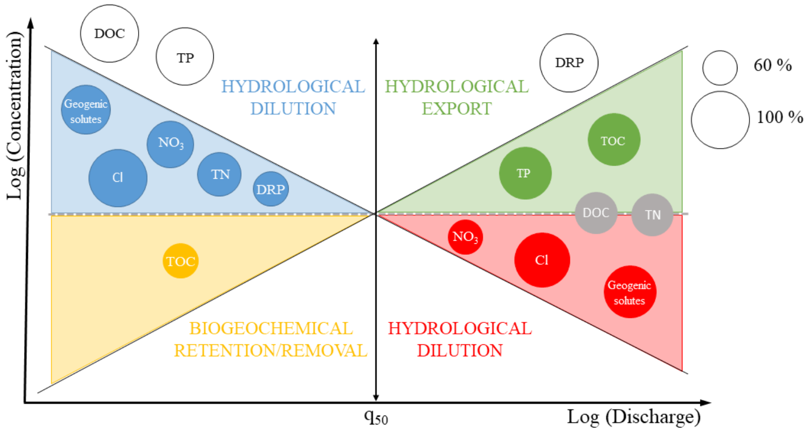

Figure 10: Solute behaviors classification in the log(C)-log(Q) space. Discharge time series is divided in low-flow and high-flow events (q_{50} = median daily discharge). Blue and red areas represent hydrological dilution behavior, while yellow area biogeochemical retention or removal and green space is representative of a hydrological export behavior. The colorless solutes outside these areas do not show any dominant behavior. The dimension of circles represents the percentage of catchments in which the dominant behavior is observed (60-100%).