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

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17 **Abstract**

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

24 While the anthropogenic impacts are clearly detectable in the concentration of certain solutes (i.e., Na⁺, Cl⁻, NO₃,
25 DRP), the influence of single catchment characteristics as geology (e.g., on Ca²⁺ and H₄SiO₄), topography (e.g.,
26 on DOC, TOC and TP), and size (e.g., on DOC and TOC) is only sometimes visible, also because of the limited
27 sample size and the spatial heterogeneity within catchments. Solute variability in time is generally smaller than
28 discharge variability and the most significant trends in time are due to temporal variations of anthropogenic rather
29 than natural forcing. The majority of solutes shows dilution with increasing discharge, especially geogenic species,
30 while sediment-bonded solutes (e.g. Total Phosphorous and Organic Carbon species) show higher concentrations
31 with increasing discharge. Both natural and anthropogenic factors affect the biogeochemical response of streams
32 and, while the majority of solutes show identifiable behaviors in individual catchments, only a minority of
33 behaviors can be generalized across the 11 catchments that exhibit different natural, climatic, and anthropogenic
34 features.

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

36

37 1. Introduction

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

52 The relationship between observed in-stream solute concentrations and discharge has been explored in various
53 catchments and with different methods in the last decades [Langbein and Dawdy, 1964; Johnson *et al.*, 1969; Hall,
54 1970; Hall, 1971; White and Blum, 1995; Evans and Davies, 1998; Calmels *et al.*, 2011]. One emerging postulate
55 is that concentration (C)-discharge (Q) relations represent the quantitative expression of the interaction between
56 catchment geomorphology, land use, hydrological processes and the solute releases, thus reflecting in lumped form
57 the complex mixing process taking place along flow paths of variable lengths and residence time [Chorover *et al.*,
58 2017]. Therefore, C - Q relations have been studied with reference to hydrological variables, e.g., hydrologic
59 connectivity and residence time [Herndon *et al.*, 2015; Baronas *et al.*, 2017; Duncan *et al.*, 2017a; Gwenzi *et al.*,
60 2017; Torres *et al.*, 2017], biological processes [Duncan *et al.*, 2017a], catchment characteristics, e.g., catchment
61 topography, land use, catchment size, and lithological properties [Musolff *et al.*, 2015; Baronas *et al.*, 2017;
62 Diamond and Cohen, 2017; Hunsaker and Johnson, 2017; Moatar *et al.*, 2017; Wymore *et al.*, 2017], as well as
63 anthropic activities [Basu *et al.*, 2010; Thompson *et al.*, 2011; Musolff *et al.*, 2015; Baronas *et al.*, 2017].

64 In a $\log(C)$ - $\log(Q)$ space, C - Q relations have been observed to be usually linear [Godsey *et al.*, 2009], so that the
65 empirical relations can be well approximated by a power-law, $C = a \cdot Q^b$, where a and b are fitting parameters
66 [Godsey *et al.*, 2009; Basu *et al.*, 2010; Thompson *et al.*, 2011; Moquet *et al.*, 2015; Moatar *et al.*, 2017; Musolff
67 *et al.*, 2017]. A very common metric, relevant also for this study, is based on the value of the b exponent, the slope

68 of the regression in the $\log(C)$ - $\log(Q)$ plot, because it is related to the concept of “chemostasis” [Godsey *et al.*,
69 2009] or “biogeochemical stationarity” [Basu *et al.*, 2010]. A catchment shows “chemostatic” behavior when
70 despite a sensible variation in discharge, solute concentrations show a negligible variability, i.e., $b \cong 0$. Conversely,
71 positive slopes (i.e., increasing concentrations with increasing discharge) would support an enrichment behavior
72 when the solute amount grows with discharge and negative slopes (i.e., decreasing concentrations with increasing
73 discharge) support a dilution behavior with solute mass that does not increase proportionally to the growing
74 discharge. A solute is typically defined transport-limited if it is characterized by enrichment, while it is called
75 source-limited in case it dilutes [Duncan *et al.*, 2017a].

76 The exact mechanisms leading to C - Q relations are, to a large extent, an open question, but these relations are
77 anyway providing insights on solute and/or catchment behavior [Godsey *et al.*, 2009; Moatar *et al.*, 2017]. The
78 concept of chemostasis emerged in studies that explored the C - Q power-law with the aim of demonstrating the
79 similarities in the export behavior of nutrients [Basu *et al.*, 2010; Basu *et al.*, 2011] and geogenic solutes [Godsey
80 *et al.*, 2009] across a range of catchments [Musolff *et al.* 2015]. These studies were mostly carried out in
81 agricultural catchments, where a “legacy storage” was supposed to exist due to antecedent intensive fertilization
82 practices [Basu *et al.*, 2010; Basu *et al.*, 2011; Hamilton, 2012; Sharpley *et al.*, 2013; van Meter and Basu, 2015;
83 van Meter *et al.*, 2016a; van Meter *et al.*, 2016b]. This storage of nutrients might have long-memory effects and it
84 was considered to buffer the variability of concentrations in streams, leading to the emergence of biogeochemical
85 stationarity [Basu *et al.*, 2011]. However, biogeochemical stationarity has been questioned outside of agriculturally
86 impacted catchments [Thompson *et al.*, 2011] and a unifying theory explaining catchment-specific C - Q behavior
87 is not available yet, considering that solutes can show different behaviors in relation to landscape heterogeneity
88 [Herndon *et al.*, 2015] and to the spatial and temporal scales of measurement [Gwenzi *et al.*, 2017]. Therefore,
89 approaching the study of solute export and C - Q relations requires the separate analysis of several solutes in as
90 many catchments as possible with the aim to find, at least, some general behavior that can be characteristic of a
91 given region or solute. The recent literature is moving toward this direction [Herndon *et al.*, 2015; Wymore *et al.*,
92 2017] with the aim to sort out the relative influence of climatic forcing, solute properties, and catchment
93 characteristics on solute behavior in search for generalizations across different catchments.

94 This study contributes to this line of research investigating a unique dataset of long-term water quality data in
95 eleven catchments in Switzerland, where multiple solutes were observed at the bi-weekly scale for multiple
96 decades with limited gaps. We perform the analysis focusing mainly on the temporal domain and by quantifying
97 magnitude, temporal trends, and seasonality of the in-stream concentrations with the goal of highlighting the long-
98 term behavior differences across the eleven catchments and investigating the drivers of such differences.

99 Specifically, we focus on the following research objectives: (i) investigating to which extent the solute
100 concentrations are influenced by anthropic activities; (ii) exploring the dependence of solute concentrations on
101 catchment characteristics; (iii) generalizing, if possible, the behaviors of selected solutes across different
102 catchments by means of the slope in the $C-Q$ relations.

103 2. Study sites

104 Observations used in this study are obtained from the Swiss National River and Survey Program (NADUF¹), which
105 represents the Swiss long-term surface water quality monitoring program. This database includes in total 26
106 monitoring stations located in different catchments. To ensure representativity and robustness of the analysis we
107 focus only on those stations with at least 10 consecutive years of water quality measurements. This restricts the
108 database to eleven catchments, the corresponding locations of which are shown in Figure 1. The resulting case
109 studies include 5 main catchments (Thur - AN, Aare - BR, Rhine – WM, Rhone – PO and Inn - SA), 3 sub-
110 catchments (Rhone – PO, Rhine – RE and Rhine – DI) and 2 small headwater catchments (Erlenbach and
111 Lümpepenbach).

112 Measurements have a temporal resolution of 14 days, which is similar to the resolution of other studies that
113 analyzed long-term water quality data. In literature, the temporal resolution of water quality observations ranges
114 namely from weekly [Duncan *et al.*, 2017a; Duncan *et al.*, 2017b; Gwenzi *et al.*, 2017; Moatar *et al.*, 2017;
115 Wymore *et al.*, 2017] to 14-days [Hunsaker and Johnson, 2017] to monthly [Basu *et al.*, 2010; Thompson *et al.*,
116 2011; Musolff *et al.*, 2015; Mora *et al.*, 2016; Moatar *et al.*, 2017] or even coarser resolution [Godsey *et al.*, 2009].
117 In fact, only, very rarely higher-frequency databases are collected and thus analyzed (e.g., Neal *et al.*, 2012; Neal
118 *et al.*, 2013; von Freyberg *et al.*, 2017a).

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

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>

126 A 14-days sampling frequency is not sufficient for an evaluation of short-term biogeochemical and transport
127 processes, which might involve solute transformation (e.g., biological processes, in-stream chemical reactions).
128 These are simply accounted for in a lumped form in the flow-proportional average concentrations collected in a
129 two-week interval. Conversely, the dataset is especially suitable for the investigation of long-term trends, due to
130 the length of the time series, which spans from 11 to 42 years (Table 1). Data are collected following ISO/EN
131 conform methods for water analysis and subsequently validated by means of an extensive quality control as
132 described in *Zobrist et al.*, 2018. In addition, we inspected the data to take into account possible errors deriving
133 from fixed detection limits, e.g., deleting the values below the detection thresholds (See Paragraph S1).

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

142 The selected catchments cover most of the Swiss territory. This is characterized by dissimilarities in terms of
143 morphology, land use, and anthropic pressure, the latter being intended as activities (e.g. fertilization of agricultural
144 lands, domestic and industrial waste water treatments, industrial sewage disposal into water), which are expected
145 to have an impact on the river biogeochemistry and to alter the natural background concentrations and their
146 seasonality. Figure 1 shows the catchments analyzed in this study as identified by the ID reported in Table 1.
147 Catchments are divided into three categories depending on the morphological zone where they are mainly located:
148 the Swiss Plateau, a lowland region in the north, the mountainous Alpine area in the centre and south, and a third
149 category that includes catchments spanning both morphologic zones. The choice of this classification criterion is
150 discussed in the Section 3.1. Geology also differs from one region to another (Figure 1c). The bedrock of northern
151 Switzerland, the Jura region, is mainly composed of calcareous rocks, while in the Alpine area crystalline silicic
152 rocks are dominant (Figure 1c). The Swiss Plateau region is instead characterized by the ‘Molasse’ sedimentary
153 rocks (Figure 1c), consisting in conglomerates and sandstones of variable composition (e.g. detrital quartz,
154 feldspars, calcite, dolomite and gypsum) [*Kilchmann et al.*, 2004]. The relative chemical weathering of carbonate
155 rock and of gypsum are respectively 12 and 40 times higher than the weathering rate of granite or gneiss [*Meybeck*,
156 1987], thus suggesting that it is a good proxy to consider the Swiss Plateau area as characterized mainly by a

157 calcareous bedrock (e.g., *Zobrist et al.*, 2018). As the maps in Figure 1d and 1e show, the prevalent land use in the
158 Swiss Plateau area is agriculture, while the Alpine area is mainly covered by forests and grasslands. Table 1
159 specifies if the share of agricultural land is cultivated either intensively, i.e. with significant fertilizer applications,
160 or extensively, e.g. as alpine grasslands, bush land and parks, which are mostly unfertilized [*Zobrist et al.*, 2018].
161 The main urban centres are concentrated in the northern Switzerland, together with most of the industrial activities,
162 which represent potential point sources of pollution. The agricultural activities, especially intensive agriculture,
163 residential and industrial areas are referred in this study as “anthropic pressure”, indicating that the sources of
164 solutes originated from these activities are other than natural. Given the much higher presence of these
165 anthropogenic factors in the northern Switzerland, the anthropic pressure follows a south-north gradient, although
166 patches of anthropic pressure are found also within the alpine valleys.

167 **3. Methods**

168 **3.1 Magnitude, seasonality and trends**

169 The magnitude of a solute is evaluated through basic statistics (i.e., median, 25th and 75th percentiles, minimum
170 and maximum values). These are computed for each solute in each catchment, with the goal of highlighting
171 differences across catchments, which are the result of catchment heterogeneities and natural and anthropogenic
172 factors affecting the quantity of a given solute.

173 The seasonality of discharge and of solute concentrations is analyzed and cross-compared to highlight differences
174 and similarities of controls that are related to the climatic seasonality and seasonality of man-induced impacts. For
175 this analysis, catchments are subdivided in the three above mentioned categories: Swiss Plateau, Alpine, and hybrid
176 catchments (Figure 1). The Swiss Plateau and Alpine catchments have substantially different hydrological regimes
177 (Figure S1, upper and bottom panels), and represent the main classes of the clusterization proposed by *Weingartner*
178 *and Aschwanden* (1992). Some of the selected catchments with large draining area include both typologies and are
179 therefore defined as “hybrid catchments”. They are characterised by a seasonality, which is intermediate between
180 the two end-members (Figure S1, central panel) because the timing of the peak is similar to the one of Alpine
181 catchments, but the magnitude is less pronounced as in the Swiss Plateau catchments. For this reason, they have
182 to be treated separately from the other two classes. The hybrid catchments have the highest percentage of lake
183 surface area in their domains (Table 1), although non-negligible lake fractions are also found in the two other
184 categories. Large lakes represent a discontinuity in the river network, reducing the fraction of catchment area
185 directly (without major water mixing effects) contributing to the observed discharge and solute dynamics. The

186 presence of large lakes contributes to the dampening of the hydro-chemical signal, but its exact quantification is
 187 not straightforward. Aware of the confounding role of large lakes, we apply this classification in order to test if
 188 the seasonality of solutes is related to the seasonality of discharge. With such an analysis we aim at isolating the
 189 effect of the discharge seasonality versus the seasonality of solute concentrations. More specifically, whenever a
 190 solute shows a seasonality different from the one imposed by climate, we investigate the potential reasons for
 191 such a difference, being it either related to specific catchment characteristics or to anthropic activities.
 192 The comparison between the seasonality of solute and discharge is made through an “index of variability” defined
 193 as the ratio between the mean monthly deviations from the mean of solute concentration and discharge
 194 respectively, where the “deviation” is determined as the average difference between the monthly means and the
 195 annual average value, resulting in the following equation:

$$196 \quad \text{Index of variability} = \frac{\sum_n \left| \frac{\text{Normalised mean of monthly deviations of concentration}}{\text{Normalised mean of monthly deviations of discharge}} \right|}{n} = \frac{\frac{\sum_{i=1}^{12} C_{i-1}}{C}}{\frac{\sum_{i=1}^{12} Q_{i-1}}{Q}}}{n},$$

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

201 Finally, we evaluated the occurrence of trends in the long-term concentration time series at monthly and annual
 202 scale using the monthly average concentration of each solute in each catchment and each year for the entire period.
 203 The statistical significance of trends was tested with the Mann-Kendall test modified to account for the effect of
 204 autocorrelation [Hamed and Rao, 1998; Kendall, 1975; Mann, 1945], fixing a significance level of 0.05. Trends
 205 are investigated and compared across catchments, in order to understand if they are consistent across Switzerland,
 206 thus suggesting the presence of clear drivers underlying the trend, or if they are just occurring in a sub-set of
 207 catchments. The time series span different periods of time, so the results might be impacted by the natural
 208 variability of discharge over the different years. This might be a potential issue, but we observed that in case of
 209 the presence of a trend in discharge (e.g. in the CH catchment, not shown), the patterns of concentrations do not
 210 show any different behavior compared to those observed in other catchments, which our analysis attributes to other
 211 external forcing (e.g., anthropic activities).

212 **3.2 Concentration-Discharge relations**

213 The empirical relation between solute concentration and discharge $C = a \cdot Q^b$ was explored separately for each
 214 solute and for each catchment with the objective of investigating solute behaviors across catchments and whether

215 this behavior can be generalized. The two variables are expected to exhibit in a log-log scale a linear relation,
216 expressed by mean of the two regression parameters a , the intercept with the same dimensions of the concentration,
217 and b , the dimensionless exponent representing the slope of the interpolating line. We focus our attention on the
218 latter, which determines the behavior of the solute. The Student's t test was applied to verify the statistical
219 significance of having a b exponent different from zero. The level of significance α was set at 0.05. When the p
220 value was lower than α , the slope identifying the log-linear C - Q relation was considered significant and quantified
221 by b , otherwise the slope was considered indistinguishable from zero, thus suggesting no evidence of a dependence
222 of concentration on discharge.

223 In each catchment, the time series of discharge were divided into two subsets using the median daily discharge q_{50}
224 to separate flow below the median (low-flows) and flows above the median (high-flows). Hourly discharge time
225 series were available from the Swiss Federal Office for the Environment (FOEN) at the same river sections and
226 for the same period of the time series of water quality provided by the NADUF monitoring program. The median
227 daily discharge was computed from the hourly series, which were aggregated to obtain daily resolution.

228 Determining the C - Q relations separately for high and low-flows allows a finer classification of the solute behavior
229 into different categories [Moatar *et al.*, 2017], than considering only the dependence on the entire range of
230 discharge. The three main behaviors – “enrichment or removal” (i.e., positive slope), “chemostatic” (i.e., near-
231 zero slope) and “dilution” (i.e., negative slope) – can indeed be the result of mechanisms controlling the runoff
232 formation and the transport mechanism. Accordingly, we have in total 9 different combinations characterizing the
233 C - Q relation across high and low flow regimes, which allow assigning distinct behaviors to a given solute.

234 For solutes that showed long-term trends over the monitoring period, we also investigated the evolution of the b
235 exponent in time. In this case, the concentration and discharge time series were divided into decades and the C - Q
236 relations over all discharge values were computed separately for each decade. The behavioral classification is
237 performed on a single b (i.e., not divided into low- and high-flow b), since, differently from the previous analysis
238 of C - Q relations, the focus is on the detection of long-term trends in solute behavior rather than on the
239 understanding of the processes leading to differences between high and low flows.

240 **4. Results**

241 **4.1 Magnitude**

242 Among the geogenic solutes, Ca^{2+} is the most abundant, most likely due to the composition of the bedrock present
243 in most of the catchments (calcite, dolomite and anhydrite/gypsum [Rodriguez-Murillo *et al.*, 2014]). In absolute
244 terms, geogenic solutes and Cl^- have the highest concentrations (≈ 10 -50 mg/L), while phosphorus species

245 concentrations (≈ 0.01 - 0.1 mg/L) are on average one to two order of magnitude less abundant than nitrogen species
246 (≈ 0.5 - 1.5 mg/L) and organic carbon (≈ 1.5 - 5 mg/L).

247 Some solutes are constituents of other species, like in the case of nutrients NO_3 of TN and DRP of TP. NO_3 is
248 often introduced in catchments as inorganic fertilizer, as DRP, which represents a readily available nutrient for
249 crops. We computed the ratio between the solute and its component for the two couples (NO_3/TN , DRP/TP) and
250 observed their pattern across the catchments (Figure 2). We take as reference values the ratios in ER catchment,
251 since, due to limited anthropogenic pressure, it represents the background concentrations of nutrients [Zobrist,
252 2010]. Variations compared to ER values might provide an indication of the ratio of nutrients coming from
253 anthropic activities. NO_3 is the major constituent of TN, since it is about 85% of TN, while DRP contributes much
254 less to TP, being only its 35%. Both have a decreasing pattern with decreasing catchment anthropogenic
255 disturbances, although in DRP/TP this pattern is more evident. DRP/TP spans from a maximum of 65% in WM to
256 a minimum of 22% in ER, while NO_3/TN has a maximum of 93% in AN and it is 63% in ER.

257 Effects of catchment characteristics and human activities on the observed stream solute concentrations can be seen
258 for certain solutes as shown by Figure 3, where each box shows the measured concentrations in the 11 catchments
259 and the last box on the right refers to all the catchments grouped together. The catchments, expressed by the
260 corresponding acronym (see Table 1), are ordered, from left to right, from the most impacted by human activity -
261 i.e., higher percentage of catchment area used for intensive agriculture - to the least impacted, which is almost
262 equivalent to considering a south-to-north gradient. The most evident effect of catchment characteristics refers to
263 the presence of Ca^{2+} and H_4SiO_4 in the stream water (Figure 3a). Despite the lower solubility of silicic rocks
264 compared to the calcareous rocks, H_4SiO_4 concentrations in the southern Alpine catchments of Inn (SA), Rhine
265 (DI) and Rhone (PO) are significantly higher than the median value across catchments. The impact of human
266 activities, instead, is more evident in Na^+ and Cl^- concentrations. These are showing, basically, the same pattern
267 across catchments (Figure 3b), indicating that they are most likely influenced by the same driver, which is the
268 spreading of salt on roads during winter months for deicing purposes. We consider the spreading of deicing salt
269 an anthropic activity related to the presence of inhabitants in a catchment. DOC and TOC concentrations are very
270 high in Lümpebach (LU) and Erlenbach (ER) catchments (Figure 3c), which are the smallest catchments with
271 the highest average yearly precipitation rate and very low anthropic presence. Thur (AN) and Aare (BR)
272 catchments also show DOC and TOC concentrations higher than the average, but in these catchments the presence
273 of wastewater treatment plants can influence TOC concentrations. Finally, nutrients, such as nitrogen species and
274 phosphorus species, which are connected with anthropic activities (fertilization, wastewater treatment plants) show
275 a relatively clear decreasing median concentrations from the most to the least impacted catchment (Figure 3d).

276 Indeed, regressing median solute concentration with the percentage of intensive agricultural land and the
277 inhabitants density (Table S1a), gives a statistically significant dependence for some nutrients (i.e., NO₃, TN,
278 DRP). Because the catchments that are mostly impacted by agricultural activities are mainly located in the Swiss
279 Plateau, a significant positive correlation between nutrients and the percentage of Swiss Plateau area of the
280 catchment exists; conversely, we observe a significant negative correlation with the percentage of the Alpine area.
281 One should note, however, that the correlation is performed on 11 catchments only, so that lack of significance
282 should be interpreted with care. Indeed, if we extend the correlation analysis to the *b* exponent derived from the
283 *C-Q* relations analysis – thus implicitly accounting for the complex interactions between catchment
284 geomorphology, land use, hydrological processes and solute releases – with the same catchment characteristics
285 (e.g., *Moatar et al.*, 2017) the correlation becomes weaker and, basically, not significant for any solute (Table S1b
286 and Table S1c).

287 **4.2 Seasonality**

288 Different climates and catchment topographies determine various hydrological responses, as we can observe in
289 Figure S1 from the analysis of discharge seasonality across the eleven catchments, expressed through the monthly
290 average streamflow normalized by its long-term average. We present the results with the catchments divided in 3
291 groups as previously explained. The partition into these classes helps in highlighting the effects of topography,
292 climatic gradient and somehow also the impact of anthropic activities since it follows a similar south to north
293 gradient. The seasonality of streamflow in Swiss Plateau catchments is determined by a combination of
294 precipitation and snowmelt. The peak flow is typically observed in spring and is not much higher than the average
295 in the other months. Alpine catchments, instead, show stronger seasonality induced by snow and ice-melt in spring
296 and summer, which generates higher streamflows than in the other months. Hybrid catchments exhibit flow peaks
297 in June-August similarly to the Alpine ones, but the deviation from the average value is less pronounced.

298 The deviations of discharge and concentration are compared using the index of variability (Section 3.1) for each
299 morphological class of catchments (Figure 4). Only few solutes show a value of the index higher than 1. This
300 indicates that seasonality of solute concentrations is generally lower or much lower than the seasonality of
301 streamflow. This is especially true for the Alpine catchments, where the marked seasonality of streamflow seems
302 to dominate the variability of concentrations. For TP this index is higher than one in Alpine catchments, and also
303 the highest compared to the other two typologies. In Swiss Plateau and hybrid catchments, instead, only solutes
304 impacted by human activity (Na⁺, Cl⁻, nitrogen species and DRP) show a ratio close or even higher than 1.

305 DOC and TOC concentrations are characterized by low indexes of variability, especially in the hybrid catchments.
306 The patterns of the index of variability across different morphologies can be classified into three categories,

307 represented by the symbols A, B and C in Figure 4. The monotonic line in A type refers to those solutes, the
308 variability index of which changes across morphologies solely as a result of the seasonality of streamflow (Ca^{2+} ,
309 Na^{2+} , K^+ and Cl^-). Type B solute (Mg^{2+} , TP, DOC and TOC) response shows a higher variability index in Alpine
310 catchments compared to types A and C, thus indicating that, among the factors controlling the seasonality of
311 biogeochemical response, there are factors that are specific to the Alpine environment, which are discussed in
312 Section 5.2. The type C pattern, instead, refers to solutes related to fertilization (NO_3 , TN and DRP) and to H_4SiO_4 ,
313 which is a product of weathering and only minimally involved in biological processes. These solutes are
314 characterized by a much lower variability index in Alpine catchments than in hybrid and Swiss Plateau catchments.
315 Difference in their regime are further discussed in Section 4.

316 The analyzed solutes show different intra-annual dynamics. For instance, despite the quite pronounced streamflow
317 seasonality of the Rhine River at Rekingen (hybrid catchment used as a representative example), solute
318 concentration patterns shows different seasonal cycles (Figure S2). Ca^{2+} , Mg^{2+} , Na^+ , K^+ , Cl^- , NO_3 and TN
319 concentrations peak in February-March and have lower values during spring-summer period, showing a pattern
320 opposite to that of streamflow. H_4SiO_4 , instead, has a shifted seasonality compared to the other solutes, peaking in
321 December-January. Phosphorus species together with organic carbon species do not show any consistent
322 seasonality over the year.

323 4.3 Trends

324 Long-term trends in the concentration time series are investigated with respect to the seasonal cycle for each year
325 separately (Figure S2). One catchment (Rhine-Rekingen) is taken as an example for illustration purposes but
326 generality of trend results is discussed in the following.

327 Focusing on the long-term horizon, different dynamics can be observed across various solutes. Some of them show
328 visible trends: for instance Cl^- has increased from 1970s to 2015, while phosphorus species have decreased
329 considerably. Some solutes have different trends across different catchments. A generalization of long-term
330 patterns is shown in Figure 5 for the three main detected behaviors. The upper panel represents the occurrence of
331 an evident trend, either increasing (as in the example of Cl^-) or decreasing (e.g., TP). Na^+ , Cl^- , DRP and TP belong
332 to this category. While Na^+ , Cl^- have increased in time, DRP and TP have decreased in the monitoring period, as
333 the monthly trends in Table S1a show (see Figure 6 for DRP only).

334 The middle panel shows a non-monotonic trend. This is typical of Mg^{2+} , which first increased in most catchments
335 (1970s-1990s) and then decreased (1990s-2015). K^+ , TN and TOC also show this type of trend in most catchments.

336 Finally, the lower panel of Figure 5 shows a number of solutes (Ca^{2+} , H_4SiO_4 , NO_3 and DOC) that do not exhibit
337 any long-term trend, although analysis on a monthly base revealed some significant trends (Table S1c).

338 4.4 C-Q relations

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

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

348 Overall, dilution is dominant for all solutes in both low- and high-flow conditions, as it occurs respectively in 65%
349 and 57% of the catchments. Therefore, even in low-flow conditions, the solute transport is mainly source limited
350 across catchments. Only sediment-related solutes (i.e., TP, TOC), show a marked transport limited behavior. The
351 label “sediment-related solutes” comes from the fact that phosphorus and organic carbon are bonded to soil
352 particles and, when soil is eroded, carbon- and phosphorus-rich soil particles are mobilized by flowing water. In
353 such conditions, soil erosion becomes one of the main contributor to the phosphorus and organic carbon load into
354 the rivers. We investigated also C-Q relations for suspended sediment concentrations and they show increasing
355 slope across all the catchments, indicating, as expected, higher erosion rates in presence of high flow conditions.
356 Only 29% of the catchment-solute combinations have different behaviors between low- and high-flow conditions
357 and therefore the C-Q relations are represented by bended lines, having different slopes between low- and high-
358 flow conditions.

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

363 Since in the trend analysis we identified four species (Na^+ , Cl^- , DRP and TP) that are characterized by remarkable
364 long-term trends, we investigated if such a significant change in magnitude has an effect on the C-Q relation
365 analyzing the temporal changes of the b exponent. The changes in the value of b across all catchments with record

366 length longer than 30 years during different decades is shown in the left panel of Figure 8, whereas the right panel
367 of Figure 8 shows an example of variation of the TP C-Q relations across decades for the human-impacted
368 catchment of Aare – BR and the Alpine catchment of Rhone - PO. Although the observed concentrations of all
369 four solutes - Na^+ , Cl^- , DRP and TP - are characterized by the presence of evident trends in time, the behaviors in
370 the C-Q relation differ. Na^+ and Cl^- have a constant b exponent across decades, while phosphorous species show
371 increasing b, which, in some catchments, leads to a switch from a behavior of dilution to one of enrichment.

372 **5 Discussion**

373 **5.1 Influences of human activities on solute concentrations**

374 The cause-effect relation between the observed in-stream concentrations and the anthropic activities is sometimes
375 evident in the concentration magnitude, seasonality, and long-term trends. Phosphorus and nitrogen are the main
376 nutrients applied for agricultural fertilization and, a decreasing pattern of their magnitude from mostly intensive
377 agricultural catchments to forested catchments is observed (Figure 3d). Indeed, taking the concentrations of NO_3
378 and DRP registered at ER as reference background of natural concentrations [Zobrist, 2010], corresponding to
379 0.20 mg/L of NO_3 , 0.38 mg/L of TN, 0.002 mg/L of DRP and 0.02 mg/L of TP, the concentrations in all the other
380 catchments are significantly higher. For example, the most impacted AN catchment recorded median
381 concentrations of 2.50 mg/L of NO_3 , 3.03 mg/L of TN, 0.06 mg/L of DRP and 0.15 mg/L of TP. Following the
382 stoichiometric composition of plants, nitrogen species concentrations are one order of magnitude higher than
383 phosphorus species concentrations (Figure 3d). Nitrogen is the main nutrient required for crop growth [Addiscott,
384 2005; Bothe, 2007, Galloway *et al.*, 2004; Zhang, 2017] and indeed NO_3 is one of the main components of
385 fertilizers applied in agriculture. NO_3 represents a large fraction of TN (Figure 2). The variability of the ratio
386 between average NO_3 and TN concentrations across the different catchments, is comparable with that estimated
387 by Zobrist and Reichert (2006), who observed a variation from 55% in Alpine rivers to 90% for rivers in the Swiss
388 Plateau. Both NO_3 to TN and DRP to TP ratios show a decreasing trend from more to less anthropic-impacted
389 catchments, the range of variability being, however, higher for phosphorus species (from about 0.6 in Thur river
390 to about 0.2 in Inn River). The DRP/TP ratios across catchments can be explained as the result of the cumulative
391 effect of two main factors: the lower DRP input due to less intensive agricultural activity in the Alpine zone and
392 the higher share of phosphorus sourced by suspended sediments contributing to TP in Alpine catchments due to
393 generally higher erosion rates.

394 Anthropic activities affect also the seasonality of certain solutes. In Figure 4, we assigned the pattern “C” to those
395 solutes (i.e., H_4SiO_4 , NO_3 , TN and DRP) characterized by a much lower index of variability in Alpine catchments

396 than in hybrid and Swiss Plateau catchments. For those solute concentrations, variability in Swiss Plateau and
397 hybrid catchments are comparable or higher than streamflow variability, while in Alpine catchments streamflow
398 seasonality is much stronger than solute seasonality. A non-negligible fraction of these solutes is introduced
399 through agricultural practices or by means of other human activities. Their input is characterized by its own
400 seasonality, which influences the solute dynamics and makes it comparable or larger than the discharge seasonality,
401 a behavior non-observable for most geogenic solutes (Figure 4). An additional evidence supporting this result is
402 represented by the patterns of the average monthly discharge and solute load (computed as the product between
403 concentration and discharge) normalized by the respective average value. This representation is made for Ca^{2+} ,
404 originated by rocks weathering, and NO_3 , mainly of anthropic origin (Figures S3a and S3b). The plot, inspired by
405 the analysis of *Hari and Zobrist* (2003), shows how the seasonality of Ca^{2+} load follows well the seasonality of
406 discharge across all catchments, while NO_3 load has its own seasonality in the catchments with the largest
407 agriculture extent, especially in the first part of the year. Indeed, in the case of NO_3 , there is no correspondence
408 between the seasonality of discharge and load (e.g. the time of maximum discharge does not coincide with the
409 time of maximum or minimum load), thus suggesting that the input is characterized by an independent seasonality.
410 Anthropic activities do not only influence the average solute concentrations and the seasonality, but also the long-
411 term dynamics. Na^+ and Cl^- show clear positive trend in time (Table S1a), largely because of the increasing
412 application of deicing salt (NaCl) [*Gianini et al.*, 2012; *Novotny et al.*, 2008; *Zobrist and Reichert*, 2006]. A clue
413 of the cause-effect relation between deicing salt application and increased Na^+ and Cl^- concentrations in stream
414 water comes from stoichiometry. The molar ratio between Na^+ and Cl^- in salt is 1:1, therefore, the closer to 1 is
415 the ratio computed on observed in-stream concentrations, the more likely deicing salt may be the driver. Figure S4
416 shows the boxplot of the Na:Cl molar ratio across catchments and it is clear that catchments with higher population
417 density show values closer to one. However, the Erlenbach (ER) and Lümpepenbach (LU) catchments, which do
418 not show any increasing long-term trend neither in Na^+ nor in Cl^- concentrations, show Na:Cl values higher than
419 one, consistently with catchments with the low population density (i.e., Rhone (PO), Rhine (DI) and Inn (SA)). In
420 this respect, *Müller and Gächter* (2011) analyzed the phenomenon of increasing Cl^- concentrations in Lake Geneva
421 basing their analysis on the NADUF data at the Rhine-Diepoldsau (DI) station. The concentrations detected by the
422 water quality monitoring station are much lower than the amount of the input of salt declared by the cantonal
423 authorities and the increasing trend characterizes the whole year and not only the winter months. These two factors
424 suggest that an accumulation effect with a long-memory in the system might exist. The salt could be stored
425 somewhere in the soil or in the groundwater and could be progressively delivered to the streams over years.
426 However, this is difficult to assert conclusively since the salt input is uncertain. Indeed, estimating the input of salt

427 used for deicing purposes is not trivial, due to the lack of reliable data [Müller and Gächter, 2011]. Official sources
428 [EAWAG, 2011] state that improved technologies have enabled a sensible decrease of the specific amount of spread
429 salt (from 40 g/m² in 1960s to 10-15 g/m² of today), but the total amount of salt still shows increasing trend, likely
430 because it is spread more often and on wider surfaces. The recent study of Zobrist *et al.* (2018) uses as a proxy for
431 salt consumption the salt production by Swiss salt refineries, and claims an increase from 360 Gg NaCl year⁻¹ in
432 the 1980s to 560 Gg NaCl year⁻¹ to the present, thus supporting the observed positive trend.

433 A positive cause-effect relation between anthropic activity and solute concentration in terms of trend is also shown
434 for phosphorus species, which decreased consistently since 1986 (Figure 6), when the phosphate ban in laundry
435 detergents was introduced in Switzerland [Jakob *et al.*, 2002; Rodriguez-Murillo *et al.*, 2014; Prasuhn and Sieber,
436 2005; Zobrist and Reichert, 2006; Zobrist, 2010].

437 A non-monotonic trend emerged from the analysis of long-term data for Mg²⁺, K⁺, TN and TOC (Figure 5).
438 Considering for example Mg²⁺, Zobrist (2010) focuses the trend analysis over the period 1975-1996 on Alpine
439 catchments and observes a similar non-monotonic increasing-decreasing pattern. Zobrist (2010) attributes this
440 pattern to an increase of water temperature, which is evident for the Rhine and Rhone rivers. For Rhine and Rhone
441 rivers, our results support the conclusion of Zobrist (2010) because at the decreasing-increasing trend of Mg²⁺
442 corresponds a reverse increasing-decreasing trend in Ca²⁺. This is consistent with the temperature dependence in
443 calcite solubility. However, in the Thur catchment (AN and HA catchments) which is mainly agricultural, the non-
444 monotonic trend of Mg²⁺, does not correspond to a trend in Ca²⁺. Since Mg²⁺ can cumulate through fertilizer
445 applications and carbonates weathering (i.e., Mg²⁺ production) can be affected by N-fertilizers and manure
446 application [Hamilton *et al.*, 2007, Brunet *et al.*, 2011], we hypothesize that fertilizers might also have an impact
447 on the Mg²⁺ long-term dynamic. In this respect, the analysis of monthly trends of Mg²⁺ (Table S1b) shows a more
448 evident increasing trend for agricultural than for non-agricultural catchments. For K⁺ the difference across the
449 gradient of agricultural pressure is not as remarkable as for Mg²⁺. Monthly trends of TN and DOC revealed
450 increasing tendency in the first months of the year (January-April) and decreasing ones in the last part of the year
451 (August-December), thus suggesting that they are induced either by streamflow trends (Birsan *et al.*, 2005) or by
452 biogeochemical processes, which have a pronounced seasonality related to temperature and moisture controls
453 rather than to human activities.

454 In summary, the anthropogenic signature is clearly detectable in the water quality of catchments with an important
455 fraction of intensive agriculture and relatively high population density, especially in the magnitude of
456 concentrations of nutrients (i.e., nitrogen and phosphorous species), in the increasing long-term trends of Na⁺ and
457 Cl⁻ and, a positive outcome of environmental regulations, in the decreasing long-term trends of phosphorous

458 species. Moreover, the seasonality of nutrients differs considerably from the seasonality of naturally originated
459 solutes (e.g., geogenic solutes).

460 **5.2 Influence of catchment characteristics on magnitude and trends of solute concentrations**

461 A statistically robust link between catchment characteristics and river biogeochemical signatures is not
462 straightforward, because the spatial heterogeneity in river catchments and the limited sample size, make the search
463 for cause-effect relations between catchment characteristics and in-stream concentrations challenging. However,
464 catchment characteristics play a role for certain solutes and we found evidence of their impact especially in the
465 magnitude and seasonality of solute concentrations. First, the geological composition of the bedrock influences
466 the weathering products, increasing Ca^{2+} concentrations in mostly calcareous catchments (northern Switzerland)
467 and of H_4SiO_4 in silicic catchments (Alpine catchments in central and southern Switzerland). The catchments DI,
468 PO and SA, which are entirely located in the Alpine area (Table 1) and mainly lay on crystalline bedrock (Figure
469 1c), have higher concentration of silicic acid (Figure 3a) along with a lower concentration of Ca^{2+} in comparison
470 to the other catchments, being the AN in the Swiss Plateau area (Table 1) an exception, which is characterized by
471 a concentration of silicic acid that is comparable to that of Alpine catchments. The influence of lithology was
472 identified before in literature, with, for instance, high Ca^{2+} concentrations in one of the tributaries of the Amazon
473 River attributed to the presence of carbonate-richer lithology in the corresponding catchment [*Baronas et al.*, 2017;
474 *Rue et al.*, 2017; *Torres et al.*, 2017].

475 In the seasonality analysis, the classification of catchments into classes helps highlighting the impact of the
476 topography on the solute variability. In the Alpine catchments, discharge seasonality generally dominates the
477 seasonality of solute concentrations, except for TP, which is related to the presence of suspended sediments in the
478 streamflow caused by higher erosion rates [*Haggard and Sharpley*, 2007]. Indeed, suspended sediment
479 concentrations, coming from erosion, are much higher in Alpine catchments, excluding the two small headwater
480 catchments LU and ER, than in the others (Figure S5). Furthermore, erosion represents a source also for DOC and
481 TOC [*Schlesinger and Melack*, 1981]. TP, DOC and TOC together with Mg^{2+} have been classified as solutes
482 belonging to “B” class (Figure 4), i.e. their concentration patterns show higher variability in Alpine catchments
483 than across other classes. The driver of Mg^{2+} variability is, however, less clear than for the others. The higher
484 variability of its concentrations in Alpine catchments in comparison to other catchments might be due to the
485 presence of glaciers. Rhone, Rhine and Inn rivers include considerable glaciated areas in their catchments and this
486 might have an effect on magnesium concentration in stream water. The chemistry of glacier water is generally
487 characterized by low water-rock contact times because the volume of water and the flow rate are high so that the

488 time water molecules interact with sediments is relatively short [Wimpenny *et al.*, 2010]. Therefore, water sourced
489 by glacier melt can have a dilution effect in terms of Mg^{2+} and this explains why Mg^{2+} concentrations are
490 significantly higher during low-flow periods than during high-flow periods. This is also consistent with the
491 observations of other studies, e.g. Ward *et al.* (1998), Wimpenny *et al.* (2010a), Wimpenny *et al.* (2010b).
492 Weathering processes in Alpine environments are also studied using isotope data (e.g. Tipper *et al.* (2012), von
493 Strandmann *et al.* (2008)). These results underlay the uncertainty on the processes determining weathering
494 products as Mg^{2+} . Besides the contribution of glacier-sourced water to streamflow and biological processes
495 affecting Mg^{2+} concentrations [Wimpenny *et al.*, 2010b], dissolution of bedrock non-proportional to its
496 composition [Kober *et al.*, 2007], which is likely to take place in presence of carbonate-poor glacial sediments
497 [McGillen and Fairchild, 2005], might also play a role. Carbonate rocks might dissolve with preferential release
498 of Mg^{2+} , which therefore contributes strongly to solute fluxes in rivers. This phenomenon has been observed also
499 in the Swiss Alps (Haut Glacier d'Arolla), where carbonate contents of sediments are of the order of 1% [Brown
500 *et al.*, 1996; Fairchild *et al.*, 1999], but their contribution to solute fluxes is much higher [McGillen and Fairchild,
501 2005].

502 Catchment size or precipitation might also influence river solute concentrations. This is evident from the behavior
503 of the Lümpenenbach (LU) and Erlenbach (ER) catchments, which are three orders of magnitude smaller than the
504 other catchments considered in the study and show median concentrations lower than those of the other catchments.
505 This is true for all solutes, except DOC and TOC, the concentrations of which are the highest in Erlenbach (ER)
506 and Lümpenenbach (LU) rivers. These catchments are situated in Alptal valley, which is characterized by more
507 humid climate (double annual precipitation), compared to other catchments. Recently, Von Freyberg *et al.* (2017b)
508 analyzed isotope data of 22 catchments across Switzerland, including LU and ER, computed the young water
509 fraction (i.e., the proportion of catchment outflow younger than approximately 2-3 months) across 22 Swiss
510 catchments and tested its correlation with a wide range of landscape and hydro-climatic indices. They inferred that
511 hydrological transport in LU and ER is dominated by fast runoff flow paths, given the humid conditions and low
512 storage capacity when compared to other catchments. DOC exports have typically been associated with near-
513 surface hydrologic flow paths [Boyer *et al.*, 1997, Tunaley *et al.*, 2016; Zimmer and McGlynn, 2018], thus offering
514 a possible explanation for the higher concentration of DOC and TOC in these catchments.

515 In summary, the comparison among catchments highlighted differences in magnitude of silicic acid and calcium,
516 likely due to the different underlying lithology. Steeper morphologies show higher sediment transport in surface
517 water, which is consistent with the observation of pronounced seasonality of sediment-binding solutes (i.e., TOC
518 and TP) in the Alpine catchments. The headwater catchments ER and LU, which are smaller and wetter than the

519 other case studies, show a peculiar behavior with enhanced DOC and TOC concentrations, likely as a consequence
520 of humid conditions, near surface and/or surface flow, and low storage capacity.

521 **5.3 Consistency of solute behaviors across catchments**

522 This study showed that concentration-discharge relations reveal nearly chemostatic behavior for most of the
523 considered solutes across catchments, i.e. analyzed solute concentrations vary a few order of magnitude less than
524 discharge (Figure S6). This outcome agrees with other studies (e.g., *Godsey et al.*, 2009; *Diamond and Cohen*,
525 2017; *Kim et al.*, 2017; *McIntosh et al.*, 2017). We found that the in-stream biogeochemical signal is highly
526 dampened, coherently with other studies [*Kirchner et al.*, 2000; *Kirchner and Neal*, 2013], but different behaviors
527 of solutes could be nonetheless detected in the $\log(C)$ - $\log(Q)$ space, thus allowing a partition into four categories,
528 as suggested by *Moatar et al.* (2017). A representation of such partitioning is offered in Figure 7, where the space
529 between the negative-slope line and the near-horizontal line represents the dilution behavior, and the space
530 delimited by the positive-slope line and the near-horizontal line represents the enrichment or removal behavior. In
531 fact for low-flow conditions (i.e. $q < q_{50}$) this is typically associated with biogeochemical processes of solute
532 removal (e.g., nitrification), while for high-flow conditions (i.e. $q > q_{50}$) it is generally associated with the capacity
533 of the flow to entrain particles containing the solute. Such a description provides a different point of view of C - Q
534 relations compared to the existing literature since the subdivision between low- and high-flow conditions allows a
535 more detailed investigation of the processes potentially determining the observed solute behaviors. However, the
536 14-days frequency sampling does not allow a direct detection of short-scale processes and especially fast flood-
537 waves. This limitation could contribute to the low percentage, only 29%, of cases in which a solute switches the
538 behavior between low-flow and high-flow conditions. Additional uncertainty is due to the choice of the median
539 daily discharge as breaking point for the curves. However, in a recent study, *Diamond and Cohen* (2017) tested
540 various breaking points for the C - Q relations of different solutes with most of the breaking points centered on
541 approximately the median flow supporting our choice. In search for generalizations, we assigned a solute to each
542 specific class if the same behavior was observed in at least 60% of the analyzed catchments. Geogenic solutes are
543 grouped in a single circle since almost all of them show a dilution behavior. Only H_4SiO_4 does not show a clear
544 signal, probably because, although to a minor extent, it is involved in complex dynamics related to biological
545 processes [*Tubaña and Heckman*, 2015], which can affect its behavior. The diluting behavior of geogenic solutes
546 is a quite well consolidated fact in the literature [*Godsey et al.*, 2009; *Thompson et al.*, 2011; *Baronas et al.*, 2017;
547 *Diamond and Cohen*, 2017; *Hunsaker and Johnson*, 2017; *Kim et al.*, 2017; *Moatar et al.*, 2017; *Winnick et al.*,
548 2017; *Wymore et al.*, 2017] and this study contributes to this body of knowledge confirming this behavior.

549 Residence time is a fundamental hydrological variable for weathering products, since it is related to the weathering
550 rates and therefore to the resulting solute concentration [Ma^her, 2010]. Catchments that show chemostatic behavior
551 (e.g., BR for Ca²⁺ or WM for H₄SiO₄) likely have average water residence times that exceed the time required to
552 reach chemical equilibrium, while a dilution behavior is expected when residence times are generally shorter than
553 required to approach chemical equilibrium [Ma^her, 2011]. Our results suggest that the concentrations of geogenic
554 solutes across the catchments are far from the equilibrium, which is likely due to relatively fast hydrological
555 response of Alpine and sub-alpine catchments also associated with substantial precipitation amounts. However,
556 very likely the residence time and the flow pathways are highly heterogeneous in Alpine catchments with water
557 from different sources having different biogeochemical characteristics [Torres *et al.*, 2017 and Baronas *et al.*,
558 2018]. Therefore, flow paths with sufficiently long residence time for reaching chemical equilibration must exist
559 but they do not leave a major signature on the examined geogenic solutes. In conclusion, there is a quite high
560 confidence in claiming that geogenic solutes are characterized by a dilution behavior.

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

563 NO₃ relations with discharge are less clear [Aguilera and Melack, 2018; Butturini *et al.*, 2008; Diamond and
564 Cohen, 2017; Hunsaker and Johnson, 2017], but this study highlighted a dilution behavior also for NO₃ in the
565 majority of catchments for both low-flow and high-flow conditions. This result partially agrees with the
566 observations of Wymore *et al.* (2017), who claimed that NO₃ shows variable responses to increasing discharge. In
567 fact, we observed that while dilution is evident in 80% of the catchments for low-flow conditions, this percentage
568 drops to 63% for high-flow conditions. Although NO₃ is one of the main components of TN (Figure 2), TN does
569 not show the same behavior. For low-flows, TN is also characterized by dilution, but for high-flows TN shows
570 chemostatic behavior in about 70% of catchments.

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

579 and suspended sediments concentration suggests that the sorption of phosphorus to particles is not the only and
580 most influencing factor of DRP dynamic.

581 TOC is the only solute characterized by enrichment in both low-flow and high-flow conditions. DOC was proved
582 by a set of studies to exhibit an enrichment behavior (e.g., *Boyer et al.*, 1996; *Boyer et al.*, 1997; *Butturini et al.*,
583 2008; *Hornberger et al.*, 1994; *McGlynn and McDonnell*, 2003; *Perdrial et al.*, 2014; *Wymore et al.* (2017)), but
584 our results are in this respect highly uncertain for low-flows and suggest a chemostatic behavior for high-flows.
585 *Wymore et al.* (2017), for instance, analyzed the biogeochemical response in the Luquillo catchment in Puerto
586 Rico and detected an enrichment behavior. This catchment is mainly covered by the tropical forest and
587 characterized by very wet conditions (≈ 4500 mm/yr or rainfall). This is the likely reason leading to higher DOC
588 concentration with increasing streamflow. The underlying mechanism could be that of a larger share of streamflow
589 coming in wet conditions from shallower soil pathways [*von Freyberg et al.*, 2017b], which are generally organic-
590 richer than the deeper horizons hosting lower DOC quantities [*Evans et al.*, 2005]. Our study seems to confirm
591 this hypothesis, as the wettest catchments analyzed in this study (Erlenbach (ER) and Lümpechenbach (LU)) show
592 enrichment of DOC at least for low-flow conditions. These are likely mainly dominated by sub-surface flow, thus
593 confirming the impact of soil wetness in the unsaturated zone on DOC behavior for undisturbed catchments
594 characterized by wet conditions.

595 The results of this study also showed that the variability of solute magnitude in the long-term can play a role in the
596 definition of the solute behavior. Na^+ and Cl^- show dilution during the entire monitoring period, despite the
597 increasing concentrations through time (Figure 8). However, DRP and TP switch from highly negative b exponent
598 of the C-Q power-law relation to even positive b (Figure 8), after the time when the measures to reduce the
599 phosphate input were introduced (Figure 6). Such measures [*Zobrist and Reichert*, 2006] lead to a conspicuous
600 decrease of DRP concentration and partially also of TP. Therefore, the fraction of DRP in TP decreased in time
601 (Figure S7) and the other TP components became more important than DRP in the definition of TP behavior.
602 Among these, the component carried with sediments might be responsible for the switch, which took place in all
603 the analyzed catchments, from dilution to enrichment across the last four decades. DRP also shows increasing
604 trend of the b exponent of the C-Q relations across decades, but only in two catchments (AN, WM) the behavior
605 switches from dilution to enrichment. This means that when DRP inputs were higher, the transport was not source
606 limited, while decreasing the input forced DRP to have a more chemostatic behavior, probably because the input
607 became so low that the phosphorus transport is controlled by a legacy of phosphorus stored in the soil, which was
608 accumulated during the years of undisciplined agricultural practices [*Sharpley et al.*, 2013; *Powers et al.*, 2016;
609 *van Meter et al.*, 2016a].

610 **6 Conclusions**

611 The long-term water quality data analysis of this study was designed for understanding the signature of catchment
612 characteristics and the influence of anthropic activities on solutes concentrations observed in Swiss rivers. The
613 analysis of magnitude, seasonality, and temporal trends revealed clear cause-effect relation between human
614 activities and certain solute concentrations (i.e., Na^+ , Cl^- , NO_3 , DRP). Indeed, changes in the anthropic forcing
615 (e.g., phosphate ban or increased deicing salt) overwhelm the natural climatic variability and are clearly reflected
616 by changes in magnitude of solutes like DRP , TP , Na^+ , Cl^- . The seasonality of anthropogenic-related solutes (i.e.,
617 NO_3 , TN , DRP and TP) in the catchments in the Swiss Plateau more impacted by human activities is clearly altered
618 compared to the seasonality of Alpine catchments.

619 The detection of the signature of catchment characteristics is less straightforward and can be only captured in a
620 quantitative but not statistically significant way due to the spatial heterogeneity of catchment characteristics and
621 the relatively small sample size (11 catchments). Although the solute export is the result of multiple complex
622 processes, catchment topography, geology and size are expected to have a role in determining solute
623 concentrations, especially of weathering solutes, whose concentrations are influenced by the bedrock composition,
624 and sediment-binding substances (i.e., TP , TOC and DOC) which have an enrichment behavior in catchments
625 characterized by steeper morphologies and higher erosion rates. While we see evidence for a role of catchment
626 characteristics, these influences are relatively minor in our analysis.

627 The analysis of the empirical $C-Q$ power-laws was used to investigate and possibly obtain a generalizable
628 classification of solute behaviors. Repeating the analysis for low-flow and high-flow conditions provides a more
629 detailed description of solute behaviors, in comparison to most of the previous literature. The variability of solute
630 concentration is generally much smaller than that of streamflow, which, in first instance, would support a
631 chemostatic behavior. However, the overall dominant behavior across solutes and catchments is dilution. For many
632 solutes, this result is consistent with other studies (i.e., geogenic solutes and Cl^-). Sediment-binding substances
633 (TP , DOC and TOC) show, however, an enrichment during high-flow events, while for other solutes it is not
634 possible to define a clear behavior (e.g., DRP).

635 Finally, we observed that anthropic activities affect not only the magnitude of concentrations of solutes in rivers,
636 but also their seasonality and long-term dynamics. Remarkable variation in long-term dynamics, moreover, might
637 also determine changes of solutes behavior in time, as we demonstrated for DRP and TP . This time-varying
638 perspective of solute behaviors represents a novelty in literature and gives a clear quantitative evidence that

639 anthropic activities might influence also the C - Q relations. Together with the small sample size, one of the main
640 limitations of the study is the coarse temporal resolution of the water quality data that prevents the direct analysis
641 of (solute) fast response times associated with flood dynamics. Luckily, the advancement of technologies in high-
642 resolution concentration measurements research [von Freyberg *et al.*, 2017a] will alleviate this limitation in the
643 future. Despite the above limitations, the above results reinforce and extend the current knowledge on the
644 biogeochemical responses of rivers, demonstrating that long-term observations allow identifying various aspects
645 of anthropic activities on the solute inputs to rivers.

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904

905 **List of Tables**

906 **Table 1:** Description of the catchments. The selected catchments are characterized by different size, elevation and average yearly precipitation. Four catchments are entirely
907 Alpine (ER, PO, DI, SA), while the others encompass different morphologies (Swiss Plateau and pre-Alpine areas). The data are sourced by the catchment descriptions included
908 in the NADUF database

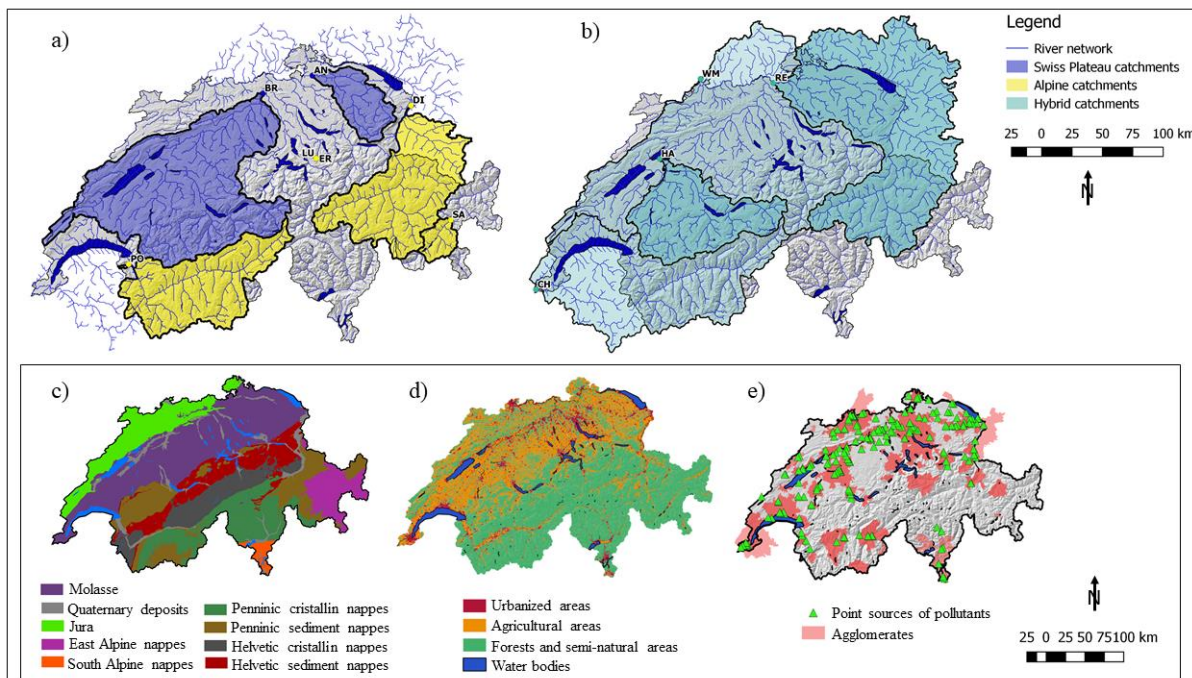
Catchment	Catchment ID	Area (km ²)	Average elevation (m a.s.l.)	Mean annual precipitation (mm/y)	Mean annual discharge (mm/y)	Lake area (%)	Morphology			Agriculture		Inhabitants density (inhab/km ²)	Period of available data	Number of consecutive years
							Swiss Plateau (%)	Alps (%)	Other (%)	Int. (%)	Ext. (%)			
Thur – Andelfingen	AN	1'696	770	1'429	880	0.1	50	23	20	51.9	10.6	222.9	1981-2015	35
Aare –Brugg	BR	11'726	1'010	1'352	847	3.6	38	23	30	35.8	17.7	181.1	1974-2015	42
Rhine–Village Neuf/Weil	WM	36'472	1'100	1'353	914	3.6	30	43	11	31.5	20.6	207.5	1977-2015	39
Rhine – Rekingen	RE	14'718	1'260	1'262	947	3.9	27	60	-	30.1	24.9	188.1	1975-2015	41
Aare – Hagneck	HA	5'104	1'370	1'506	1'106	2.1	25	52	23	23.9	29.2	147.3	1977-1982 1988-1990 1994-1996 2003-2015	13
Rhone – Chancy	CH	10'323	1'580	1'335	1'042	5.8	-	77	10	14.4	23.9	167.9	1977-1982 1986-2015	30
Lümpenenbach	LU	0.94	1'300	2'127	1'879	0	-	100	-	21.3	55.8	0	2005-2015	11
Rhine - Diepoldsau	DI	6'119	1'800	1'319	1'196	0.4	-	100	-	8	46.9	54.9	1976-2015	40
Rhone - Porte du Scex	PO	5'244	2'130	1'372	1'101	0.4	-	100	-	6.1	31.7	58.5	1974-2015	42
Inn - S Chanf	SA	618	2'466	1'063	1'036	1.6	-	100	-	3.3	43	27.5	1998-2015	18
Erlenbach	ER	0.76	1'300	2'182	1'660	0	-	100	-	2.9	52.5	0	2005-2015	11

909 **Table 2:** Results of the C-Q relations analysis. The symbols "+", "-" and "=" refer to the possible behavior
 910 combinations described in Figure 7, while the numbers indicate how many catchments exhibit a specific
 911 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 ²⁺	0	0	0	0	0	0	0	0	11
	H ₄ SiO ₄	1	1	0	1	1	2	0	0	5
	K ²⁺	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

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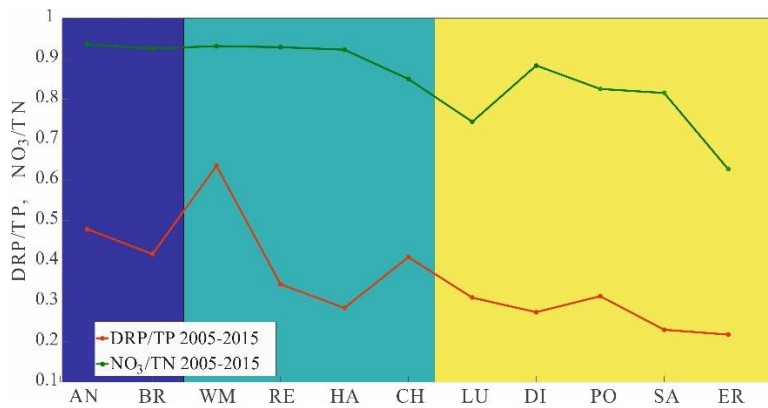
913 **Figures**



914

915 **Figure 1:** Map of NADUF monitoring stations and description of the study sites. The upper panel represents the
 916 study sites. a) Swiss Plateau (blue) and the Alpine catchments (yellow), b) the catchments spanning both regions,
 917 hybrid catchments (light blue). The bottom panel describes the study sites in terms of c) macro-geological classes,
 918 d) land cover and e) anthropic pressure.

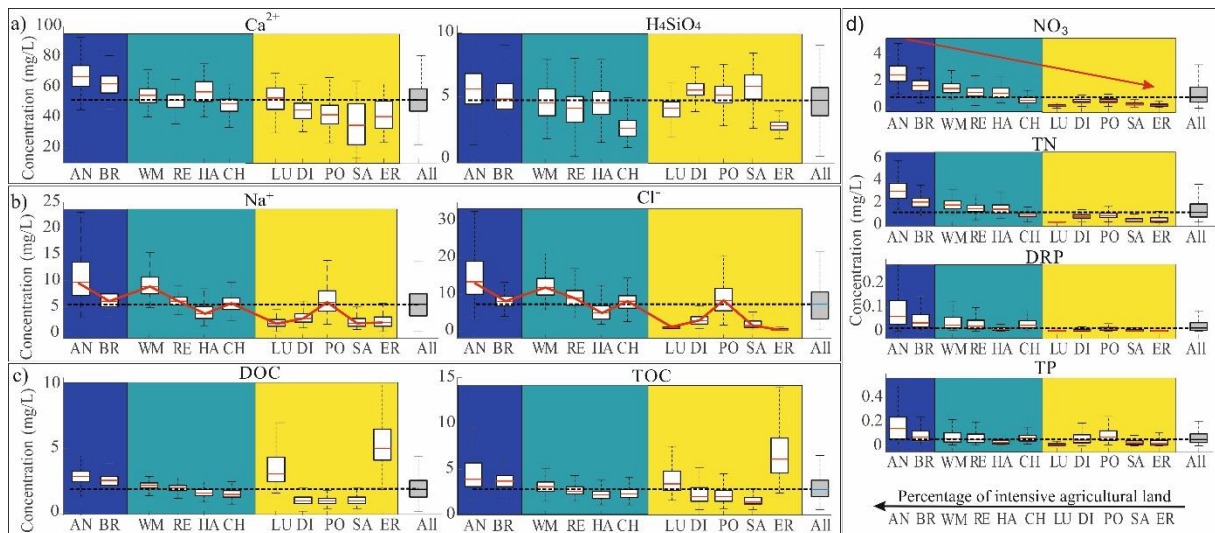
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920

921 **Figure 2.** Ratios of DRP/TP (red) and NO₃/TN (green) across catchments computed on the period 2005-2015.
 922 Both the patterns show a decreasing trend from more to less anthropogenically affected catchments (left-to-right
 923 of x axes). This pattern is more evident for phosphorus. Background colors refer to the catchment classification
 924 explained in Session 3.1.

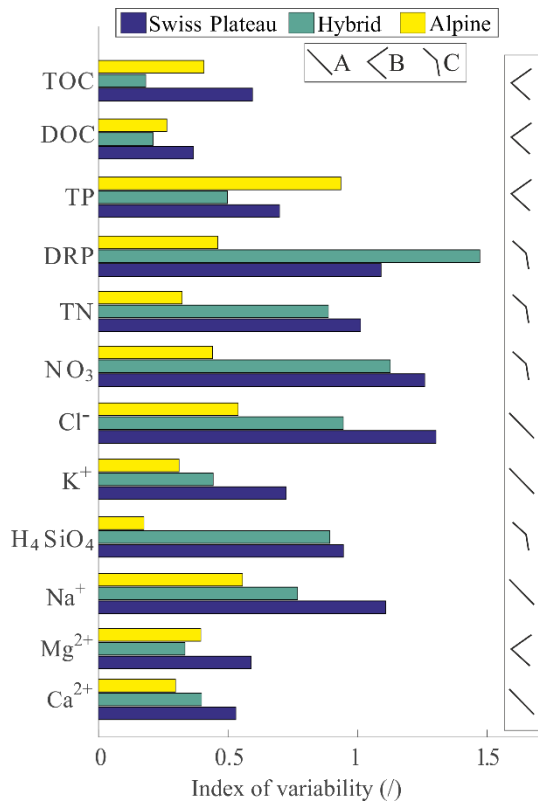
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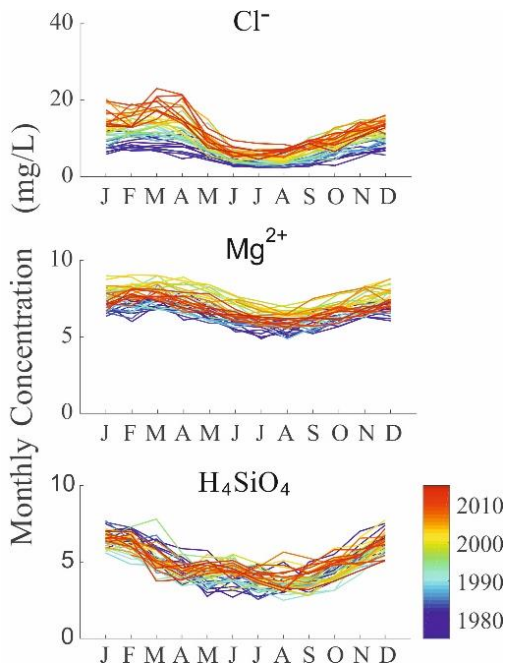
927 **Figure 3:** Boxplot of measured concentrations across catchments. The grey box on the right of each subplot refers
 928 to the concentrations computed from all the observations of all the catchments. The black horizontal dashed line
 929 represents the median of all the measurements across all the catchments. Panel a) shows the effect of bedrock
 930 geological composition on Ca²⁺ and H₄SiO₄ concentrations. Panel b) shows the pattern of Na⁺ and Cl⁻
 931 concentrations across catchments. Panel c) shows the DOC and TOC concentrations. Panel d) shows the decreasing
 932 trend of nutrients median concentrations. The catchments are ordered by increasing percentage of land used for
 933 intensive agriculture, as shown in the bottom table and the background colors refer to the catchment classes: Swiss
 934 Plateau (blue), hybrid (light blue) and Alpine (yellow) catchments.

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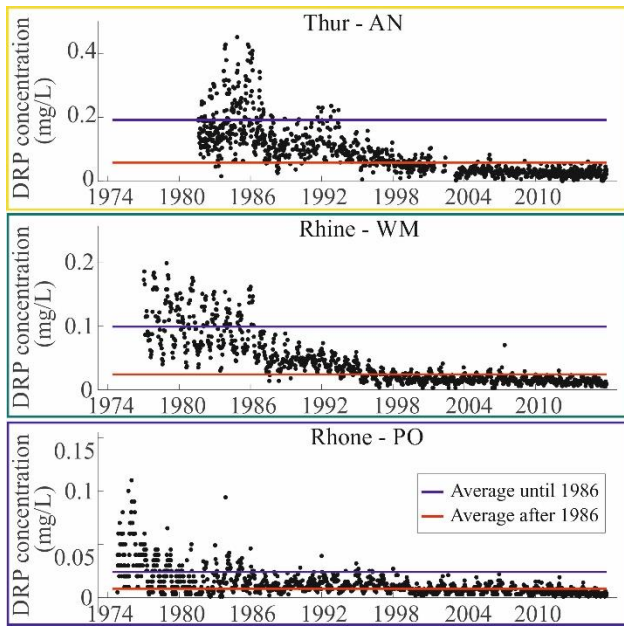


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937 **Figure 4:** Bar plot of the index of variability. Each bar represents the average monthly variability of average
 938 concentration relatively to discharge variability per catchment class. The colors of the bars differentiate catchment
 939 morphologies: blue for Swiss Plateau, aqua-green for hybrid and yellow for Alpine catchments. The A, B and C
 940 represent the observable patterns of the index of variability across the three classes. Type A is the result of the
 941 different seasonality of discharge dominating the response. Type B refers to those solutes with an index of
 942 variability much higher in the Alpine catchments than in the others. Type C represents solutes with the index of
 943 variability higher in Swiss Plateau catchments than in the other classes.



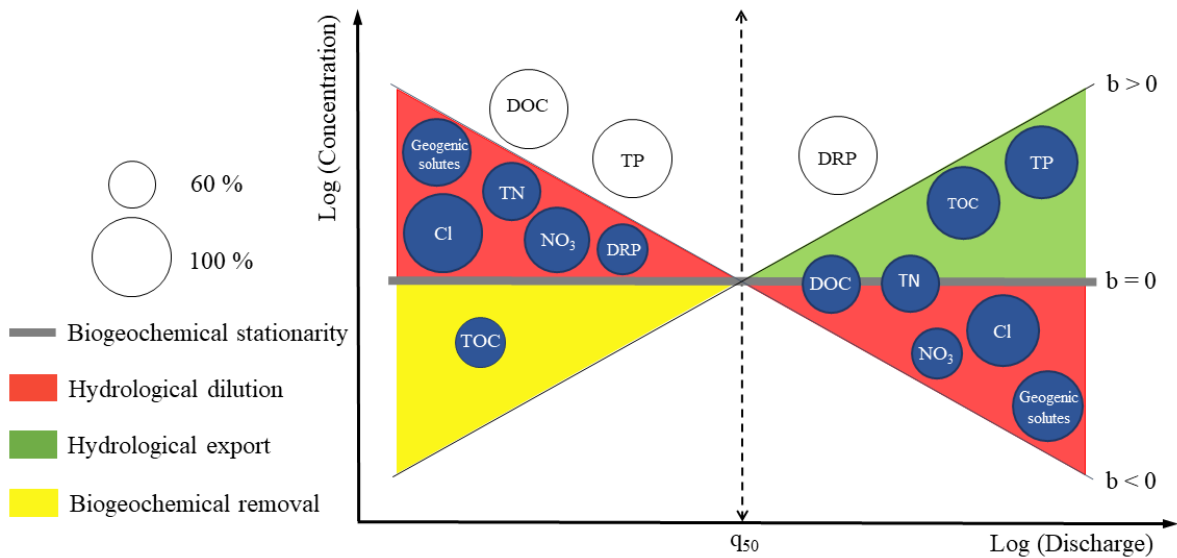
944 **Figure 5:** Three exemplary long-term patterns of solute concentrations. The upper box represent a clear
 945 increasing trend, the middle box a non-monotonic trend (firstly increasing and then decreasing), while the
 946 bottom box shows the absence of any trend. The patterns are shown for the station of Aare – Brugg as an
 947 exemplary case.



948

949 **Figure 6.** Observed DRP concentrations in three catchments characterized by different classes (i.e. Thur-AN,
 950 Rhine-WM, Rhone-PO). The blue line represents the mean until 1986, whereas the red line represents the mean
 951 after 1986 and until the end of the monitoring period. After the introduction of the phosphate ban in 1986, the DRP
 952 concentrations have shown an evident decrease.

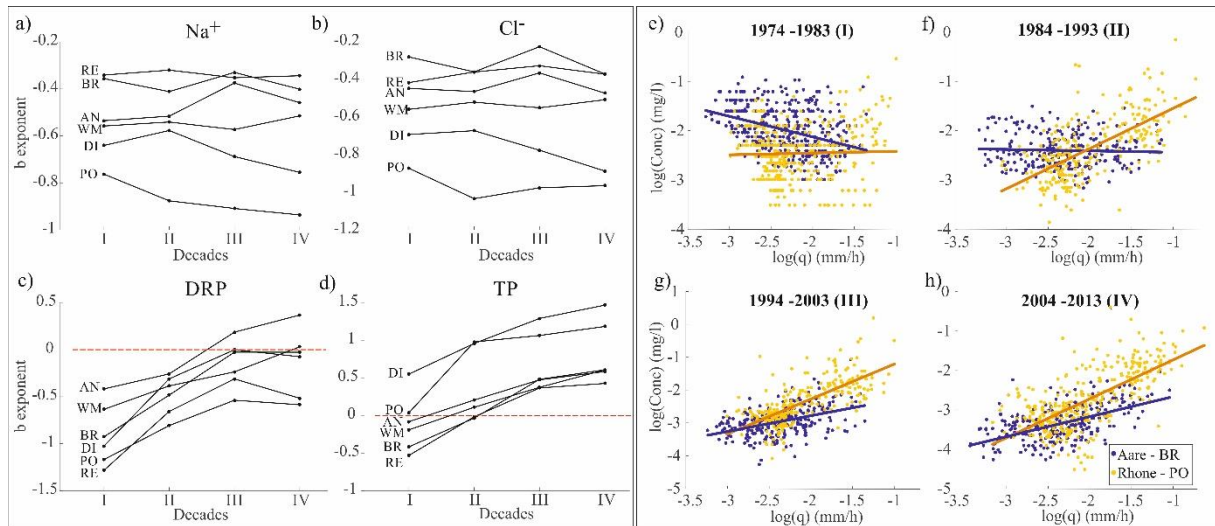
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955 **Figure 7:** Solute behaviors classification in the log(C)-log(Q) space. The definitions are derived from the
 956 classification of *Moatar et al.* (2017), which is based on the value of b , the slope of the regression line in the
 957 log(C)-log(Q) space. Discharge time series is divided in low-flow and high-flow events based on q_{50} the median
 958 daily discharge. Red areas represent hydrological dilution behavior, yellow areas represent biogeochemical
 959 removal for low flows, while green areas represent hydrological export behavior. The grey horizontal line crossing
 960 the axes origin represents the near-zero slope area, i.e., it is representative of -biogeochemical stationarity. The
 961 colorless solutes outside these areas do not show any dominant behavior. The dimension of circles represents the
 962 percentage of catchments in which the dominant behavior is observed (from 60 to 100%).

963



964 **Figure 8:** Analysis of temporal variations of the b exponent. The left plots represent the values of b exponent of
 965 the C-Q empirical relation ($C = aQ^b$) of a) Na^+ , b) Cl^- , c) DRP and d) TP across four decades from 1974 to 2013
 966 ((i) 1974-1983, (ii) 1984-1993, (iii) 1994-2003 and (iv) 2004-2013) across all the catchments with monitoring
 967 period longer than 30 years. The dashed red line represents the zero threshold (i.e., biogeochemical stationarity).
 968 The right panel represents two examples of how the C-Q relations vary across the decades e) 1974-1983, f) 1984-
 969 1993, g) 1994-2003 and h) 2004-2013. The C-Q relations refer to the catchments BR (Swiss Plateau, in blue) and
 970 PO (Alpine, in yellow) for the total phosphorus.