

Water Chemistry of Swiss Alpine Rivers

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Abstract Average concentrations of dissolved nutrients (NO_3 , DRP, K) in the large alpine rivers Rhine, Rhône, Ticino, and Inn, and in small alpine streams and glacier streams, are low compared to those in midland rivers. Concentrations of NO_3 in the large rivers clearly exceed background concentrations. In spite of limited anthropogenic activities in alpine catchments, DRP concentrations in large rivers exhibited a downward trend over the last 30 years. Time series of NO_3 concentrations were first increasing and then leveled off. Export coefficients of NO_3 and DRP in alpine streams fall in the range of those estimated for nonagricultural lands and forests on the Swiss Plateau.

The chemical weathering rate of rock-forming minerals in alpine catchments is about $165 \pm 45 \text{ g m}^{-2} \text{ y}^{-1}$, corresponding to an ablation rate of about 0.06 mm y^{-1} . Rates are dominated by the reaction of carbonate-containing rocks with CO_2 and the dissolution of anhydrite, whereas the weathering of silicate minerals contributes little. Total chemical weathering rates are in the same range as the export rate of fine sediments, as part of physical weathering products. In this respect, alpine rivers differ distinctly from lowland running waters. Long-term observations also revealed small changes in concentrations and loads of geochemical constituents. An increase in water temperature may be one driver for these changes, although other factors also play a role.

Keywords Export coefficients, Nutrients, Temporal trend, Water quality, Weathering

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Abbreviations

Ca	Calcium
CO ₂	Carbon dioxide
DRP	Dissolved reactive phosphorous
H ₄ SiO ₄	Silicic acid
K	Potassium
Mg	Magnesium
NO ₃	Nitrate
P	Phosphorous
SS	Suspended solids
TP	Total phosphorous

1 Introduction

1.1 *Specific Characters of Alpine Rivers*

Alpine rivers in Middle Europe represent a special aquatic ecosystem and their characters differ greatly from those of lowland rivers (see [1], this volume). Alpine rivers have their sources in mountain regions where the land is covered with snow for several months of the year and where glaciers can exist in high altitude areas. As a result, water discharge decreases to a minimum in winter and a

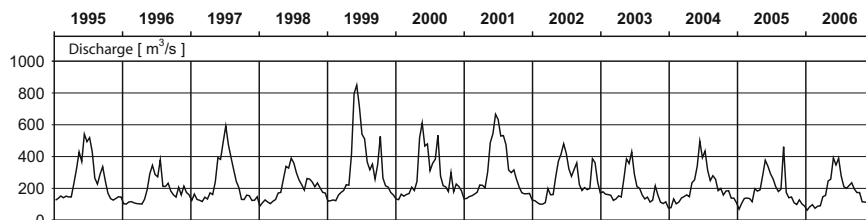


Fig. 1 Seasonal pattern of water discharge in the alpine Rhine (Diepoldsau) from 1995 to 2006 [3]

maximum discharge occurs during snowmelt in early summer (Fig. 1). During this period, much sand, silt and clay, as well as gravel, are transported downstream by turbulent flows, i.e. the river water is turbid, and exhibits a deep grey color and a high concentration of suspended solids (SS). In winter, alpine running waters mostly have clear waters and a laminar flow.

A temperate-humid climatic zone surrounds the Alps. Due to orographic rains, yearly precipitation rates may increase regionally to over 2 m y^{-1} , whereby summer precipitation rates can exceed those in winter (for details see Figs. 6 and 8, [2], this volume). The runoff from alpine catchments generally varies between 0.9 and 1.4 m y^{-1} , i.e. in the range of $28\text{--}45 \text{ L s}^{-1} \text{ km}^{-2}$ ([2, 3], this volume), depending on region and year. This high discharge rate illustrates a typical property of alpine running waters. Rates are considerably greater than in lowland middle European rivers such as the Elbe, Seine ($0.20 \pm 0.05 \text{ m y}^{-1}$) and also water inputs into the sea by the rivers Danube, Rhine, and Rhône ($0.25\text{--}0.56 \text{ m y}^{-1}$) [4].

Presently, a large part of the river water in alpine regions is used for producing hydroelectric power. This abstraction of water may drastically change the flow regime in some segments of rivers. In addition, hydropeaking (rapid changes in water discharge due to temporary running of hydroelectric power stations) may strongly impair the ecological condition of these running waters [5]. Wehren ([6], this volume) provides more detail regarding disturbances due to human interventions.

1.2 Processes Regulating Water Composition

Figure 2 shows processes and factors that regulate water quality.

The condition or state of a natural water body can be characterized by a set of measurable physical, chemical, and biological parameters and a description of observed phenomena. The condition results from the various inputs of diffuse and point sources from natural and anthropogenic origins. These inputs may be transformed from the place of input to the place of measurement depending on the character of the catchment and parameter. Water quality always reflects

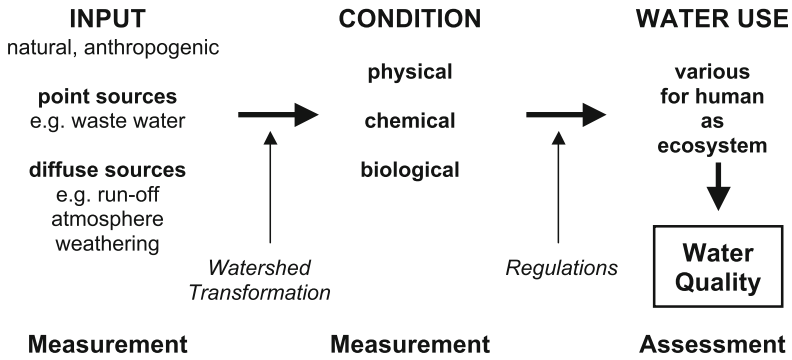


Fig. 2 Schematic representation of the relationship between input into a river, condition (state), water use, and water quality

an interpretation of data gained by observing the water condition. This assessment must be accomplished according to the goal of the water use and regulations, such as the EU Water Framework Directive [7] or the Swiss Water Protection Ordinance [8].

The water composition of alpine rivers is strongly influenced by natural diffuse inputs originating from rock weathering. Weathering processes are defined as the alteration of rocks in the top crust of the earth; it is mainly an interaction of water with rocks [9, 10]. Water can act through physical and chemical processes.

In physical weathering, the rock is broken apart by frost heaving, glacial plucking, and abrasion in running waters. The products of these processes are solid particles (rock debris) exhibiting various sizes (boulder, gravel, sand, and silt). In alpine regions, the subsoil consists mainly of these weathering products. A percentage of the smaller particles are flushed downhill by surface runoff, thus representing the SS in running waters. Therefore, alpine rivers exhibit a large load of SS during high water discharge caused by snowmelt or heavy rainfall. Physical weathering also increases the surface area of the rock and debris exposed to chemical weathering.

Chemical weathering describes the interactions of rock-forming minerals with water and its solutes (protons, carbonic acid, complexing agents) [9]. For the most abundant rocks, calcareous rocks and silicates, such as granitoid rocks, chemical weathering can be considered as acid–base reactions in which the rock-forming minerals represent the base and the dissolved reactants act as the acid, especially dissolved CO₂. Other minerals, such as gypsum, simply undergo dissolution reactions in water (Table 1).

Biological weathering involves the disintegration of rock and its minerals by the chemical and physical actions of living organisms, for example plant roots or bacteria, which can dissolve minerals by oxidation or reduction processes [11].

The rates of chemical weathering reactions increase with temperature as all chemical processes. This effect has been confirmed in laboratory experiments and field studies involving silicate rocks [12]. Weathering reactions occur at mineral

Table 1 Important weathering reactions in order of ease of chemical weathering and solubility, which goes along with the reaction rate of the mineral dissolution, except for bacterial mediated pyrite oxidation [9, 10]

Rock-forming mineral	Equation	Solubility
Halite (Sylvine)	$\text{NaCl (KCl)} \rightleftharpoons \text{Na}^+ (\text{K}^+) + \text{Cl}^-$	High
Gypsum	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O} \rightleftharpoons \text{Ca}^{2+} + \text{SO}_4^{2-} + 2\text{H}_2\text{O}$	High
Calcite	$\text{CaCO}_3 + \text{H}_2\text{CO}_3 \rightleftharpoons \text{Ca}^{2+} + 2\text{HCO}_3^-$	Intermediate
Dolomite	$\text{CaMg}(\text{CO}_3)_2 + 2\text{H}_2\text{CO}_3 \rightleftharpoons \text{Ca}^{2+} + \text{Mg}^{2+} + 4\text{HCO}_3^-$	Intermediate
Silicates	Primary minerals + $\text{H}_2\text{CO}_3 \longrightarrow \text{Base cations} + \text{H}_4\text{SiO}_4 + \text{HCO}_3^- + \text{Al}(\text{OH})_3 + \text{secondary minerals}$	Slight
Quartz	$\text{SiO}_2 + 2\text{H}_2\text{O} \rightleftharpoons \text{H}_4\text{SiO}_4$	Slight
Apatite	$\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2 + 6\text{H}_2\text{O} \rightleftharpoons 4 \text{Ca}_2(\text{HPO}_4)(\text{OH})_2 + 2\text{Ca}^{2+} + 2\text{HPO}_4^{2-}$	Low
Pyrite	$\text{FeS}_2 + 3.75\text{O}_2 + 2.5\text{H}_2\text{O} \longrightarrow \text{Fe}(\text{OH})_3 + 2\text{SO}_4^{2-} + 2\text{H}^+$	

Notes:

CO_2 consumed by weathering reactions represents a sink for atmospheric CO_2

Dissolution of pyrite can also be mediated by bacteria. Weathering reaction listed for silicates is elementary only

surfaces; therefore, the overall rate relies on the size of the wetted surface of the mineral particle and the water flow regime. Hence, comparisons between mineral dissolution rates determined in the laboratory and in the field reveal large discrepancies with orders of magnitude lower rates in the field [9, 13, 14]. In addition, environmental factors such as the mineral supply from the breakdown of rocks [15] or runoff [16, 17] can influence weathering rates occurring in natural systems. Factors that govern weathering rates can also be described by two kinds of weathering regime [18]. In a transport-limited regime, physical erosion is low and produces fewer new reactive surfaces of minerals. In addition, it leads to an excess of soil that depresses the chemical weathering of bedrock. In a weathering-limited regime, high physical erosion restricts soil formation and continuously creates new reactive surfaces that can be weathered chemically. Weathering rates of carbonates and silicates also depend on the partial pressure of CO_2 at the location where reactions proceed in soil and aquifers. The solubility of calcite and dolomite is inversely proportional to temperatures found in natural aquatic environments [19]. All these processes and factors must be considered when assessing whether climate effects change weathering rates and its implication regarding the regulation of atmospheric CO_2 [12, 15, 18, 19].

In alpine rivers, dilution will govern the impairment from pollution loads by point or diffuse sources such as treated wastewaters or runoff from agricultural lands. This dilution effect decreases gradually when rivers enter the lower altitude range of a watershed.

1.3 Data

In the field of water protection, small and medium-sized alpine running waters are rarely monitored, since their impairment by pollution is considered small. Therefore, the database of nutrients for such rivers relies on ecological research projects [20–23]. The National Long-Term Surveillance of Swiss Rivers (NADUF) [23] monitors the larger alpine rivers Rhine, Rhône, Ticino, and Inn, and yields data on nutrients and geochemical constituents as well. To highlight the specific chemical condition of alpine rivers, relevant data, including the Thur River for comparison, are included in the following discussion. The Thur flows through a part of the eastern Swiss Plateau (Swiss Midlands) where major intensive agricultural activities occur. The Thur has its source in the alpine region of the Säntis massif.

Rivers listed in Table 2 and shown in Fig. 3 incorporate a broad range of characteristics, including water discharge, catchment area, land cover, land use, and the number of people living in the catchment. Land use and population reflect the potential pollution intensity, whereas the percentage of intensively used agricultural land in the catchment or the number of inhabitants per unit water discharge are major pollution stress factors. They also represent important diffuse and point sources of pollution.

Table 2 Character of alpine catchments for which chemical data are discussed

River station	Water discharge $\text{m}^3 \text{s}^{-1}$ mean Q	Basin area km^2	% Barren	% Forest	% ext. used	% int. used	% settl.	Inhab. per mean Q	Basin altitude m.a.s.l. mean	References
Six glacier streams	0.6–4	20–50	~85	~5	~10	0	0	0	~2,900	[22]
Versegères	~0.6	15	19.0	18.1	61.0	1.2	0.7	30	2,065	[20]
Calancasca	~4	108	34.3	20.9	43.2	1.0	0.6	70	1,965	[20]
Arvigo										
Erlenbach	0.027	0.76	0.0	33.7	61.3	5.0	0.0	0	1,348	[23]
Rhine	244	6,116	20.2	23.0	46.0	8.1	2.8	1,500	1,790	[23]
Dipoldsau										
Rhône	190	5,236	41.6	16.9	32.6	6.0	2.8	1,500	2,123	[23]
Porte-du-Scex										
Inn	24	617	47.6	6.2	41.3	3.2	1.7	630 ^a	2,462	[23]
S-Chanf										
Ticino	71	1,617	19.3	33.8	40.9	3.1	2.9	1,000	1,635	[23]
Riazzino										
Thur	48	1,704	1.5	25.6	18.4	45.7	8.8	6,300	768	[23]
Andelfingen										

^aWithout seasonal guests

Notation for land uses:

Barren: land with no vegetation, e.g. snow fields, glacier, bedrock, rock debris, surface waters

Forest: dense forest, can be exploited, not fertilized

Ext. used: land covered with vegetation, which is not or only scarcely used and not fertilized

Int. used: agricultural land that is fertilized strongly, e.g. arable land, pastures, and vineyards

Settl.: human settlements, e.g. villages, roads, and industrial areas

The six glacier rivers are situated pairwise in three regions, the Val Roseg in Graubünden, Alps of Uri, and the Bernese Alps, their land use is a rough estimate

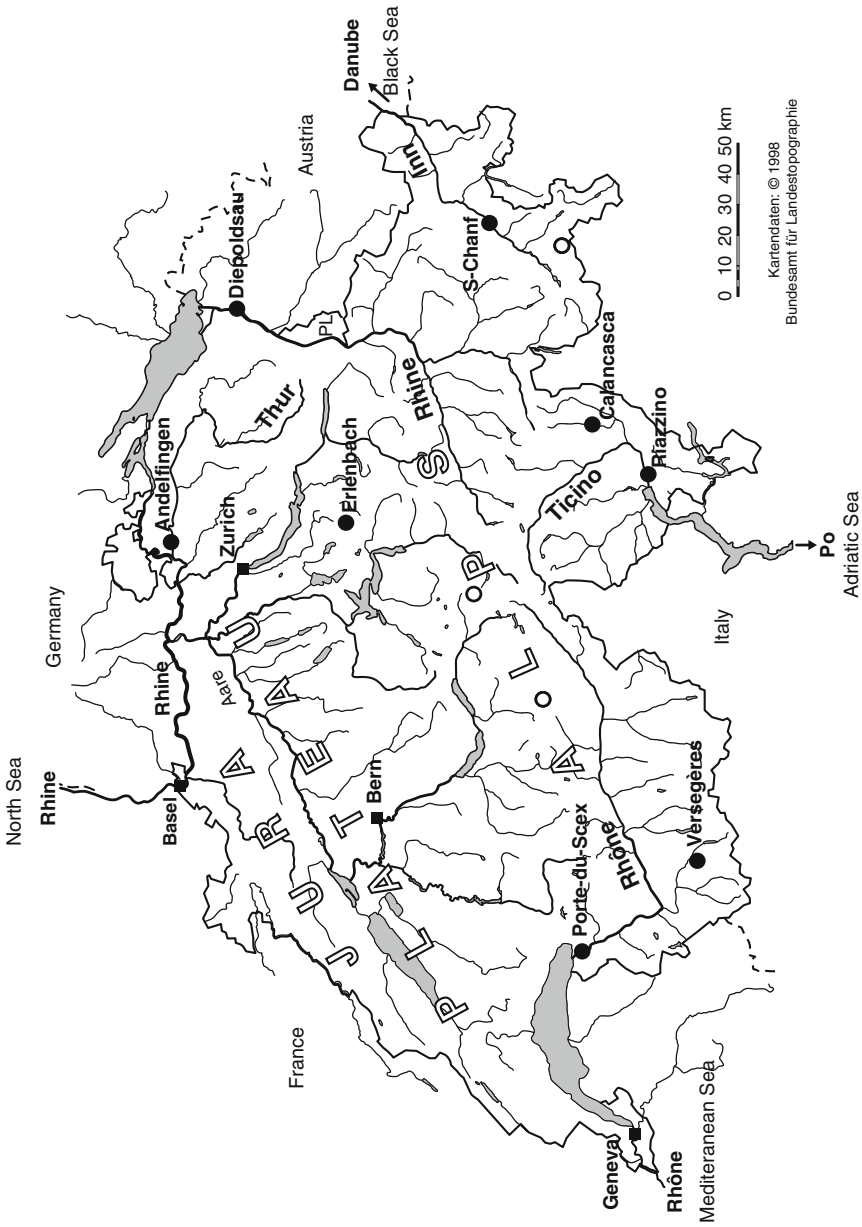


Fig. 3 Map of Switzerland and river stations from which chemical data are used in this contribution, *circle* only. Running waters from the Alps flow in all four directions and in four different seas

1.4 Objectives

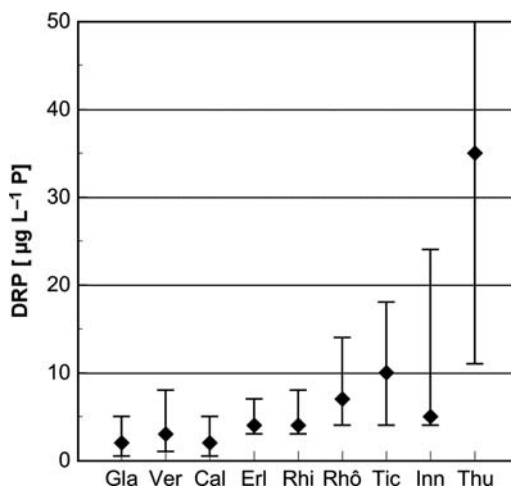
The following sections aim to illustrate the key words displayed in Fig. 2 using measured data and to discuss the important processes regulating the observed water conditions. The change in nutrient concentrations in Swiss alpine running waters will be reported proceeding from high alpine regions to lower alpine valleys. Data gained from the long-term monitoring NADUF program facilitate the identification of significant trends in nutrient concentrations and loads as well as geochemical parameters. The reasons for observed trends will be discussed in the framework of water pollution control measures taken, and climate change. Data used also enable us to calculate export coefficients for nutrients characterizing the different land uses and to estimate geochemical weathering rates.

2 Current Chemical Conditions

2.1 Phosphorous

Concentrations of dissolved reactive phosphorous (DRP) (Fig. 4) in glacier streams, and the two small streams Calancasca and Versegères, fell in the range of a few

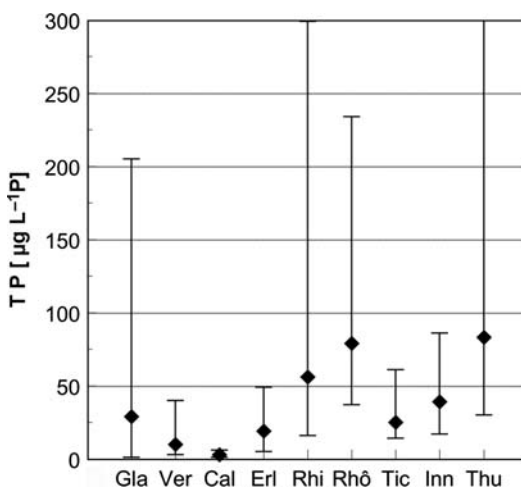
Fig. 4 Concentration ranges (5%, 50%, and 95% percentiles) of DRP in six glacier streams (Gla), two alpine streams Versegères and Calancasca (Ver, Cal), one prealpine stream Erlenbach (Erl), three alpine rivers Rhine (Rhi), Rhône (Rhô), and Ticino (Tic) and the midland river Thur (Thu). Note: Database: glacier streams altogether 90 grab samples (1998/99), Versegères 27 grab samples (1980/81), Calancasca 34 grab samples (1980/81), Erlenbach 52 continuous and flow proportional weekly samples (2005), Ticino continuous and flow proportional biweekly samples 1997–1999 Rhine, Rhône, and Thur continuous and flow proportional biweekly samples 2001–2005



$\mu\text{g L}^{-1}$ P. Values were just above the analytical detection of the method applied in these three surveys. Human activities in these catchments are very small; therefore concentrations measured reflect natural background values of alpine running waters in the Swiss Alps. Concentrations can be considered being due to the weathering of phosphate-containing minerals and small atmospheric inputs. The lower average altitude of the Versegères catchment may explain the somewhat higher concentrations of DRP in this stream in relation to those in the glacier streams and Calanca stream; that is by more active vegetation. The increase in average DRP in the Erlenbach stream to $4 \mu\text{g L}^{-1}$ P compared to the three other rivers may also be caused by the higher detection limit of the analytical method applied in this survey. The average DRP concentrations in the large rivers Rhine, Rhône, Ticino, and Inn were still low considering the existing inputs from treated wastewater and runoff from agricultural land. These low average DRP concentrations result from the water protection measures taken in Switzerland to decrease phosphorous (P) inputs into surface waters [24], especially into lakes where eutrophication occurred [25]. Trend analysis of P concentrations in Swiss rivers [26], including alpine rivers, exemplified in Fig. 5, have clearly shown the decrease in P loads. The high content of SS also favors low concentrations of dissolved P in alpine rivers due to sorption of P to particles. Therefore, in rivers exhibiting high concentrations of fine particles, the potential bioavailable load of P can be underestimated by using measured DRP data [27]. Figure 4 also clearly displays the difference in the DRP concentration between natural rivers and slightly impaired running waters and the River Thur, which lies in a catchment on the Swiss Plateau where nearly half of the catchment area is used by intensive agriculture and the input of treated wastewater is significant.

Concentrations of total phosphorous (TP) mostly exceeded those of DRP and exhibit a different pattern (Fig. 5). During high flow conditions, concentrations of TP and SS both show high values that indicate a good correlation between these two chemical parameters. As an extreme, the weekly sample during a high flow event

Fig. 5 Concentration ranges (5%, 50%, and 95% percentiles) of total phosphorous (TP) in five glacier streams (Gla), two alpine streams (Ver, Cal), one prealpine stream (Erl), three alpine rivers Rhine (Rhi), Rhône (Rhô), and Ticino (Tic) and the midland river Thur (Thu). Database see legend for Fig. 4



that occurred in the alpine Rhine in August 2005 exhibited a TP concentration of $2,550 \mu\text{g L}^{-1}$ P and a SS concentration of 2.52 g L^{-1} . This means that 78% of the yearly load of TP and 63% of the SS were discharged during this peak flow. Speciation data from the glacier streams and the Versegères and Calancasca [20, 22] showed that the total dissolved fraction of phosphorous is only slightly higher than the DRP concentration, but clearly less than the TP. Therefore, it can be assumed that the main fraction of the P load present as TP measured in alpine rivers is not bioavailable to algae when these waters are discharged into lakes.

2.2 Nitrogen

Nitrate (NO_3) concentrations (Fig. 6) observed in the glacier streams and the Versegères, Calancasca, and Erlenbach reflect the contemporary background values in alpine running waters. Concentrations are mainly due to atmospheric inputs of inorganic nitrogen compounds such as ammonium (NH_4) and NO_3 . The higher atmospheric nitrogen deposition rate in the southern Alps than in the northern region [28] may explain the higher NO_3 concentration in the Calancasca stream. Concentrations in the alpine rivers, Rhine to Inn, exceeded background values, indicating a small but clear anthropogenic impairment. NO_3 concentrations in the Thur were above those measured in alpine running waters. They indicate the high nitrogen inputs from fertilized agricultural lands [29].

The median ammonium concentration in the glacier streams, the Versegères and the Calancasca equaled $10\text{--}15 \mu\text{g L}^{-1}$ N, whereas ammonium levels mostly went over the median in summer. The median values of nitrite (NO_2) were low in the range of $1\text{--}2 \mu\text{g L}^{-1}$ N. Concentrations of dissolved organic nitrogen in glacier streams were about one third of that of NO_3 . Therefore, ammonium and nitrite contributed little to the background concentration of total dissolved nitrogen

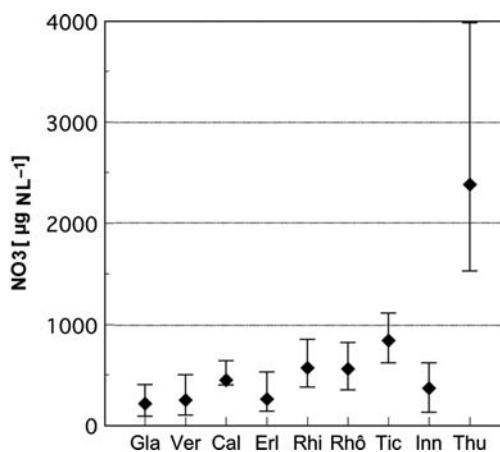


Fig. 6 Concentration ranges (5%, 50%, and 95% percentiles) of nitrate in six glacier streams (Gla), two alpine streams (Ver, Cal), one prealpine stream (Erl), three alpine rivers Rhine (Rhi), Rhône (Rhô), and Ticino (Tic) and the midland river Thur (Thu)

content in natural alpine rivers. In addition, concentrations of nitrite and ammonia, that is produced in the pH-dependent equilibrium with ammonium, remained well below the toxicity level for salmonoids in fresh waters [30]. The content of particulate nitrogen in glacier streams was <10% of that of NO_3 or total nitrogen. In the alpine rivers, Rhine to Inn, NO_3 amounted to 70–85% of the total nitrogen [26]. In the case of the Thur, nitrate made up over 90% of the total nitrogen. This means that the other nitrogen fractions mentioned above contribute little to the total nitrogen load in Swiss rivers.

2.3 Other Nutrients

In waters, silicic acid (H_4SiO_4) represents an important nutrient for diatoms. Potassium (K) also acts as a nutrient for aquatic plants, although it is rarely limiting. Their concentrations in alpine rivers are strongly governed by the chemical weathering of silicates (rock-forming minerals) such as biotite, K-feldspar, and clay minerals. Concentrations of K and H_4SiO_4 observed in alpine rivers (Fig. 7) reflect qualitatively the relative abundance of silicates in the catchment. Highest values, medians and 95% percentiles, were reported in the Ticino, a catchment covered mainly with silicates, gneiss, and granites. The lowest concentrations were observed in the Erlenbach, a catchment exhibiting calcareous rocks, mainly flysch (calcareous sandstones with clay-rich schists), which also contain some clay. The relatively high range of K in the Thur, a catchment dominated by calcareous rocks, mainly molasses, can be explained by inputs from fertilized agricultural lands.

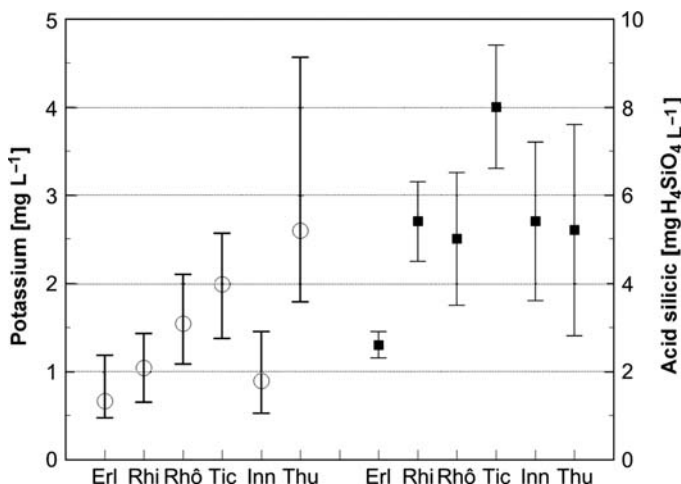


Fig. 7 Concentration ranges (5%, 50%, and 95% percentiles) of potassium and silicic acid in one prealpine stream (Erl), three alpine rivers Rhine (Rhi), Rhône (Rhô), and Ticino (Tic) and the midland river Thur (Thu)

3 Trends

3.1 Introduction

The long-standing data series obtained by the NADUF program allowed the evaluation of changes and trends in nutrient concentrations and loads. The mathematical model chosen describes the time series in concentration and load as a yearly sinusoidal function, representing the seasonal fluctuation and the linear change with time. The regression calculation with the data measured gives the average yearly trend and the average amplitude in seasonal variation. In addition, the calculation also estimates the standard deviations of the regression coefficients [26]. Trends and amplitude are considered significant if the correlation coefficient of the regression is statistically significant at the 95% level and the 95% confidence intervals of the linear trend or amplitude do not include zero. This kind of time-series analysis allows detecting small but significant linear trends down to 0.1% per year depending on the chemical parameter and water flow regime.

3.2 Phosphorous

The long-term time series in DRP concentrations, exemplified in Fig. 8, showed a clear decrease in most Swiss rivers and a downward step in 1986, the year in which

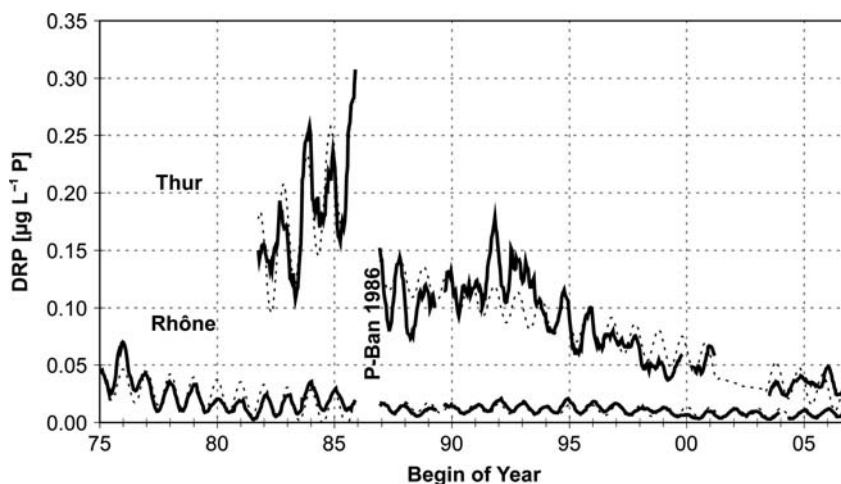


Fig. 8 Influence of the P-ban in detergent to the moving averages over a period of 22 weeks (*solid line*) for DRP concentration in the Thur and Rhône. Sinusoidal regression curves (*dashed line*) before and after the ban

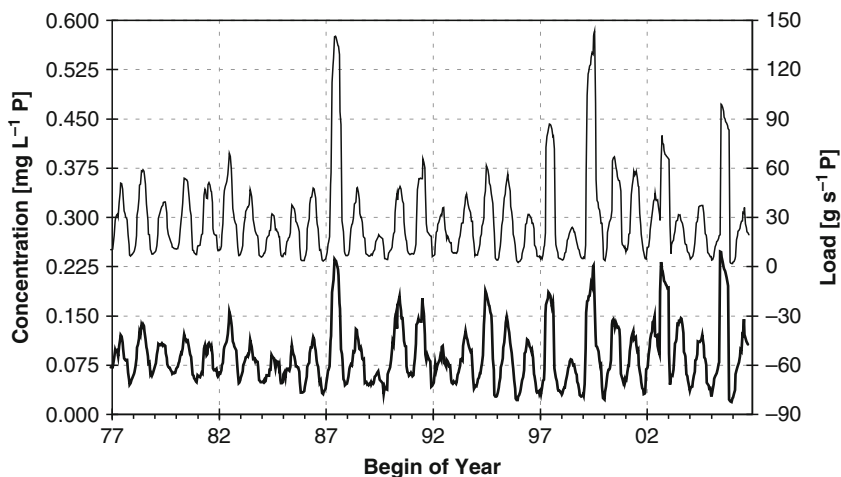


Fig. 9 Moving average over a period of 22 weeks for TP concentration (*lower curve*) and load (*upper curve*) in the Rhine from 1977 to 2006

the P-ban in detergent was enforced. The yearly decrease in the Rhône amounted to $2.3 \mu\text{g L}^{-1} \text{P}$ in the period 1975–1985, it decreased to $0.3 \mu\text{g L}^{-1} \text{P}$ afterwards. In the River Thur, an increase was noted in the short measuring period before the P-ban. After 1986, the DRP concentration clearly decreased at a yearly rate of $5.5 \mu\text{g L}^{-1} \text{P}$. However, in the last two years the downward trend appeared to level out. In alpine rivers, decreases in DRP concentrations and loads were usually small but mostly statistical significant [26]. Trends estimated in the alpine Rhine are similar to those in the Rhône.

TP concentrations and loads displayed strong seasonal fluctuations (Fig. 9). In addition, peak flow resulted in high TP concentrations and loads. The trend analysis yielded no statistically significant change over the measuring period of 30 years in the Rhine or 32 years in the Rhône. However, at shorter intervals, some significant changes could be recognized, such as in the period from 1977 to 1986.

Siegrist and Boller [24] estimated that the P-ban in detergents resulted in a decrease of P input of $2,600 \text{ t P y}^{-1}$ (390 g P s^{-1}) by wastewaters into Swiss surface waters. Referring this decrease to the alpine Rhine catchment (proportional to the number of inhabitants), a reduction in P-load of 145 t y^{-1} ($4.5 \text{ g s}^{-1} \text{P}$) can be expected, giving an average concentration decrease of $18 \mu\text{g L}^{-1} \text{P}$. For the alpine Rhône, this decrease would equal $110 \text{ t y}^{-1} \text{P}$ ($3.6 \text{ g s}^{-1} \text{P}$), resp. $19 \mu\text{g L}^{-1} \text{P}$ and for the Thur $120 \text{ t y}^{-1} \text{P}$ ($3.7 \text{ g s}^{-1} \text{P}$), resp. $77 \mu\text{g L}^{-1} \text{P}$. The measured decreases in P in the alpine Rhine and Rhône (Fig. 8) were not as large as those expected by the P-ban, although the P input by detergents in wastewaters occurs mainly in the form of DRP. The higher decrease found in the Thur may be attributed to P control measures taken on agricultural lands and in enhanced P elimination in wastewater

treatment plants. Two factors may explain why the effect of the P-ban could not be clearly detected by monitoring TP: The decrease in the P load in the alpine rivers due to the P-ban was small compared to the total measured TP load, and the strong yearly fluctuation in measured TP loads and concentrations may mask the decrease. The main source of TP in alpine running waters originates from soil particles that are flushed during heavy rainfalls or by snowmelt into running waters.

3.3 Nitrate

NO_3 concentrations and loads in the Rhône, as well as in the Rhine, showed clear trends (Fig. 10). From the mid-1970s to the end of the 1980s, both concentrations and loads increased significantly in the range of 2–5%, that is 9–14 $\mu\text{g L}^{-1}$ N per year. From the 1990s to 2006, concentrations and loads decreased significantly in the Rhône, about 0.5% per year, whereas decreases in the Rhine were insignificant. This downward trend of NO_3 is probably due to a change in agricultural practices, as they adapted the input of fertilizer to the need of the crops and avoiding fallow fields in winter. During the entire measuring period from 1975 to 2006, NO_3 concentrations increased significantly, 0.4% per year in the Rhône and 0.2% per year in the Rhine. The NO_3 loads did not change significantly in either river, although the water discharge in the Rhine decreased 0.5% per year.

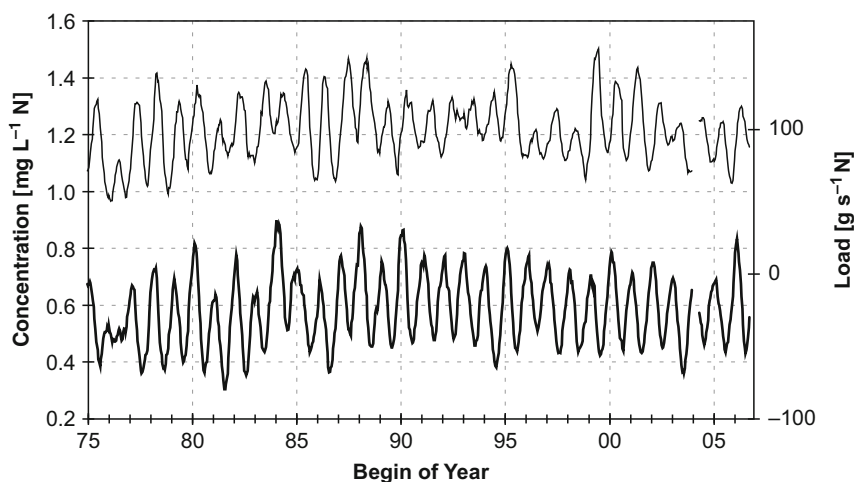


Fig. 10 Moving average (period 22 weeks) of nitrate concentration (*lower curve*) and load (*upper curve*) in the Rhône from 1975 to 2006

3.4 Water Temperature and Geochemical Parameters

Water temperatures measured continuously at the sampling stations of the Rhine and Rhône have increased significantly. In the River Rhine, the increase amounted to 0.031°C or 0.43% per year or 0.95°C in 30 years (Fig. 11), and in the River Rhône the average increase was 0.023°C or 0.34% per year or 0.69°C in 30 years. In rivers on the Swiss Plateau [26, 31], temperature increases mostly were over 0.4% per year. Figure 11 displays a remarkable temperature increase in the period 1987–1992 when the water discharge was low. Therefore, one might argue that the temperature increase was due to the change in water discharge. Indeed, the heat flux in the Rhine as well as in the Rhône did not change significantly over the measuring period from 1975 to 2006. However, this result would be inconsistent with the warming effect of running waters expected by increased air temperature (see [2], this volume). When discussing the causes of water temperature changes in alpine rivers, one must consider that temporal and spatial changes in water flow provoked by hydroelectric power stations could also influence the water temperature regime to an extent not yet evaluated [31].

In the context of the discussion raised in the literature on the impact of global warming on weathering [e.g. 12, 15, 18], it will be interesting to evaluate the concentration and load changes of geochemical constituents in alpine rivers. Time series analysis described in Sect. 3.1 allows the analysis of their changes in the Rhine and Rhône River. Measuring periods in the other alpine rivers cited were too short to yield meaningful results.

Quantitatively, the most important weathering product, bicarbonate expressed as alkalinity, exhibited a small, but statistically significant, decrease of $2.6 \mu\text{mol L}^{-1}$

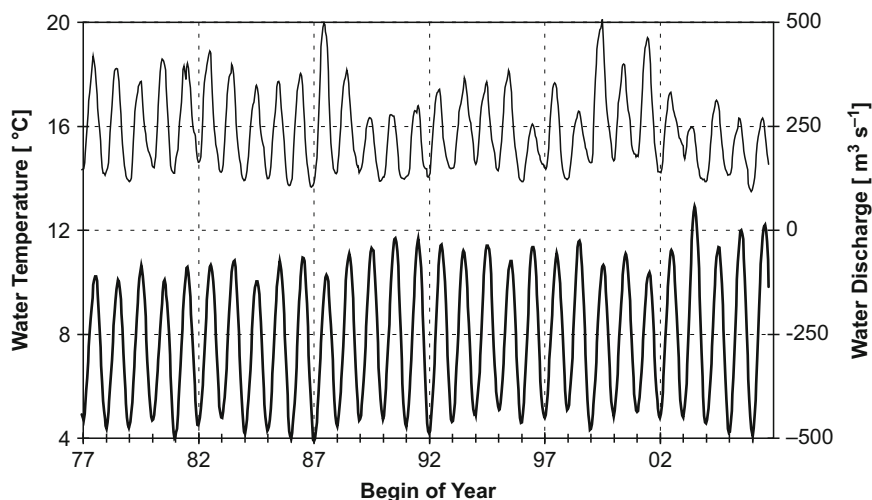


Fig. 11 Moving average (period 22 weeks) of water temperature (*lower curve*) and water discharge (*upper curve*) in the Rhine

per year; equivalent to 0.13% of the alkalinity observed in the Rhine and 0.20% of that in the Rhône. These declines can be explained quantitatively by the diminishing solubility of calcite with increasing temperature [32]. The load of alkalinity in the Rhine diminished slightly by 0.32% per year, caused by the decrease in the water discharge of 0.47% per year from 1977 to 2006. In contrast, the alkalinity load in the Rhône exhibited no change. The main ionic counterpart of bicarbonate in natural waters, calcium and magnesium, exhibited a different behavior. Mg concentrations increased notably and significantly; $1.5 \mu\text{mol L}^{-1}$ per year or 0.72% in the Rhône and $2.3 \mu\text{mol L}^{-1}$ or 0.72% in the Rhine. Mg loads also became greater in both rivers, as has been observed in most rivers monitored in the NADUF programme [26]. It can be hypothesized that the observed increase is due to the release of Mg from soils brought in by applied fertilizers containing Mg as a minor ingredient. Ca concentrations, on the other hand, decreased insignificantly by $0.34 \mu\text{mol L}^{-1}$ per year in the Rhone and significantly by $1.1 \mu\text{mol L}^{-1}$ per year in the Rhône. In general, these decreases were consistent with the temperature dependence in calcite solubility. Calcium loads decreased significantly 0.19% per year in the Rhône and 0.52% in the Rhine. The opposite time trend of the two earth-alkaline ions observed in the Rhône yielded no significant patterns in concentration and load of the sum of both ions, that is total hardness. With regard to the Rhine River, the concentration in total hardness increased slightly and the load decreased as caused by the decline in water discharge.

The opposite trend in concentrations of the earth-alkaline ions induced a remarkable and statistically significant change in the magnesium to calcium ratio (Fig. 12). It is worth mentioning that the seasonal minimum in the ratio occurs in summer when Mg and Ca also show their minima. The relatively larger seasonal decrease in

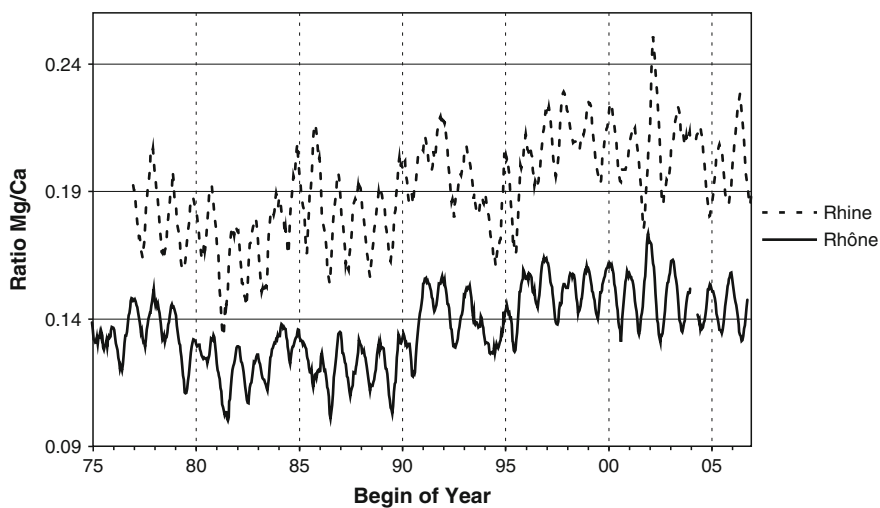


Fig. 12 Moving average over a period of 22 weeks of the molar ratio Mg to Ca in the Rhône and Rhine from the 1970s to 2006

Mg than in the Ca concentration causes the summer minimum in the ratio. Mg to Ca ratios did not rise evenly over the measuring period. In the years 1987–1997, a clear increase occurred. In the last 7 years, changes were leveling. The increase in the Mg to Ca ratio has been observed in most of the other rivers monitored by the NADUF program [26].

From 1975 to 2006, the concentration of H_4SiO_4 , the weathering product of silicates and clays, diminished slightly but significantly by $0.13 \mu\text{mol L}^{-1}$ or 0.23% per year in the Rhône and nonsignificantly in the Rhine ($0.03 \mu\text{mol L}^{-1}$). Loads of H_4SiO_4 decreased significantly by 0.6% per year in both rivers. The calculated downward trends in H_4SiO_4 are contradictory to expected increases in the weathering rate of silicates due to observed increases in air and water temperatures.

K, a weathering product and fertilizer ingredient, exhibited a strong increase in all Swiss rivers. In the Rhône, this amounted to $17 \mu\text{g L}^{-1}$ or 1.5% per year and $9.4 \mu\text{g L}^{-1}$ or 1.1% per year in the Rhine. Trends in loads were also highly significant. This large increase in K can be best explained by a small release from the large K deposit built up in soils fertilized over the last few decades [26].

4 Mass Fluxes

4.1 Export Coefficients

Export coefficients per unit area of the catchment and per unit time characterize the mass flow (load) of a river water constituent at the outlet of the catchment. For conservative constituents, that is for which no relevant biogeochemical transformation processes are occurring in the river water, the export at the outlet is equal to the sum of all inputs into the river coming from the various point and diffuse sources. This assumption can be regarded as a valuable approximation in alpine rivers for most of the chemical parameters discussed. Export coefficients allow comparing different catchments in size, land use, or other characters describing a basin.

DRP, NO_3 , and TP export coefficients listed in Table 3 exhibited about the same relative size pattern between rivers like their concentrations depicted in Figs. 4, 6, and 7, since specific water discharges between rivers fell into the same size range. DRP and NO_3 coefficients calculated for the small and remote catchments (glacier streams, Versegères, Calancasca, and Erlenbach) did not vary significantly. These differences between the four catchments cannot be related to the differences in land cover reported in Table 2. A Bayesian estimation [29] of DRP and NO_3 export coefficients for each kind of the five input sources stated in Table 2, using the whole long-term NADUF data set, gave very similar values for the three categories of land cover (barren land, dense forest, and extensively used land), but with large confidence intervals. In these calculations, mean values for DRP varied between 4 and $6 \text{ mg P m}^{-2} \text{ y}^{-1}$ and those of NO_3 between 360 and $480 \text{ mg N m}^{-2} \text{ y}^{-1}$, when taking the load calculation mode. Coefficients for intensively used agricultural land

Table 3 Export coefficients for water, nutrients, and suspended solids

Parameter	Water discharge		NO ₃	DRP		TP		SS	
	m ³ m ⁻² y ⁻¹	Mean		mg m ⁻² y ⁻¹	Mean	mg m ⁻² y ⁻¹	Mean	mg m ⁻² y ⁻¹	Mean
Unit			mg m ⁻² y ⁻¹		mg m ⁻² y ⁻¹		mg m ⁻² y ⁻¹		g m ⁻² y ⁻¹
River			Mean		Mean		Mean		Median
Gla	~1.5		~350		~110		n.d		n.d
Ver	1.26		280		20		n.d		n.d
Cal	1.17		540		3.4		n.d		n.d
Erl	1.31		400		65		31		27
Rhi	1.17		619		167		55		51
Rh�	1.24		663		166		88		60
Tic	1.53		1,210		47		25		7
Inn	1.08		312		63		12		1
Thu	0.86		2,240		141		57		14

n.d.: no data, river abbreviation see legend Fig. 4

Database: For glacier streams, Versg eres and Calanca: mean load calculated as mean discharge times mean concentration. For the other rivers, loads represent means and medians, respectively, of biweekly water discharge proportional samples over the whole measuring period

were distinctly higher, $41 \text{ mg P m}^{-2} \text{ y}^{-1}$ and $2,900 \text{ mg N m}^{-2} \text{ y}^{-1}$, respectively. The contribution of inhabitants, including settlements, amounted to $0.16 \text{ kg P inhab}^{-1} \text{ y}^{-1}$ and $2.1 \text{ kg N inhab}^{-1} \text{ y}^{-1}$, giving $9.6 \text{ mg P m}^{-2} \text{ y}^{-1}$ and $126 \text{ mg N m}^{-2} \text{ y}^{-1}$ for the most populated alpine catchment, the alpine Rhine. The sum of the five Bayesian partial coefficients fitted reasonably well with the measured NO_3 export coefficient for the larger and populated alpine catchments listed in Table 3. In contrast, most observed DRP coefficients fell below the sum of the Bayesian coefficients. This effect might be due to the partial sorption of DRP on SS. Observed DRP and NO_3 export coefficients for the Thur catchment, with its high percentage of agricultural land and higher population density, clearly exceeded those of the other catchments.

TP export coefficients showed a different pattern. They were strongly related to those of SS, that is turbidity. This flow is governed by the physiographical condition of the catchment and the type of bedrock. Mean and median values of TP and SS export coefficients differed greatly. This effect is due to the very high concentrations measured during periods of high water discharge and peak flows.

4.2 Weathering Rates

Weathering rates of rock-forming minerals can be estimated by using a simple input–output box model, whereas the atmospheric deposition [26] represents the input into the catchment and the output are the loads measured at the outlet of the basin, that is at the measuring station. The difference between input and output is assigned to the products formed by chemical weathering taking place with rock-forming minerals in soils and aquifers, represented by the dissolved water constituents. Conversion processes of geochemical parameters occurring in rivers are neglected since they are considered small. Rates of minerals weathered are calculated by the aid of the stoichiometric relations given in Table 1. The exact reconstruction procedure is described in [10] and applied in [26]. Average loads over the measuring period at each station were deployed to estimate weathering rates depicted in Fig. 13.

Weathering of sedimentary rocks, containing calcite, dolomite, and anhydrite, clearly dominated in all catchments (Fig. 13), and also in the Ticino and Inn catchment where bedrock of silicates, mainly granites and gneiss, cover a major part of the basin. This effect is due to a much lower dissolution rate per unit area of land surfaces or mineral surfaces per unit time of silicates compared to calcareous rocks [19]. Meybeck [33] found that the world average relative chemical erosion rate of carbonate rock is 12 times and that of gypsum or anhydrite is 40 times higher than the weathering rate of granite or gneiss.

Large differences in the proportion of silicate bedrock in catchments presented only weakly influenced the silicate-weathering rate for the whole basin (see silicates bar in Fig. 13). In the Ticino basin, mostly covered with silicate bedrock, the rate increased to $100 \text{ mmol m}^{-2} \text{ y}^{-1}$ ($40 \text{ g m}^{-2} \text{ y}^{-1}$). This value was in the range

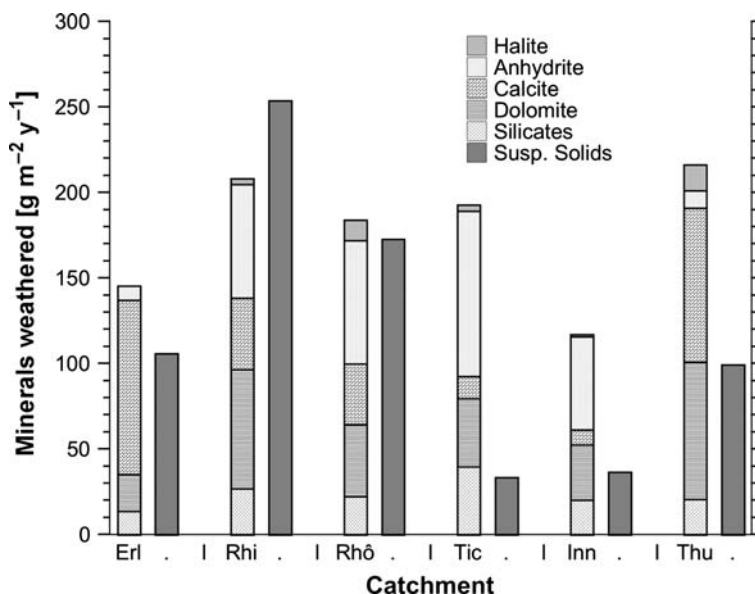


Fig. 13 Minerals weathered chemically and suspended solids weathered physically in alpine catchments and Thur basin. Abbreviation of rivers, see legend for Fig. 4

found in glacier streams in alpine crystalline catchments [34]. In the Rhine and Rhône catchments, silicate-weathering rates were 68 and 56 $\text{mmol m}^{-2} \text{y}^{-1}$ (27 and 22 $\text{g m}^{-2} \text{y}^{-1}$). In the Erlenbach and Thur catchments, having no silicate bedrock, silicate-weathering rates estimated from the load of silicic acid, H_4SiO_4 , amounted to 35 and 52 $\text{mmol m}^{-2} \text{y}^{-1}$, respectively. This inconsistency can be resolved by assuming that carbonate lithologies also contain clays and quartz in the rock and overlying soils, which will be weathered. Indeed, Bluth and Kump [16] have shown that a carbonate lithology also exhibits a clear flux of H_4SiO_4 . Taking their empirical relationship between the flux of H_4SiO_4 and water runoff gained from 101 river basins, each draining a primary lithology, the Thur, as a basin with carbonate rocks, would have a silicate chemical denudation rate of 113 $\text{mmol m}^{-2} \text{y}^{-1}$ and the Ticino, taken as a granitic basin, would exhibit a rate of 194 $\text{mmol m}^{-2} \text{y}^{-1}$. These rates estimated by the relationships shown in [16] clearly exceed those measured in rivers displayed in Fig. 13. The positive relationship between chemical weathering rates and runoff found by Bluth and Kump [16] also highlights the importance of the formation of new reactive particles by physical weathering as regulating factors for chemical weathering rates.

In contrast to the fate of silicates, a catchment exhibiting a small area of so-called “Bündner Schiefer,” a sandy-marly schist containing soluble anhydrite or gypsum, will produce a remarkably high weathering rate for the entire basin. This effect arises in the alpine catchments of the Ticino, Rhine, and Rhône. The occurrence of “Bündner Schiefer” also causes sulfate concentrations in the range of 0.5 – 1 mmol L^{-1} in rivers. Natural and anthropogenic atmospheric sulfur

deposition [28], as well as pyrite oxidation, contribute little to the sulfate concentration in Swiss rivers [26]. Weathering rates calculated for halite indicate primarily the anthropogenic input of sodium chloride from its diverse uses such as road salting, use in ion exchangers in water-softening equipment, and in animal and human wastes. In the Erlenbach catchment, exhibiting negligible pollution sources, the weathering rate of halite fell to zero. Observed chloride concentrations in the Erlenbach stream were in the range of 0.5 mg L^{-1} ; denoting atmospheric wet and dry deposition.

Total chemical weathering rates reported in Fig. 13 varied between 119 and $212 \text{ g m}^{-2} \text{ y}^{-1}$. They correspond to annual denudation rates between 0.045 and 0.075 mm per year. Rates in the alpine catchments of Rhine, Rhône, and Ticino clearly exceeded those estimated for the whole basin (River Po in Ticino) by Gaillardet et al. [18]; they cite 53, 109, $126 \text{ g m}^{-2} \text{ y}^{-1}$, respectively. Chemical weathering rates of alpine rivers were well above the world average, $24 \text{ g m}^{-2} \text{ y}^{-1}$ cited in [18] or $23 \text{ g m}^{-2} \text{ y}^{-1}$ given in [13]. This fact highlights the importance of runoff and the formation of new reactive particles by physical weathering as regulating factors for chemical weathering rates. Alpine rivers discussed here exhibited slightly higher chemical weathering rates than alpine rivers in the Himalaya [34, 35].

In the catchments of the large alpine river Rhine and Rhône and the Erlenbach stream, chemical and physical weathering rates estimated from SS loads fell in the same range. Physical weathering rates in the Inn and Ticino basin were even smaller than the corresponding chemical rates. Physical weathering rates shown in Fig. 13 were below those reported for rivers in the Himalaya [34, 35]. The estimated river inputs of sediments into oceans, the world average physical erosion rate, amounts to $226 \text{ g m}^{-2} \text{ y}^{-1}$ according to [13].

The physical erosion rates shown in Fig. 13 were estimated from data of SS loads. To be correct, they do not represent the total sediment yield transported with the river water. The latter is commonly interpreted as physical erosion or denudation rate. The continuous and water discharge proportional sampling device discriminates larger particles, which contribute strongly to the total load during peak water flows. Therefore, loads of solids gained by this sampling device undervalue up to a factor of three in high flood years the mean sediment transport rate of alpine basins cited in [3] obtained with grab samples. However, estimations of suspended sediment loads based on grab samples also exhibit a distinct uncertainty due to the extrapolation procedure related to periods of peak water flows not sampled [36].

5 Conclusion

The chemical data presented clearly show the special character of alpine running waters compared to those in the midland and lowlands. The high water flow in these systems and the low anthropogenic activities produce only a small impact from pollution of nutrients and results mostly in their good chemical status. This

prerequisite for having a good ecological status is hampered by short-term changes in their water flow regime provoked by hydroelectric power production. Nutrient export coefficients in alpine streams fall in the range of those estimated for nonagricultural lands and forests on the Swiss Plateau. Trend analysis for nutrients confirmed the success of permanent efforts to decelerate the anthropogenic cycle of nitrogen and phosphorous in alpine regions. Long-term observations also revealed small changes in concentrations and loads of geochemical constituents in alpine rivers and therefore slightly affecting chemical weathering rates. The measured gradual temperature increase is likely one cause for these changes in the geochemical condition. However, other factors also will play an important role for explaining observed changes in concentrations and loads of geochemical constituents.

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