

Research papers

Discharge and temperature effects on weathering fluxes in alpine and perialpine basins in Switzerland

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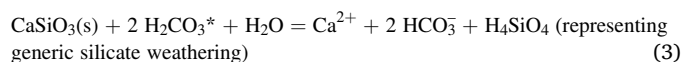
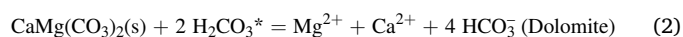
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ABSTRACT

Chemical weathering exerts a key control on atmospheric CO₂ and hence on Earth's temperature. Knowledge of the influence of discharge and temperature on weathering product loads and fluxes through rivers is important to evaluate the possible influence of climate change on weathering. The role of hydrology on such loads and fluxes is clear, but the effect of temperature is difficult to investigate, particularly in big rivers. We use long term (1974–2015) measurements of hydrological and chemical parameters in 20 Swiss stations in large, median-sized, and small rivers. This is to calculate the effect of discharge and temperature on annual loads in each station and in mean fluxes of silicic acid (SA) and calcium linked to carbonate (Ca_{car}) considering all 20 stations together. SA and Ca_{car} loads are good proxies of carbonate and silicate weathering. Mean annual loads of SA and Ca_{car} depend mostly on discharge. They decrease with temperature when the dependence is evaluated by univariate linear regression. Multiple linear regression analysis, however, reveals that the real influence of temperature, when taking into account discharge, is positive in several cases for SA and is mostly non-significant for Ca_{car}. Runoff and lithology are the main positive factors on SA fluxes, whereas temperature is the main positive factor in Ca_{car} fluxes. In both cases, the fraction of impounded water in the catchment is the main negative influence. No significant temporal trend in loads are detected in 18 out of the 20 stations despite the general increase of water temperature, which is consistent with the small effect of temperature on loads found in the present work.

1. Introduction

Chemical weathering exerts a major influence in Earth's climate via the control of atmospheric CO₂ by the carbonate–silicate cycle (Kasting, 2019). Weathering processes are the main source of geogenic solutes into rivers. Basic cations (principally Ca²⁺), silicic acid (H₄SiO₄) and alkalinity are liberated in these processes:



Inorganic carbon from carbonate dissolution flows to the oceans, where eventually it precipitates as calcium carbonate and gives back to the atmosphere the CO₂ incorporated in the dissolution of carbonate in land. In contrast, silicate dissolution by CO₂ constitutes a net long-term

carbon sink when the inorganic carbon released precipitates as carbonate in the ocean (Kasting, 2019). Recently, Liu and co-workers pointed out that some CO₂ from carbonate weathering is taken up by freshwater organisms before reaching the sea; this process is also a carbon sink (Liu et al., 2010; Liu et al., 2018). Changes in weathering rates could have important effects on the global carbon cycle. In the past, these changes were slow compared with current rates. The accelerated increase in CO₂ atmospheric concentrations and temperatures and changes in precipitations can imply significant increases in weathering (Gislason et al., 2009; Beaulieu et al., 2012) and associated carbon sinks.

Long-term time series of weathering product loads in rivers provide key data to study the influence of discharge and temperature –and thus of global change– on weathering processes. The influence of climate on weathering has been studied for many years, mostly by analysing the solute concentrations and fluxes in large (Meybeck, 1979; 1981) and small rivers (Meybeck, 1986; White and Blum, 1995). Large rivers do not generally show any dependence of silicate weathering products on temperature (Huh et al., 1998; White et al., 1999). Positive correlations

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with temperature of dissolved silica concentrations have been observed in small granitic basins (White and Blum, 1995; Oliva et al., 2003; Sun et al., 2019) and of fluxes of weathering products in basaltic basins in Iceland (Gislason et al., 2009). Positive relationships of relative chemical weathering rates with temperature exist in big rivers when rivers dominated by carbonate weathering (Gaillardet et al., 1999) are not considered. Weathering fluxes increase with precipitation, runoff and temperature, and discharge is the main factor influencing composition and fluxes in rivers (Kump et al., 2000). Weathering also depends on erosion rates (Raymond, 2017 and others before); the effects of temperature and precipitation are higher in “weathering limited” conditions (fast erosion rates compared to weathering rates) rather than in “erosion limited” ones (slow erosion rates compared to weathering rates) (West et al., 2005; Raymond, 2017). The residence time of water in the basin provides an additional control over weathering rates because the dissolution of carbonates is much faster than that of silicates (Meybeck, 1987). This implies that equilibrium conditions are normally achieved in carbonated areas but not in siliceous environments where water residence times might be too short to reach equilibrium in the dissolution of the silicates. These effects may be reflected in weather fluxes (Maher, 2010; 2011).

Connecting trends in weathering products with trends in the weathering processes that originate them is not straightforward. On the one hand, solutes liberated by chemical weathering have often an active (bio)geochemical role on river basins, which complicates the identification of the climate signal. Strong human influences can also blur the weathering-concentration relationship. On the other hand, environmental drivers such as discharge and temperature may be strongly coupled in determining fluxes of the products, which make difficult the identification of the effective cause of increased/decreased weathering.

The influence of temperature in mineral weathering is not easy to evaluate by studying the variation of concentrations and fluxes at different temperatures. As pointed out by Clow and Mast (2010), chemical weathering rates are well correlated with lithology and runoff (Hartmann et al., 2010; Jansen et al., 2010) but the relation with temperature is confounded by discharge and other effects also temperature-dependent (e.g., soil characteristics and vegetation). To situate the observed variations, of weathering products with temperature and discharge, in context, it is important to be acquainted with the theoretical processes of carbonate and silicate dissolution and their temperature and discharge dependences. A short description can be found in the Supplementary Information file.

In the present work we aim to understand the roles of discharge and temperature on the loads and weathering fluxes (annual load by basin surface unit) of carbonates and silicates, and to look for other possible additional environmental drivers of these loads and fluxes, in 20 alpine and perialpine catchments in Switzerland. The accurate determination of chemical weathering fluxes needs frequent sampling and long enough sampling periods (Hindshaw et al., 2011). In this context, Swiss NADUF solute concentration data series provides an invaluable opportunity to study environmental changes in Swiss catchments because it provides long, consistent temporal series of many parameters (e.g., temperature, discharge) and solute concentration data (more than 1,000 data points in some sampling stations).

Our study includes alpine and perialpine areas. Alpine areas show characteristics that differentiate them from other basins in temperate zones (Wehren et al., 2010) making them particularly interesting when looking for possible effects of climate change. These areas are characterised by a high runoff (more than 1 m per year) due to the effect of relief on precipitation and the presence of glaciers, with effects on erosion, weathering and discharge regime of rivers. Erosion and weathering are intense in alpine areas making climate change effects on chemical weathering potentially more intensive in mountain river basins (Gislason et al., 2009). At the same time, other effects tend to decrease weathering: big areas in alpine basins are bare rock or have thin soils with sparse vegetation, which could influence weathering via

short water residence times in the basin and less CO₂ production in soils. Perialpine catchments show the influence of rain, temperature and snow in different degrees depending on basin altitude. In the more pluvial regimes there is a lesser seasonal discharge than in alpine basins (characterised by pronounced maximum discharge in summer, due to snow and glacier melting, and a minimum in winter), with a maximum in winter-spring. Runoff is still high, due to high rainfall, and soils are more profound and vegetated.

2. Area of study

Twenty measurement stations have been chosen in the alpine basins of the rivers Rhine (Diepoldsau), Rhone (Porte du Scex), Inn (S-Chanf and Martina) and Ticino (Riazzino), and the perialpine basins of Rhine, Rhone, Aare, Reuss, Thur, Glatt, Sarine, Birs, Limmat, Kleine Emme, Sitter, Sense and Murg (15 stations). The area covered represents most of the Swiss territory and includes some French, Austrian and German areas. Geographic and land use data of basins have been taken from <https://www.hydrodaten.admin.ch/en/>.

All data are taken from the NADUF (Swiss National River Monitoring and Survey Programme) (<https://www.bafu.admin.ch/bafu/de/home/themen/wasser/zustand/wasser-messnetze/nationale-beobachtung-g-oberflaechengewaesserqualitaet-nawa-/nationale-dauerbeobachtung-g-fluessgewaesser-naduf.html>) (Fig. SI2). The main characteristics of the sampling points as well as the time periods considered are shown in Table 1, while their location is shown in Fig. 1. Dates of discharge-weighted concentrations and loads of alkalinity, Ca and silicic acid (SA), as well as water temperature and discharge have been taken from NADUF (Table 2). NADUF programme supplies a set of discharge-weighted solute concentration and solute load (calculated as product of mean discharge during the two weeks period and concentration) time series, discharge-weighted, in the main Swiss rivers, which is long (6 to 41 years), regular (two weeks integrated values), homogeneous (same procedures of data acquisition in all the stations), and traceable (documented changes of analytical methods) (Zobrist et al., 2018).

We can distinguish three morphological regions in Switzerland, which draw three parallel bands from North to South: Jura, Swiss Plateau, and Alps. Lithologically, Jura region is calcareous, Swiss Plateau is mainly made of “molasses”, a mixture of sedimentary rocks, calcareous and crystalline, and Alps has a dominant presence of crystalline bedrocks, with important evaporite and calcareous areas. All regions are included in this study.

3. Methods

We have chosen Ca and SA loads as representative of carbonate and silicate weathering, respectively. Ca from silicates is a minor Ca source in our 20 stations due to the dominant carbonate lithology in the basins (with the exception of the Ticino basin) (Zobrist et al., 2004); thus, the ratio SA:Ca is always <0.1 (Table 2). In the seven stations studied by Zobrist et al. (2018), which are also included in the present work, they estimated that the weathering of calcareous minerals gives more than 90% of measured alkalinity. Thus, we will not consider Ca emanating from silicates.

A significant portion of Ca comes from calcium sulphates (anhydrite, gypsum), especially in alpine stations. We can estimate the quantity of Ca coming from carbonates (calcite and dolomite) by subtracting sulphate from total Ca concentrations. We will refer to this parameter as Ca_{car}. The perfect correlation of alkalinity with (Ca_{car} + Mg) concentrations (Fig. SI1) confirms the validity of our approach. Atmospheric inputs to chemical content of SA and Ca in rivers have not been considered, as they should be minor (Zobrist et al., 2004).

Two parameters are studied: loads (bi-weekly and annual) and fluxes of SA and Ca_{car}. As loads are strongly dependent on discharge, and this might confound the influence of temperature, we have also considered the discharge-normalized mean annual loads, that is, the mean annual

Table 1
Sampling stations and their characteristics (Rodríguez-Murillo et al (2015) and BAFU^a).

River	Station	Station code	Coordinates ^a	Basin drainage area / km ²	Average basin altitude / m.a.s.l.	Water discharge / m ³ s ⁻¹	Runoff / m yr ⁻¹	Mean annual water temperature / °C	Period	Number of bi-weekly periods
Rhône	Porte du Scex	PS	557660/ 133280	5,220	2,130	187 ± 89	1.13	7.2	1974–2015	1,045
	Chancy	CH	486600/ 112340	10,294	1,580	351 ± 133	1.08	11.6	1977–2015	875
	Diepoldsau	RD	766280/ 250360	6,119	1,800	231 ± 132	1.19	8.0	1984–2015	823
Rhine	Rekingen	RR	667060/ 269230	14,718	1,260	450 ± 166	0.964	11.6	1975–2015	1,043
	Village Neuf/ Weil	VN	611740/ 272310	36,472	1,100	1,078 ± 408	0.951	12.4	1977–2015	1,007
Thur	Andelfingen	AN	693510/ 272500	1,696	770	47 ± 31	0.874	10.7	1981–2015	819
Aare	Brugg	BR	657000/ 259360	11,750	1,010	322 ± 134	0.864	11.8	1974–2015	1,008
	Bern	BE	600710/ 198000	2,969	1,610	126 ± 72	1.34	10.4	1975–1996	225
Inn	S'chanf	IS	795800/ 165910	618	2,466	21.7 ± 19	1.11	5.0	2000–2015	427
	Martina	IM	830640/ 197190	1,945	2,350	59.3 ± 43	0.961	5.5	1982–1988	195
Ticino	Riazzino	TI	713670/ 113500	1,611	1,640	72.7 ± 50	1.42	9.0	1978–2015	444
	Guemmenen	GU	585100/ 199240	1,880	1,130	54.7 ± 28	0.918	9.9	1987–2015	326
Limmat	Gebenstorf	GE	660530/ 260770	2,415	1,130	102 ± 45	1.33	12.0	1979–2015	461
Reuss	Mellingen	ME	662830/ 252580	3,382	1,240	141 ± 75	1.31	11.5	1975–2015	488
Birs	Muenchenstein	MU	613570/ 263080	911	740	15.3 ± 11	0.530	10.9	1983–2015	459
Glatt	Rheinsfelden	GL	678040/ 269720	416	498	8.47 ± 4.3	0.642	12.4	1977–2015	836
Kleine Emme	Littau	KE	664220/ 213200	477	1,050	15.2 ± 10.3	1.00	9.0	1982–2005	343
Sitter	Appenzell	SA	749040/ 244220	74.4	1,256	3.15 ± 2.02	1.34	7.5	2006–2013	171
Sense	Thoerishaus	ST	593350/ 193020	351	1,071	8.37 ± 5.46	0.752	9.5	2003–2015	153
Murg	Frauenfeld	MF	709540/ 269660	213	597	3.80 ± 2.44	0.563	10.9	2007–2013	127

^a Data from: Verzeichnis_der_eidgenoessischenhydrometrischenstationenaufende2.pdf. Available at: <https://www.bafu.admin.ch/bafu/de/home/themen/wasser/zustand/wasser-messnetze/basismessnetz-wassers-tand-und-abfluss-an-oberflaechengewaessern.html>.

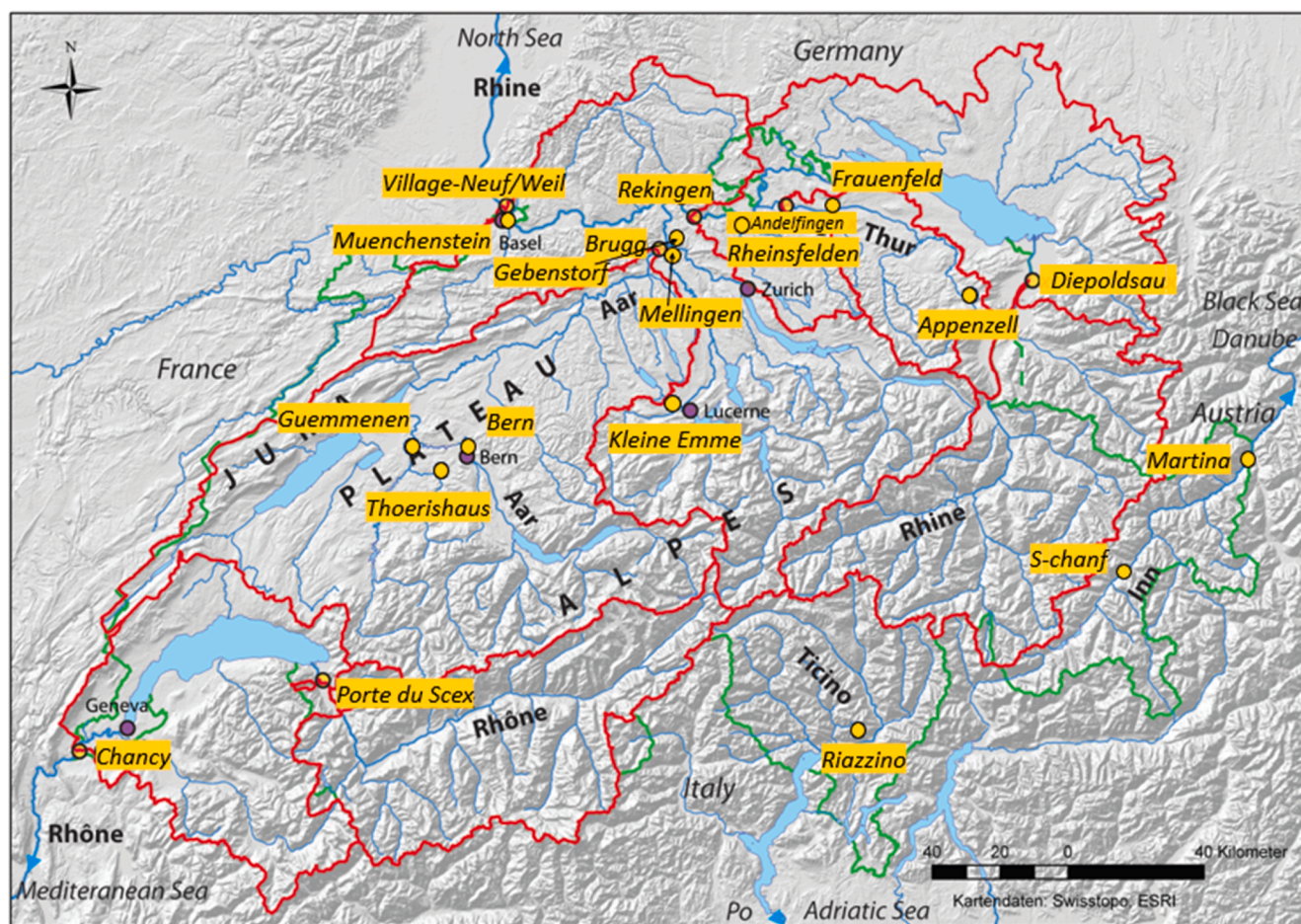


Fig. 1. Location of the 20 NADUF stations considered in the work.

Table 2

Mean solute concentrations and weathering fluxes for the 20 stations studied.

Station	[Alk] / meq L ⁻¹ (Mean ± SD)	[SA] / μmol L ⁻¹ (Mean ± SD)	[Ca] / mmol L ⁻¹ (Mean ± SD)	[Ca _{car}] / mmol L ⁻¹ (Mean ± SD)	% [SA]/[Ca]	Alk flux / t km ⁻² yr ⁻¹	SA flux / t km ⁻² yr ⁻¹	Ca flux / t km ⁻² yr ⁻¹	Ca _{car} flux / t km ⁻² yr ⁻¹	Mg flux / t km ⁻² yr ⁻¹
PS	1.45 ± 0.25	52.8 ± 9.8	1.05 ± 0.21	0.483 ± 0.099	5.0	96.8	5.52	44.5	20.5	6.02
RD	1.99 ± 0.25	57.1 ± 6.2	1.11 ± 0.16	0.629 ± 0.085	5.2	140	6.40	50.1	28.4	9.69
IS	1.15 ± 0.31	59.4 ± 12	0.895 ± 0.35	0.233 ± 0.051	6.6	61.2	5.36	27.6	7.19	5.78
IM	1.51 ± 0.31	53.3 ± 8.3	0.919 ± 0.23	0.384 ± 0.093	5.8	79.3	4.55	29.4	12.3	7.01
RR	2.66 ± 0.30	43 ± 13	1.26 ± 0.13	0.953 ± 0.139	3.4	154	3.79	48.0	36.3	8.99
VN	2.74 ± 0.28	47 ± 14	1.36 ± 0.14	1.07 ± 0.14	3.5	155	4.18	50.4	41.0	7.27
BR	3.04 ± 0.34	51 ± 13	1.54 ± 0.16	1.27 ± 0.17	3.3	154	4.05	51.5	42.5	5.76
CH	1.97 ± 0.24	26.5 ± 9.0	1.20 ± 0.12	0.720 ± 0.118	2.2	127	2.66	50.2	30.1	6.57
AN	4.09 ± 0.51	57 ± 16	1.67 ± 0.21	1.55 ± 0.19	3.4	210	4.96	57.1	52.9	11.4
TI	1.01 ± 0.20	83.6 ± 11	0.922 ± 0.23	0.257 ± 0.063	9.1	75.3	10.6	43.7	12.2	7.08
BE	2.24 ± 0.23	33.3 ± 11	1.24 ± 0.13	0.937 ± 0.103	2.7	176	3.96	64.3	48.6	6.32
GU	3.37 ± 0.31	65.5 ± 9.7	1.77 ± 0.15	1.41 ± 0.13	3.7	185	5.62	63.7	50.7	6.72
GE	2.52 ± 0.24	32.2 ± 15	1.17 ± 0.11	0.986 ± 0.114	2.8	204	3.94	62.2	52.4	8.67
ME	2.26 ± 0.26	31.7 ± 12	1.10 ± 0.12	0.948 ± 0.111	2.9	173	3.75	55.4	47.7	5.34
MU	4.13 ± 0.27	70.3 ± 15	2.17 ± 0.15	1.97 ± 0.143	3.2	132	3.53	45.3	41.1	2.26
GL	4.15 ± 0.41	75.0 ± 15	1.78 ± 0.19	1.51 ± 0.19	4.2	165	4.62	46.6	39.5	10.17
KE	3.06 ± 0.47	59.3 ± 12.9	1.46 ± 0.21	1.33 ± 0.19	4.1	174	5.61	54.4	49.6	4.95
SA	3.08 ± 0.36	38.3 ± 6.9	1.41 ± 0.16	1.36 ± 0.16	2.7	251	4.92	75.6	73.0	5.86
ST	3.35 ± 0.29	83.4 ± 11.9	1.79 ± 0.13	1.32 ± 0.15	4.7	154	6.03	53.0	39.7	6.58
MF	5.15 ± 0.32	84.5 ± 18.7	1.93 ± 0.17	1.77 ± 0.19	4.4	185	4.87	46.1	42.3	13.10

concentrations, and we have calculated their dependence on discharge and temperature. Univariate (temperature or discharge) and multiple (temperature and discharge) linear regressions have been used to characterise temperature and discharge dependency of loads and concentrations in each watershed. Multiple linear regression, when the

conditions for its application are met, can discriminate between the influences of discharge and temperature.

Water temperature has been used as a surrogate of average basin temperature. Soil temperature would be the most appropriate parameter to study concentration dependence on temperature but data are not

available. Water temperature integrates temperatures from distinct basin zones. Water temperatures are higher than air temperatures in winter and lower than air temperatures in summer; this is also the case with soil temperatures.

The global weathering in the different basins (Table 2) has been evaluated through the calculation of weathering fluxes ($\text{t yr}^{-1} \text{ km}^{-2}$) in each basin using the mean basin bi-weekly loads along the whole time period and the basin area. Multiple linear regressions of fluxes of SA and Ca_{car} in the 20 basins studied have been calculated by considering six parameters that represent significant effects in weathering in the basins as independent variables:

- fraction of water in lakes and reservoirs (E) as proxy of the influence of SA retention by lakes and reservoirs; E is obtained as $100 \times (\text{Sum of water volume in basin lakes and reservoirs (W)}) / (W + \text{yearly water output of the station (O)})$. Water volumes are from Swisstopo (<https://www.swisstopo.admin.ch/en/maps-data-online/maps-geodata-online.html>), adding up the capacities of lakes and reservoirs $> 1 \text{ hm}^3$ in the basin. Only Swiss lakes and reservoirs have been considered, except for the Alpine Rhine basin (Diepoldsau), where Austrian Ill River watershed has been taken into account (International Commission for the Hydrology of the Rhine Basin (KHR/CHR), 2009);
- the concentration of dissolved reactive phosphorous as proxy of the loss of SA by diatoms associated to eutrophy;
- SA and Ca_{car} as indicators of basin lithology;
- runoff (R), estimated as the mean annual discharge during the measurement period divided by the basin surface;
- slope (B) of the c - Q relationship for SA and Ca_{car} (Fig. SI3) in log scale; $c = a Q^B$ relationships with c : concentrations, Q discharge and a and B constants for each basin (Fig. SI4), they are commonly used to characterise hydrological solute responses;
- temperature, which influences many of the previous variables and is itself a fundamental environmental variable.

The values of all these parameters are in Table 3. In order to obtain meaningful regressions, the maximum number of independent variables in the multiple regression calculations were restricted to three (Green, 1991). Regressions with all possible combinations of one, two and three-independent variables were performed with XLSTAT software and the best regression (i.e., highest R^2) chosen.

Temporal trends have been calculated using the non-parametric Seasonal Mann-Kendall method (Gibbons and Coleman 2001).

Multiple linear correlations and other statistical calculations were performed with XLSTAT (<https://www.xlstat.com/en/solutions/basic>) and PAST software (Hammer et al., 2001) (nhm.uio.no/english/research/infrastructure/past/).

4. Results

Solute loads depend principally on discharge in all stations. The linear relationship of bi-weekly loads with discharge is highly statistically significant ($p < 10^{-4}$) and generally high in all the stations, particularly for Ca_{car} (Table SI1). Linear correlations of mean annual loads-mean annual discharges are also very significant ($p < 0.01$) in all stations. Load-discharge plots always show positive slopes (Table SI1 and Fig. 2; in this figure only the 15 stations later analysed by multiple linear regression are shown).

The effect of temperature on bi-weekly loads (Table SI1) is weak, except, for Ca_{car} , in PS, RD, IS, IM, and BE, ME, which show a clear increase of loads with temperature. There is a decrease of loads with temperature in some stations: MU, GL, MF (Ca_{car}) and GE (SA). In the rest, a small decrease or increase of loads with temperature ($R^2 < 0.1$) is observed. SA loads in stations after big lakes (CH, BE, BR, ME, GE, RR, and VN) usually decrease with temperature.

Linear regression of annual loads on temperature have been calculated for 19 of the 20 stations (MF has only three complete years with

Table 3

Mean annual values of some environmental and climatic variables for the 20 stations studied.

Station	E^a	$[\text{DRP}]^b$ / mg P L^{-1}	B^c SA	B^c Ca_{car}
PS	17.8	0.013	-0.234	-0.0443
RD	9.5	0.005	-0.0856	0.0111
IS	31.2	0.013	-0.174	-0.0294
IM	20.5	0.006	-0.110	-0.0218
RR	77.6	0.029	-0.333	-0.0818
VN	74.5	0.043	-0.0902	-0.0141
BR	73.6	0.043	-0.0328	-0.0388
CH	88.9	0.030	-0.0781	-0.0267
AN	0.0671	0.116	0.168	-0.0268
TI	6.97	0.008	-0.0823	-0.117
BE	74.7	0.011	-0.204	-0.0977
GU	16.5	0.014	-0.0813	0.00159
GE	65.8	0.059	-0.251	0.00129
ME	78	0.031	-0.205	-0.0945
MU	0	0.063	0.0240	0.0384
GL	35.7	0.288	-0.205	0.0707
KE	0	0.032	-0.00491	-0.139
SA	0.6	0.013	0.0128	-0.0363
ST	0.882	0.004	-0.0542	0.0392
MF	0	0.034	0.185	0.126

^a Fraction of water in lakes and reservoirs.

^b Dissolved reactive phosphorous.

^c $c = a Q^B$ relationship with c : concentrations, Q discharge and a and B constants.

annual load data and has been discarded). The relationship is negative in the majority of cases and, in particular, in all statistically significant stations, both for SA and Ca_{car} . Mean annual loads as a function of mean annual temperature are shown for 15 of the 20 basins in Fig. 3; R^2 values for the regression with temperature are in Table SI1. Ca_{car} and SA annual loads decrease generally when temperature increases. Ca_{car} annual loads decrease significantly with temperature (univariate linear regression, $p < 0.05$) in ten stations of covering alpine and subalpine basins (PS, RD, IS, AN, MU, RR, VN, CH, BR, ME) while SA annual loads do it in six stations (PS, RD, AN, MU, CH, BR). No station shows significant increases with temperature.

Independent variables have been checked for collinearity calculating the variance inflation factor (VIF). VIF are always less than five, which ensures a tolerable collinearity (<https://www.ncss.com/wp-content/themes/ncss/pdf/Procedures/NCSS/Multiple-Regression-Basic.pdf>). Heteroskedasticity has been corrected using the adjusted Newey-West method (Newey and West, 1987). Normal distributions of residuals were assessed with the Shapiro-Wilk method. The hypothesis of normal distribution cannot be rejected at a significance level of 0.05 in any annual load series, except for Ca_{car} in two stations (IS and KE). For bi-weekly load series, the distributions of residuals are generally non-normal. We have introduced the variable T^2 to take into account the non-linearity of the relationship load-temperature, and transformed the dependent variable and discharge by taking their logarithms. In this case, a strong collinearity between T and T^2 unavoidably arises and we needed to "centre" the variable T , subtracting the mean of temperature values from each temperature, but residual distributions are still non-normal in many cases, even taking into account the interaction terms of the three variables (QT , QT^2 , TT^2). We also used the loads and the variable Q^B instead of their logarithms, but this does not eliminate the non-normality of the residuals. We thus decided to use the annual loads only, to eliminate this problem.

Multiple linear regressions using bi-weekly and annual data as dependent variables and temperature and discharge as independent variables have been performed. Only the 15 stations with more than ten years of data available have been considered for annual load regressions, which is reasonable for two independent variables given the R^2 values obtained (Green, 1991). We used the value of the standardized

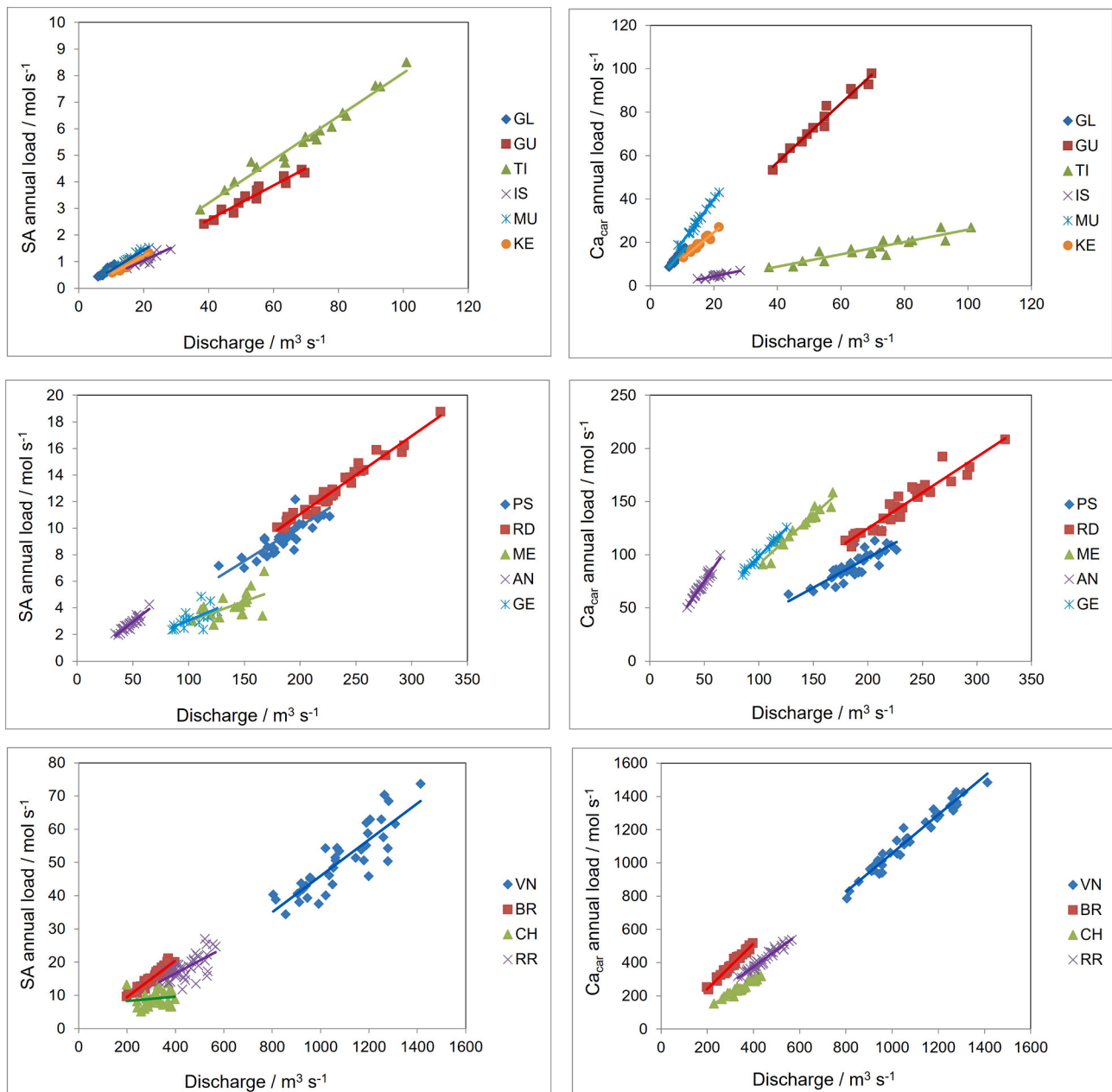


Fig. 2. Dependence of mean annual SA and Ca_{car} loads on mean annual discharges for the 15 stations with more than ten years of data available.

coefficients of discharge and temperature in the regression of annual loads to evaluate their relative importance and compute also their significance (Table 4). In a few cases, the best regression, as judged by the value of R^2 , is a single one (with discharge); in the majority of cases, the temperature contribution is not significant or small compared to discharge. Five stations present a significant positive effect on SA loads (TI, GE, ME, RR, VN) and one on Ca_{car} loads (GL). Only in two stations (MU, CH) is there a significant negative effect of temperature on SA load and only in one (VN), there is a negative effect of temperature on Ca_{car} load.

Multiple linear regressions of the mean annual concentrations (loads normalized by discharge) of SA and Ca_{car} on mean annual discharge and temperature (Table S12) show that the temperature contribution to SA concentrations is significantly positive in TI, GE, RR and VN, and negative in MU and CH, as it was the case with loads. The temperature contribution to Ca_{car} concentrations is not significant in any of the 15 stations. The standardized coefficients for T , which represent the

contributions of the temperature to loads and concentrations, have similar values within the corresponding uncertainties.

Weathering of carbonates and silicates, represented by $(\text{Ca}_{\text{car}} + \text{Mg})$ and SA fluxes respectively (Table 2), have been compared to published weathering data in other basins. Carbonate weathering intensities ($0.503\text{--}2.674 \text{ mmol L}^{-1}$, mean: $1.39 \pm 0.58 \text{ mmol L}^{-1}$) are typical of carbonated basins (Gaillardet et al., 1999). Silicate weathering intensities are given in this work as silicic acid (H_4SiO_4) fluxes, and can be compared with the data of big basins and small granitic catchments given by West and co-workers (West et al., 2005, Table 2) as SiO_2 fluxes. The value for “Swiss Alps” in that table ($9.91 \text{ t SiO}_2 \text{ km}^{-2} \text{ yr}^{-1}$), taken from Hosein et al. (2004), is higher than our average flux ($3.07 \pm 1.01 \text{ SiO}_2 \text{ km}^{-2} \text{ yr}^{-1}$) when expressed as SA flux. However, Hosein’s value is not directly comparable to ours as it corresponds to two small glaciated crystalline catchments. On the other hand, our value is well in the range of other alpine catchments in West et al. (2005).

The best regression for SA fluxes is that with R , [SA] and E ($R^2 =$

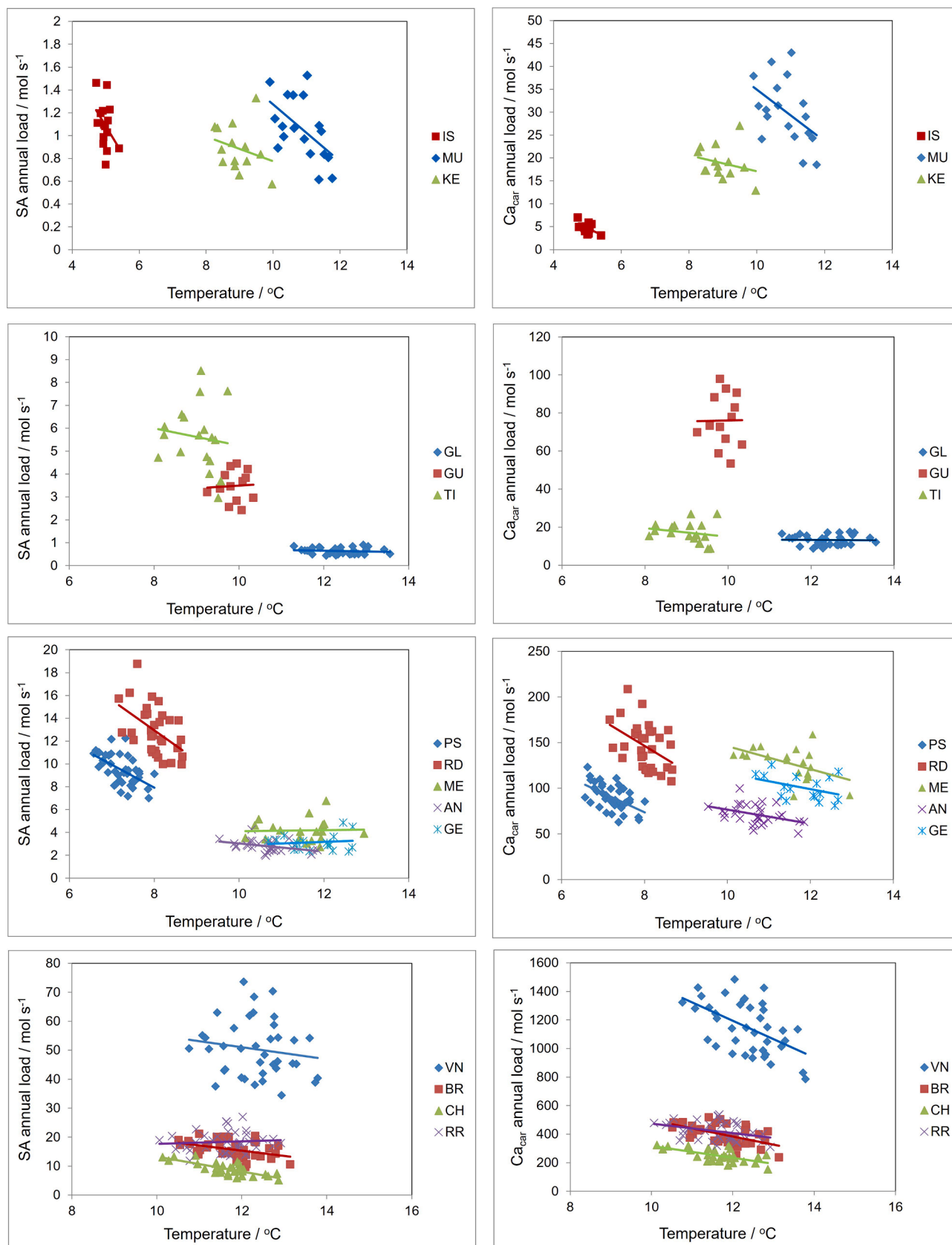


Fig. 3. Dependence of mean annual SA and Ca_{car} loads on mean annual temperatures for the 15 stations with more than ten years of data available.

Table 4
Influence of temperature on mean annual loads of SA and Ca_{car} for the 20 stations studied. Univariate (temperature) and multiple linear regression results (R^2 and standardized coefficients). *: $0.05 > p > 0.01$; **: $0.01 > p > 0.001$; ***: $p < 0.001$. nc: temperature not considered in the best regression. Statistically significant values ($p < 0.05$) in bold.

Station	SA mean annual loads				Ca_{car} mean annual loads			
	Univariate linear regression vs T^a		Multivariate linear regression		Univariate linear regression vs T^a		Multivariate linear regression	
	R^2	T standardized coefficient	Q standardized coefficient	Q standardized coefficient	R^2	T standardized coefficient	Q standardized coefficient	Q standardized coefficient
PS	0.716	0.147	0.767***	0.767***	0.715	-0.133	0.776***	0.776***
RD	0.967	0.046	1.01***	1.01***	0.920	0.100	1.01***	1.01***
IS	0.793	nc	0.906***	0.906***	0.875	-0.123	0.880***	0.880***
TI	0.981	0.084**	1.01***	1.01***	0.829	nc	0.916***	0.916***
GU	0.946	0.114	0.978***	0.978***	0.974	0.07	0.991***	0.991***
GE	0.482	0.482*	0.790**	0.790**	0.969	nc	0.985***	0.985***
ME	0.419	0.456*	0.814**	0.814**	0.924	nc	0.965***	0.965***
MU	0.959	-0.119**	0.921***	0.921***	0.986	nc	0.994***	0.994***
GL	0.909	nc	0.955***	0.955***	0.964	0.093*	0.989***	0.989***
KE	0.950	nc	0.977***	0.977***	0.953	nc	0.978***	0.978***
BR	0.880	0.116	0.999***	0.999***	0.976	-0.034	0.970***	0.970***
AN	0.868	nc	0.934***	0.934***	0.949	nc	0.975***	0.975***
CH	0.914	-0.336***	0.723***	0.723***	0.935	-0.085	0.917***	0.917***
RR	0.562	0.411**	0.826**	0.826**	0.941	nc	0.971***	0.971***
VN	0.815	0.319***	1.01***	1.01***	0.966	-0.085*	0.941***	0.941***

^a Sign of the correlation and S: statistically significant. Complete results in Table S11.

0.871). The standardized coefficients, which represent the influence of each independent variable on the flux, are 0.840, 0.831 and -0.307, respectively; all of them significant ($p < 0.05$). The best regression for Ca_{car} flux is that with temperature, E and R ($R^2 = 0.509$). The corresponding standardized coefficients are 1.02, -0.711 and 0.387; the influence of R is not significant ($p = 0.053$).

Very few significant temporal trends have been found in the data series considered (Fig. S12; Table 5): bi-weekly SA loads decrease at the two Rhone River stations (PS and CH) and in IM, and bi-weekly Ca_{car} loads decrease at CH. No significant trends have been observed in the other stations.

5. Discussion

5.1. Temperature and discharge intertwined effects

The measured loads and fluxes of weathering products in rivers are the result of the direct temperature effect on mineral chemical weathering as well as of many factors (e.g., atmospheric deposition on the basin, direct anthropic inputs, biological transformations, ionic exchange processes in soils, biological assimilation, glacier retreat, reduced snow cover, dam construction, river canalisation, etc.). In general, our quantitative or even qualitative knowledge of those processes is poor, which is an obvious reason for the conflicting results in the study of weathering fluxes in rivers and their relationship to temperature (White and Blum, 1995; Huh et al., 1998; White et al., 1999; Oliva et al., 2003; Gislason et al., 2009). Moreover, the effect of temperature on weathering is confounded by the effect of discharge on loads. In spite of all these factors, is it still possible to detect the effect of temperature on weathering?

Plots of annual load-temperature and annual load-discharge do not suggest any non-linear effect and -clearer in the load-discharge plots- an acceptable linear relationship is observed in the majority of cases (Figs. 2 and 3). The relationships annual loads on temperature are negative in most cases and, particularly, in all significant ones, both for SA and for Ca_{car} . This may appear surprising for SA because temperature enhances kinetics of silicate dissolution. In fact, only Gislason et al (2009) performed an analysis differentiated by rivers 'like the one presented here' including many years of mean annual data for each of their rivers. These authors found a positive significant correlation of loads and temperature in almost all the studied rivers. Their results, however, cannot be considered as directly comparable to ours because their basins were almost 100% basaltic and their temperatures very low, not

Table 5

Temporal trends of bi-weekly SA and Ca_{car} loads. Significant trends in bold (statistically significant level 5% corresponds to $|Z| = 1.96$).

	Z SA	Z Ca_{car}
PS	-2.37	-1.68
RD	0.224	1.29
IS	0.801	0.443
IM	-2.21	-1.44
RR	1.75	-0.147
VN	0.729	-1.37
BR	-0.399	-1.78
CH	-4.16	-2.77
AN	-0.325	-0.478
TI	0.0903	-0.535
BE	-1.77	1.18
GU	-1.02	-0.956
GE	1.79	-0.456
ME	0.861	-0.606
MU	-0.816	0.0432
GL	-1.26	-0.634
KE	-0.621	-0.484
SA	0.430	0.755
ST	1.23	1.34
MF	0.603	1.27

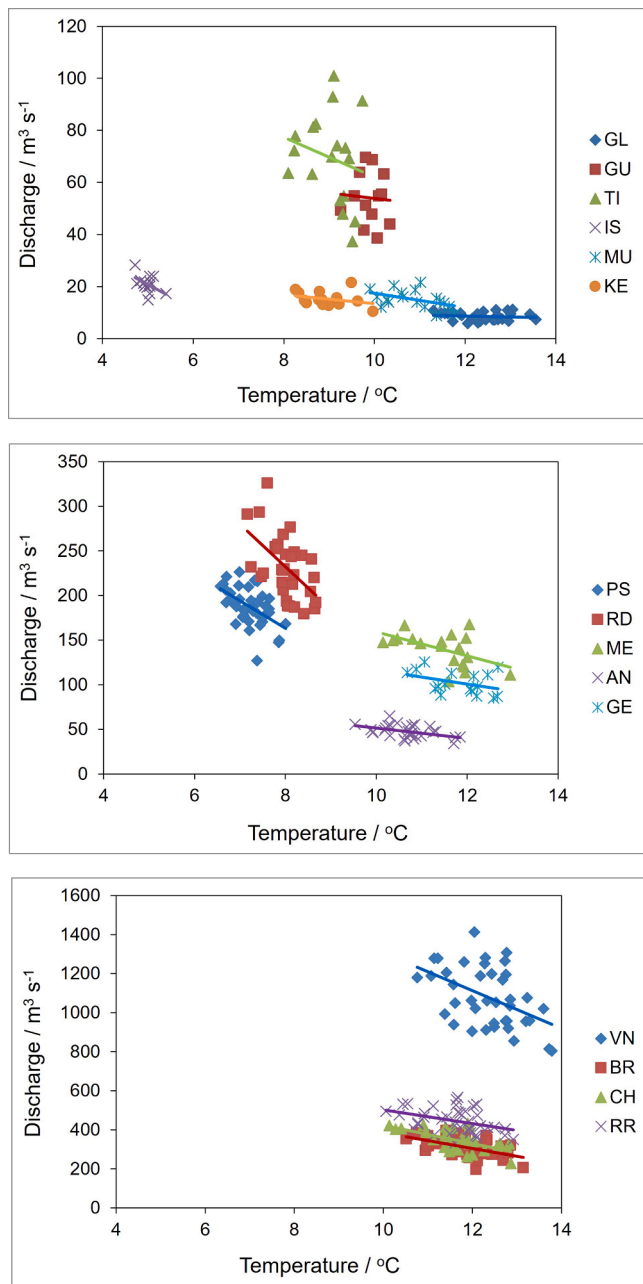


Fig. 4. Dependence of mean annual discharges on mean annual temperatures for the 15 stations with more than ten years of data available.

overlapping with ours. In addition, human influence is probably much stronger in our case.

However, just evaluating univariate load-temperature correlations might give misleading information on the influence of temperature on loads because it assumes that both effects are independent and additive. Indeed, the coupling of discharge and temperature makes it advisable to perform a multiple linear regression of loads on discharge and temperature to explore any possible cross-effect of those two variables on weathering loads. Contrary to the univariate load-temperature correlations (Table S11), in the results of the multiple regressions of loads on temperature and discharge, the inclusion of discharge results in a negligible effect of temperature in the majority of stations (Table 4), although five stations present a significant positive effect on SA annual loads (TI, GE, ME, RR, VN) and one on Ca_{car} annual loads (GL). Only in two stations (MU, CH) is there a significant negative effect of temperature on SA annual loads and only in one (VN) a negative effect of

temperature on Ca_{car} annual load is observed. An explanation for the differences between univariate and multiple regression results can rely on the negative relationship of discharge and temperature in all stations (Fig. 4). Our results, therefore, clearly show that a multiple linear regression treatment is needed to discern temperature and discharge effects.

The influence of temperature on annual loads is generally positive but only important (as deduced from the values of standardized coefficients (Table 4)) in the case of SA in the post big lakes stations of GE, ME, RR, VN and CH, positive in the first four and negative in CH. This station shows a significant decrease of discharge and SA load in the period of sampling, which could explain the result. Perturbation of SA dynamics in large lakes is the cause for the other. For Ca_{car} annual loads, the influence of temperature is small (0.1 or less).

In conclusion, on a basin per basin basis, discharge is the dominant influence on annual loads of both SA and Ca_{car} (Eiriksdottir et al., 2013). The acceleration of silicate and carbonate dissolution as temperature increases is hidden by the effect of discharge.

Measuring possible changes in weathering inside a catchment eliminates the confounding effects of differences in lithology, soils, relief and vegetation among basins, which complicate the interpretation of data (Gislason et al., 2009). Can comparison among basins furnish a further insight?

5.2. What weathering fluxes and their comparison with annual loads tell us

Runoff and lithology ([SA]) exert the main positive influences on SA annual fluxes, and temperature is the main positive influence on Ca_{car} fluxes in our basins. The fraction of impounded water in the basin exerts a negative influence on both SA and Ca_{car} weathering fluxes. Our basin lithology heterogeneity allows for the effect of lithology on SA weathering to be detected; this is an advantage compared with studies where basins chosen share a similar lithology. Comparison of these results with those of annual loads in each basin give interesting insights but requires to consider that variables E , B and mean concentrations are constant parameters in each basin but not among basins. Whereas runoff or discharge (its equivalent in the univariate basin load regressions) are the main drivers of single basin SA annual loads and all basin SA fluxes, runoff influence is not significant in all basin Ca_{car} fluxes but discharge is the main variable in single basin regressions. In contrast to SA, almost half Ca_{car} variability in fluxes is unexplained by temperature, impounded water and runoff.

Temperature is the main variable behind Ca_{car} fluxes while its influence in each basin is variable and generally small. This is easy to understand if we consider that the range of temperatures covered in each basin is small (i.e., giving not significant effects and inter-basin variability) while much higher when considered all together (i.e., the diversity of the many basins included in this work allows the detection of effects otherwise hidden). In Ca_{car} fluxes, positive temperature effects correspond to mean annual temperatures up to 12.4 °C, which are situated in the increasing part of the general “banana” concentration-temperature relationship ($T < 15$ °C) (see Sup. Info file), thus agreeing with theoretical expectations.

It is probable that variables such as E substitute for the effect of temperature in the general regression of SA fluxes. In fact, stations with high temperature effects in annual loads are located after big lakes (GE, ME, CH, RR, VN, see table 4), with high E values. Probably, we are not detecting in them the effect of silicate weathering but those of SA perturbations in big lakes.

5.3. What temporal trends suggest

Statistically significant temporal trends on several solute concentrations have been observed in Swiss surface waters (Rodríguez-Murillo et al 2015; Zobrist et al 2018; Botter et al 2019) and mostly attributed to

direct anthropic influences. In the case of the weathering products studied in the present work, however, very few significant temporal trends have been found: bi-weekly SA loads decrease at the two Rhone River stations (PS and CH) and in IM, and bi-weekly Ca_{car} loads decrease at CH (Table 5). No significant trends have been observed in other stations. The general significant increase of water temperature (Zobrist et al., 2018) is not mirrored by an increase of weathering in the basins, in line with the conclusions by Zobrist and co-workers. Indeed, the lack of significant temporal trends in weathering loads is consistent with the small effect of temperature on loads observed in the present work. Obviously, this does not mean that human effects are not acting on weathering loads and fluxes but rather that the effect on weathering of human-caused temperature increase in the last decades is small compared to the sum of all acting effects and that these processes themselves do not result in significant temporal changes in most of weathering loads in Swiss basins.

6. Conclusions

Long term (1974–2015) hydrological and chemical data in 20 stations in Swiss rivers of contrasting characteristics allowed us to evaluate the effect of discharge and temperature on annual silicic acid (SA) and calcium linked to carbonate (Ca_{car}) loads in each station and in mean fluxes considering all 20 stations together. Our results show that multiple linear regression analysis (temperature and discharge) reveal that influence of temperature, when taking into account discharge, is different from the one obtained from univariate linear regression on temperature and discharge. This ‘real’ influence of temperature is positive in several basins for SA and mostly non-significant for Ca_{car} . Runoff and lithology are the main positive factors on SA fluxes, whereas temperature is the main positive factor in Ca_{car} fluxes with the fraction of impounded water in the catchment being the main negative influence for both solutes. No temporal trend in loads are detected in 18 out of the 20 stations considered.

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Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.jhydrol.2022.127995>.

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