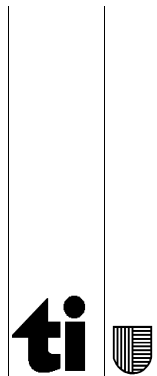

Results from the participation of Switzerland to the International Cooperative Programme on Assessment and Monitoring Effects of Air Pollution on Rivers and Lakes (ICP Waters)

Biannual report 2021-2022

Ufficio dell'aria, del clima e delle energie rinnovabili
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Executive Summary

The Convention on Long-Range Transboundary Air Pollution (CLRTAP) of the UN Economic Commission for Europe (UNECE) was concluded in Geneva in 1979 and entered into force in 1983. It comprises eight protocols on the reduction of specific air pollutants. Switzerland has ratified all the protocols, and is actively involved in a variety of CLRTAP bodies. In addition to its Executive Body, the CLRTAP operates in three main working groups and programmes in which Switzerland is actively involved: Working Group on Strategies & Review, European Monitoring & Evaluation Programme (EMEP), Working Group on Effects (WGE). The WGE promotes international cooperation on research into, and the monitoring of, the impacts of air pollutants on human health and the environment. This scientific activities are carried out by six international cooperation programmes (ICPs) plus a working group focusing on health-related impacts of air pollution (Task Force on Health). The effects of cross-border air pollution on aquatic ecosystems are studied by the International Cooperative Programme on Assessment and Monitoring Effects of Air Pollution on Rivers and Lakes (ICP Waters). In Switzerland, because of the abundance of crystalline bedrock many surface waters in the northern Canton Ticino are sensitive to acidification. The same region is highly affected by long-range transport of atmospheric pollutants originating from the plain of the River Po, in Italy, one of the most urbanized and industrialized areas of Europe. Therefore, mainly chemical but also biological parameters of mountain lakes and high-altitude stretches of rivers and streams in this area are examined. These investigations are carried out by the Office for Air, Climate and Renewable Energies of the Canton of Ticino on behalf of the Federal Office for the Environment (FOEN) and under the umbrella of ICP Waters. Results of these investigations are reported to the ICP Waters programme center and regularly published in specific reports.

Significant time trends were observed for rainwater concentrations of sulphate, nitrate and ammonia as well as for acidifying and eutrophying deposition. As a consequence of reduced SO₂ emissions, sulphate concentrations and depositions decreased significantly at all sites particularly between 1980's and 2010. After 2010 concentrations of sulphate decreased less. Since 1990, annual mean sulphate concentrations decreased from around 75 meq m⁻³ (Locarno Monti and Lugano) to 10-15 meq m⁻³ at all sites and sulphate depositions from 110 meq m⁻² to 13-23 meq m⁻². Concentrations and depositions of nitrate also decreased significantly at all sites (8 out of 9), mainly between 2000 and 2010. This can mainly be attributed to the reduction of NO_x emissions. Concentrations and depositions of ammonium also slightly decreased at some sites after 2000 (concentrations at 5 out of 9 sites and depositions at 8 out of 9 sites). Consequently, during the last 35 years annual mean concentrations of Gran alkalinity increased significantly at all sites from values ranging from -54 to -8 meq/m³ (1988-1992) to values ranging from 9 to 44 meq/m³ (2018-2022) and deposition of potential acidity decreased from values ranging from 93 to 272 meq/m² to values ranging from 22 to 111 meq/m². Accordingly, yearly mean rainwater pH increased from values ranging from 4.3 to 4.7 during 1988-1992 to values ranging between 5.5 and 6.2 more recently (2018-2022). Compared to the 1980's, the rainwater quality does nowadays vary less among the monitoring sites.

In agreement with trends of rainwater concentrations and depositions from the 1980's until present, concentrations of sulphate and nitrate decreased in most lakes, leading to an increase of alkalinity and pH. While concentrations of sulphate decreased mainly at the beginning of the monitoring period (1980's-2000), concentrations of nitrate decreased

particularly after 2000. Lake water concentrations of aluminum also decreased in many lakes, especially in the most acidic lakes (pH < 6): Lago Tomé (from 37-50 $\mu\text{g l}^{-1}$ to 11-26 $\mu\text{g l}^{-1}$), Lago del Starlaresc da Sgiof (from 74-106 $\mu\text{g l}^{-1}$ to 25-55 $\mu\text{g l}^{-1}$) and after 2012 in Laghetto Gardiscio (from 27-62 $\mu\text{g l}^{-1}$ to 10-22 $\mu\text{g l}^{-1}$ since 2000).

Next to decreasing deposition of acidifying pollutants, also the climate change is significantly affecting the lake water chemistry, especially those directly influenced by thawing cryospheric features (e.g. rock glaciers). In these lakes concentrations of both sulphate and base cations are increasing, not changing however the downward and upward trends of alkalinity and pH, respectively.

River water chemistry also responded to the emission reductions of S and N. The time trend analysis revealed that from 2000 to 2022 concentrations of sulphate and nitrate decreased significantly in river Maggia, Vedeggio and Verzasca and Gran alkalinity increased significantly in river Vedeggio and Verzasca.

Since the ultimate goal of emission control programmes is biological recovery (e.g. the return of acid sensitive species that have disappeared) and the restoration of biological functions that have been impaired during the course of acidification, macroinvertebrates as bioindicators have been studied in two of the most acidic lakes (Lago del Starlaresc da Sgiof, Lago Tomé). A biological recovery over time could not yet be observed. None of the analysed biological indicators (number of total taxa, of EPT taxa (=Ephemeroptera+Plecoptera+ Trichoptera), of chironomid taxa and neither the relative abundances of EPT taxa increased with time, nor single more acid sensitive species appeared with time.

Riassunto

La Convenzione sull'inquinamento atmosferico a lunga distanza (CLRTAP) della Commissione economica per l'Europa delle Nazioni Unite (UNECE) è stata stipulata a Ginevra nel 1979 ed è entrata in vigore nel 1983. Comprende otto protocolli concernenti la riduzione di specifici inquinanti atmosferici. La Svizzera ha ratificato tutti i protocolli e partecipa in modo attivo in diversi gremi della CLRTAP. Oltre all'organo esecutivo la CLRTAP opera in 3 principali gremi: Working Group on Strategies & Review, European Monitoring & Evaluation Programme (EMEP), Working Group on Effects (WGE). Il gruppo di lavoro WGE promuove la collaborazione internazionale nell'ambito della ricerca e della sorveglianza degli effetti degli inquinanti atmosferici sulla salute umana e sull'ambiente. Questi lavori scientifici sono svolti attraverso sei Programmi cooperativi internazionali (ICP) nonché un gruppo di lavoro che indaga sugli effetti degli inquinanti sulla salute (Task Force on Health). Gli effetti dell'inquinamento atmosferico transfrontaliero sugli ecosistemi acquatici sono studiati dal Programma di valutazione e osservazione degli effetti dell'inquinamento atmosferico su fiumi e laghi (ICP Waters). In Svizzera, a causa della geologia prevalentemente cristallina, molte acque superficiali nel nord del Canton Ticino sono sensibili all'acidificazione. Siccome la stessa zona è influenzata fortemente dal trasporto a lunga distanza di inquinanti atmosferici provenienti dalla Pianura Padana, una delle zone maggiormente urbanizzate in Europa, l'Ufficio dell'Aria, del Clima e delle Energie Rinnovabili del Canton Ticino monitora regolarmente la chimica, ma anche parametri biologici di laghi alpini e tratti di fiumi ad alta quota su incarico dell'Ufficio Federale per l'Ambiente (UFAM) nell'ambito dell'ICP Waters. I risultati di questo monitoraggio sono regolarmente pubblicati in specifici rapporti.

Trend temporali significativi sono stati osservati per le concentrazioni di ioni nelle precipitazioni e per le deposizioni. Grazie alla riduzione delle emissioni di SO₂, le concentrazioni e le deposizioni di solfato sono diminuite in modo significativo in tutti i punti di prelievo in particolare prima tra gli anni 1980 e il 2000. Dopo il 2010 le concentrazioni sono diminuite meno drasticamente. Dal 1990, le concentrazioni medie annue sono diminuite da circa 75 meq m⁻³ (Locarno Monti and Lugano) a valori di 10-15 meq m⁻³ in tutte le stazioni di campionamento e le deposizioni da 110 meq m⁻² a valori inferiori a 13-23 meq m⁻². A causa della diminuzione delle emissioni di NO_x, anche le concentrazioni e le deposizioni di nitrato sono diminuite significativamente ovunque, perlopiù tra il 2000 e il 2010. Pure le concentrazioni e le deposizioni di ammonio sono diminuite leggermente in alcuni punti dopo il 2000 (5 stazioni su 9 per le concentrazioni e 8 stazione su 9 per le deposizioni). Conseguentemente, negli ultimi 35 anni le concentrazioni di alcalinità sono aumentate in modo significativo in tutti i punti di monitoraggio da valori medi annui che potevano variare da -54 a -8 meq/m³ a valori che oggi variano da 9 a 44 meq/m³ (2018-2022) e le deposizioni di acidità potenziale sono diminuite da valori che variavano da 93 a 272 meq/m² a valori che variano da 22 a 111 meq/m². Analogamente il pH medio annuo delle acque piovane è aumentato da valori che variavano da 4.3 a 4.7 tra il 1988 e il 1992 a valori che oggi variano tra 5.5 e 6.2 (2018-2022). Rispetto all'inizio del monitoraggio negli anni 1980's la qualità dell'acqua piovane varia meno tra i siti di campionamento.

Similmente ai trend delle concentrazioni nelle precipitazioni e delle deposizioni atmosferiche, dagli anni 1980's ad oggi, le concentrazioni di solfato e nitrato sono diminuite in quasi tutti i laghi, causando un aumento dell'alcalinità e del pH. A differenza delle concentrazioni di solfato, che sono diminuite principalmente all'inizio del periodo di

monitoraggio (1980's-2000), le concentrazioni di nitrato sono diminuite soprattutto dopo il 2000. Anche le concentrazioni di alluminio disciolto sono diminuite soprattutto nei laghi maggiormente acidi ($\text{pH} < 6$): nel Lago di Tomé (da $37\text{-}50 \mu\text{g l}^{-1}$ a $11\text{-}26 \mu\text{g l}^{-1}$), nel Starlaresc da Sgiof (da $74\text{-}106 \mu\text{g l}^{-1}$ a $25\text{-}55 \mu\text{g l}^{-1}$), nel Laghetto Gardiscio ($27\text{-}62 \mu\text{g l}^{-1}$ a $10\text{-}22 \mu\text{g l}^{-1}$).

Accanto alla diminuzione delle deposizioni di inquinanti acidificanti anche il cambiamento climatico sta influenzando in modo significativo la chimica dei laghi, particolarmente quelli influenzati direttamente dallo scioglimento di formazioni criosferiche (es: ghiacciai rocciosi). In questi laghi entrambe le concentrazioni di solfato e dei cationi basici stanno aumentando, non cambiando però il trend in discesa e in salita dell'alcalinità e del pH, rispettivamente.

La riduzione delle emissioni di zolfo e azoto si riflette anche nella chimica dei fiumi. L'analisi delle tendenze temporali ha mostrato una diminuzione delle concentrazioni di solfato e nitrato nei fiumi Maggia, Vedeggio e Verzasca e un aumento dell'alcalinità nei fiumi Vedeggio e Verzasca dal 2000 al 2022.

Siccome il fine ultimo delle misure per ridurre le emissioni è la ripresa della biologia, per esempio il ritorno di specie sensibili all'acidificazione precedentemente scomparsi e il ripristino delle funzioni biologiche che sono state alterate durante il processo di acidificazione, si è deciso di studiare anche i macroinvertebrati come bioindicatori in due dei laghi più acidi (Lago del Starlaresc da Sgiof, Lago Tomé). Non si è potuto osservare un recupero della biologia nel tempo. Nessuno degli indicatori biologici analizzati (numero totale di taxa, numero di taxa EPT (=Ephemeroptera+Plecoptera+ Trichoptera), numero di taxa di chironomidi, né l'abbondanza relative dei taxa EPT è aumentato nel tempo e neppure sono apparse nel tempo specie più sensibili all'acidificazione.

Riassumendo, nonostante le concentrazioni di acidità e delle sue deposizioni sono diminuite in modo significativo nella maggior parte dei laghi e dei fiumi, le acque maggiormente sensibili all'acidificazione non si sono ancora riprese completamente. È necessario quindi diminuire ulteriormente le emissioni atmosferiche, in particolare di NO_x e NH_3 .

I Introduction

The International Cooperative Programme on Assessment and Monitoring Effects of Air Pollution on Rivers and Lakes (ICP Waters) was established under the United Nations Economic Commission for Europe's Convention on Long-Range Transboundary Air Pollution (CLRTAP) in 1985, when it was recognized that acidification of freshwater systems provided some of the earliest evidence of the damage caused by sulphur emissions. The monitoring programme is designed to assess, on a regional basis, the degree and geographical extent of the impact of atmospheric pollution, in particular acidification on surface waters. The monitoring data provide a basis for documenting effects of long-range transboundary air pollutants on aquatic chemistry and biota. An additional important programme activity is to contribute to quality control and harmonization of monitoring methods. The Programme is planned and coordinated by a Task Force under the leadership of Norway. Up to now data from about 20 countries in Europe and North America are available in the database of the Programme Centre. Switzerland joined the Programme in 2000 on behalf of the Swiss Federal Office for the Environment with the support of Canton Ticino.

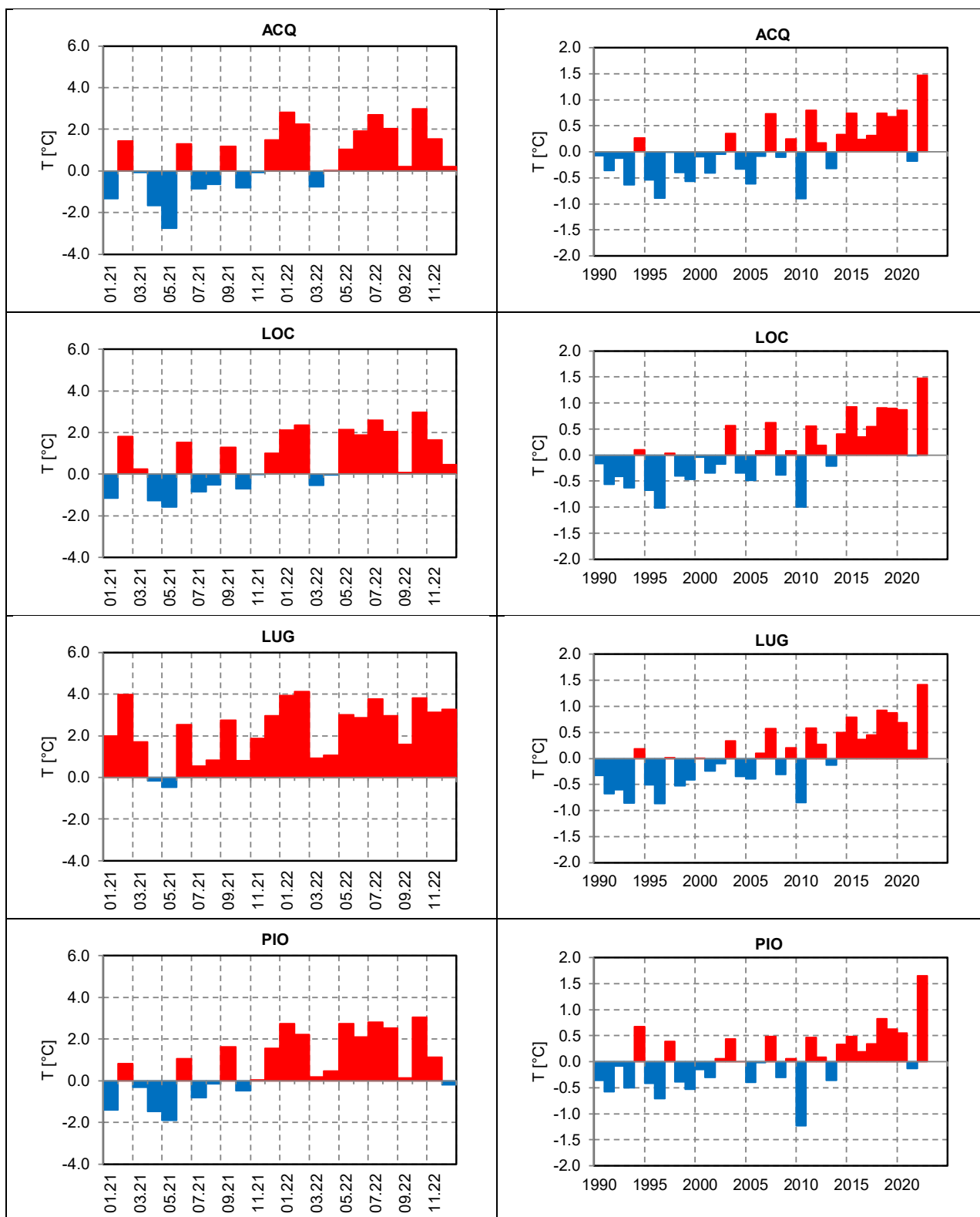
I.1 Climatic parameters during 2021-2022

Unlike the years before, during 2021 the mean temperatures in Switzerland have not been particularly high (MeteoSwiss 2022). In the Canton of Ticino the annual mean temperatures were close to the norm values of the period (1992-2020) (Fig. 1.1). The colder temperatures in the months of January, April and May compensated the higher temperatures in February, June, September and December. At the southern side of the Alps (Ticino and Engadine) the precipitations during 2021 were on average slightly lower than the norm values, with values above the norm only in January and July, while in the rest of the country they were abundant with locally lots of snow in winter and one of the wettest summer ever registered (MeteoSwiss 2022).

Instead, 2022 has been the warmest year in Switzerland since the beginning of the measurements in 1864 (MeteoSwiss 2023) and with scarce precipitations. In the Canton of Ticino the yearly mean precipitations ranged between 50% and 70% of the actual norm values (Fig. 1.2). At most sites monthly precipitations have been below the norm values from autumn 2021 until the end of 2022.

As a consequence the high altitude ecosystems have been influenced only little by snow melt during 2022 and the river discharges have been low during the entire 2022 (see following paragraphs).

Figure 1.1 Monthly mean (2021-2022) and yearly mean (1991-2022) temperature deviation from the norm values (1991-2020) at the wet deposition sampling sites with MeteoSwiss climate data in the Canton of Ticino. Site acronym as defined in Table 2.1



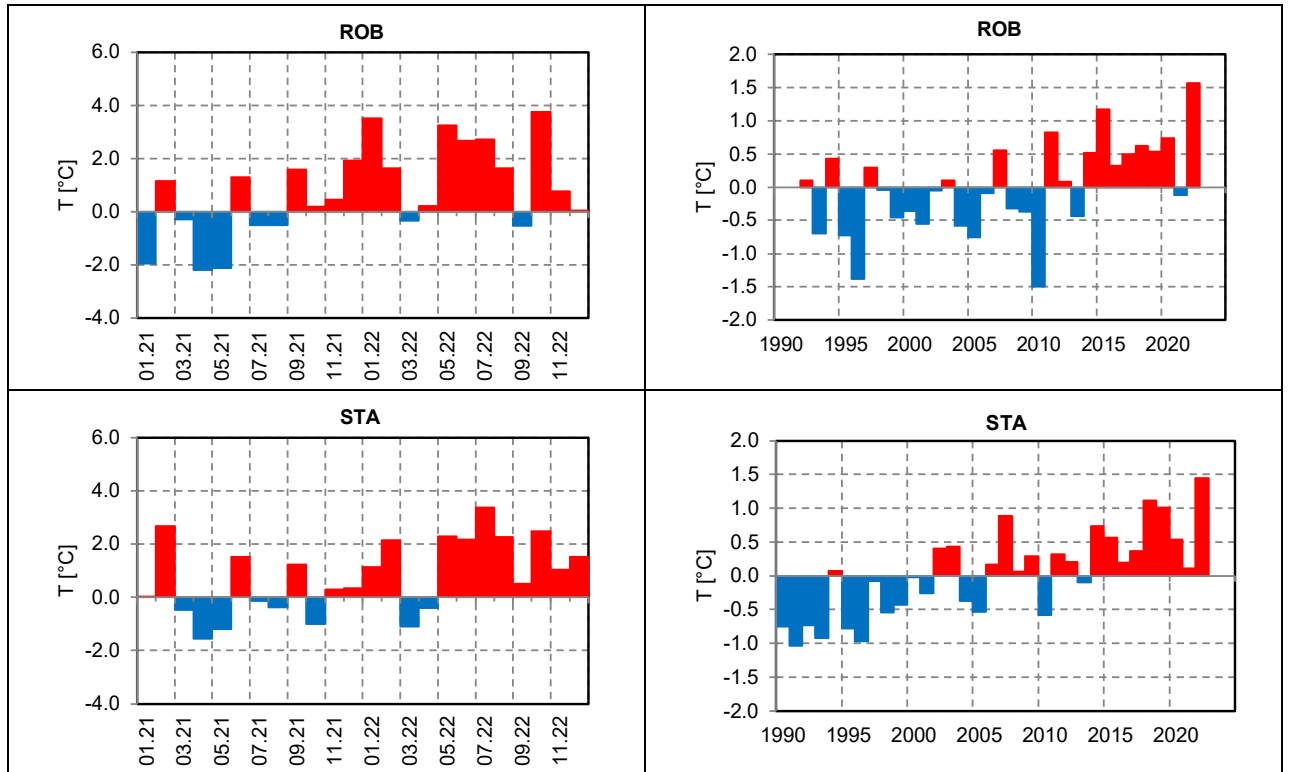
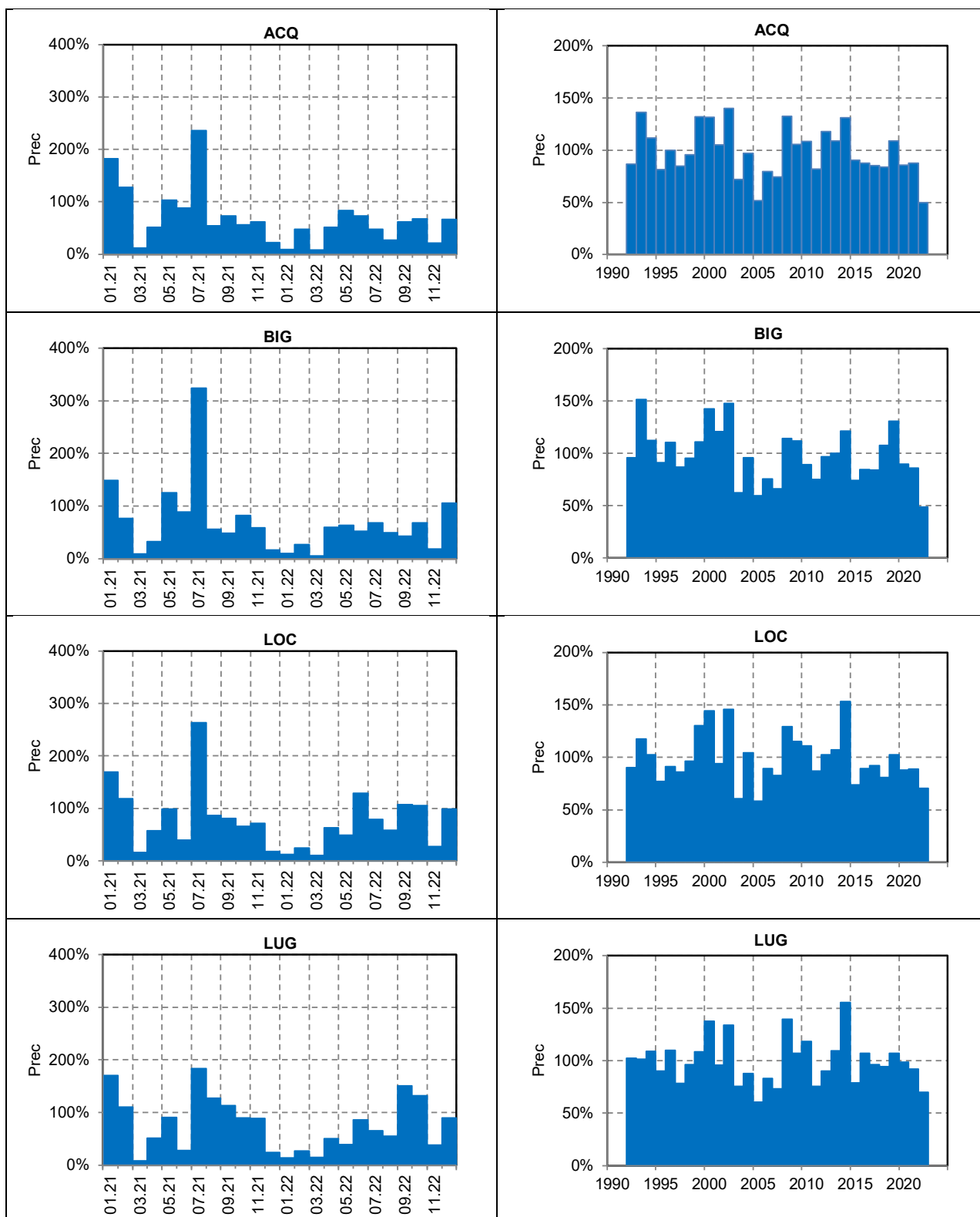
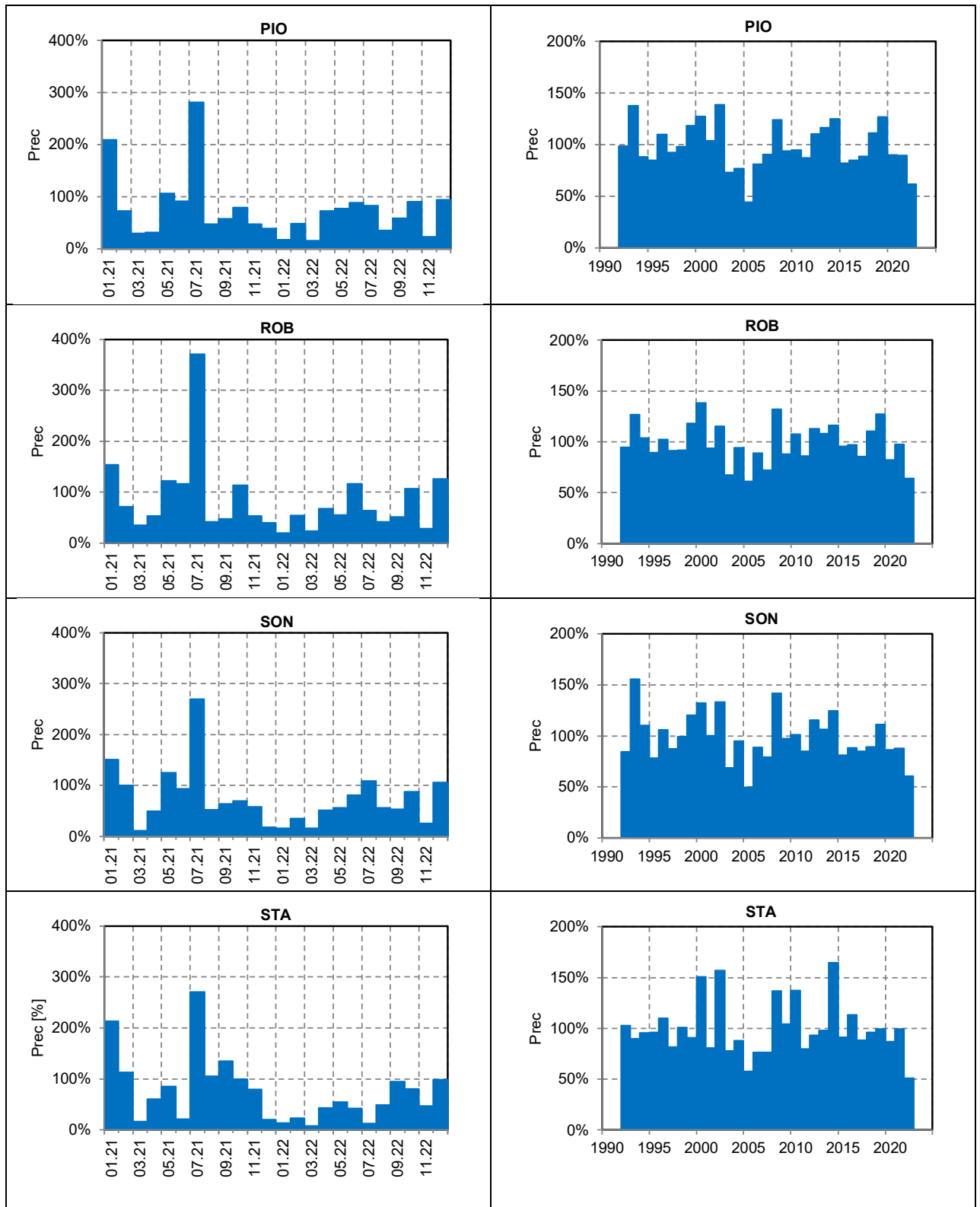


Figure 1.2 Monthly (2021-2022) and yearly (1991-2022) percent precipitation relative to the norm values (1991-2020) at the wet deposition sampling sites with MeteoSwiss climate data in the Canton of Ticino. Site acronym as defined in Table 2.1





2 Study sites

The study area is located in the southern part of the Alps in the Canton of Ticino in Switzerland. Precipitation in this region is mainly determined by warm, humid air masses originating from the Mediterranean Sea, passing over the Po Plain and colliding with the Alps. The lithology of the northwestern part of this canton is dominated by base-poor rocks especially gneiss. As a consequence soils and freshwaters in this region are sensitive to acidification.

In order to assess the impact of long-range transboundary air pollution, monitoring of water chemistry has been conducted in 20 acid sensitive high-altitude lakes and in the 3 Alpine rivers MAG VED and Vezasca. Wet deposition has been monitored at 11 sampling sites distributed over all the Canton of Ticino. Macroinvertebrates as bioindicators were sampled in 2 of the most acidic lakes (STA, TOM, see Table 2.3).

The lake's watersheds are constituted mainly by bare rocks with vegetation often confined to small areas of Alpine meadows. The selected Alpine lakes are situated between an altitude of 1690 m and 2590 m and are characterized by intensive irradiation, a short vegetation period, a long period of ice coverage and by low nutrient concentrations. The sampling points of the selected rivers are located at lower altitudes (610-918 m). They are influenced by larger catchment areas and therefore less sensitivity toward acidification than the lakes.

The geographic distribution of the sampling sites (wet deposition, rivers and lakes) are shown in Fig. 2.1, while their main geographic and morphometric parameters are resumed in Tab. 2.1, 2.2 and 2.3.

Figure 2.1 Sampling sites (Relief map: © Swisstopo)

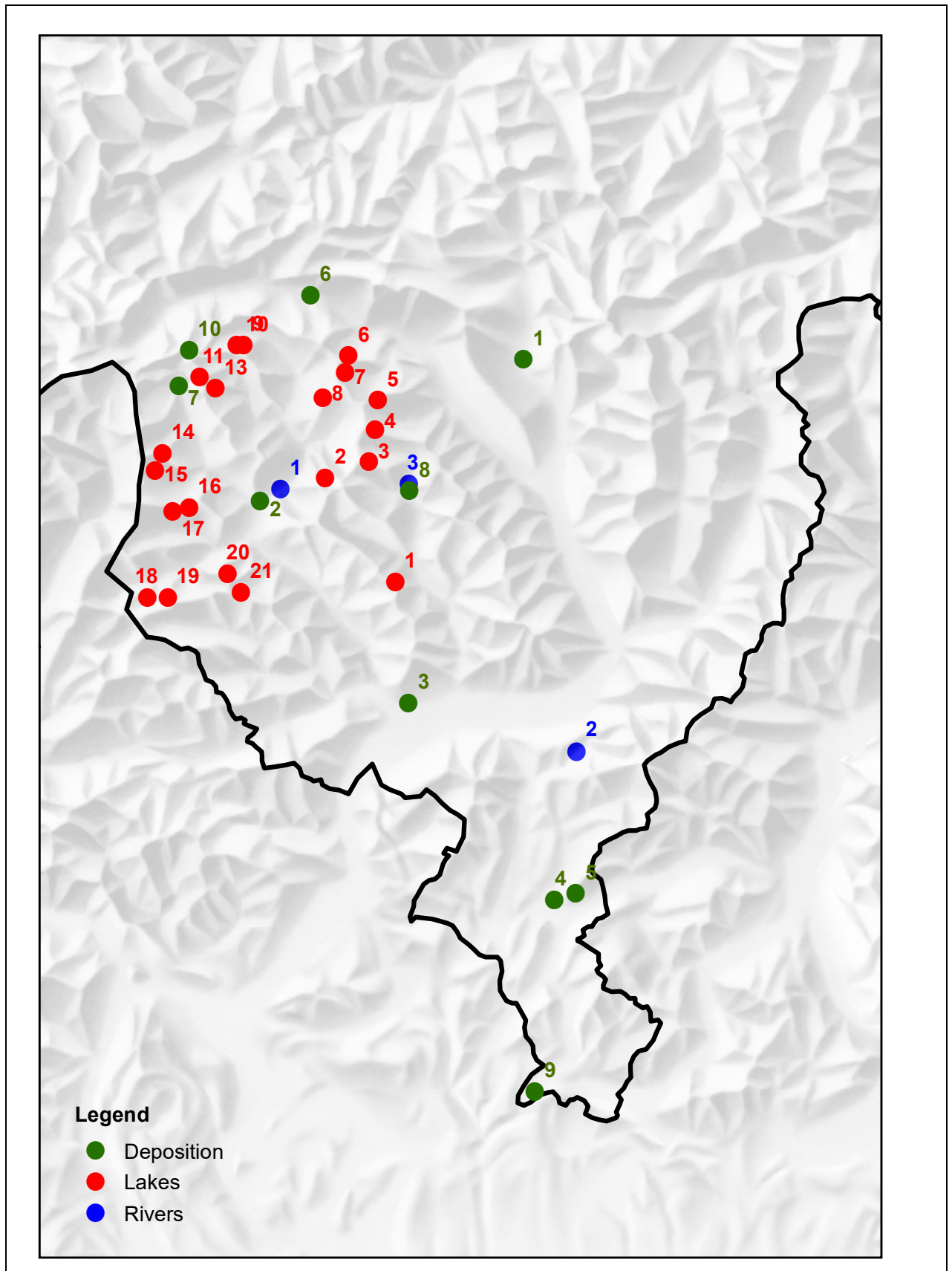


Table 2.1 Geographic and morphometric parameters of the wet deposition sampling sites

Sampling site number	Code	Sampling site	CH1903 LV03 (m)		WGS84		Altitude m a.s.l.
			Longitude	Latitude	Longitude	Latitude	
1	ACQ	Acquarossa	714998	146440	8°56'12"	46°27'41"	575
2	BIG	Bignasco	690205	132257	8°59'17"	46°00'32"	443
3	LOC	Locarno Monti	704160	114350	8°47'17"	46°10'27"	366
4	LUG	Lugano	717880	95870	8°57'18"	46°00'24"	273
5	BRE	Monte Brè	719900	96470	8°59'17"	46°00'32"	925
6	PIO	Piotta	695882	152270	8°41'17"	46°30'54"	990
7	ROB	Robiei	682540	143984	8°30'51"	46°26'43"	1890
8	SON	Sonogno	704250	134150	8°47'14"	46°21'05"	918
9	STA	Stabio	716040	77970	8°55'52"	45°51'36"	353
10	CRI	Cristallina	683526	147305	8°31'34"	46°28'19"	2575

Table 2.2 Geographic and morphometric parameters of the studied river sites

River number	River code	River name	Sampling site	CH1903 LV03 (m)		WGS84		Altitude m a.s.l.	Catchment area km ²
				Longitude	Latitude	Longitude	Latitude		
1	MAG	MAG	Brontallo	692125	134375	8°38'8"	46°21'16"	610	ca. 189
2	VED	VED	Isonne	719900	109800	8°59'24"	46°07'45"	740	20
3	VER	VER	Sonogno	704200	134825	8°47'33"	46°21'24"	918	ca. 27

Table 2.3 Geographic and morphometric parameters of the studied lakes

Lake number	Lake code	Lake name	CH1903 LV03 (m)		WGS84		Altitude m a.s.l.	Catchment area ha	Lake area ha	Max depth m
			Longitude	Latitude	Longitude	Latitude				
1	STA	Lago del Starlaresc da Sgiöf	702905	125605	8°46'25"	46°16'26"	1875	23	1.1	6
2	TOM	Lago di Tomè	696280	135398	8°41'23"	46°21'47"	1692	294	5.8	38
3	POR	Lago dei Porchieisc	700450	136888	8°44'39"	46°22'33"	2190	43	1.5	7
4	BAR	Lago Barone	700975	139813	8°45'06"	46°24'07"	2391	51	6.6	56
5	GAR	Laghetto Gardiscio	701275	142675	8°45'22"	46°45'22"	2580	12	1.1	10
6	LEI	Lago della Capannina Leit	698525	146800	8°43'17"	46°27'55"	2260	52	2.7	13
7	MOR	Lago di Morghirolo	698200	145175	8°43'00"	46°27'03"	2264	166	11.9	28
8	MOG	Lago di Mognòla	696075	142875	8°41'19"	46°25'49"	2003	197	5.4	11
9	INF	Laghetto Inferiore	688627	147855	8°35'34"	46°28'34"	2074	182	5.6	33
10	SUP	Laghetto Superiore	688020	147835	8°35'05"	46°28'34"	2128	125	8.3	29
11	NER	Lago Nero	684588	144813	8°32'22"	46°26'58"	2387	72	12.7	68
13	FRO	Lago della Froda	686025	143788	8°33'29"	46°26'24"	2363	67	2.0	17
14	ANT	Laghetto d'Antabia	681038	137675	8°29'32"	46°23'08"	2189	82	6.8	16
15	CRO	Lago della Crosa	680375	136050	8°28'60"	46°22'16"	2153	194	16.9	70
16	ORS	Lago d'Orsalia	683513	132613	8°31'24"	46°20'23"	2143	41	2.6	16
17	SCH	Schwarzsee	681963	132188	8°30'11"	46°20'10"	2315	24	0.3	7
18	POZ	Laghi dei Pozzöi	679613	124200	8°28'17"	46°15'52"	1955	33	1.1	4
19	SFI	Lago di Sfille	681525	124213	8°29'46"	46°15'52"	1909	63	2.8	12
20	SAS	Lago di Sascòla	687175	126413	8°34'11"	46°17'01"	1740	90	3.2	5
21	ALZ	Lago d'Alzasca	688363	124488	8°35'05"	46°15'58"	1855	110	10.4	40

3 Water chemistry analysis

3.1 Introduction

Acid deposition in acid sensitive areas can cause acidification of surface waters and soils. Because of its particular lithology (base-poor rocks especially gneiss) and high altitudes (thin soil layer and low temperatures) the buffer capacity of the northwestern part of the Canton of Ticino is low. This area is therefore very sensitive to acidification. Acidification can be defined as a reduction of the acid neutralizing capacity of soils (=alkalinity) or waters. Alkalinity is the result of complex interactions between wet and dry deposition and the soil and rocks of the watershed and biologic processes. A commonly used threshold for surface water acidification for alkalinity (or ANC=acid neutralizing capacity) is 20 µeq/l, originally set based on responses of fish and invertebrate populations to acidification (Lien et al. 1987, CLRTAP 2017). In fact, critical loads of acidity for Swiss Alpine lakes have been calculated based on critical ANC values of 20 µeq/l (Posch et al. 2007). Since concentrations of soluble aluminum start to increase below a pH of ca. 6.3, it is generally assumed that first signs of changes in the biological communities due to acidification appear, when pH drops below 6 (Wright et al. 1975).

3.2 Sampling methods

Rainwater has been sampled at weekly intervals with wet-only samplers. The first sampler of this type was installed at LOC in 1988. Other samplers followed in 1989 (LUG), in 1990 (ACQ, PIO, STA), in 1995 (BRE), in 1996 (ROB) in 2001 (BIG, SON). The altitudes of these sites vary between 353 and 1890 m a.s.l. In 2017 a wet-only sampler has also been installed at CRI (2575 m). Since the hut is inhabited only periodically, weekly sampling is not always possible.

Between the 1980's and the 1990's surface water of totally 62 lakes was sampled irregularly. From 2000 a subgroup of 20 acid sensitive lakes has been sampled every year: between 2000 and 2005 twice a year (once at beginning of summer, once in autumn), between 2006 and 2018 three times a year (once at the beginning of summer, twice in autumn), from 2019 again only two times a year (twice in autumn). River water has been sampled monthly since 2000. From 2022 sampling of the rivers MAG and VED were interrupted and monitoring continued only at the more acid sensitive river VER.

3.3 Analytical methods

Measured parameters, conservation methods, analytical methods and quantification limits are summarized in Tab. 3.1. The data quality was assured by participating regularly at national and international intercalibration tests. In addition, data were only considered if the calculation of the ionic balance and the comparison of the measured with the calculated conductivity corresponded to the quality requests indicated by the programme manual of ICP Waters (ICP waters Programme Centre 2010). Furthermore, the data were checked for outliers. If available, as for metals, dissolved concentrations were compared with total concentrations.

Table 3.1 Measured parameters, conservation methods, analytical methods, quantification limits. CA, PC, GF, PP stay for cellulose acetate, polycarbonate, glass fibre and polypropylene, respectively

Parameter	Acronym	Filtration	Conservation	Method	Limit of quantification
pH		No	No	potentiometry	0.02
conductivity	Cond	No	No	potentiometry	1 $\mu\text{S cm}^{-1}$
Gran alkalinity	GranAlk	No	No	potentiometry	0.001 meq l ⁻¹
Ca ²⁺	Ca	CA filter	PP bottle, 4°C	ion cromatography	0.06 mg l ⁻¹
Mg ²⁺	Mg	CA filter	PP bottle, 4°C	ion cromatography	0.01 mg l ⁻¹
Na ⁺	Na	CA filter	PP bottle, 4°C	ion cromatography	0.01 mg l ⁻¹
K ⁺	K	CA filter	PP bottle, 4°C	ion cromatography	0.08 mg l ⁻¹
NH ₄ ⁺	NH ₄	CA filter	PP bottle, 4°C	ion chromatography (precipitations)	0.030 mg N l ⁻¹
NH ₄ ⁺	NH ₄	CA/GF filter	PP bottle, 4°C	UV/VIS (lakes, rivers)	0.012 mg N l ⁻¹
SO ₄ ²⁻	SO ₄	CA/GF filter	PP bottle, 4°C	ion cromatography	0.08 mg l ⁻¹
NO ₃ ⁻	NO ₃	CA/GF filter	PP bottle, 4°C	ion cromatography	0.02 mg N l ⁻¹
NO ₂ ⁻	NO ₂	CA/GF filter	PP bottle, 4°C	ion cromatography	0.2 $\mu\text{g N l}^{-1}$
Cl ⁻	Cl	CA/GF filter	PP bottle, 4°C	ion cromatography	0.1 mg l ⁻¹
soluble reactive P	SRP	CA/GF filter	PP bottle, 4°C	ion cromatography	2 $\mu\text{g P l}^{-1}$
total P	P _{tot}	No	glass bottle, persulphate mineralisation	UV/VIS	32 $\mu\text{g P l}^{-1}$
soluble reactive Si	SiO ₂	CA/GF filter	PP bottle, 4°C	ICP-MS	0.06 mg SiO ₂ l ⁻¹
total N	N _{tot}	No	glass bottle, persulphate mineralisation	UV/VIS	0.15 mg N l ⁻¹
DOC	DOC	PC filter	brown glass bottle	IR-catalytic oxidation and combustion	0.05 mg C l ⁻¹
labile Al	Al _{sol}	PC filter	acid washed PP bottle, +HNO ₃ , 4°C	ICP-MS	1.0 $\mu\text{g l}^{-1}$
total Al	Al _{tot}	No	acid washed PP bottle, +HNO ₃ , 4°C	ICP-MS	1.0 $\mu\text{g l}^{-1}$
soluble Pb	Pb _{sol}	PC filter	acid washed PP bottle, +HNO ₃ , 4°C	ICP-MS	0.1 $\mu\text{g l}^{-1}$
total Pb	Pb _{tot}	No	acid washed PP bottle, +HNO ₃ , 4°C	ICP-MS	0.1 $\mu\text{g l}^{-1}$
soluble Cd	Cd _{sol}	PC filter	acid washed PP bottle, +HNO ₃ , 4°C	ICP-MS	0.1 $\mu\text{g l}^{-1}$
total Cd	Cd _{tot}	No	acid washed PP bottle, +HNO ₃ , 4°C	ICP-MS	0.1 $\mu\text{g l}^{-1}$
soluble Cu	Cu _{sol}	PC filter	acid washed PP bottle, +HNO ₃ , 4°C	ICP-MS	0.1 $\mu\text{g l}^{-1}$
total Cu	Cu _{tot}	No	acid washed PP bottle, +HNO ₃ , 4°C	ICP-MS	0.1 $\mu\text{g l}^{-1}$
soluble Zn	Zn _{sol}	PC filter	acid washed PP bottle, +HNO ₃ , 4°C	ICP-MS	0.1 $\mu\text{g l}^{-1}$
total Zn	Zn _{tot}	No	acid washed PP bottle, +HNO ₃ , 4°C	ICP-MS	0.1 $\mu\text{g l}^{-1}$
soluble Cr	Cr _{sol}	PC filter	acid washed PP bottle, +HNO ₃ , 4°C	ICP-MS	0.1 $\mu\text{g l}^{-1}$
total Cr	Cr _{tot}	No	acid washed PP bottle, +HNO ₃ , 4°C	ICP-MS	0.1 $\mu\text{g l}^{-1}$
soluble Ni	Ni _{sol}	PC filter	acid washed PP bottle, +HNO ₃ , 4°C	ICP-MS	0.1 $\mu\text{g l}^{-1}$
total Ni	Ni _{tot}	No	acid washed PP bottle, +HNO ₃ , 4°C	ICP-MS	0.1 $\mu\text{g l}^{-1}$
soluble Fe	Fe _{sol}	PC filter	acid washed PP bottle, +HNO ₃ , 4°C	ICP-MS	1.0 $\mu\text{g l}^{-1}$
total Fe	Fe _{tot}	No	acid washed PP bottle, +HNO ₃ , 4°C	ICP-MS	1.0 $\mu\text{g l}^{-1}$

3.4 Data handling

Monthly and yearly mean concentrations in precipitation were calculated by weighting weekly concentrations with the sampled precipitation volume, while monthly and yearly wet depositions were calculated by multiplying monthly and yearly mean concentrations with the precipitation volume measured at a meteorological sampling station close to the sampling site. This procedure has been chosen in order to avoid underestimation of monthly and yearly depositions due to occasionally missing weekly samples. In particular, for the sampling sites, data from the pluviometric stations of MeteoSwiss (ACQ → Comprovasco, LOC → Locarno Monti, LUG → Lugano, BRE → Lugano, PIO → Piotta, ROB → Robiei, STA → Stabio) and of the Canton Ticino (BIG → Cavigno, SON → Sonogno) have been chosen.

Since between 2015 and 2022 the concentrations and depositions of nitrate at ROB were occasionally influenced by the emission of a generator close to the sampling site, the concentration of nitrate without the local emissions were estimated from the nearby Italian sampling site Devero (distance = 23 km, DEV). The monthly and yearly mean concentrations in rainwater at DEV were provided by the Institute of Ecosystem Study (Verbania Pallanza, Italy). Since at ROB GranAlk and pH were influenced by the elevated NO_3 concentrations, concentrations of GranAlk in the absence of the local pollution source were approximated with ANC by subtracting the sum of the acid anions SO_4 , NO_3 , Cl from the base cations Ca, Mg, Na and K plus NH_4 , while pH values could not be reconstructed.

The deposition of the potential acidity was calculated subtracting GranAlk (ANC at ROB from 2015) from twice NH_4 .

3.5 Statistical methods used for trend analysis

Trend analyses were performed with the Mann-Kendall test to detect temporal trends in wet deposition and lake and river water chemistry. For wet depositions a seasonal Mann-Kendall test (Hirsch et al. 1982) was performed on monthly mean concentrations and depositions. For river chemistry the seasonal Mann-Kendall test was performed on monthly measurements. For both wet deposition and river chemistry a correction among block was considered (Hirsch and Slack 1984). For lake chemistry a simple Mann-Kendall test was performed on autumn concentrations (Mann 1945). The two sided tests for the null hypothesis that no trend is present were rejected if p-values were below 0.05.

Estimates for temporal variations of wet depositions, river and lake water chemistry were quantified with the seasonal Kendall slope estimator (Gilbert 1987). All trend analyses were calculated with the CRAN package “rkt 1.4” (Marchetto 2015).

3.5.1 Wet deposition

Spatial variation

Annual average rainwater concentrations of the main chemical parameters and their yearly deposition rates during 2021 and 2022 are shown in Tab. 3.2 (in red the approximated values in the absence of the local NO₃ pollution source at ROB).

Table 3.2 Yearly mean rainwater concentrations and depositions in 2021 and 2022.

Sampling site	Year	Precipitation MétéoCH (mm)	Analysed precipitation (mm)	Cond 25°C (µS cm ⁻¹)	pH	Ca		Mg		Na		K		NH ₄		HCO ₃		SO ₄		NO ₃		Cl		GranAlk	Potential acidity		
						Concentration (meq m ⁻³)	Deposition (meq m ⁻²)	Concentration (meq m ⁻³)	Deposition (meq m ⁻²)	Concentration (meq m ⁻³)	Deposition (meq m ⁻²)	Concentration (meq m ⁻³)	Deposition (meq m ⁻²)	Concentration (meq m ⁻³)	Deposition (meq m ⁻²)	Concentration (meq m ⁻³)	Deposition (meq m ⁻²)	Concentration (meq m ⁻³)	Deposition (meq m ⁻²)	Concentration (meq m ⁻³)	Deposition (meq m ⁻²)	Concentration (meq m ⁻³)	Deposition (meq m ⁻²)	Concentration (meq m ⁻³)	Deposition (meq m ⁻²)	Concentration (meq m ⁻³)	Deposition (meq m ⁻²)
ACQ	2021	1121	917	9	5.8	28	32	4	4	4	4	2	2	32	35	34	38	12	13	18	20	6	5	32	35		
	2022	636	627	9	6.1	19	12	3	2	5	3	2	1	42	27	31	20	12	7	20	13	4	3	31	34		
BIG	2021	1494	1249	10	5.8	36	54	4	6	7	10	3	4	33	49	35	52	14	21	21	32	7	10	33	49		
	2022	846	696	11	6.2	20	17	3	3	6	5	3	2	51	43	36	30	13	11	25	21	6	5	35	57		
LOC	2021	1612	1427	10	5.8	22	35	4	6	7	11	2	3	37	60	26	41	13	24	23	37	7	11	26	86		
	2022	1283	1167	10	6.0	14	18	3	4	8	10	1	2	53	68	33	42	16	17	23	30	7	9	32	96		
LUG	2021	1444	1159	9	5.6	21	30	4	6	7	10	2	2	34	50	22	32	13	19	22	31	8	12	20	70		
	2022	1096	871	13	6.2	21	23	5	5	9	10	2	2	67	73	45	49	16	18	30	33	9	9	44	98		
BRE	2021	1444	1297	8	5.9	22	31	4	6	7	10	2	3	29	42	22	32	12	17	19	27	7	11	21	54		
	2022	1096	1011	12	6.1	20	22	4	5	9	10	4	5	56	62	40	44	14	15	26	28	8	9	39	80		
PIO	2021	1302	1046	10	5.9	30	39	3	4	20	27	1	2	29	38	33	43	11	15	16	21	21	27	32	34		
	2022	895	790	10	6.1	26	24	3	3	8	8	1	1	37	33	38	34	12	11	16	15	8	7	38	33		
ROB	2021	2352	1952			18	42	3	6	5	13	2	4	25	59	15	34	11	26	14	32	3	8	24	61		
	2022	1541	1325			16	25	3	4	3	4	1	1	20	31	4	5	10	15	16	25	3	4	14	41		
SON	2021	1832	1545	10	5.9	34	62	4	7	5	9	2	3	37	67	42	77	12	22	19	34	5	10	41	59		
	2022	1270	962	9	6.0	14	18	3	3	4	5	1	2	43	55	30	38	11	14	20	25	4	5	29	72		
STA	2021	1542	1402	10	5.8	21	33	4	6	8	12	2	3	43	67	28	44	14	22	24	37	8	13	27	92		
	2022	1350	676	12	6.0	17	13	5	4	9	7	4	3	60	47	39	31	13	11	27	22	8	6	38	64		

In general, ion concentrations of anthropogenic origin (SO₄, NO₃, NH₄) still decrease with increasing latitude and altitude. The gradients, however, are not as pronounced as they were at the beginning of the measurements. In 2021 and 2022, the highest concentrations of the sum of SO₄, NO₃ and NH₄ were measured at STA in 2021 and LUG in 2022, and the lowest at ROB in both years. The correlation with latitude and altitude reflects the influence of long-range transboundary air pollution moving along a south to north gradient from the Po plain toward the Alps and the distance from pollution sources.

Wet deposition of atmospheric pollutants depends on their concentration and the amount of precipitation. Highest precipitation usually occurs in the north-western part of Canton Ticino. The reason for this distribution are air masses rich in humidity that move predominantly from southwest toward the southern Alps and the particular orography of the area that causes a steep raise of the air masses to higher altitudes. During 2021 and 2022, the highest deposition rates of the sum of SO₄, NO₃ and NH₄ occurred at STA in 2021 and at LUG in

2022 and the lowest at ROB in both years. The highest annual mean deposition of potential acidity occurred at STA in 2021 and at LUG and LOC in 2022; the lowest at ACQ and PIO in both years.

Seasonal variation

Fig. 3.1 shows the amount of monthly precipitation at each sampling site during 2021 and 2022 and the average values during the last decade 2011-2020. Seasonal variations of monthly mean rainwater concentrations of the main chemical parameters are presented in Fig. 3.2.

Average monthly precipitation is normally low from December to March and higher between May and November. Compared to the average values, precipitation was significantly higher in January, July, September (Sottoceneri: LUG, STA) 2021, in June 2022 at LOC, in September/October 2022 at LUG and in December 2022 at ROB and significantly lower in March/April 2021, in June 2021 at LOC and in most of the months after fall 2021.

During 2011-2020 average SO_4 concentrations were higher in summer and lower in winter. This follows the oxidation rate of SO_2 to SO_4 (highest in summer and lowest in winter) and at high altitudes also the seasonality of thermal convection (occasionally absence of vertical transport in winter).

Monthly mean concentrations of NO_3 during 2011-2020 were highest in March and lowest in November and December. The NO_3 peak at the end of the winter is most probably the result of the high concentrations of NO_2 in winter, the already increasing oxidation rates of NO_x to NO_3 in spring (lowest in winter and highest in summer) and at high altitudes the absence of vertical transport of pollutants induced by thermal convection.

The seasonality of monthly mean concentrations of NH_4 during 2011-2020 was very similar to that of SO_4 . Hedin et al. (1990) explained this similarity with a chemical coupling between NH_4 and SO_4 , with acidic SO_4 aerosols acting as a vehicle for long-range transport of NH_4 . Seasonal variations in NH_4 concentrations at sites distant from major sources of NH_4 emissions thus may be influenced strongly by the supply of SO_4 aerosol and by seasonal variations in emissions and oxidation of SO_2 .

Concentrations of Cl are almost identical to concentrations of Na, because the main source is sea salt, with exceptions in winter especially at PIO and occasionally at SON due to spreading of salts on the roads.

Concentrations of Ca+Mg+K, during 2011-2020 they tended to be higher in spring and to be similar at all sites. Similar behaved concentrations of GranAlk, indicating that concentrations of Ca+Mg+K heavily influence the seasonality of alkalinity. Rainwater pH is usually also higher in spring/summer.

In general, compared to the previous decade, during 2021 and 2022 concentrations of SO_4 were slightly lower, concentrations of NO_3 similar and concentrations of NH_4 slightly higher during 2022. The higher concentrations during 2022 could be related higher evaporation rates of ammonia from agriculture due to the particularly elevated temperatures. GranAlk and pH were in general higher during both 2021 and 2022 compared to the data of the previous decade. In fact, during 2021 and 2022 only 5% and 0%, respectively of the analysed rainwater samples had pH values below 5, while they were 9% between 2011 and

2020. Similarly, during 2021 and 2022 37% and 32%, respectively of the samples had pH values between 5.5 and 6 and 57% and 68%, respectively higher than 6.0. These percentages were only 48% and 42%, respectively during 2011-2020.

Single concentration peaks can often be attributed to small precipitation volumes (example: concentration peaks in March 2021). Others, especially as regards Ca+Mg+K and Gran Alk can be related to alkaline rain events (e.g. deposition of Saharan dust). Alkaline rain events occurred in February 2021 (MeteoSwiss 2022) and probably in June 2021.

Monthly variations of wet depositions behave in general similar to monthly variations of concentrations, with the difference that the amount of precipitation gains further importance (Fig. 3.3). Average (2011-2020) monthly depositions of SO₄, NO₃ and NH₄, Ca+Mg+K and the potential acidity are normally higher during the warm months when both concentrations and precipitations are higher.

Figure 3.1 Monthly precipitations during 2021-2022 (left) and monthly mean precipitations during 2011-2020 (right)

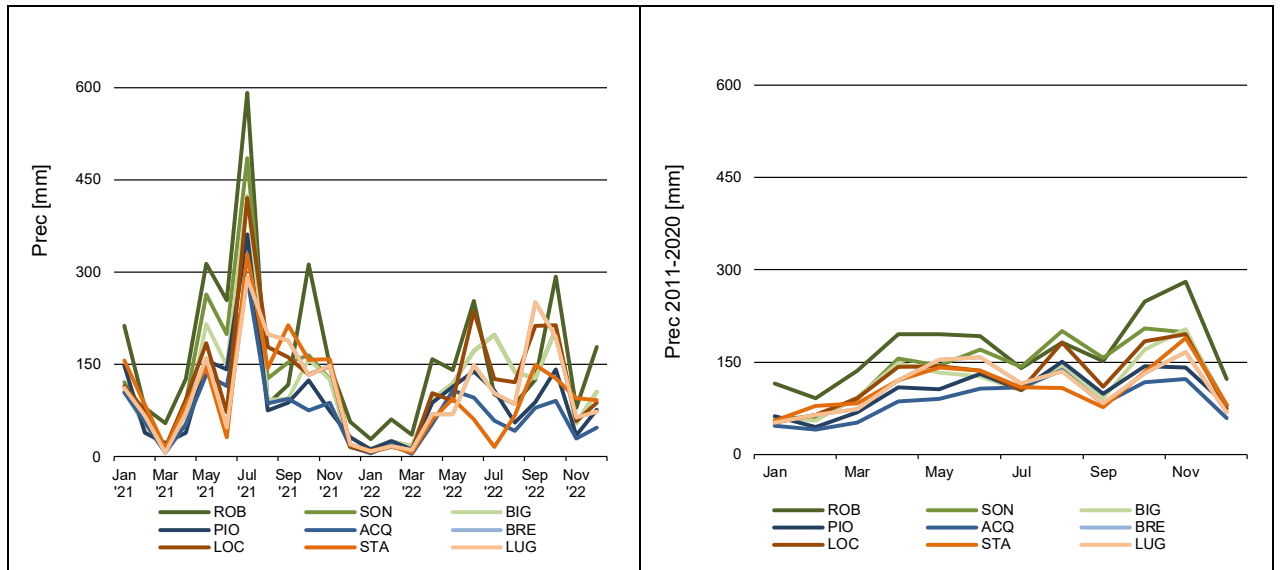
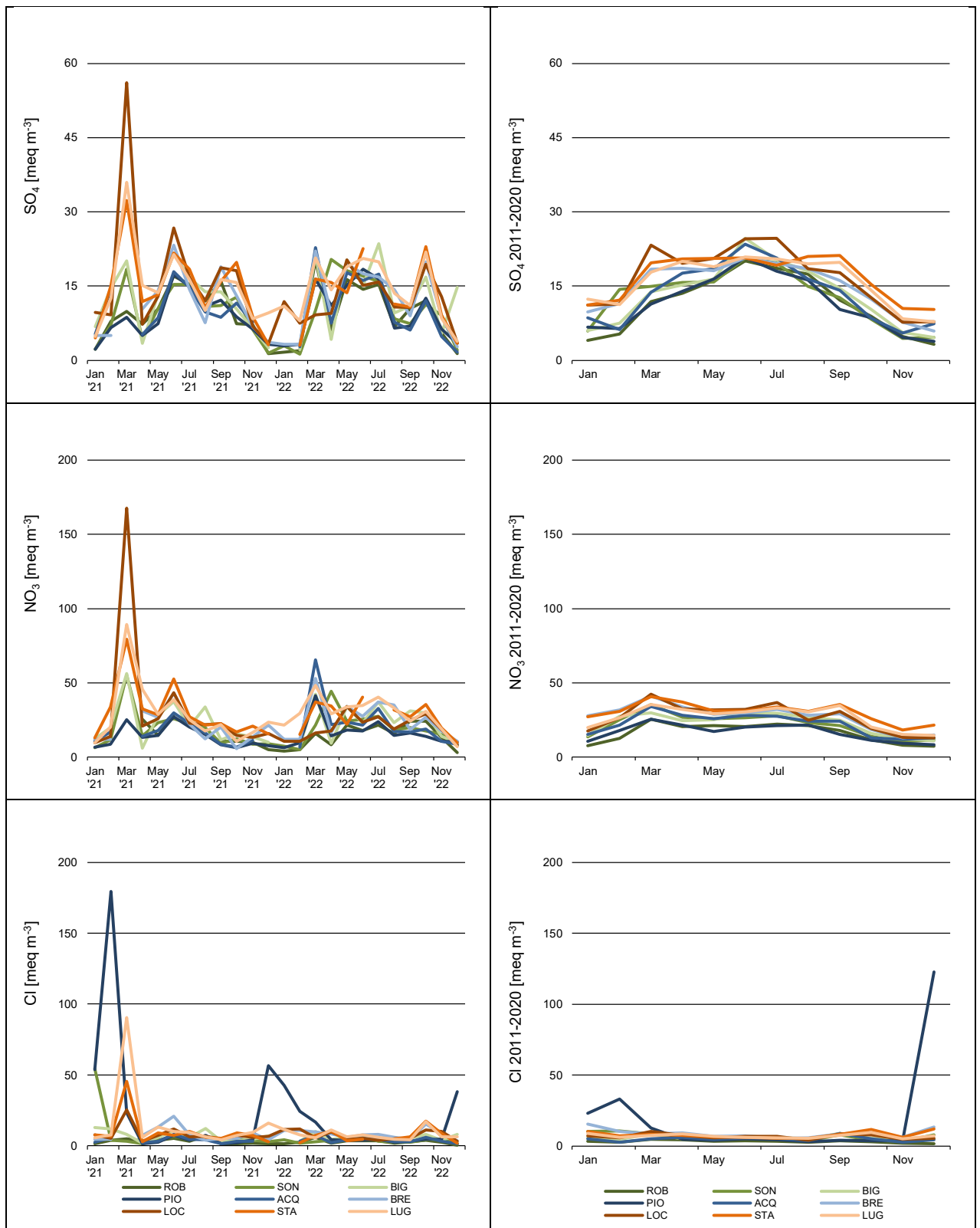


Figure 3.2 Monthly mean rainwater concentrations during 2021-2022 (left) during 2011-2020 (right)



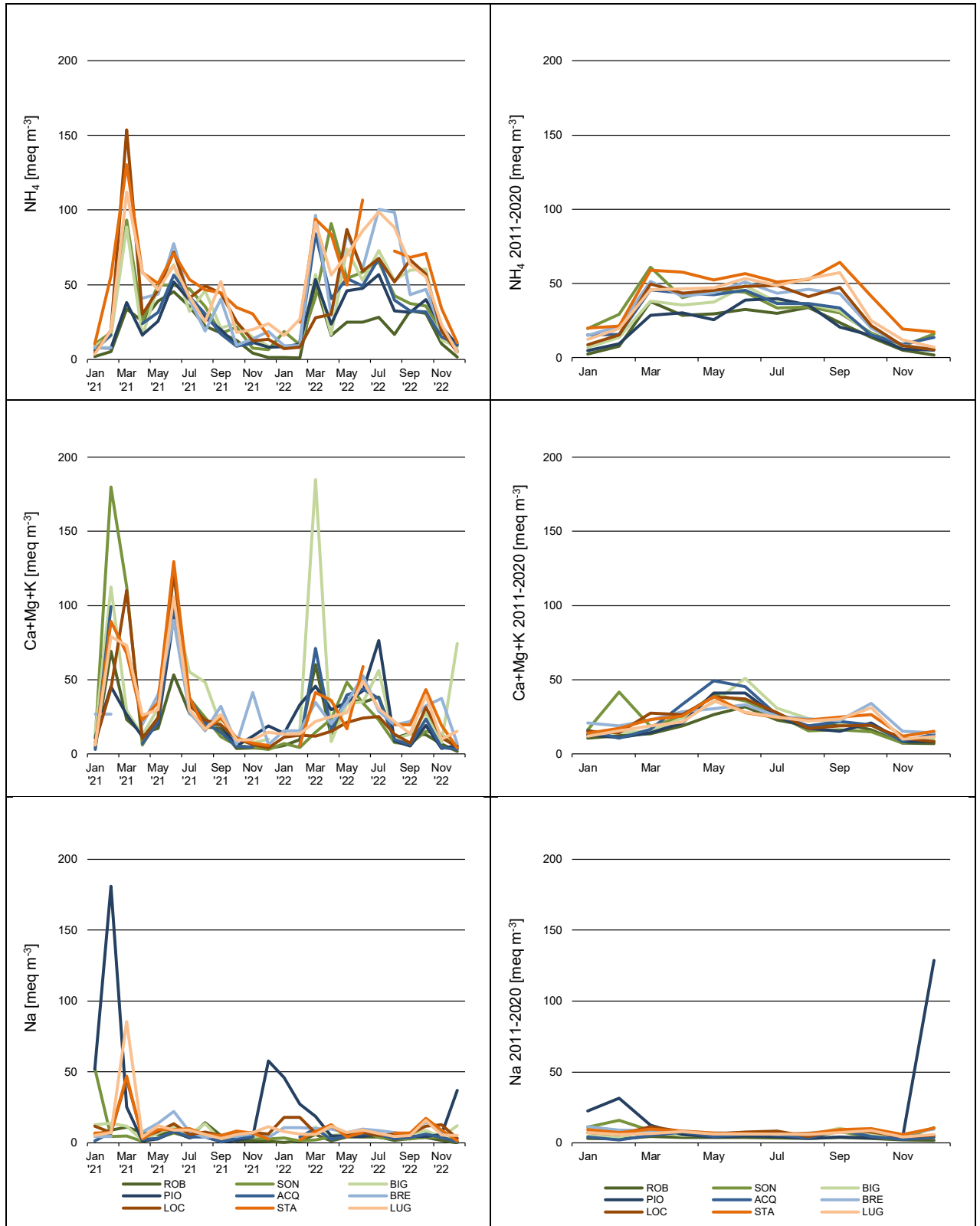
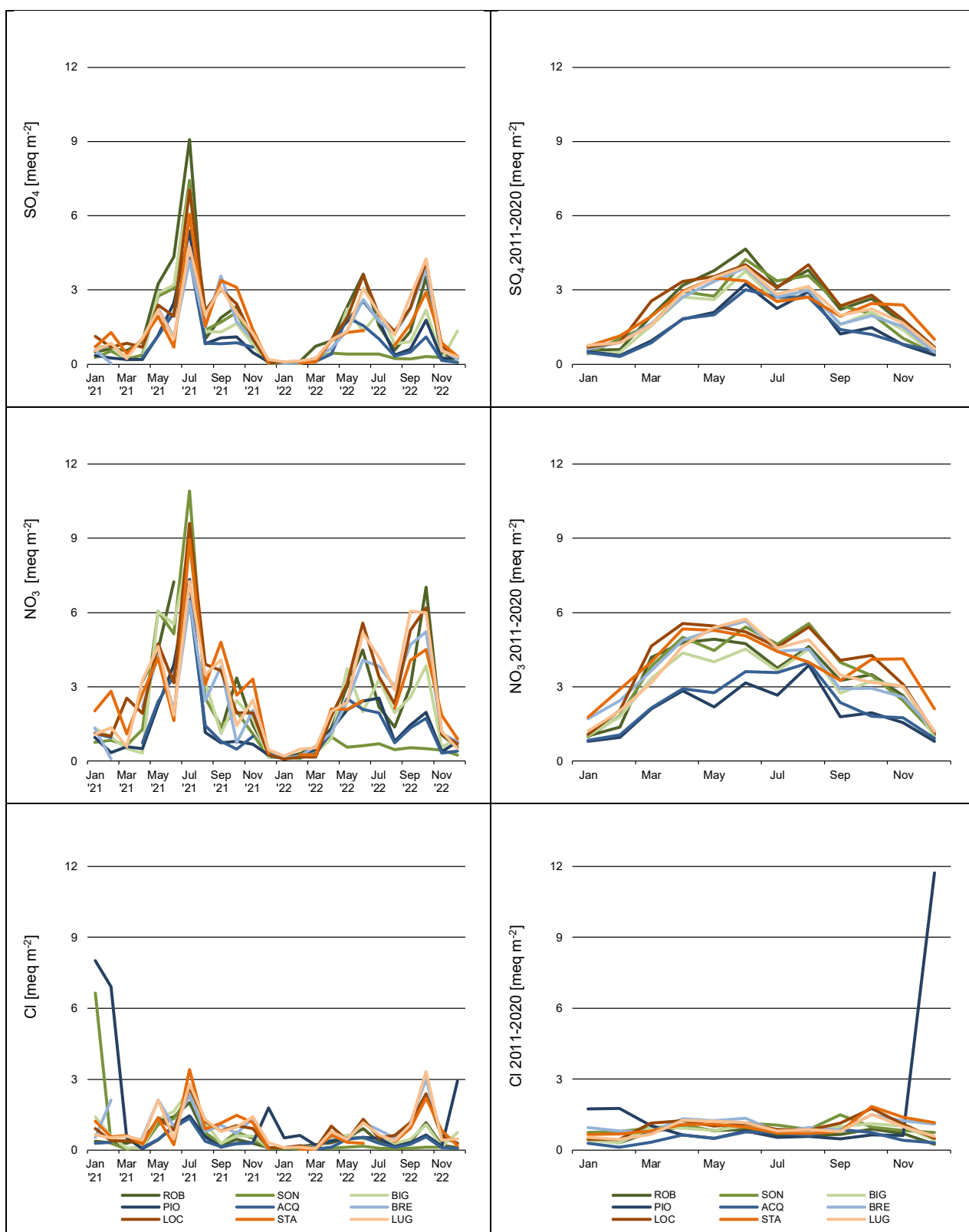
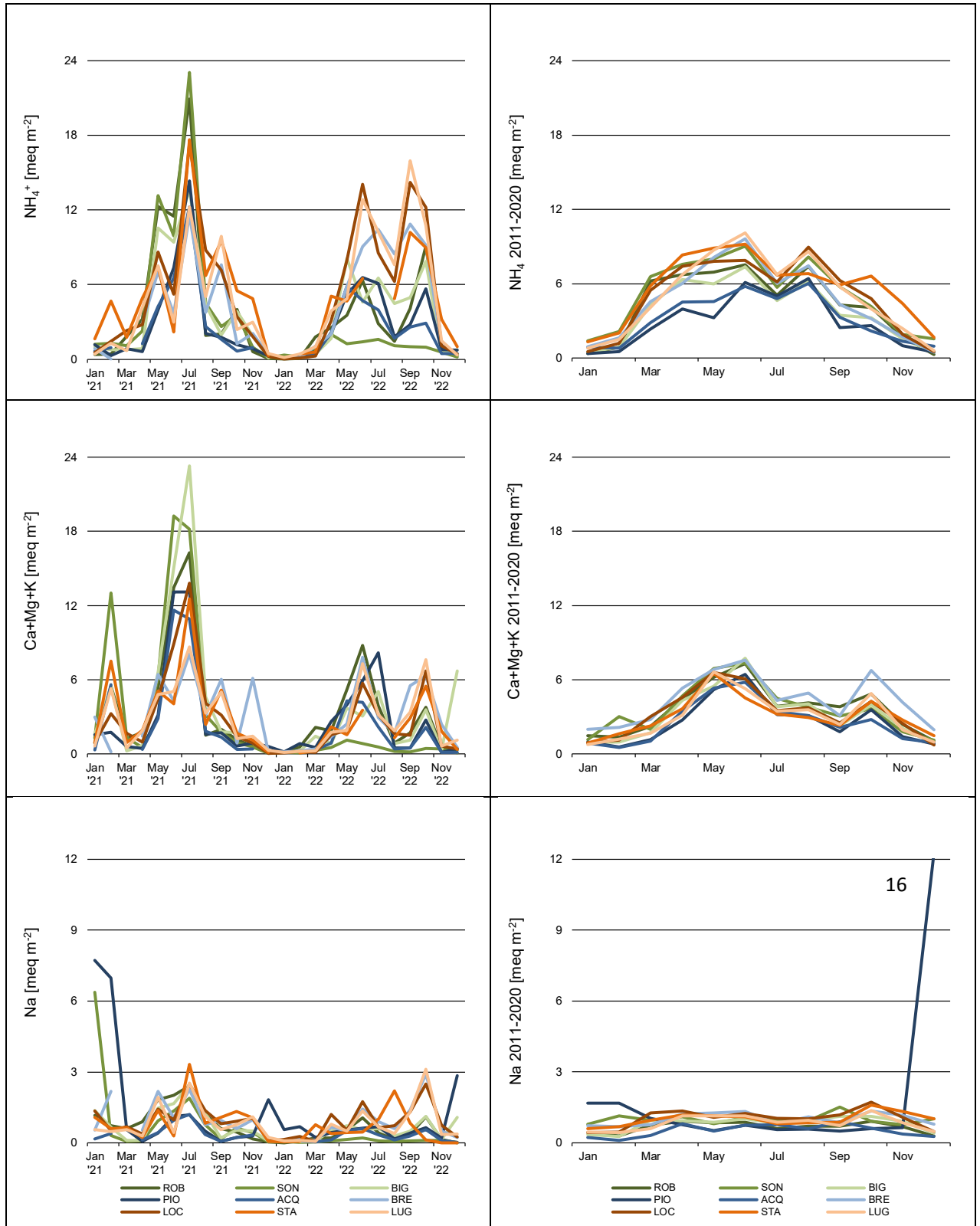
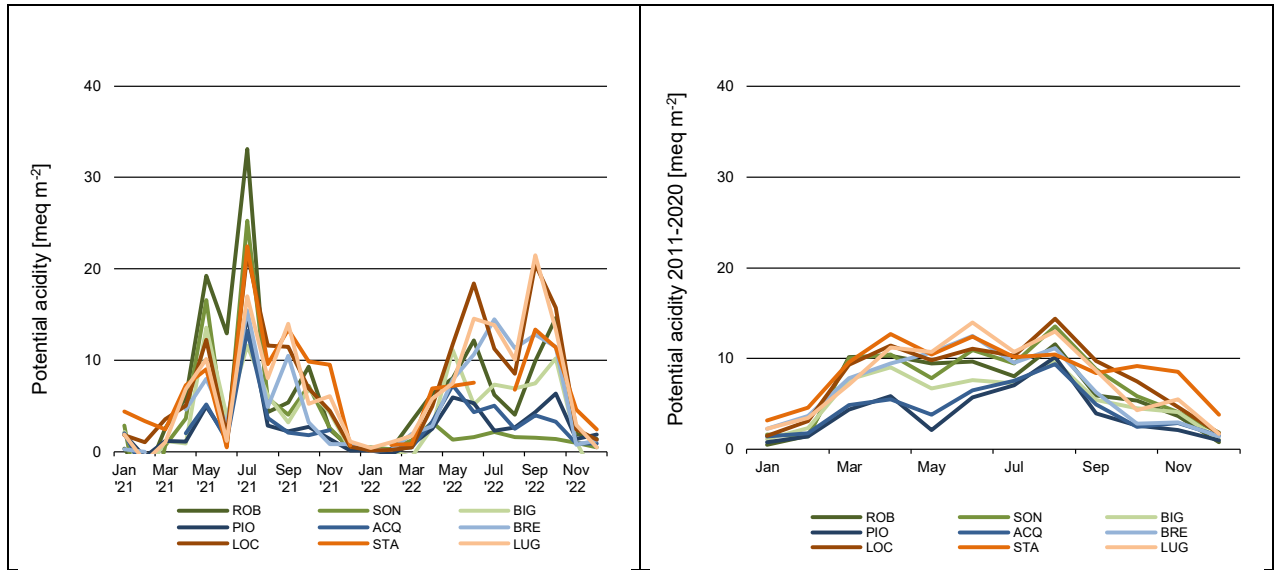




Figure 3.3 Monthly mean depositions during 2021-2022 (left) during 2011-2020 (right)



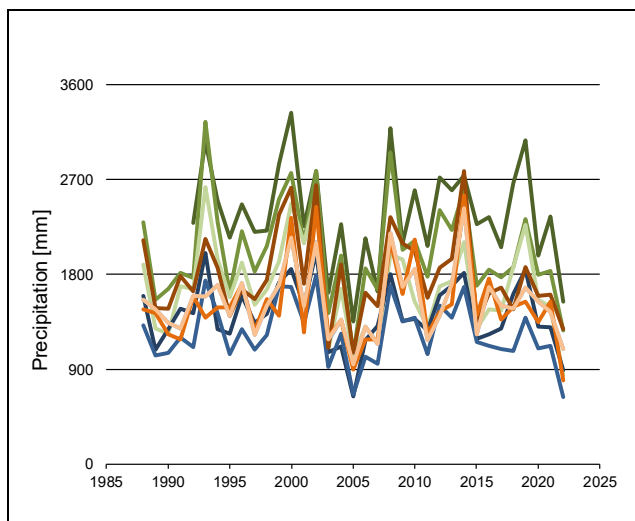




Temporal variations

The amount of yearly precipitations at each sampling site is presented in Fig. 3.4. Yearly precipitation was average during 2021 and significantly lower than average during 2022. Annual mean rainwater concentrations and depositions of the main chemical parameters since 1988 are shown in Fig. 3.5.

Figure 3.4 Yearly precipitations



Temporal trends for some of the measured parameters are immediately visible. The most pronounced trend show concentrations and depositions of SO_4 with a steep decrease after 1990 particularly until 2015 at all sampling sites. This is a direct consequence of reduced SO_2 emissions. A smaller decrease can be seen for concentrations and depositions of NO_3 particularly between 2000 and 2015 and even smaller for NH_4 . As already mentioned the exceptional high concentrations of NH_4 in 2022 may be related to higher evaporation rates of ammonia from agriculture due to the particularly warm and dry summer. Concentrations and depositions of $\text{Ca}+\text{Mg}+\text{K}$ also decreased and alkaline rain events became less frequent. Concentrations and depositions of Na and Cl were higher at the beginning of the 1990s. Frequent sea salt episodes due to storms in the Atlantic have been then reported in coastal areas in Northern European countries (Wright and Jenkins 2001). It is possible that this events slightly influenced the rain quality in Switzerland as well. On the other hand, it is also known that due to measures taken to reduce the emissions of S, the emission of HCl from combustion processes also decreased (Evans et al. 2011). However, the strong correlation between Na and Cl rather suggests sea salt to be the main source of the high concentrations at the beginning of the 1990's. The concentration peaks of SO_4 and base cations (Ca, Mg, Na, K) at LUG in 2010 were the consequence of the volcanic eruption at Eyafjellajokull (Iceland) in April 2010.

Concentrations of GranAlk increased at all sites. In general, concentrations of Gran alkalinity increased from values around -40 and -30 meq m^{-3} to values around between 15 and 30 meq m^{-3} . Because of the GranAlk increase, average pH increased from values around 4.3 in the 1990's to values ranging between 5.6 and 5.8 .

Trends of rainwater concentrations were analysed for four different time periods: from 1988-1991 until 2022, from 1988-1991 until 2000, from 2000 until 2010, and from 2010 until 2022

(Tab. 3.3). Since trends of depositions are “disturbed” by the precipitation volumes that vary irregularly through time, trends in depositions were calculated only for the entire monitoring period in order to level out as much as possible the influence of rainwater volume.

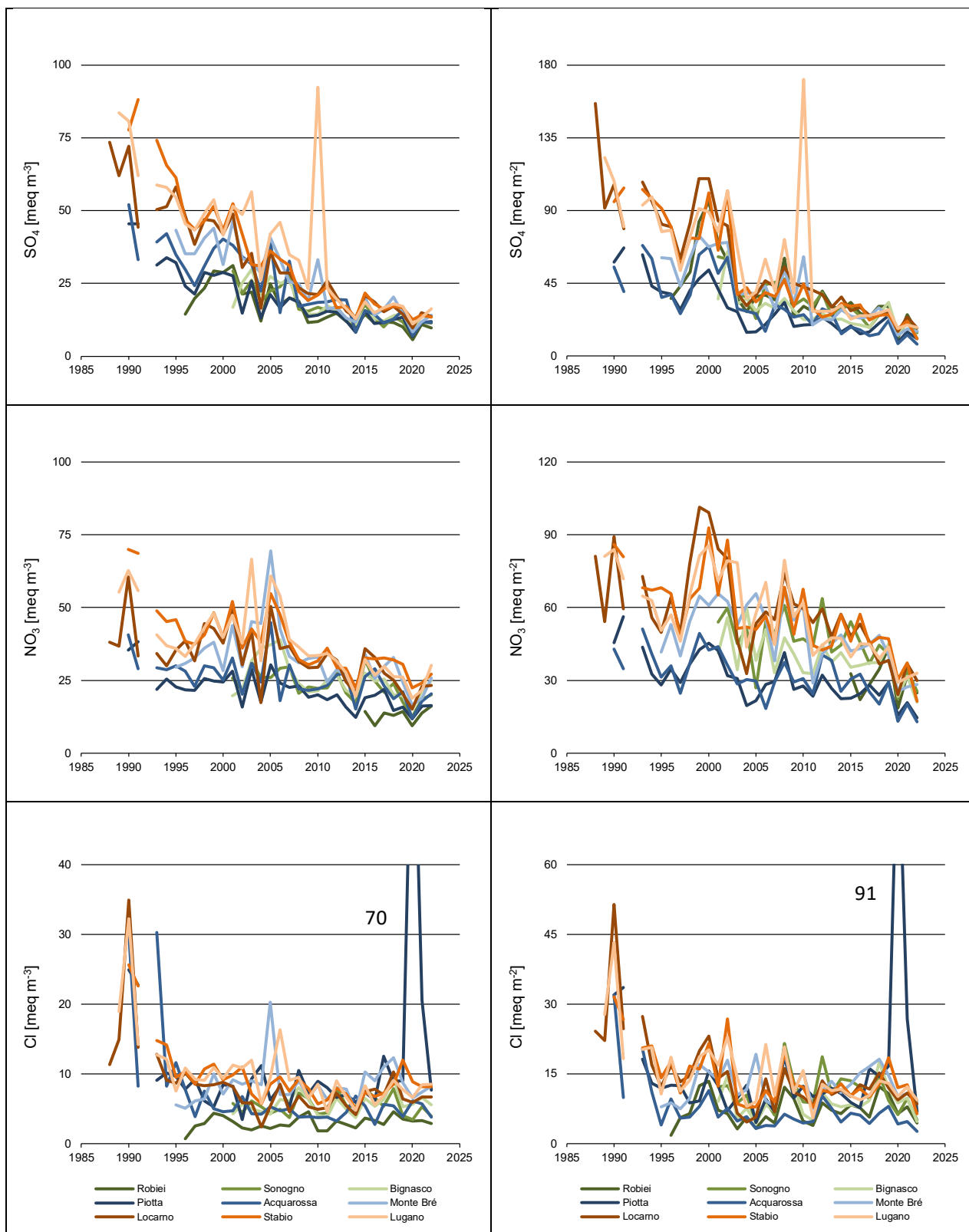
SO₄ concentrations decreased significantly at all sites. The highest change in concentrations occurred at the most polluted sites LOC, LUG and STA and during the first two analysed time periods (from 1988-1991 until 2000 and from 2000 until 2010). After 2010 concentrations of SO₄ still decreased significantly at all sites but much less. Concentrations of NO₃ also decreased significantly at all sites particularly between 2000 and 2010 and less after 2010. Concentrations of NH₄ decreased significantly at five sites and mainly between 2000 and 2010. The sum of Ca, Mg and K also decreased significantly at five sites and for most of them mainly during 2000-2010.

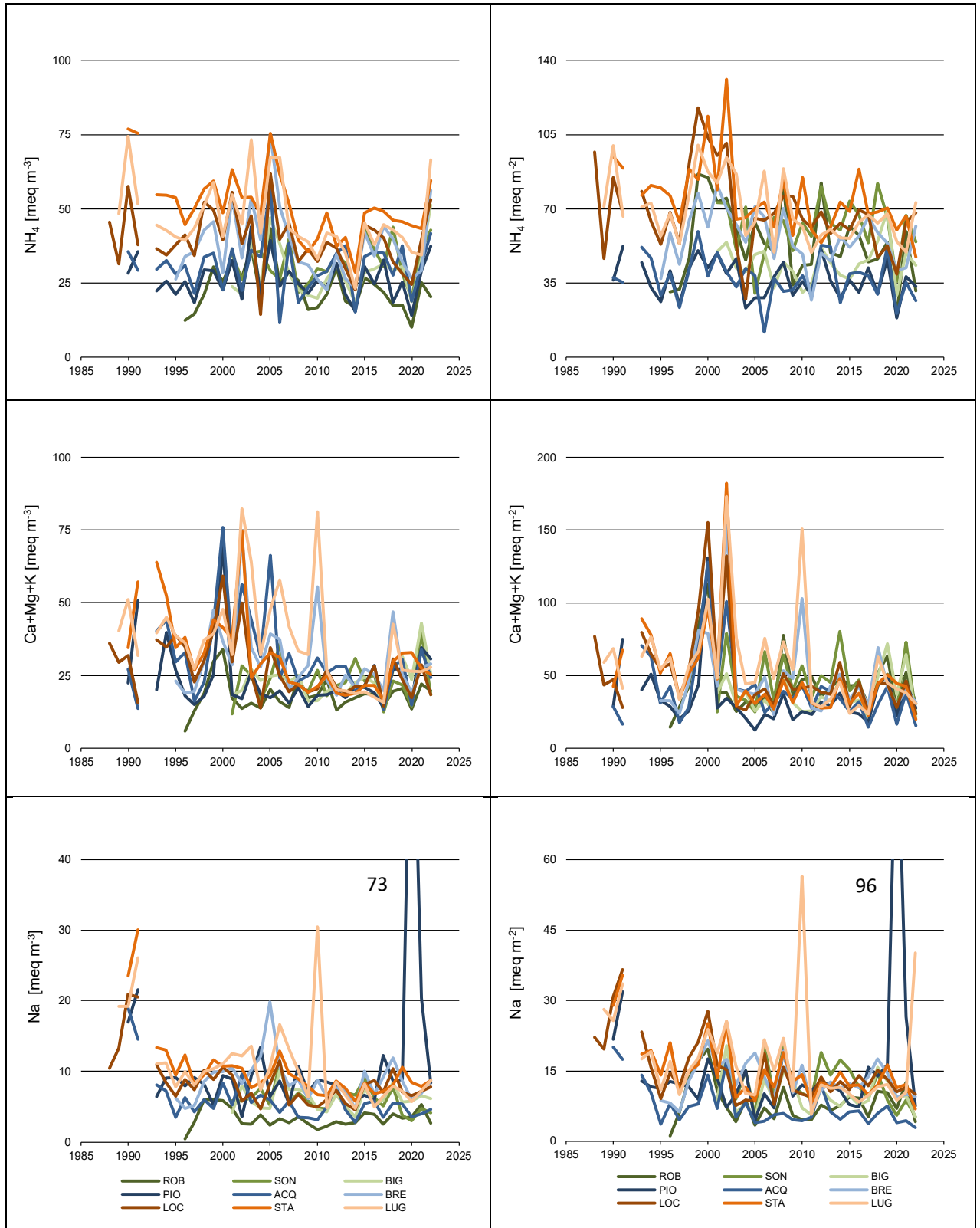
The concentrations of Na and Cl decreased at most sites, especially between the 1990s and 2000. Since 2010 the concentrations of Na and Cl are increasing again (significant trends at 4 sites and positive trend slopes at 8 sites). This increase occurred mainly during the winter months (from October to March, see Tab. 3.4). Sea-salt episodes in near-coastal surface waters in Northern Europe have been shown to be correlated with the North Atlantic Oscillation (NAO) index (Skjelkvåle 2003). The North Atlantic Oscillation (NAO) Index describes the large-scale weather systems in the north Atlantic Ocean which influence weather patterns in Europe, particularly in winter. Since about 2013 the NAO index reached again the high levels that characterised the beginning of the 1990's. (<https://www.cpc.ncep.noaa.gov/products/precip/CWlink/pna/nao.shtml>). It is very probable that the slight increase of Na and Cl concentrations, that we observe in Southern Switzerland in winter is related to this phenomena. An increase of NAO Index has been predicted by Hulme et al. (2002) for the next 60 years, implying that warm, westerly conditions in winter may become more prevalent.

The concentrations of the hydrogen ions decreased significantly at all sites, particularly at the beginning of the monitoring period (1980/1990-2000), but even after although less dramatically. The concentrations of GranAlk increased significantly at all sites during the entire monitoring period.

Deposition of SO₄, NO₃, hydrogen ions and potential acidity decreased significantly at all sites, deposition of NH₄ decreased significantly at all sites except BIG and deposition of the base cations decreased significantly at most sites.

Figure 3.5 Annual mean rainwater concentrations (left), depositions (right) and rainwater pH





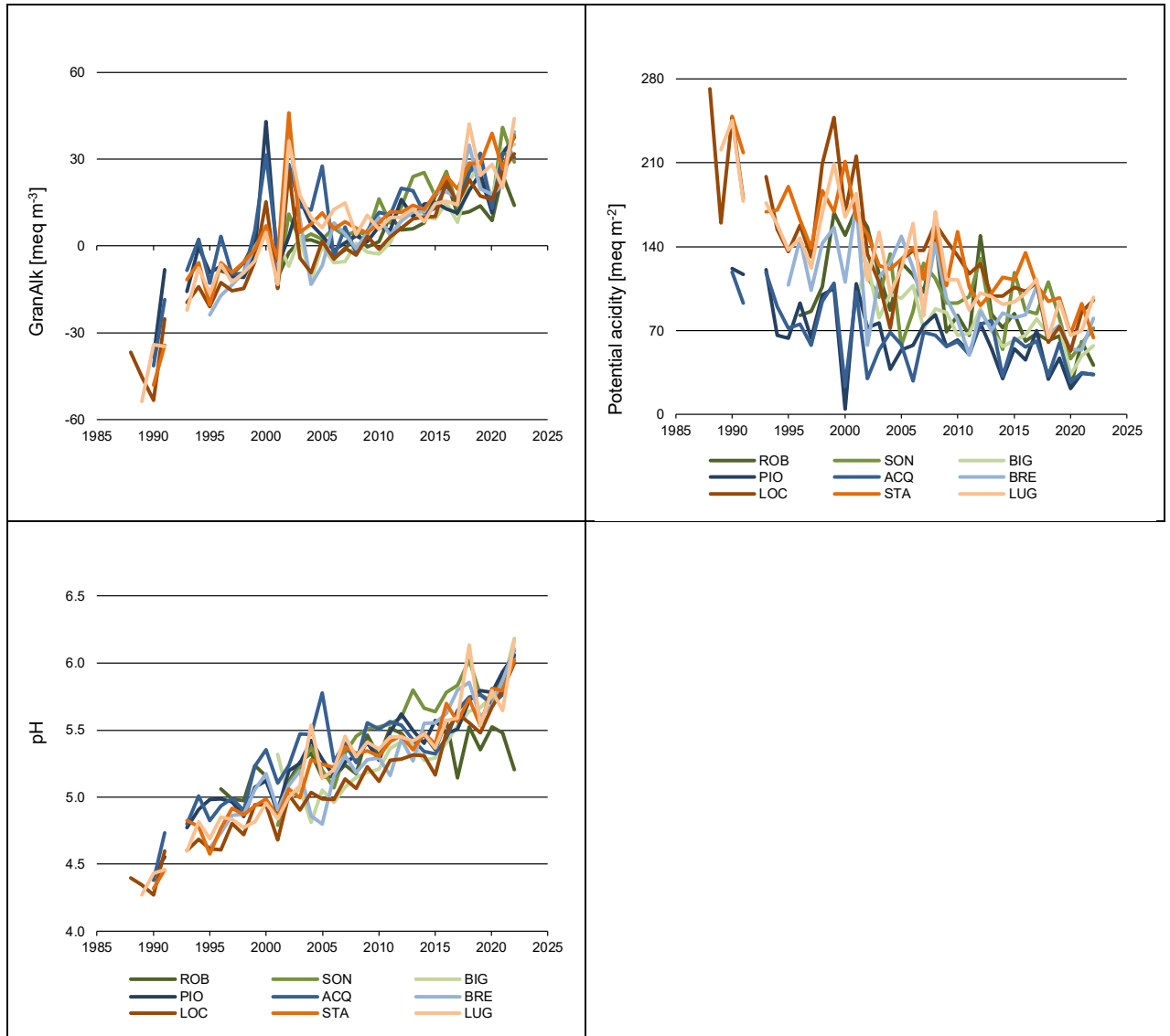


Table 3.3 Changes in rainwater concentrations (in meq m⁻³ yr⁻¹) and depositions (in meq m⁻² yr⁻¹) during the indicated time periods. Red rates indicate significant trends

CONC (meq m ⁻³ yr ⁻¹)	Period	SO ₄ beginning-2022			NO ₃ beginning-2022			Cl beginning-2022			NH ₄ beginning-2022			Ca+Mg+K beginning-2022			Na beginning-2022			H beginning-2022			GranAlk beginning-2022		
ACQ	1990-2022			-1.11			-0.55			-0.09			-0.17			-0.61			-0.10			-0.32			1.26
BIG	2001-2022			-0.60			-0.59			0.02			0.02			0.05			0.02			-0.43			1.75
BRE	1995-2022			-1.12			-0.59			0.07			-0.12			-0.05			0.07			-0.48			1.92
LOC	1988-2022			-1.67			-0.85			-0.16			-0.40			-0.44			-0.10			-0.94			2.12
LUG	1989-2022			-1.77			-0.80			-0.16			-0.33			-0.66			-0.18			-0.58			1.91
PIO	1990-2022			-0.71			-0.51			-0.05			-0.12			-0.26			-0.06			-0.46			1.24
ROB	1996-2022			-0.56			-0.36			0.00			-0.22			-0.08			-0.02						0.84
SON	2001-2022			-0.57			-0.45			-0.03			0.01			-0.17			-0.08			-0.20			1.23
STA	1990-2022			-1.76			-0.81			-0.12			-0.32			-0.53			-0.12			-0.48			2.00

CONC (meq m ⁻³ yr ⁻¹)	Period	SO ₄			NO ₃			Cl			NH ₄			Ca+Mg+K			Na			H			GranAlk																		
		'80/'90-00	00-10	10-22	'80/'90-00	00-10	10-22	'80/'90-	00-10	10-22	'80/'90-00	00-10	10-22	'80/'90-00	00-10	10-22	'80/'90-00	00-10	10-22	80/90-00	00-10	10-22	80/90-00	00-10	10-22																
ACQ	1990-2022	-1.41	-2.14	-0.64	-1.04	-0.76	-0.61	-0.82	-0.22	0.04	-1.05	-0.93	0.10	-0.47	-2.09	-0.81	-0.38	-0.35	0.05	-2.29	-0.06	-0.15	4.61	-0.42	1.12																
BIG	2001-2022		-1.27	-0.28			-1.19			-0.60			0.15	0.13			-1.20			0.34			-0.44	0.43			0.15	0.13			-0.56	-0.28			0.42	2.02					
BRE	1995-2022			-1.65			-0.44			-0.08			-0.56			-0.08			0.17			-0.77			0.56			-0.65	0.52			-0.21	0.17			-0.48	-0.20			1.96	2.17
LOC	1988-2022	-2.40	-2.46	-0.69	-0.71	-1.58	-1.22	-0.43	-0.31	0.24	-0.53	-1.50	0.03	-0.62	-1.25	-0.18	-0.42	-0.56	0.30	-3.48	-0.76	-0.25	2.56	0.98	1.94																
LUG	1989-2022	-2.78	-3.07	-0.58	-1.22	-1.47	-0.49	-0.70	-0.31	0.18	-0.11	-1.69	0.68	0.09	-1.61	0.14	-0.65	-0.65	0.07	-2.85	-0.42	-0.11	3.76	1.39	1.27																
PIO	1990-2022	-1.43	-1.01	-0.21	-0.62	-0.58	-0.49	-0.46	-0.14	0.09	-0.11	-0.70	0.22	-0.87	-0.89	0.65	-0.55	-0.21	0.07	-1.63	-0.31	-0.24	2.43	0.10	1.86																
ROB	1996-2022			-1.17			-0.23			-0.43			-0.50			-0.02			0.09			-1.17			-0.17			-0.48	0.19			-0.21	0.11			-0.28			0.44	0.55	
SON	2001-2022			-1.14			-0.40			-0.66			-0.61			-0.12			-0.06			-0.88			-0.07			-0.65	-0.21			-0.35	-0.09			-0.42	-0.08			0.57	0.80
STA	1990-2022	-3.44	-2.48	-0.51	-2.07	-1.11	-0.32	-0.97	-0.14	0.13	-0.85	-1.32	0.91	-2.17	-1.38	0.49	-1.28	-0.06	0.11	-2.65	-0.47	-0.08	4.30	1.72	1.92																

DEP (meq m ⁻² yr ⁻¹)	Period	SO ₄ beginning-2022			NO ₃ beginning-2022			Cl beginning-2022			NH ₄ beginning-2022			Ca+Mg+K beginning-2022			Na beginning-2022			H beginning-2022			Potential acidity beginning-2022		
ACQ	1990-2022			-1.16			-0.75			-0.10			-0.29			-0.57			-0.11			-0.37			-1.58
BIG	2001-2022			-0.62			-0.67			0.00			-0.04			0.05			-0.02			-0.46			-2.00
BRE	1995-2022			-1.34			-0.92			0.06			-0.28			-0.12			0.02			-0.63			-2.58
LOC	1988-2022			-2.24			-1.27			-0.20			-0.54			-0.49			-0.12			-1.34			-3.81
LUG	1989-2022			-2.29			-1.04			-0.17			-0.41			-0.75			-0.20			-0.85			-2.91
PIO	1990-2022			-0.66			-0.49			-0.06			-0.12			-0.14			-0.08			-0.46			-1.30
ROB	1996-2022			-1.16			-0.90			-0.01			-0.39			-0.10			-0.04						-1.75
SON	2001-2022			-0.99			-1.23			-0.12			-0.58			-0.44			-0.22			-0.36			-2.18
STA	1990-2022			-2.23			-1.24			-0.16			-0.48			-0.64			-0.16			-0.64			-3.12

Table 3.4 Changes in Cl and Na concentrations (in meq m⁻³ yr⁻¹) in the winter and summer semester from 2010 to 2022. Red rates indicate significant trends

Site	Cl		Na	
	winter	summer	winter	summer
ACQ	0.16	-0.03	0.19	-0.07
BIG	0.30	-0.04	0.30	-0.04
BRE	0.47	0.03	0.47	0.03
LOC	0.43	0.43	0.09	0.09
LUG	0.29	0.07	0.29	0.07
PIO	0.34	0.00	0.36	-0.05
ROB	0.16	0.01	0.25	0.01
SON	-0.05	-0.08	-0.07	-0.10
STA	0.33	0.04	0.28	0.02

Comparison between the sampling sites ROB and CRI hut

To have an idea how rainwater chemistry changes at altitudes above the until then highest sampling site ROB (1890 m a.s.l.), in spring 2017 another wet-only sampler was placed on the roof of the Cristallina hut (2575 m a.s.l., CRI), aware that at this very isolated site sampling could be performed only intermittently, more precisely during the stay of the custodian. Fig. 3.6 and 3.7 show the comparison between the monthly concentrations measured at the CRI and at ROB and at the Italian site DEV, respectively from April 2017 to September 2017 and from April 2019 to December 2019, January 2021, from June to October 2021, from December to April 2022, from June to October 2022, December 2022. Concentrations of Cl, K and Na at CRI were similar to those measured at ROB and DEV. Concentrations of NH_4 were similar to the concentrations at ROB, but slightly lower at DEV. Concentrations of SO_4 , Ca, Mg and slightly NO_3 were lower at CRI compared to both ROB and DEV, suggesting a decrease with altitude of the concentrations of these ions

Figure 3.6 Comparison between the monthly rainwater concentrations at CRI and at ROB during 2017, 2019, 2021, 2022

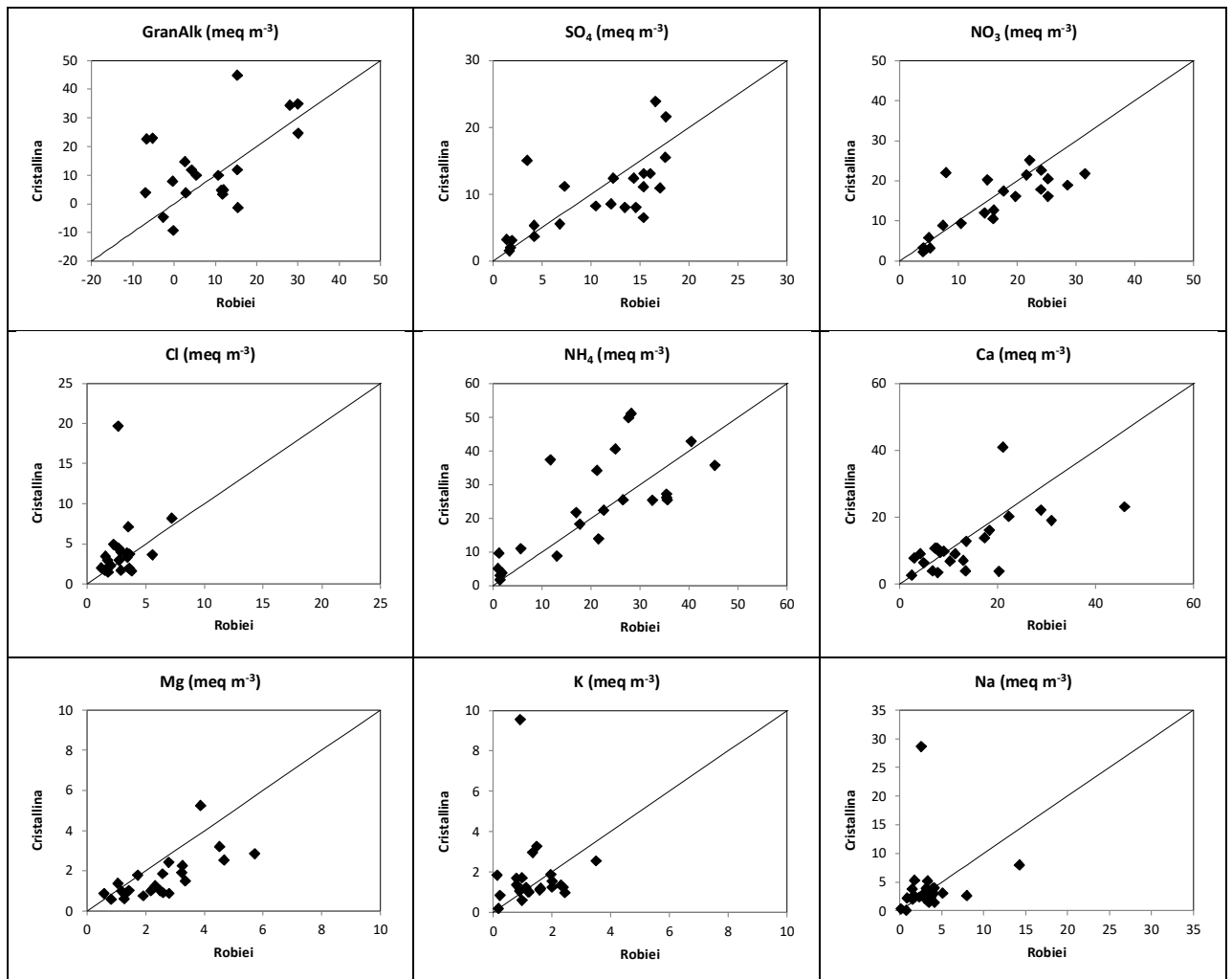
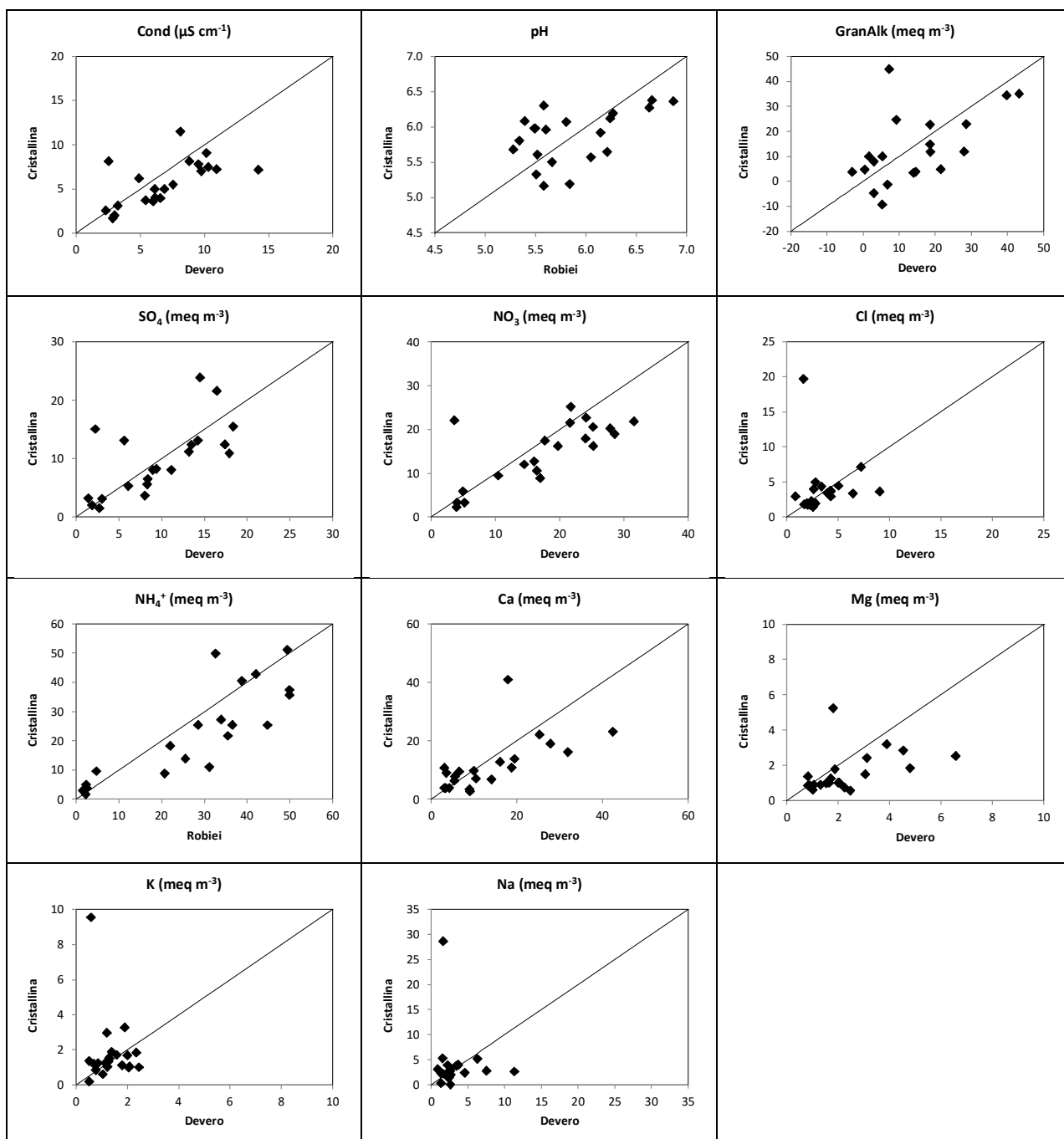


Figure 3.7 Comparison between the monthly rainwater concentrations at Cristallina and at Devero during 2017, 2019, 2021, 2022

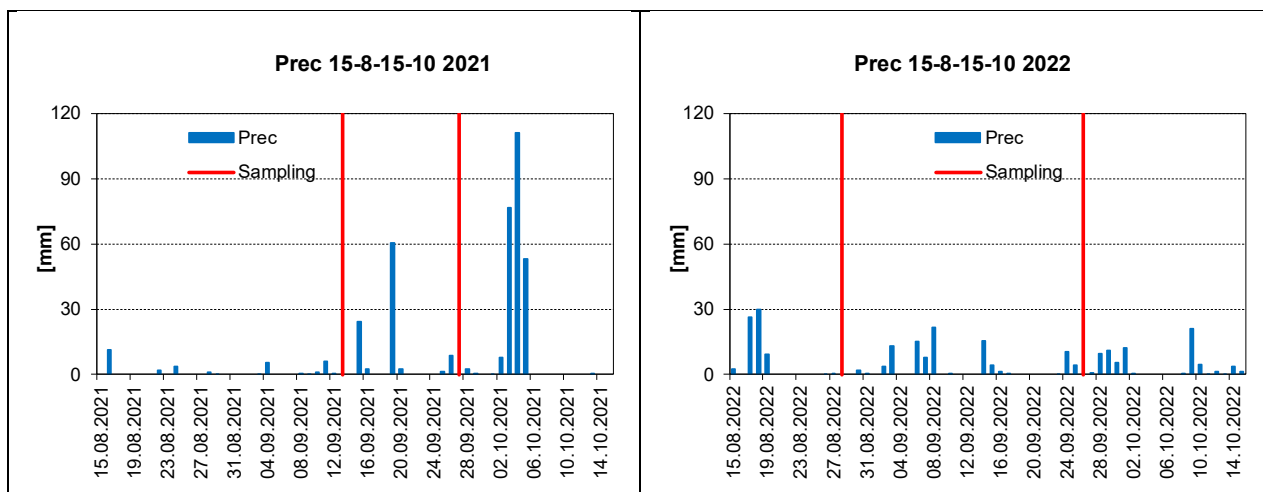


3.5.2 Alpine lakes

Introduction

During the last two years, lake sampling occurred on the 13th and 27th of September 2021, the 28th of August 2022 and the 26th of September 2022. Fig. 3.8 shows the daily precipitation volumes at ROB during the lake sampling periods. None of the samplings was preceded by heavy rain events.

Figure 3.8 Daily precipitation at ROB during the sampling months in 2021 and 2022. Sampling dates are indicated with red bars.



Spatial variations

Average autumn concentrations of the main chemical parameters measured in lake surface water are presented in Tab. 3.5.

During 2021 Cond at 25°C varied between 6 and 37 $\mu\text{S cm}^{-1}$, GranAlk between 0 and 89 meq m^{-3} , pH between 5.6 and 9.3, Ca between 20 and 185 meq m^{-3} , SO_4 between 10 and 261 meq m^{-3} , NO_3 between 1 and 24 meq m^{-3} , TN between 0.2 and 0.5 mg N l^{-1} , dissolved DOC 0.1 and 1.1 mg C l^{-1} , SiO_2 between 0.4 and 3.6 $\text{mg SiO}_2 \text{ l}^{-1}$ and Al_{sol} between 3 and 48 $\mu\text{g l}^{-1}$. 15% of the autumn samples were characterized by GranAlk below 20 meq m^{-3} and 6% by pH's below 6.

During 2022 conductivity at 25°C varied between 6 and 36 $\mu\text{S cm}^{-1}$, GranAlk between 1 and 114 meq m^{-3} , pH between 5.6 and 8.6, calcium between 19 and 185 meq m^{-3} , SO_4 between 10 and 234 meq m^{-3} , NO_3 between 2 and 28 meq m^{-3} , TN between 0.2 and 0.5 mg N l^{-1} , DOC between 0.3 and 1.4 mg C l^{-1} , SiO_2 between 0.9 and 3.2 mg l^{-1} and Al_{sol} between 2 and 41 $\mu\text{g l}^{-1}$. 15% of the autumn samples were characterized by GranAlk below 20 meq m^{-3} and 5% by pH's below 6.

According to the European surface water quality standards of Pb_{sol} and Ni_{sol} were below the environmental standards for annual means (Directive 2008/105/EC; Pd_{sol} : 7.2 $\mu\text{g l}^{-1}$, Ni_{sol} : 20 $\mu\text{g l}^{-1}$).

According to the critical values defined by the Environmental Protection Agency of the United States (EPA 2018), concentrations of Al_{tot} chronically exceeded the critical values

that depend on concentrations of DOC, pH and hardness in lake STA (critical value: $\sim 47 \mu\text{g l}^{-1}$) and in lake GAR (critical value: ca. $8 \mu\text{g l}^{-1}$). Aluminum is found in most soils and rocks and is the third most abundant element in the earth's crust. At high altitude lakes the main aluminum source is weathering. Elevated levels of aluminum can affect some species' ability to regulate ions, like salts, and inhibit respiratory functions, like breathing. Aquatic plants are generally less sensitive to aluminum than fish and other aquatic life. The bioavailability of aluminum is dependent on the chemistry of the water. The more bioavailable the aluminum is, the more likely it is to cause a toxic effect. The water chemistry parameters that have the greatest impact on aluminum's bioavailability are pH, total hardness and DOC. At low pH values aluminum is in general more bioavailable. The lowest aluminum solubility occur at pH 6-7, with higher solubility below and above this range. However, at higher values, the hardness of the water is also higher and in general, more ions are present in the water that compete with aluminum and make it less bioavailable. Aluminum also binds to DOC, making the aluminum less bioavailable to aquatic organisms. Therefore high DOC values also reduce the bioavailability of aluminum. (<https://www.epa.gov/sites/default/files/2018-12/documents/aluminum-final-national-recommended-awqc.pdf>)

Table 3.5 Average lake surface water concentrations in autumn 2021 and 2022. Values below the quantification limit were preceded with <.

Parameter	Year	STA	TOM	POR	BAR	GAR	LEI	MOR	MOG	INF	SUP	NER	FRO	ANT	CRO	ORS	SCH	POZ	SFI	SAS	ALZ
Temp (°C)	2021	14	12	8	10	10	10	10	10	11	11	10	10	10	12	9	9	14	12	13	13
	2022	14	12	8	11	11	11	12	12	12	12	11	11	11	13	10	10	14	13	14	14
Cond 25°C (µS cm ⁻¹)	2021	5.6	7.4	26.7	9.0	7.0	36.3	15.7	21.8	8.2	8.1	17.5	14.6	11.6	6.2	9.9	12.7	8.0	7.2	8.9	14.6
	2022	5.9	8.6	28.1	9.2	6.8	35.3	15.6	24.2	10.1	9.0	18.3	15.7	13.5	6.9	10.5	13.3	9.3	9.2	9.8	15.9
pH	2021	5.7	6.1	7.0	6.4	5.6	6.6	6.8	9.1	7.1	7.0	6.9	6.9	7.2	6.6	7.0	6.8	6.8	6.7	6.5	7.1
	2022	6.1	6.2	7.0	6.4	5.6	6.6	6.8	7.6	7.0	7.9	6.9	7.0	7.2	6.7	7.0	7.2	6.7	7.0	6.9	7.2
GranAlk (meq m ⁻³)	2021	4	10	85	22	2	32	51	80	40	39	75	68	72	31	52	62	50	35	30	88
	2022	15	15	91	25	1	40	58	106	55	51	81	78	94	36	57	66	65	51	41	102
Ca (meq m ⁻³)	2021	20	39	179	57	24	179	91	118	54	54	115	106	85	41	69	89	53	47	46	93
	2022	19	41	176	48	21	168	79	130	56	49	110	103	91	37	60	83	51	50	43	92
Mg (meq m ⁻³)	2021	6	5	17	6	10	77	20	27	7	7	16	9	6	5	7	9	9	8	13	16
	2022	7	6	18	6	9	68	19	30	8	8	16	9	6	5	8	10	9	9	13	17
Na (meq m ⁻³)	2021	11	12	23	11	8	23	16	29	11	11	16	13	17	10	14	15	15	14	14	20
	2022	13	15	24	12	8	25	17	33	15	13	17	14	20	12	15	16	19	18	16	22
K (meq m ⁻³)	2021	3	4	14	5	6	15	13	14	7	7	12	7	6	4	5	7	4	3	8	12
	2022	4	4	15	6	7	18	16	17	11	9	15	9	9	5	6	9	6	4	10	16
NH ₄ (meq m ⁻³)	2021	1	0	0	1	1	1	0	0	0	0	1	1	0	0	1	0	0	0	1	1
	2022	3	1	1	1	1	2	1	1	1	1	2	1	1	1	1	1	1	1	1	2
SO ₄ (meq m ⁻³)	2021	17	22	126	38	34	253	70	85	19	17	65	43	14	10	14	24	17	17	21	28
	2022	17	24	125	37	33	228	63	94	24	20	68	45	15	11	14	22	18	20	21	29
NO ₃ (meq m ⁻³)	2021		22	13	12	10	8	10	9	13	13	9	14	17	14	18	22	2	9	21	13
	2022	11	27	18	12	9	9	10	8	11	9	9	14	16	14	22	27	2	9	20	12
NO ₂ (µg N l ⁻¹)	2021	1	1	1	2	1	1	1	1	2	1	1	1	2	2	3	2	0	1	2	2
	2022	1	3	2	1	1	1	1	3	1	1	1	1	2	2	3	3	0	1	2	2
Cl (meq m ⁻³)	2021	4	4	3	3	3	3	3	3	3	3	2	3	3	3	4	4	4	4	3	4
	2022	5	4	3	3	3	3	3	4	3	3	3	3	3	3	4	4	4	4	3	4
SRP (µg P l ⁻¹)	2021	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2
	2022	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2	8	<2	<2	<2	<2	<2	<2	<2	<2
P _{tot} (µg P l ⁻¹)	2021	<32	<32	<32	<32	<32	<32	<32	<32	<32	<32	<32	<32	<32	<32	<32	<32	<32	<32	<32	<32
	2022	<32	<32	<32	<32	<32	<32	<32	<32	<32	<32	<32	<32	<32	<32	<32	<32	<32	<32	<32	<32
N _{tot} (mg N l ⁻¹)	2021	0.32	0.46	0.28	0.26	0.22	0.24	0.34	0.39	0.33	0.34	0.21	0.30	0.34	0.28	0.39	0.40	0.23	0.25	0.46	0.30
	2022	0.36	0.47	0.37	0.28	0.22	0.26	0.24	0.26	0.32	0.32	0.21	0.30	0.35	0.28	0.46	0.51	0.21	0.24	0.49	0.30
DOC (mg C l ⁻¹)	2021	1.1	0.7	0.3	0.3	0.1	0.4	0.3	0.7	0.8	0.8	0.3	0.3	0.5	0.3	0.5	0.4	1.0	0.8	0.7	0.6
	2022	1.4	0.5	0.4	0.3	0.3	0.5	0.4	0.5	0.7	1.3	0.4	0.5	0.8	0.4	0.8	0.4	1.2	0.9	1.0	0.8
SiO ₂ (mg l ⁻¹)	2021	1.3	1.7	2.6	1.2	0.7	2.4	2.0	3.3	1.0	1.0	1.9	1.2	2.2	1.6	1.3	1.9	2.1	1.6	1.6	2.7
	2022	1.9	2.3	3.2	1.5	0.9	2.4	2.2	3.1	1.7	1.7	2.3	1.8	2.6	1.7	2.1	2.4	2.7	2.4	2.2	2.1

Parameter	Year	STA	TOM	POR	BAR	GAR	LEI	MOR	MOG	INF	SUP	NER	FRO	ANT	CRF	ORS	SCH	POZ	SFI	SAS	ALZ
Al _{sol} (µg l ⁻¹)	2021	42.5	12.0	3.7	4.3	14.9	3.9	5.5	14.1	10.7	10.6	3.8	7.0	8.8	4.2	8.5	10.3	28.4	18.9	22.0	10.7
	2022	36.8	11.3	3.0	4.6	9.8	12.4	11.3	11.2	5.5	18.6	4.9	7.9	8.8	2.8	8.4	7.4	27.2	14.2	21.2	11.4
Al _{tot} (µg l ⁻¹)	2021	57.6	24.0	6.1	8.4	19.2	14.0	31.1	17.9	20.3	19.8	7.4	10.2	17.5	8.2	15.8	16.5	52.0	24.7	33.8	14.0
	2022	60.1	16.6	5.1	9.5	13.2	22.4	78.6	17.6	14.4	27.9	10.3	12.0	16.7	5.2	15.6	13.5	40.1	20.1	35.4	17.6
Pb _{sol} (µg l ⁻¹)	2021	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
	2022	<0.1	<0.1	<0.1	<0.1	<0.7	<4.3	<0.3	<0.3	<0.1	<0.1	<0.2	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Pb _{tot} (µg l ⁻¹)	2021	0.2	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
	2022	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Cd _{sol} (µg l ⁻¹)	2021	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
	2022	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Cd _{tot} (µg l ⁻¹)	2021	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
	2022	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Cu _{sol} (µg l ⁻¹)	2021	0.3	0.2	0.2	0.1	0.2	0.3	0.3	0.3	0.2	0.1	0.1	<0.1	<0.1	<0.1	0.1	<0.1	<0.1	0.1	0.2	<0.1
	2022	0.3	<0.1	<0.2	<0.1	0.2	<0.3	0.3	0.3	0.1	0.2	0.1	<0.1	<0.2	<0.1	0.2	0.1	0.1	0.1	0.1	0.2
Cu _{tot} (µg l ⁻¹)	2021	0.3	0.2	0.2	0.2	0.2	0.4	0.4	0.3	0.2	0.2	0.1	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.2	0.2	0.1
	2022	0.5	0.2	0.2	0.1	0.3	0.6	0.6	0.5	0.2	0.2	0.2	0.2	<0.2	<0.1	0.2	0.1	0.2	0.1	0.3	0.2
Zn _{sol} (µg l ⁻¹)	2021	2.8	1.8	0.3	0.6	1.2	0.9	0.5	0.1	0.7	0.2	0.4	0.6	0.8	0.4	0.5	0.5	0.3	0.7	0.9	0.3
	2022	2.3	1.0	0.7	0.5	5.1	1.6	0.8	0.8	0.7	1.1	1.6	0.3	3.5	1.1	2.2	0.4	0.6	0.6	1.6	0.9
Zn _{tot} (µg l ⁻¹)	2021	2.9	2.0	0.3	0.8	1.3	1.1	0.9	0.5	1.0	0.5	0.4	0.8	1.1	0.5	0.8	0.7	0.5	0.8	1.0	0.4
	2022	2.4	1.1	0.7	0.6	5.2	1.8	1.2	1.1	0.8	1.1	1.7	0.4	3.9	1.1	2.4	0.5	0.7	0.7	1.7	1.0
Cr _{sol} (µg l ⁻¹)	2021	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
	2022	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.2	<0.1	<0.1	<0.1	<0.1	<0.1	<0.2	<0.1
Cr _{tot} (µg l ⁻¹)	2021	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
	2022	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.2	<0.1	<0.1	<0.1	<0.1	<0.1	<0.3	<0.1	<0.2	<0.1	<0.1	<0.1	<0.2	<0.1
Ni _{sol} (µg l ⁻¹)	2021	0.2	0.1	<0.1	0.1	1.5	14.0	0.5	0.4	<0.1	<0.1	0.2	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	0.1	0.2	<0.1
	2022	0.2	0.1	<0.1	0.1	1.3	8.4	0.4	0.5	<0.1	<0.1	0.2	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	0.2	<0.1
Ni _{tot} (µg l ⁻¹)	2021	0.2	0.1	<0.1	0.1	1.5	14.2	0.5	0.5	<0.1	<0.1	0.2	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	0.2	<0.1
	2022	0.2	<0.1	<0.1	<0.1	1.3	8.4	0.5	0.5	0.1	<0.1	<0.2	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	0.2	<0.1
Fe _{sol} (µg l ⁻¹)	2021	7.7	<1.2	<1.0	1.2	8.6	2.4	3.4	5.6	<1.0	<1.1	1.5	1.9	<1.0	<1.0	<1.0	<1.0	3.4	2.3	9.4	2.4
	2022	11.6	<1.0	<1.0	1.7	5.4	17.4	10.3	13.8	<1.0	4.1	2.4	3.2	<1.3	<0.6	1.4	1.8	2.1	2.1	20.4	3.2
Fe _{tot} (µg l ⁻¹)	2021	18.2	6.4	2.3	4.0	11.6	13.9	31.0	18.3	<8.6	10.5	4.3	4.6	7.9	2.9	7.0	4.9	9.6	4.7	20.5	4.6
	2022	25.4	3.3	2.4	4.4	8.2	28.4	75.6	42.2	7.6	11.0	6.0	5.9	6.5	2.4	7.1	5.7	12.7	4.9	40.5	7.1

Fig. 3.9 and Fig. 3.10 compares the main parameters measured during 2021 and 2022 with their mean values from 2011 to 2020.

Differences in the lake surface water temperature are mainly determined by their altitude. Highest average temperatures during 2011-2020 were measured in ALZ, STA, Lago dei POZ, SFI. Lowest temperatures were measured in POR. Interestingly, several higher situated lakes had higher temperatures than POR. The presence of thawing cryospheric features in the latter can be an explanation. Compared to the means of the previous decade temperatures during 2021 and 2022 were significantly higher. The increasing air temperatures and the low rainfalls that characterized the last two years that limited the water renewal in the lakes most probably contributed to the warming of the lakes. Temperatures were particularly high during the sampling that occurred at the end of August 2022.

Highest concentrations of SO₄ during 2021 and 2022 were measured in lakes characterized by thawing cryospheric features, that probably enhanced weathering of S (POR, LEI, MOG, NER, MOR). In fact, concentrations of SO₄ are mainly determined by S deposition, in some lakes also by weathering of S containing rocks and partially also by the release of legacy deposits of old atmospheric S (Steingruber in prep.). Compared to 2011-2020 the concentrations of SO₄ in the lakes impacted by cryospheric features were even higher, while they were similar in the other lakes.

Concentrations of NO_3 during 2021-2022 were similar to those of 2011-2020. Concentrations of NO_3 depend on the atmospheric deposition of N, the retention of N in the catchments and the transformation of DIN into organic N (especially in the lakes). In fact, differences of concentrations among the lakes were mainly determined by different N retention capacities of the catchments and by differences in the proportion of the transformation of inorganic nitrogen into organic nitrogen.

Cl is known to be a conservative parameter and it mainly derives from atmospheric deposition (from emissions of HCl and from sea salts). Compared to the means of 2011-2020, the concentrations were higher during 2021 and 2022. The highest chloride concentrations occurred at the lakes with the highest temperature, suggesting a relation between the two parameters. In fact, the chloride concentrations of the August 2022 sampling, when lake water was warmest, correlated significantly with the water temperature (Pearson correlation coefficient = 0.57), suggesting that evapotranspiration may partially explain the differences in the concentrations among the lakes.

The concentrations of the base cations in the lakes are mainly determined by the extent of weathering in the catchments and by the release/retention from/at the base cation exchange sites. High concentrations of base cations normally characterize lakes with elevated alkalinities and pH's, as well. Most lakes impacted by cryosperic features (POR, LEI, MOR, MOG) have higher concentrations of Ca and Mg, than expected from their alkalinities and pH's. Compared to the values of the previous decade the concentrations of the base cations of 2021 and 2022 were slightly higher. Several mechanisms can be imagined: concentration effects due to evapotranspiration or lack of dilution because of low precipitation, increase of weathering, effect of recovery from acidification. The topic is discussed further in the paragraph of the temporal trends.

During 2021 and 2022 none of the lakes had concentrations of GranAlk below 0 meq m^{-3} , while GranAlk constantly above 50 meq m^{-3} were measured in lakes ANT, MOG, ALZ, NER, POR, FRO, SCH and MOG. All other 12 lakes were at least temporary sensitive to acidification ($0 < \text{GranAlk} < 50 \text{ meq m}^{-3}$). Compared to the means of 2021-2022 the GranAlk during 2021 and 2022 were mostly slightly higher.

The pH's of the lakes were also mostly higher during 2021 and 2022 compared to the averages of the previous decade. Exceptionally high pH's were measured in lake MOG especially during both 2021 samplings (9.3 and 8.9) and in lakes SUP and in POZ during the first sampling of 2022 (8.6 and 7.3, respectively). This high values may have been temporarily caused by a high photosynthetic activity. Concentrations of SRP in these lakes were mostly below $1 \mu\text{g P l}^{-1}$ and are typical of oligotrophic lakes ($< 1 \mu\text{g P l}^{-1}$), however it is very probable that the unusual high water temperatures of the last two years have enhanced the primary production in some Alpine lakes.

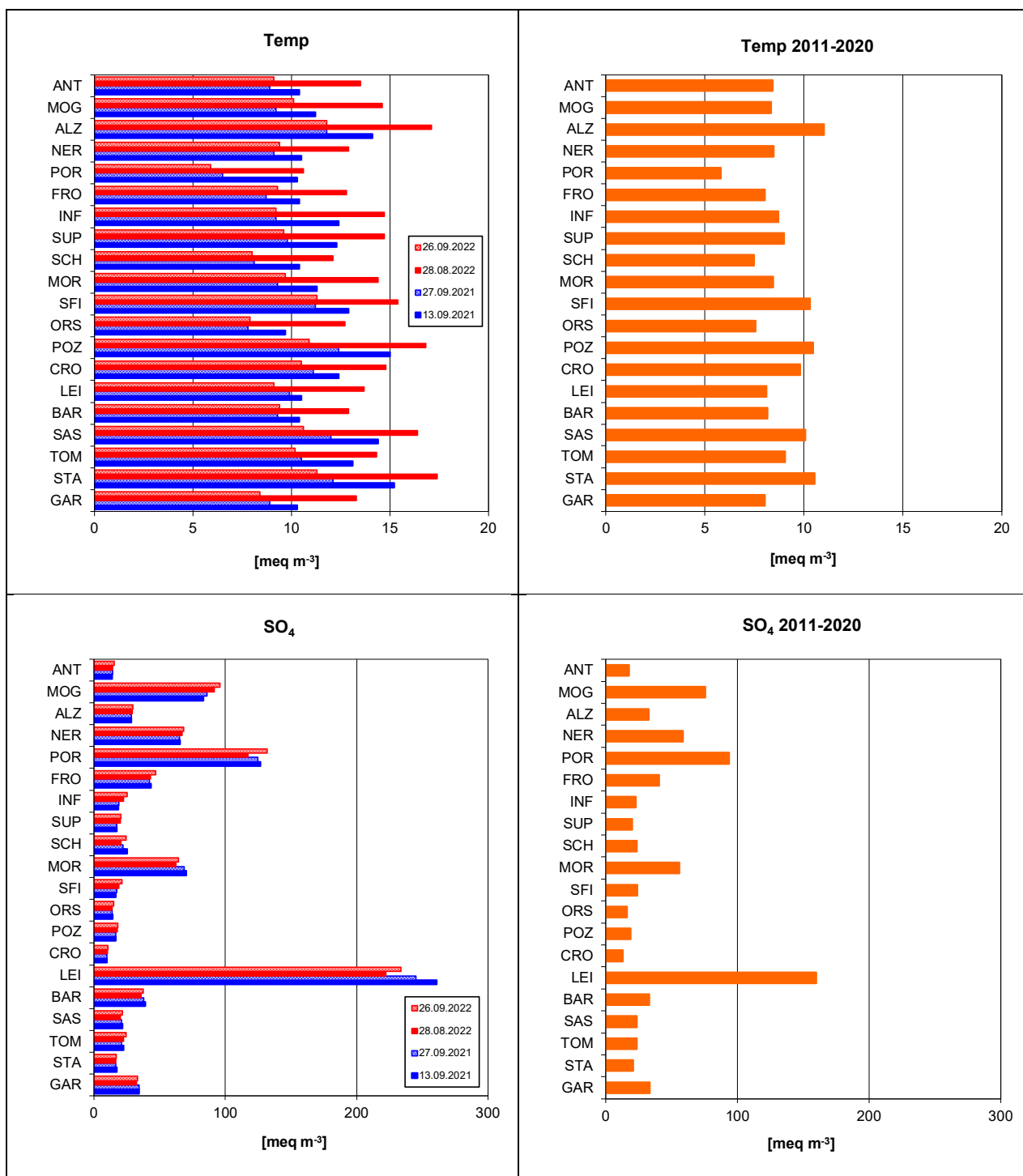
Highest concentrations of Al_{sol} were normally measured in the lakes with low pH. In fact, the mean concentrations in lakes STA, GAR, SAS and TOM during 2011-2020 were $45 \pm 14 \mu\text{g l}^{-1}$, $31 \pm 15 \mu\text{g l}^{-1}$, $20 \pm 9 \mu\text{g l}^{-1}$ and $19 \pm 5 \mu\text{g l}^{-1}$, respectively. Compared to these values, concentrations of Al_{sol} during 2021 and 2022 remained relatively stable in lake STA ($40 \pm 6 \mu\text{g l}^{-1}$) and lake SAS ($22 \pm 4 \mu\text{g l}^{-1}$) but were significantly lower in lake GAR ($12 \pm 3 \mu\text{g l}^{-1}$) and lake TOM ($10 \pm 2 \mu\text{g l}^{-1}$). With exception of lake STA, the pH's of the other three lakes were

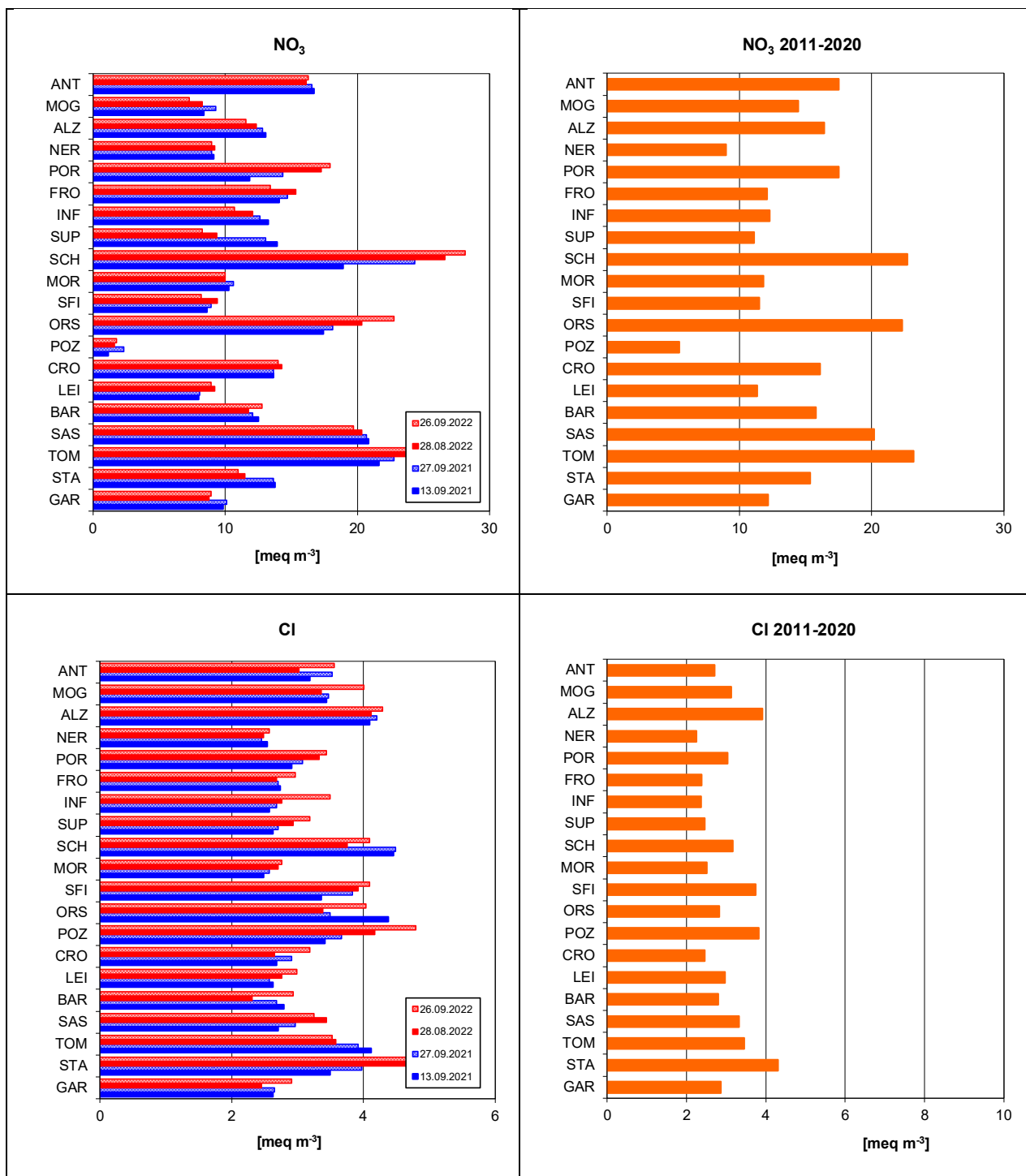
higher during 2021 and 2022 compared to the mean of the previous decade (STA: 5.9 vs 5.8 ± 0.2 , SAS; 6.5 vs 6.2 ± 0.2 , GAR: 5.6 vs 5.4 ± 0.1 , TOM: 6.1 vs 5.9 ± 0.1). The lack of a further decrease of aluminum in lake SAS is probably related to the fact that its pH is above 6. In this range concentrations of aluminum react less to changes in pH.

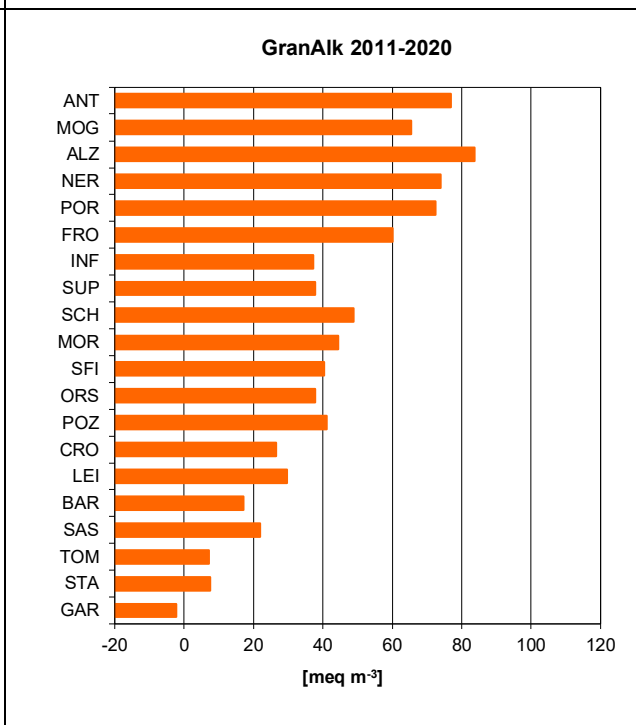
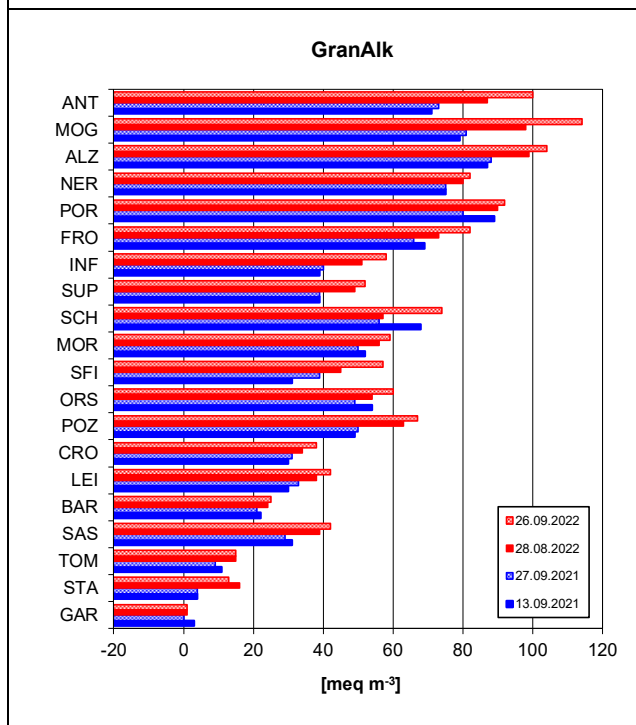
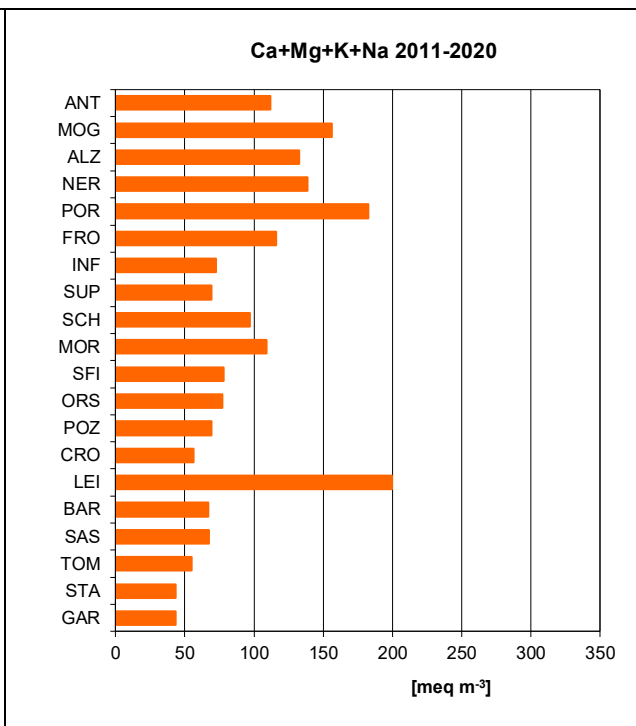
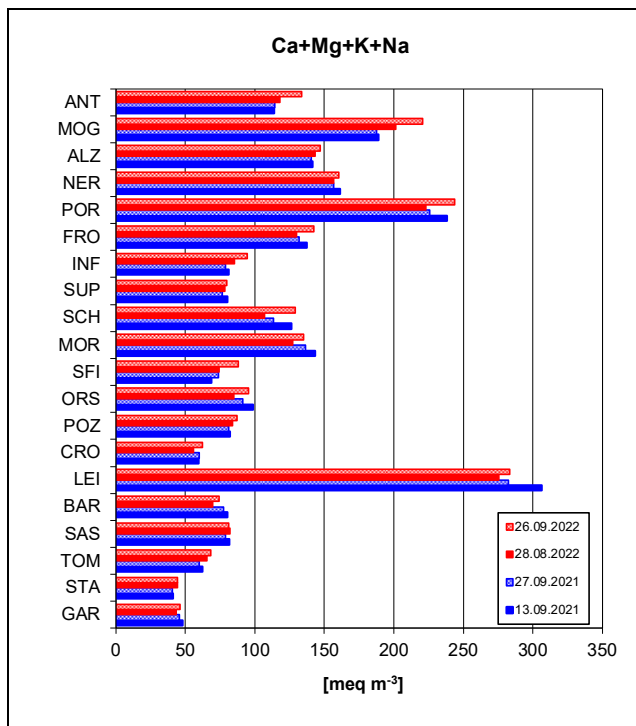
Concentrations of SiO_2 were in general higher at lakes characterized by higher concentrations of base cations (correlation: 0.69 and 0.62 in 2021 and 2022, respectively) and GranAlk (correlation: 0.66 and 0.75 in 2021 and 2022, respectively), indicating that differences in the concentrations of the lakes are mainly determined by the amount of weathering in the catchments. With exception of the samples of the 27th September 2021, that were surprisingly low, the silica concentrations during 2021 and 2022 were slightly higher than during the previous decade. Similar to what observed for the base cations, several mechanisms might explain this phenomena: concentration effects due to evapotranspiration, lack of dilution because of low precipitation, increase of weathering.

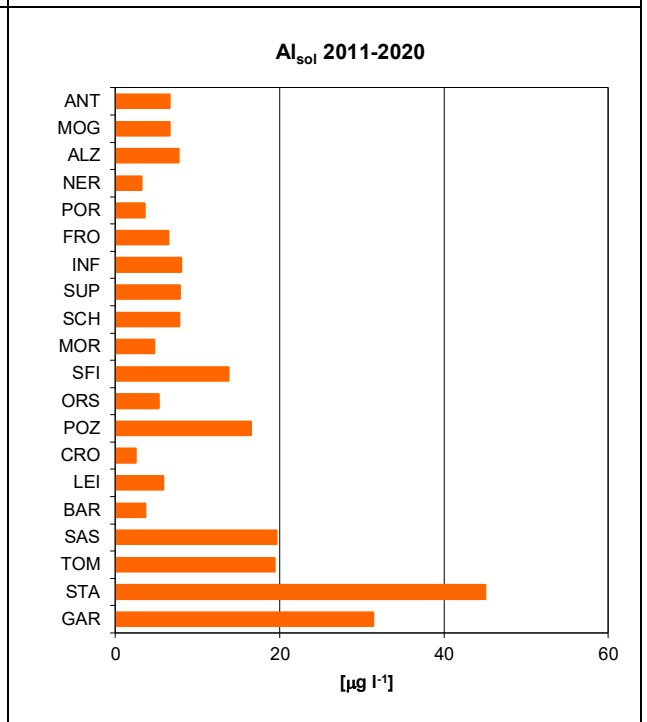
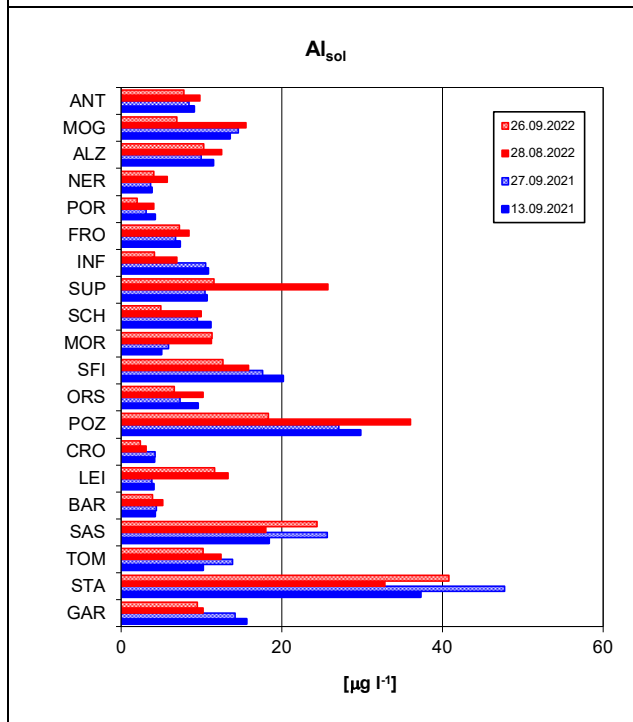
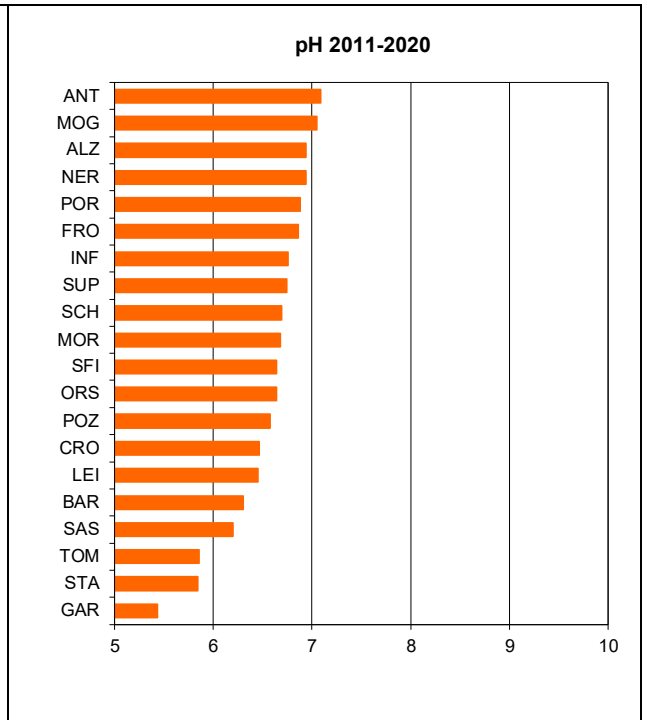
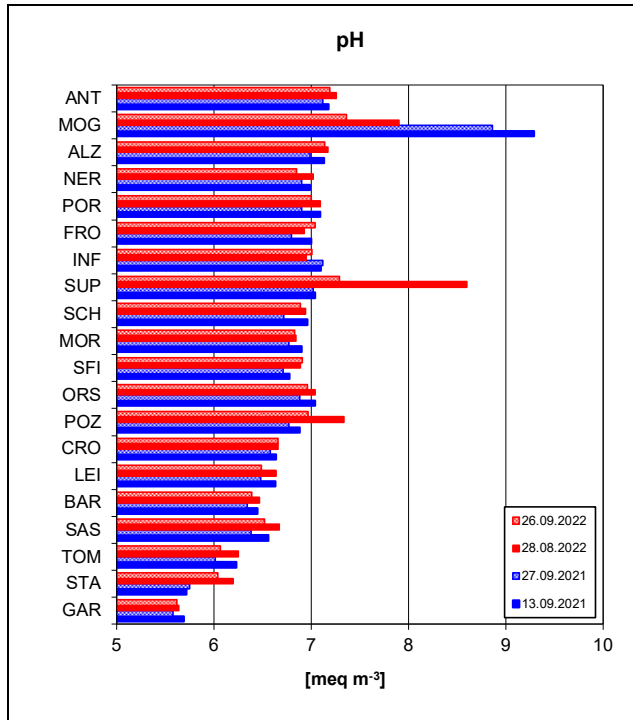
Concentrations of DOC were always low ($< 1.5 \text{ mg C l}^{-1}$). Shallow lakes situated at lower altitudes are generally characterized by slightly higher values of DOC (STA, POZ, SAS, SUP). Concentrations of 2021 were in the same range as those of the previous decade, while the highest concentrations of 2022 (STA, POZ, SAS, SUP, SFI) were significantly higher than the means of 2011-2020. In these lakes concentrations of DOC during 2022 were also significantly higher than those measured during 2021. Similarly, in these lakes the relative difference of pH between 2022 and 2021 was also highest, particularly during the first sampling at the end of August. This suggests that in these lakes because of the exceptional high temperatures at the end of August 2022, the primary production has been particularly high causing high values of pH and high values of DOC as a consequence of decomposition processes of dead material. The same phenomena may have occurred in lake MOG during 2021.

Figure 3.9 Concentrations of the main chemical parameters in 20 Alpine lakes during 2021 and 2022 and their average autumn values between 2011 and 2020.









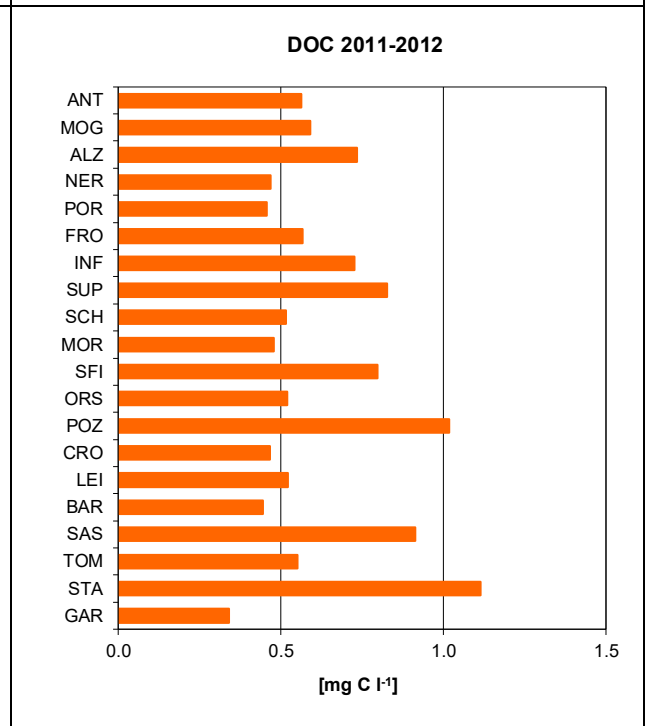
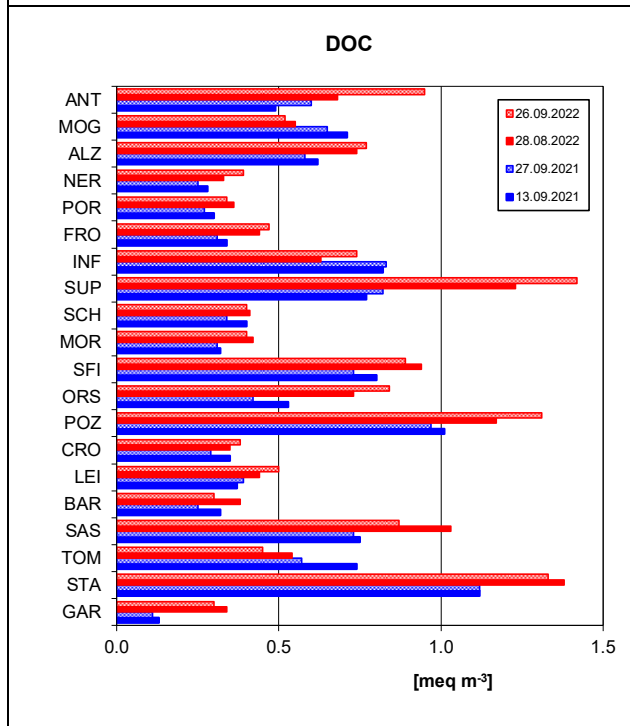
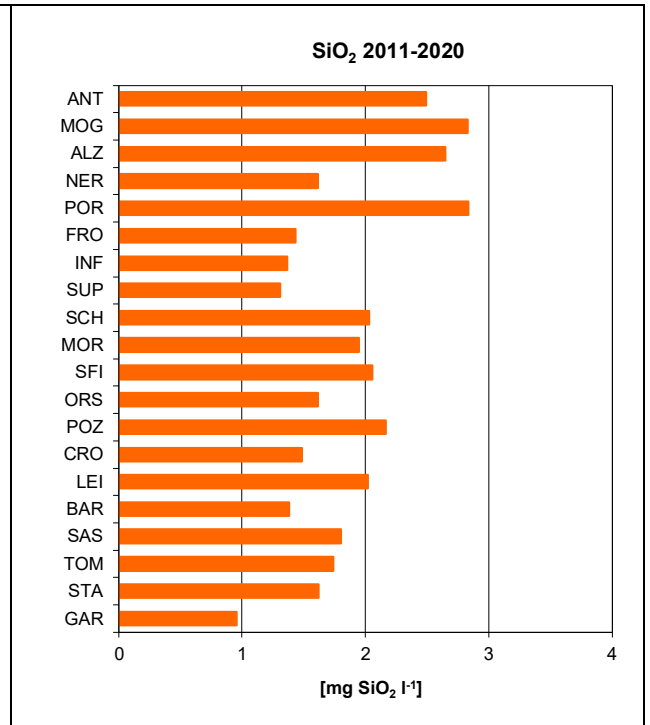
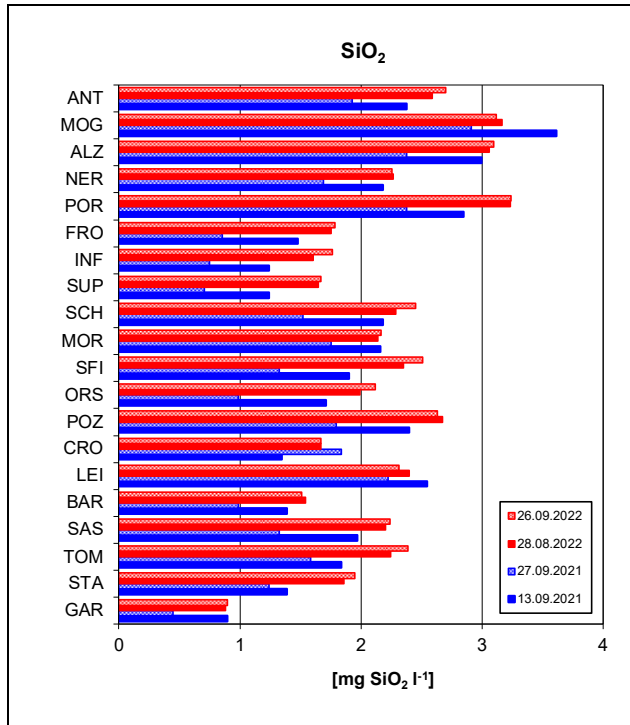
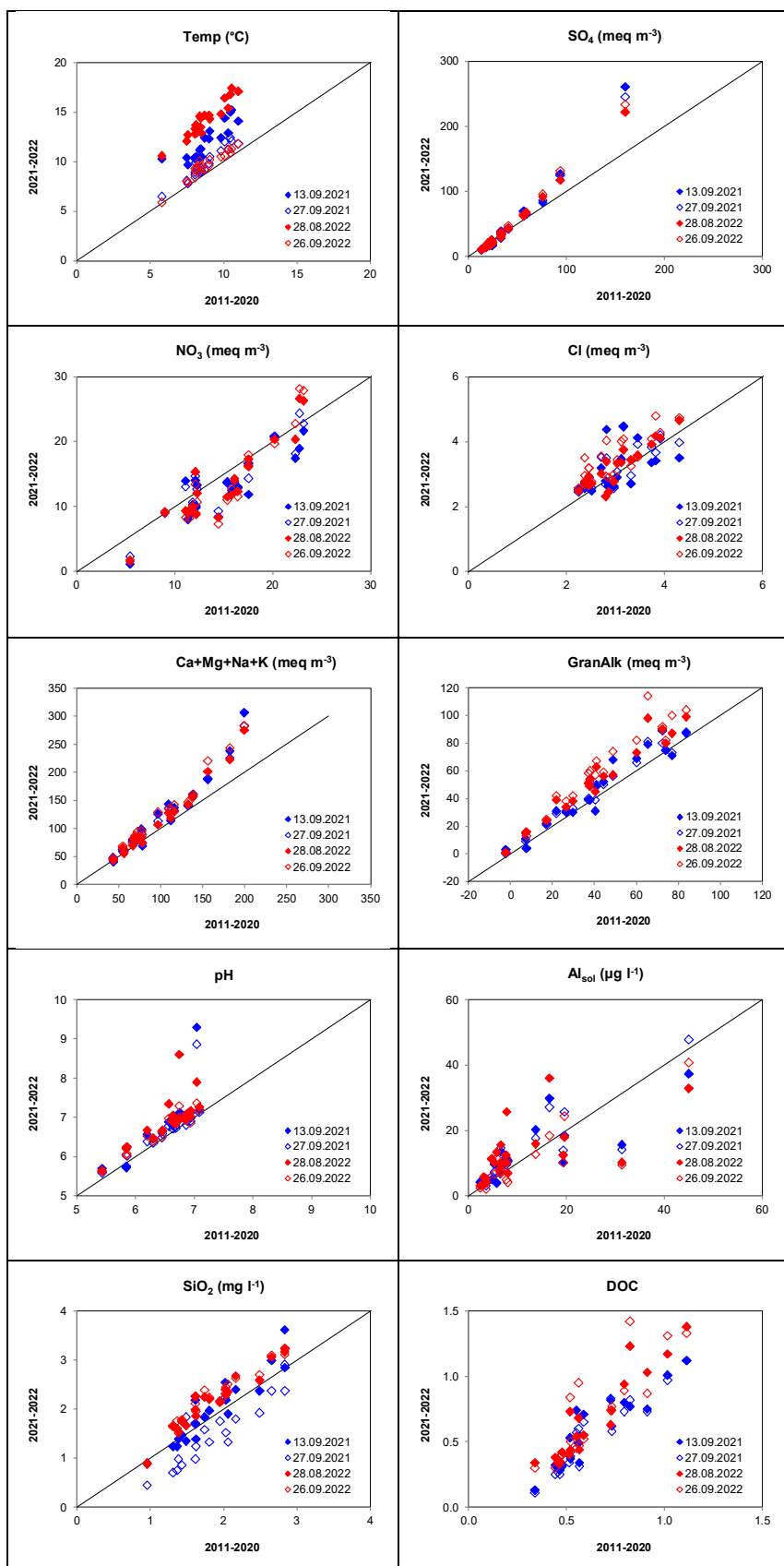


Figure 3.10 Concentrations of the main chemical parameters in 20 Alpine lakes during 2021 and 2022 vs. their average autumn values between 2011 and 2020.



Temporal variations

In order to show temporal variations of lake water quality, autumn median temperature and water concentrations of SO_4 , NO_3 , Cl, the base cations Ca, Mg, Na, K, GranAlkalinity, pH, Al_{sol} , SiO_2 , DOC and their corresponding boxplots are represented in Fig. 3.11. Only years, where all 20 Alpine lakes have been monitored are shown. After the 1980's, median SO_4 concentrations decreased in most lakes. This can be attributed to reduced SO_x emissions and the associated decrease in SO_4 depositions. Concentrations of NO_3 also decreased because of reduced emissions of NO_x . As a consequence of the reduced depositions, concentrations of Cl also decreased in the lakes. The strongest decrease in SO_4 and NO_3 occurred between the 1980's and 2015. The concentrations of the base cations also decreased until about 2015 because of the replenishment of the base cation exchange sites, typically occurring in catchments recovering from acidification. Since the stabilisation of the SO_4 and NO_3 concentrations, the base cations started to increase again. Because of the decrease of especially SO_4 and NO_3 concentrations and more recently the increase in the base cation concentrations. GranAlk and the pH increased. As a consequence, in the three most acidic lakes concentrations of Al_{sol} decreased continuously from 2000 to 2022 (Fig. 3.12). In lake STA the concentrations decreased from 80-100 to 25-70 $\mu\text{g l}^{-1}$, in lake TOM and in lake GAR from around 40 $\mu\text{g l}^{-1}$ to below 15 $\mu\text{g l}^{-1}$.

Results of a detailed trend analysis of the main parameters are presented in Tab. 3.6. Trends were calculated for the entire monitoring period (1980s-2022), from the beginning of monitoring until the stabilisation of the SO_4 and NO_3 concentrations (2015) and from 2015 to 2022. For aluminium, we calculated the trends from 2000 to 2022 only for the most acidic lakes with the highest aluminium concentrations because at the beginning of the aluminium measurements (2000) the detection limit was high (7 $\mu\text{g l}^{-1}$) and the analysis of the lakes with smaller aluminium concentrations therefore less reliable.

Due to the decreasing SO_4 and NO_3 depositions, concentrations of SO_4 decreased significantly in 15 lakes and of NO_3 in all lakes. Concentrations of Cl also decreased significantly in 13 lakes. For SO_4 and Cl the highest decrease occurred between the 1980's and 2015. In fact, the decrease in concentrations was stronger during '80s-15 than during '80s-22. Differently, the trend slopes of NO_3 were similar during '80s-22 and '80s-15, indicating a more homogenous decrease of the concentrations with time. After 2015 the trends were not significant anymore. However, the trend slopes of SO_4 and NO_3 were still negative in 9 and 12 lakes, respectively suggesting a lower, but continuing decrease in many lakes. Similar as observed for depositions. the trend slopes of Cl were positive in 19 lakes (1 significantly), suggesting an increase of the concentrations after 2015, probably as a result of an increase of the storms during winter in the North Atlantic.

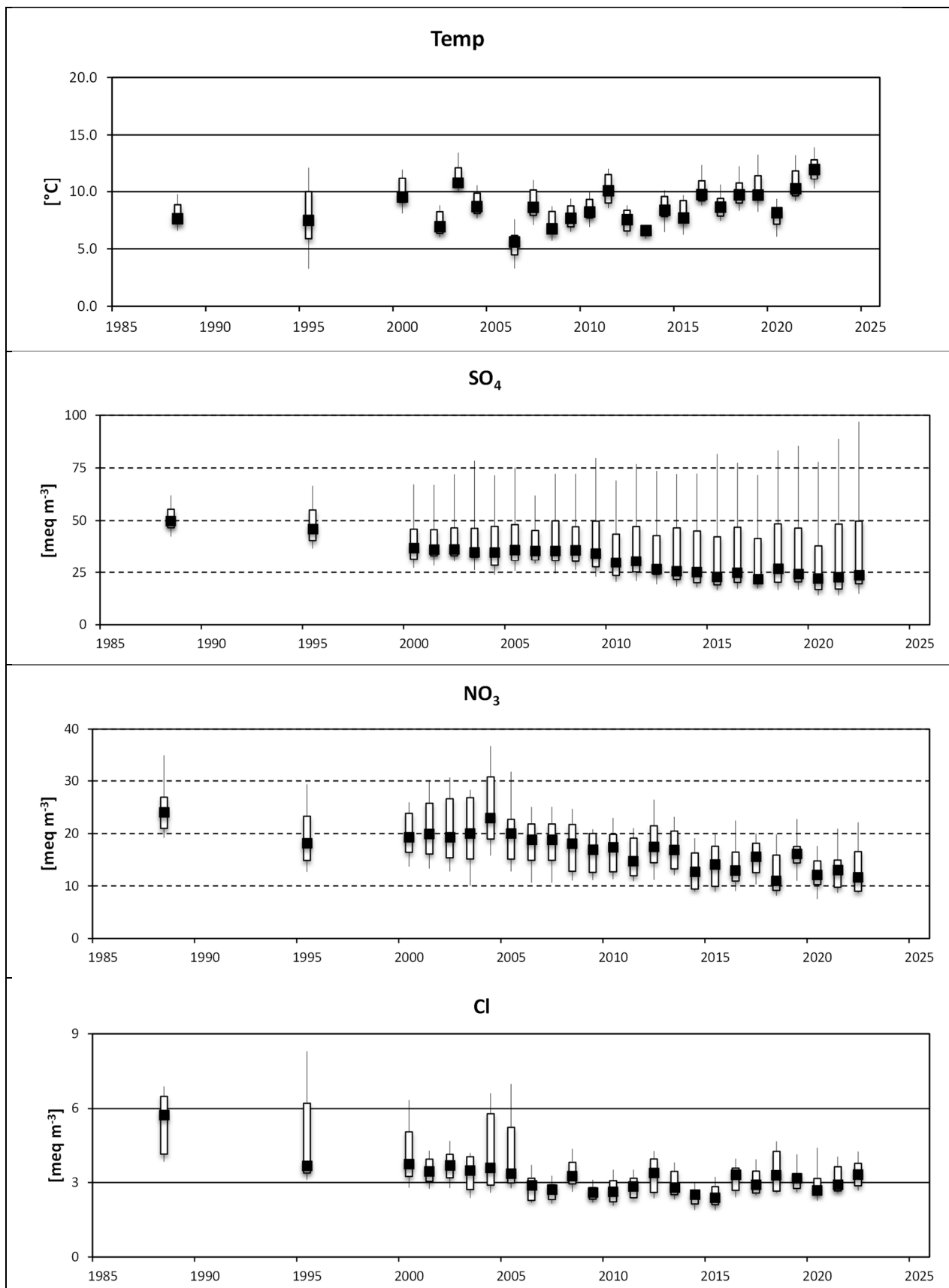
In half of the lakes the concentrations of the base cations decreased significantly. This is a common phenomenon in freshwaters recovering from acidification. The base cation exchange sites in the catchments get replenished, causing a decrease of the base cation concentrations in the lakes. The decrease was stronger during '80s-15 than during '80s-22, because of an increase of the base cations after 2015 (significant increasing trend in 8 lakes and positive trend slopes in 19 lakes. The recent increase of base cations in freshwaters recovering from acidification has been observed at numerous ICP wares sites (ICP waters report in prep.). The reason is not yet clear, but enhanced weathering related to climate change is hypothesized. However, we would then also expect a general increase of the SiO_2 concentrations. During '80s-22 SiO_2 increased significantly in 7 lakes, from which only 4 are

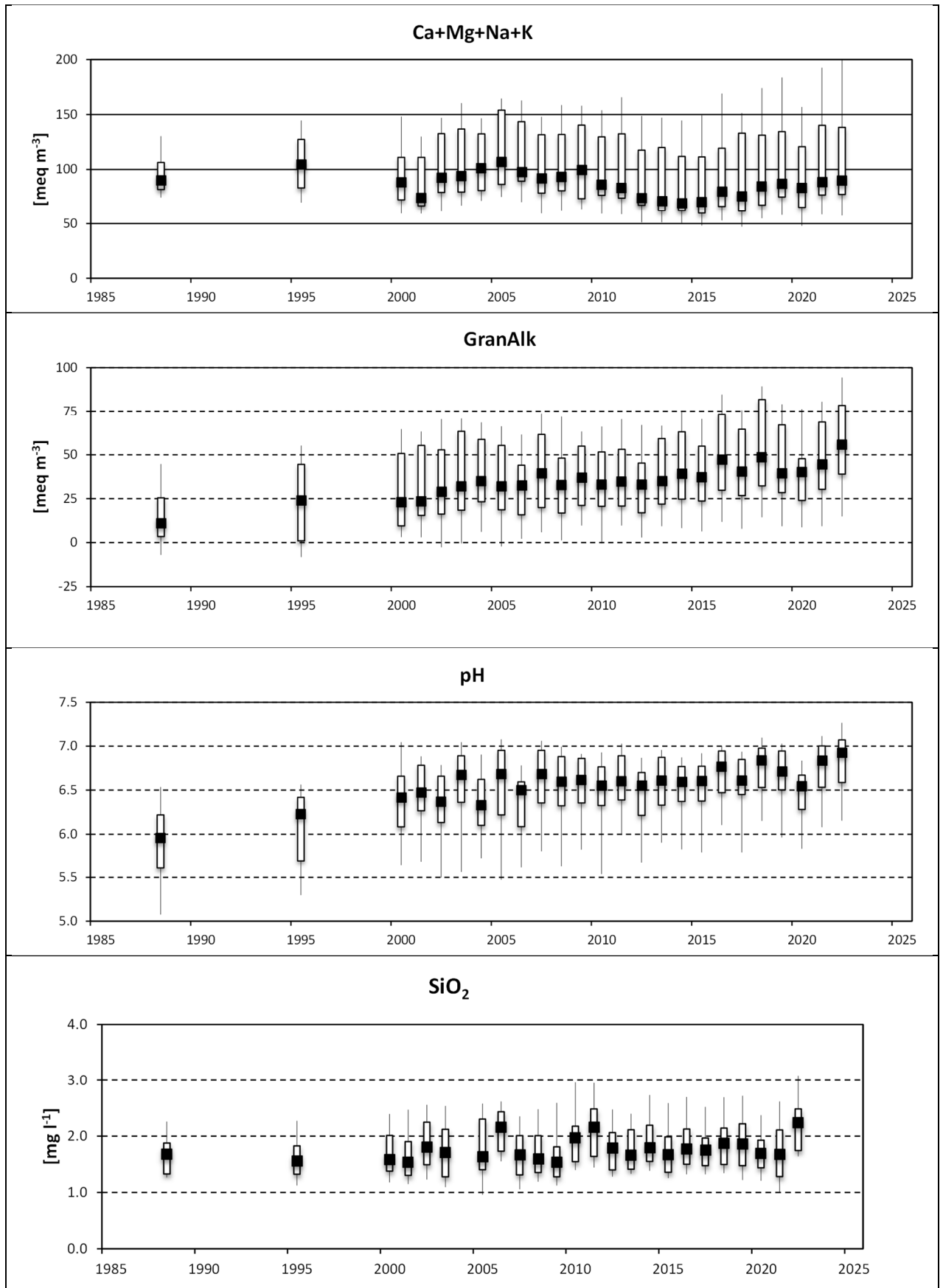
not influenced by melting rock glaciers (discussed below) and the comparison of the trend slopes of '80s-22 and '80s-15 do not suggest a stronger increase after 2015. Interesting is the fact that the base cations started to increase when the concentrations of SO_4 and NO_3 stabilized. It is possible that the increase of the base cations is related to the stabilisation of SO_4 and NO_3 , suggesting that the base cations are now increasing toward a new steady state concentration as predicted by the theory of recovery from acidification (Galloway 1983). An overlap of the recovery process with enhanced weathering is also imaginable.

Differently to most lakes, in five lakes (POR, LEI, MOR, MOG, NER) concentrations of SO_4 increased significantly with higher trend slopes after 2015. In the same lakes, the increase of the base cations has been particularly pronounced, in lakes LEI already from 2000 on and even more after 2015, suggesting a positive relation between the increase of the concentrations of SO_4 and the base cations. Climate change leading to melting of permafrost and rock glaciers (Scapozza and Mari 2010) might be the reason (Thies et al. 2007). Steingruber et al. (2020 and in prep.) hypothesized that the thawing of permafrost in the rock glacier affects the flow path of groundwater enabling its contact with fresh highly weatherable minerals increasing the overall weathering rate and shifting the relative ionic composition in the discharge toward the ions that originate from the most soluble minerals.

The decrease of acidic deposition also caused a significant increase of GranAlk in most lakes (80's-22: 19 lakes). The trend slopes of 80's-22 and 80's-15 were similar indicating a continuous increase during the monitoring period. Also after 2015 GranAlk increased significantly in 4 lakes and the trend slopes were positive in 19 lakes. The increase of GranAlk after 2015, when concentrations of SO_4 and NO_3 stabilized is related to the increase of the base cation concentrations. The fact that in the lakes strongly impacted by cryospheric features (POR, LEI, MOR, MOG, NER) GranAlk also continued to increase, indicates that the release of SO_4 in these catchments is largely neutralized by the simultaneous release of base cations.

Figure 3.11 Temporal variations of the main parameters measured in 20 Alpine lakes from 1988 to 2022. Boxplots show the median and the 10th, 25th, 75th, 90th percentiles of autumn mean values.





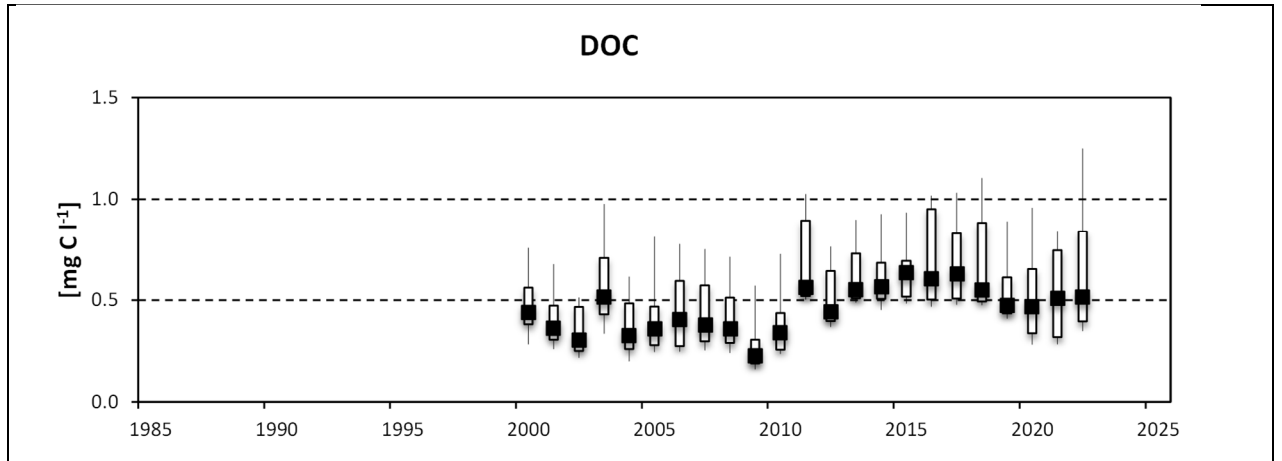


Figure 3.12 Temporal variations of dissolved aluminum from 1988 to 2022 in the three most acidic lakes (mean autumn values).

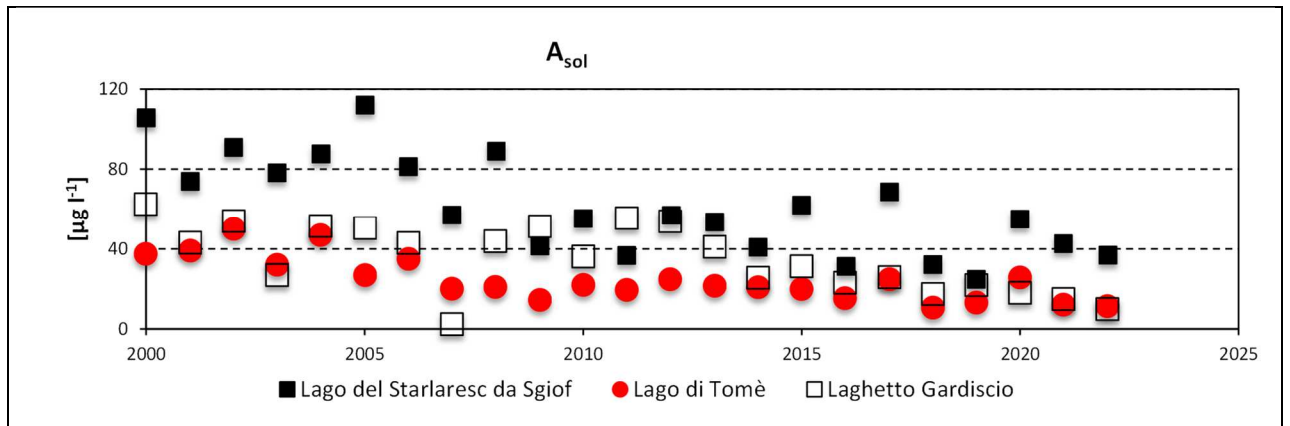


Table 3.6 Changes in lake water concentrations during the indicated time periods. Red values indicate significant trends. All changes are expressed in mg l^{-1} with exceptions of SiO_2 and Al_{dis} that are expressed in $\text{mg l}^{-1} \text{ yr}^{-1}$ and $\mu\text{g l}^{-1}$, respectively.

Lake	SO_4			NO_3			Cl			Ca+Mg+Na+K			GranAlk			H			SiO_2			Al_{dis}	
	80-22	80-15	15-22	80-22	80-15	15-22	80-22	80-15	15-22	80-22	80-15	15-22	80-22	80-15	15-22	80-22	80-15	15-22	88-22	80-15	15-22	00-22	15-22
STA	-1.14	-1.33	-0.35	-0.57	-0.47	-0.82	-0.07	-0.11	-0.02	-0.99	-1.11	-0.13	0.85	0.85	0.73	-0.325	-0.471	-0.007	0.010	0.010	0.035	-2.67	-2.71
TOM	-0.80	-0.91	0.10	-0.44	-0.44	0.35	-0.03	-0.06	0.11	-0.89	-1.23	1.88	0.44	0.38	0.73	-0.076	-0.067	-0.144	-0.001	0.000	0.058	-1.23	-0.69
POR	1.10	0.38	3.32	-0.44	-0.44	-0.39	-0.02	-0.05	0.01	1.15	-0.24	7.84	1.01	0.57	2.00	-0.001	-0.005	0.027	0.008	0.020	0.022		-0.01
BAR	-0.36	-0.44	0.57	-0.37	-0.25	-0.22	-0.05	-0.07	-0.01	-0.32	-0.50	1.78	0.64	0.55	0.95	-0.034	-0.039	-0.023	0.002	0.008	-0.013		0.26
GAR	-0.22	-0.23	0.02	-0.31	-0.20	-0.42	-0.04	-0.06	-0.02	-0.35	-0.31	0.22	0.30	0.26	0.25	-0.163	-0.104	-0.335	0.001	0.008	-0.005	-2.04	-2.70
LEI	4.50	2.61	10.87	-0.24	-0.26	-0.14	-0.03	-0.05	-0.06	4.41	2.64	12.15	0.50	0.47	0.71	-0.005	-0.009	0.014	0.020	0.019	0.056		0.24
MOR	0.48	0.31	1.08	-0.16	-0.16	0.00	-0.02	-0.06	0.06	0.88	0.62	5.11	0.87	0.73	1.50	-0.003	-0.004	0.026	0.017	0.017	0.040		0.45
MOG	0.49	0.39	2.10	-0.30	-0.16	-0.97	-0.02	-0.04	0.08	0.55	0.35	8.02	0.45	-0.14	3.63	0.000	-0.000	0.068	0.009	0.017	0.036		0.90
INF	-0.80	-0.97	0.18	-0.42	-0.43	0.11	-0.04	-0.09	0.09	-0.79	-1.09	2.72	0.67	0.48	1.80	-0.006	-0.008	0.037	0.000	0.003	0.028		0.02
SUP	-0.76	-0.86	0.03	-0.41	-0.37	0.14	-0.04	-0.07	0.07	-0.30	-0.30	2.14	0.92	0.88	0.90	-0.010	-0.014	0.080	0.007	0.012	-0.002		0.37
NER	0.14	0.03	1.05	-0.11	-0.11	0.12	-0.04	-0.06	0.07	0.48	0.26	4.13	0.73	0.65	0.29	-0.001	-0.003	0.021	0.017	-0.014	0.080		0.33
FRO	-0.29	-0.32	0.67	-0.18	-0.27	0.20	-0.01	-0.04	0.09	0.43	0.11	2.52	0.93	0.65	1.38	-0.004	-0.006	0.040	0.003	0.004	0.034		0.30
ANT	-0.65	-0.76	-0.43	-0.32	-0.29	-0.10	-0.04	-0.10	0.09	-0.10	-0.19	1.76	0.79	0.57	-0.67	-0.003	-0.003	0.029	0.011	0.013	-0.026		0.16
CRO	-0.76	-0.85	-0.27	-0.22	-0.16	-0.15	-0.04	-0.07	0.11	-0.37	-0.61	1.20	0.82	0.67	0.94	-0.016	-0.025	-0.001	0.007	0.005	0.023		0.19
ORS	-0.79	-0.96	-0.15	-0.31	-0.25	-0.45	-0.03	-0.10	0.09	0.06	-0.40	3.06	1.24	1.00	2.13	-0.022	-0.042	0.037	0.008	0.012	-0.014		0.39
SCH	-0.96	-1.14	-0.20	-0.21	-0.26	0.27	-0.04	-0.07	0.20	-0.82	-1.44	2.39	0.65	0.48	3.06	-0.004	-0.007	0.031	0.004	0.003	0.016		0.10
POZ	-0.91	-1.12	-0.06	-0.21	-0.10	-0.45	-0.04	-0.09	0.16	-0.53	-0.86	3.04	0.50	0.33	3.00	-0.002	-0.004	0.114	0.012	0.015	0.060		1.61
SFI	-0.91	-0.97	-0.60	-0.22	-0.23	-0.41	-0.04	-0.08	0.08	-0.65	-0.73	0.97	0.68	0.66	0.00	-0.007	-0.010	0.089	0.010	0.016	-0.019		0.51
SAS	-0.96	-1.01	-0.04	-0.32	-0.24	0.62	-0.07	-0.13	0.00	-0.92	-1.24	2.95	0.54	0.38	1.85	-0.012	-0.015	0.056	0.004	0.010	0.027		2.04
ALZ	-0.95	-0.96	-0.29	-0.11	-0.06	-0.67	-0.06	-0.09	0.16	-0.27	-0.27	3.59	0.92	0.90	1.50	-0.002	-0.003	0.038	0.019	0.020	0.044		0.70

3.5.3 Alpine rivers

Introduction

Sampling occurred in river MAG and VED until 2021 and in river VER, the most acid sensitive, until 2022. River water was sampled in 2021 and 2022 during the following days: 18.1.21, 9.2.21, 2.3.21, 29.3.21, 11.5.21, 14.6.21, 13.7.21, 9.8.21, 7.9.21, 11.10.21, 16.11.21, 13.12.21, 18.1.22, 15.2.22, 15.3.22, 12.4.22, 10.5.22, 7.6.22, 12.7.22, 9.8.22, 13.9.22, 11.10.22, 15.11.22, 13.12.22.

Spatial variations

Annual mean concentrations of the chemical parameters measured in river MAG, VED and VER during 2021 and 2022 are shown in Tab. 3.7. Cond, GranAlk, concentrations of Ca, and SO₄ were highest in river MAG, followed by VED and VER. As discussed in Steingruber and Colombo (2006), differences in catchment areas and geology are the main cause for differences in concentrations among rivers. In fact, the catchment area of river MAG is 7 and 10 times larger than the watersheds of river VER and VED, respectively, implying a longer average water residence time and higher average weathering. Differences in water chemistry of rivers VED and VER are more related to their different catchment geology. Similarly to the catchment of river MAG, the watersheds of river VED and VER are very poor in carbonate containing rocks. But while the catchment of river VER is characterized by the presence of relatively young rocks that were formed during the orogenesis of the Alps (60 millions years ago), the geology of the catchment of river VED is much older (300 millions to 2.5 milliards years). Therefore much more weathered and fractured, increasing the surface that can interact with water from precipitations. Interestingly, highest concentrations of nitrate were measured in river VED followed by river VER and MAG. This is mainly due to the different N input concentrations, as the N retention capacities did not vary greatly among the catchments. In fact, from 2018-2022, the average total evaporation corrected N concentrations in the rainwater falling on the watershed of river VED, VER and MAG were 109, 61 and 55 meq m⁻³, respectively and the N retention during the same time period was 28% in river VER, 25% in river VED and 23% in river MAG (Steingruber 2023).

During 2021 average GranAlk was 296 meq m⁻³ in river MAG, 174 meq m⁻³ in river VED and 73 meq m⁻³ in river VER. Based on these data river VER and river VED have low alkalinities (50-200 meq m⁻³), but no river is sensitive to acidification. The same is suggested by their minimum GranAlk that were always > 0 meq m⁻³. The average pH during 2021 was 7.4 river MAG, 7.1 in river VED and 6.8 in river VER. Their minimum pH's were not much lower (MAG: 6.8, VED: 7.0, VER: 6.6). The analysed metals were all below the critical concentrations.

Table 3.7 Average concentrations in river water during 2021 and 2022. Values based on at least one sample below the quantification limit were preceded with <

Parameter	Year	MAG	VED	VER
Temp (°C)	2021	8	7	8
	2022			8
Cond 25°C (µS cm ⁻¹)	2021	57	45	22
	2022			26
pH	2021	7.4	7.1	6.8
	2022			6.9
GranAlk (meq m ⁻³)	2021	296	174	73
	2022			87
Ca (meq m ⁻³)	2021	352	224	125
	2022			142
Mg (meq m ⁻³)	2021	52	77	18
	2022			21
Na (meq m ⁻³)	2021	70	84	30
	2022			35
K (meq m ⁻³)	2021	36	15	14
	2022			17
NH ₄ (meq m ⁻³)	2021	0.6	0.4	0.4
	2022			0.7
SO ₄ (meq m ⁻³)	2021	166	115	64
	2022			78
NO ₃ (meq m ⁻³)	2021	31	68	40
	2022			44
NO ₂ (µg NI ⁻¹)	2021	0.5	0.6	0.3
	2022			0.4
Cl (meq m ⁻³)	2021	33	41	5
	2022			9
SRP (µg P l ⁻¹)	2021	2.9	2.8	2.3
	2022			2.0
N _{tot} (mg N l ⁻¹)	2021	0.6	1.0	0.7
	2022			0.7
DOC (mg C l ⁻¹)	2021	0.8	0.6	0.6
	2022			0.3
SiO ₂ (mg l ⁻¹)	2021	5.2	7.5	4.2
	2022			4.5

Parameter	Year	MAG	VED	VER
Al _{sol} (µg l ⁻¹)	2021	17.2	10.9	15.3
	2022			5.1
Al _{tot} (µg l ⁻¹)	2021	40.1	17.5	27.1
	2022			7.5
Pb _{sol} (µg l ⁻¹)	2021	<0.1	<0.1	<0.1
	2022			<0.1
Pb _{tot} (µg l ⁻¹)	2021	<0.1	<0.2	<0.1
	2022			<0.1
Cd _{sol} (µg l ⁻¹)	2021	<0.1	<0.1	<0.1
	2022			<0.1
Cd _{tot} (µg l ⁻¹)	2021	<0.1	<0.1	<0.1
	2022			<0.1
Cu _{sol} (µg l ⁻¹)	2021	0.4	0.6	0.3
	2022			0.2
Cu _{tot} (µg l ⁻¹)	2021	0.5	0.6	0.4
	2022			0.2
Zn _{sol} (µg l ⁻¹)	2021	0.9	1.6	0.8
	2022			0.4
Zn _{tot} (µg l ⁻¹)	2021	0.6	2.0	1.1
	2022			0.5
Cr _{sol} (µg l ⁻¹)	2021	<0.1	<0.1	<0.1
	2022			<0.1
Cr _{tot} (µg l ⁻¹)	2021	<0.1	<0.1	<0.1
	2022			<0.1
Ni _{sol} (µg l ⁻¹)	2021	0.2	1.0	<0.1
	2022			0.1
Ni _{tot} (µg l ⁻¹)	2021	0.2	1.0	<0.2
	2022			0.1
Fe _{sol} (µg l ⁻¹)	2021	<3	2.3	<2.0
	2022			<1.0
Fe _{tot} (µg l ⁻¹)	2021	<25	8.1	<14.2
	2022			<3.5

Seasonal variations

Fig. 3.13 shows the daily mean discharges of the rivers MAG, VED and VER during 2021 and 2022 and the average values during 2011-2020. Discharges are usually low during winter, highest in spring because of frequent precipitation and snow melt, average during summer and higher again in autumn. Compared to the daily median values of the previous decade, the discharges during 2021 were in the same range of order and those of 2022 mostly lower because of the low precipitations.

The temperature and the concentrations of the main chemical parameters in river water during the sampling days in 2021 and 2022 and their average values during 2011-2020 are shown in Fig. 3.14.

During 2011-2020 the seasonality was characterized by concentrations of SO_4 , $\text{Ca}+\text{Mg}+\text{Na}+\text{K}$, chloride, Gran alkalinity, SiO_2 and pH that are normally lower during spring/summer when river discharge is higher and more elevated during the rest of the year. Because water quality of surface waters and rain differ greatly, Steingruber and Colombo (2006) suggested that a dilution of SO_4 , $\text{Ca}+\text{Mg}+\text{Na}+\text{K}$, Cl and a combination of dilution and consumption of alkalinity occurs during rain events and/or snowmelt. River pH decreases during rain events because of the rain acidity. Concentrations of NO_3 are higher in winter compared to summer and can increase during high flow events. More than one factor are responsible for this variations in concentrations e.g. higher values during winter because of lower discharge (less dilution), lower retention (uptake by vegetation and algae, denitrification) and occasionally higher values during precipitation events or snowmelt because of leakage from soils. Concentrations of aluminum are higher in spring and autumn when discharge is higher, suggesting leakage from soils, probably enhanced by lower pH values during these occasions. The high winter Cl concentrations in river VED and MAG are caused by the use of road salt. Concentrations of DOC are lowest during the cold month when the biological activity is low therefore also the mineralisation of organic matter is lowest.

The concentrations of the main chemical parameters during 2021 and 2022 were in general in the same range as the means of 2011-2020. Only in river MAG during May and July 2021, when monitoring occurred during a rain event, the concentrations of SO_4 , Cl, $\text{Ca}+\text{Mg}+\text{Na}+\text{K}$, GranAlk and SiO_2 were lower than average, because of the dilution with rainwater. At the same time in river MAG the pH was lower because of the rainwater acidity and the concentrations of aluminum and DOC were higher as consequence of soil leaching.

Figure 3.13 Daily mean discharge during 2021 and 2022 (red) and daily median discharge (green) during 2011-2020 of the rivers MAG, VED and VER and the precipitation volumes close to the sampling sites. The vertical line correspond to the sampling dates.

The discharge of the river VED at Isonne and the precipitation at Isonne were measured by the Canton of Ticino (UCA 2001-2023). The discharge of the river VER at Sonogno was estimated by the discharge measured at Lavertezzo by the BWG (2001-2004) and by the FOEN (2005-2023) and the precipitation at Sonogno by the Canton of Ticino (UCA 2001-2023). The discharge of the river MAG was measured at Brontallo by Ofima and the precipitation at Caveragno by the Canton of Ticino (UCA 2001-2023).

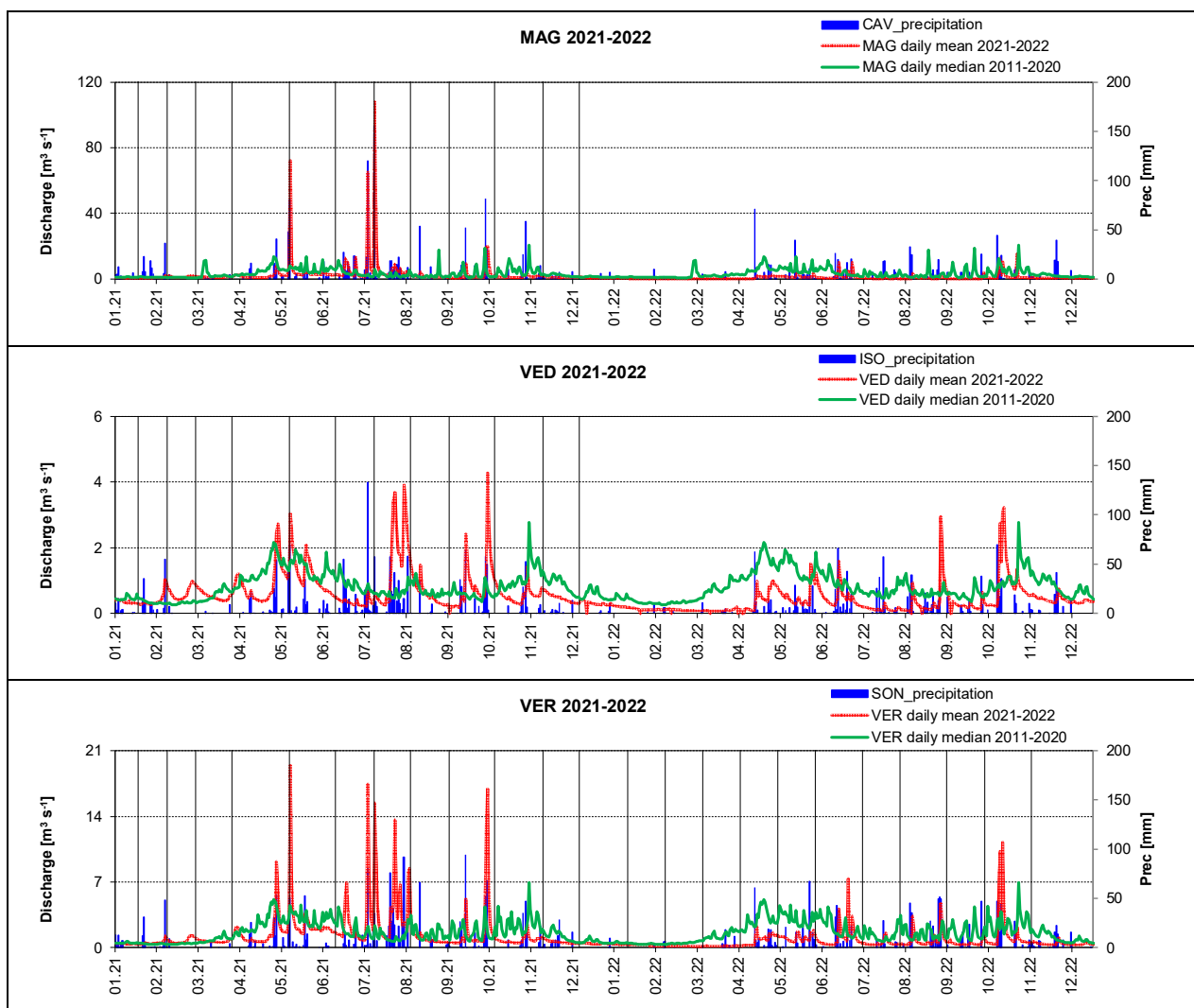
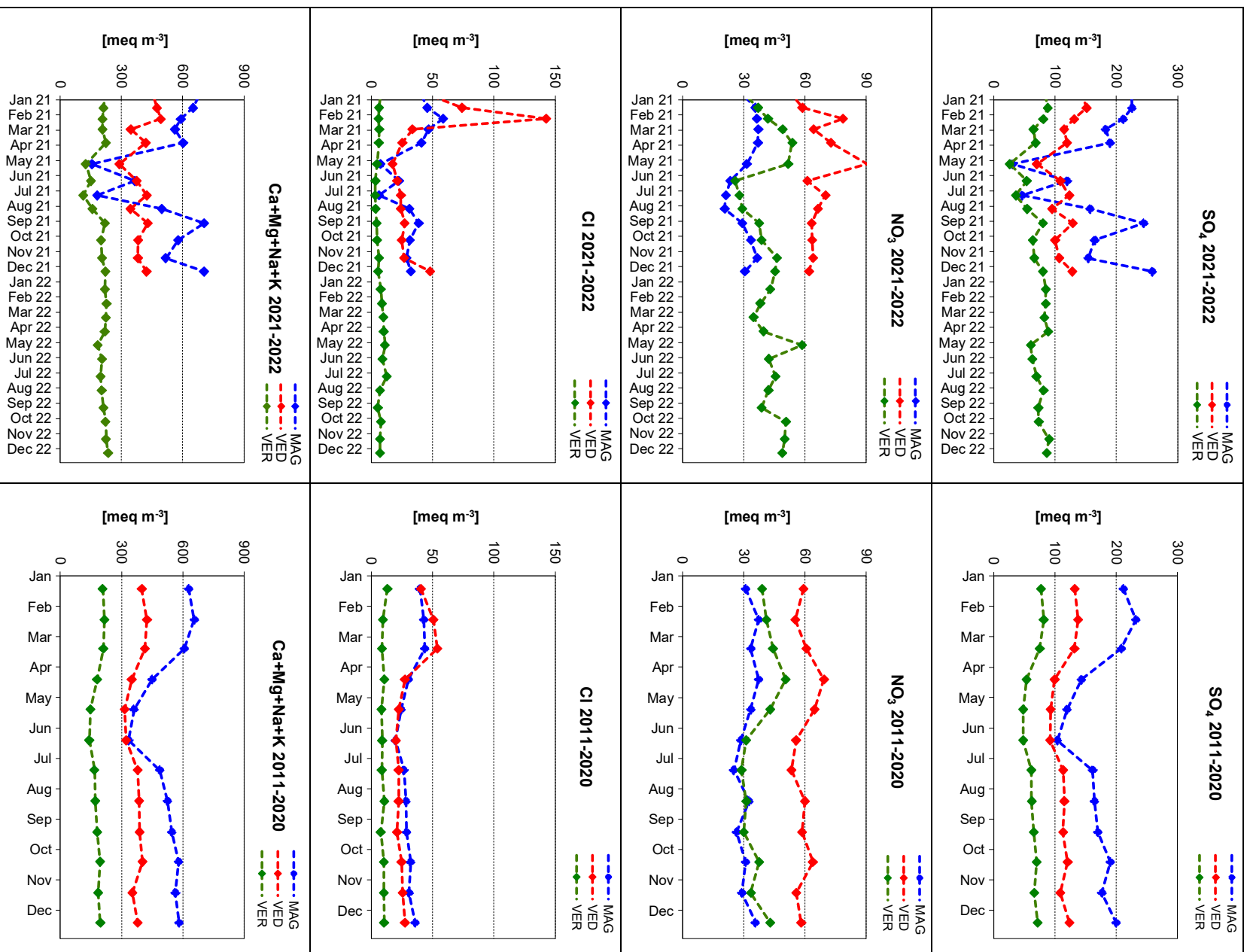
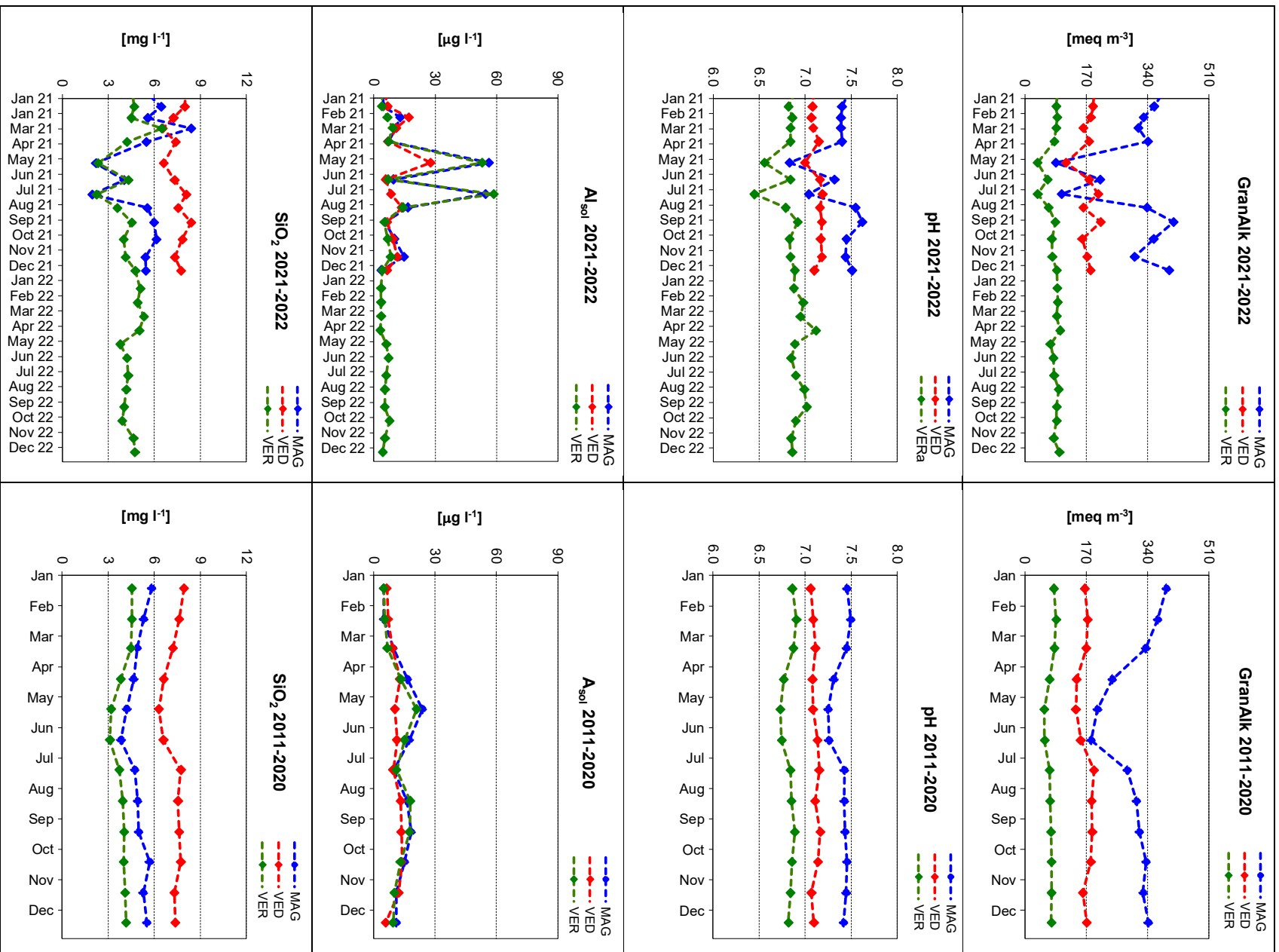
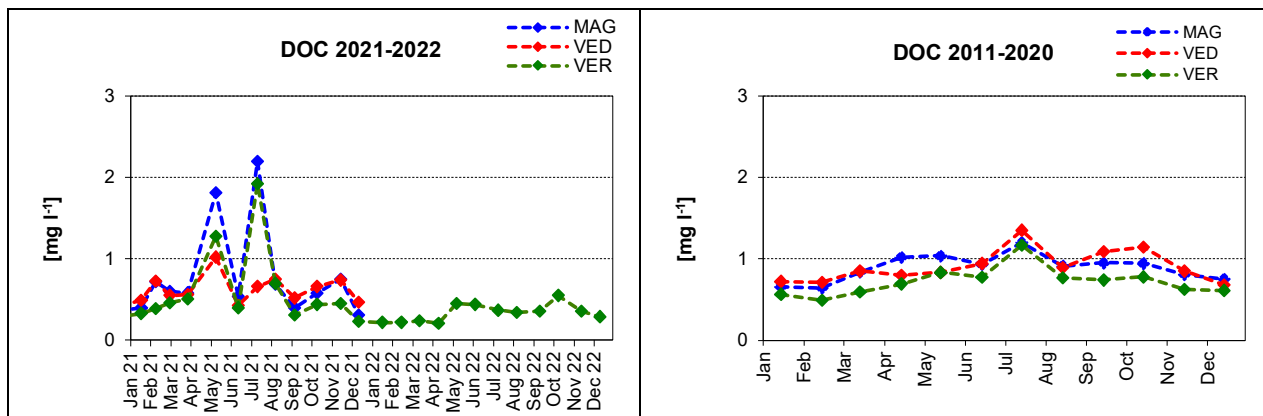


Figure 3.14 Concentrations of the main chemical parameters in river water during the sampling days in 2021 and 2022 and their average values during 2011-2020.







Temporal variations

The temporal variations of the monthly average discharges from 2000 to 2022 are presented in Fig. 3.15 and of the temperature and the concentrations of the chemical parameters in Fig. 3.16.

Similar to what observed for chemistry, also in rivers, concentrations of SO₄ and during the last few years also of NO₃ decreased. However, as observed for the seasonal variations of the river chemistry, concentrations are very much related to the river discharge and temporal trends in the river chemistry is difficult to detect at a glance. We therefore performed a seasonal Mann-Kendall test for the entire monitoring period (MAG and VED: 2000-2021, VER: 2000-2022). Results of the trend analysis are shown in Tab. 3.8. Over the entire monitoring period, concentrations of SO₄ and NO₃ decreased significantly in all three rivers. GranAlk increased significantly in river VED and VER and almost in river MAG (p=0.06) and concentrations of the hydrogen ions decreased significantly only in river VED.

Figure 3.15 Monthly mean discharge in river water from 2000 to 2022.

The discharge of river VED at Isonne was measured by the Canton of Ticino (UCA 2001-2023), the discharge of river VER at Sonogno was estimated by discharge values measured at Lavertezzo by BWG (2001-2004) and by FOEN (2005-2023), the discharge of river MAG at Brontallo was estimated from values measured at Brontallo by Ofima.

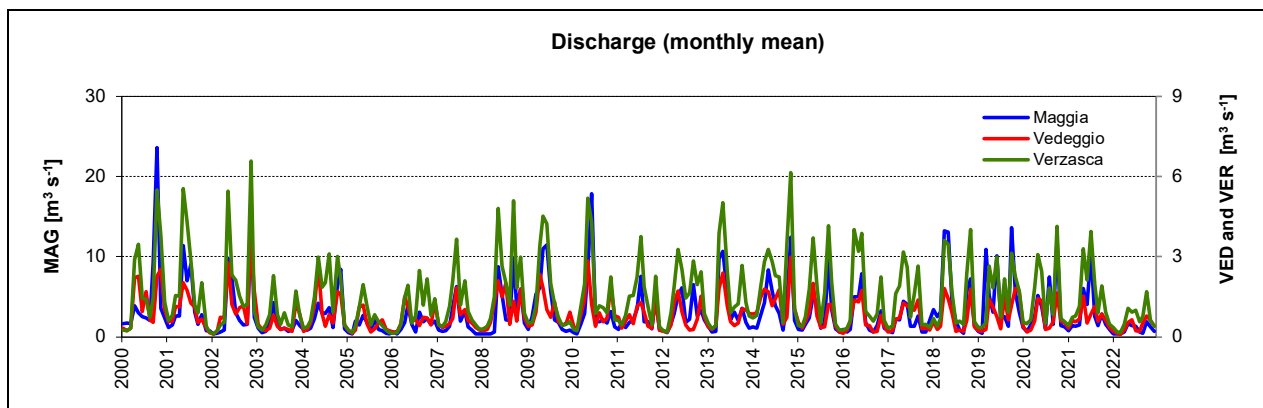
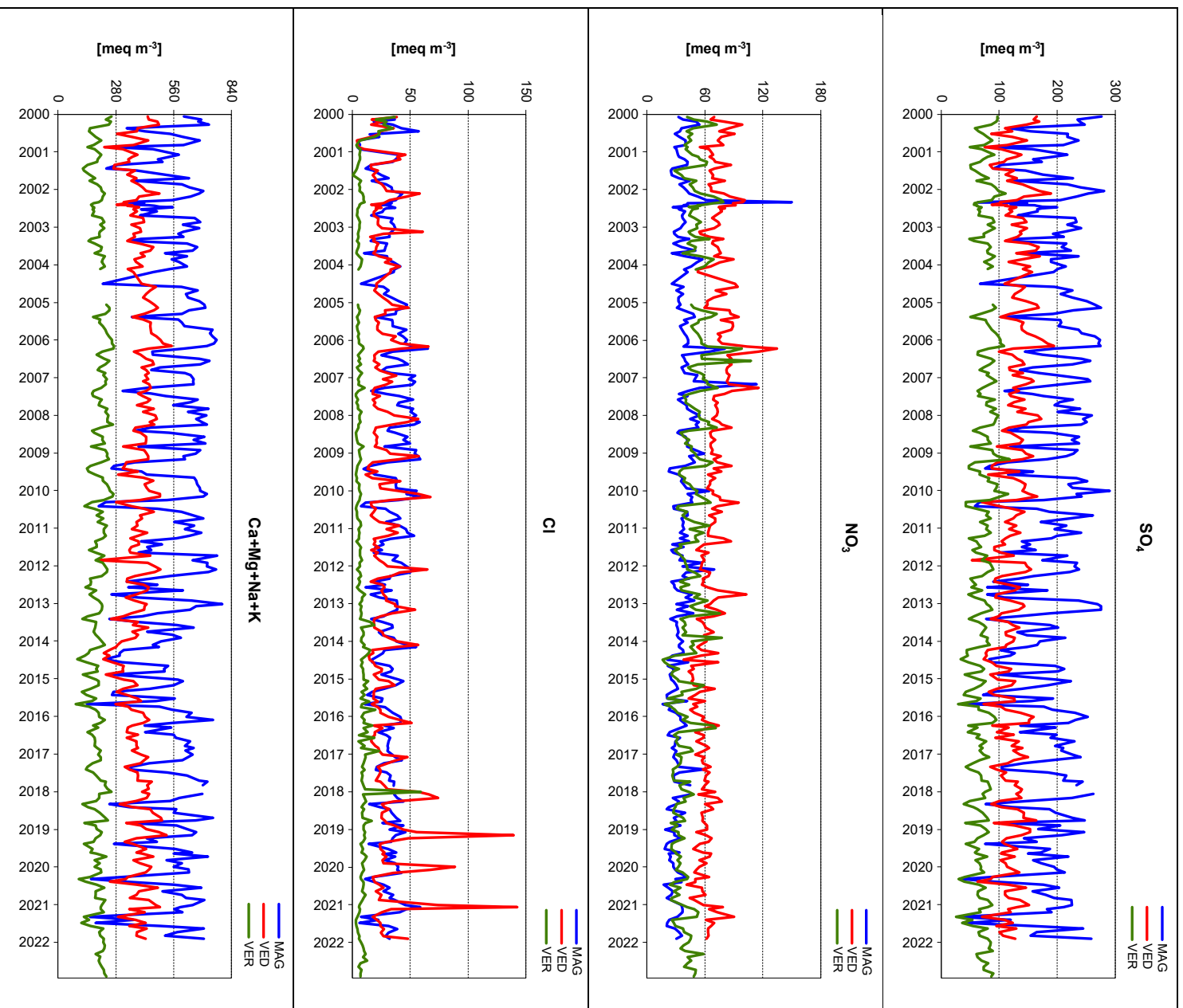
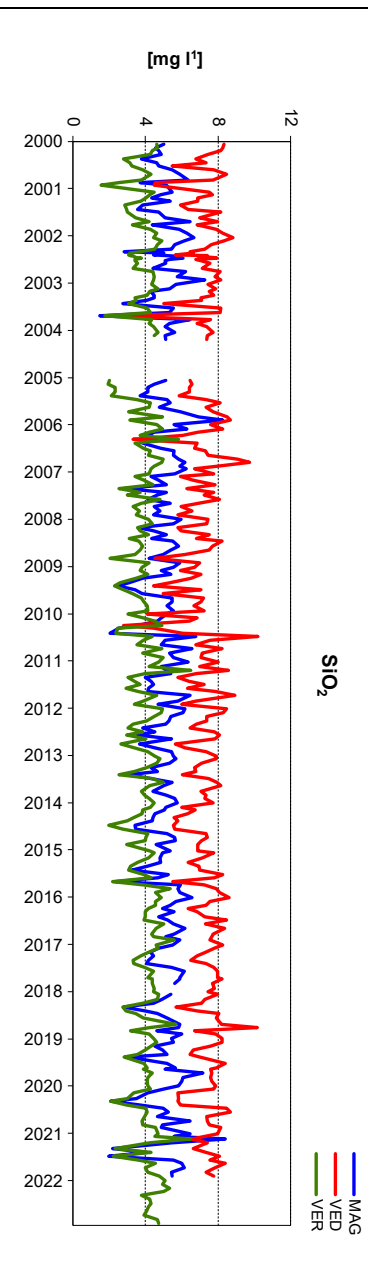
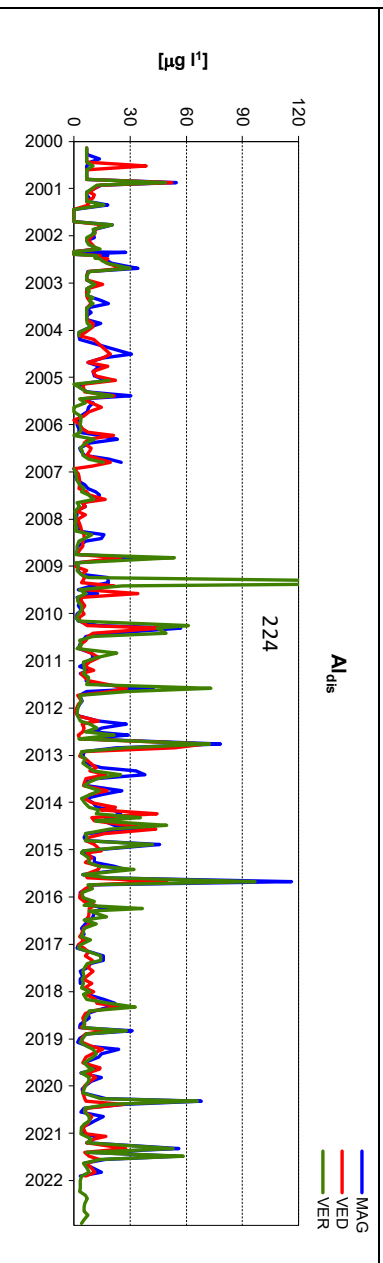
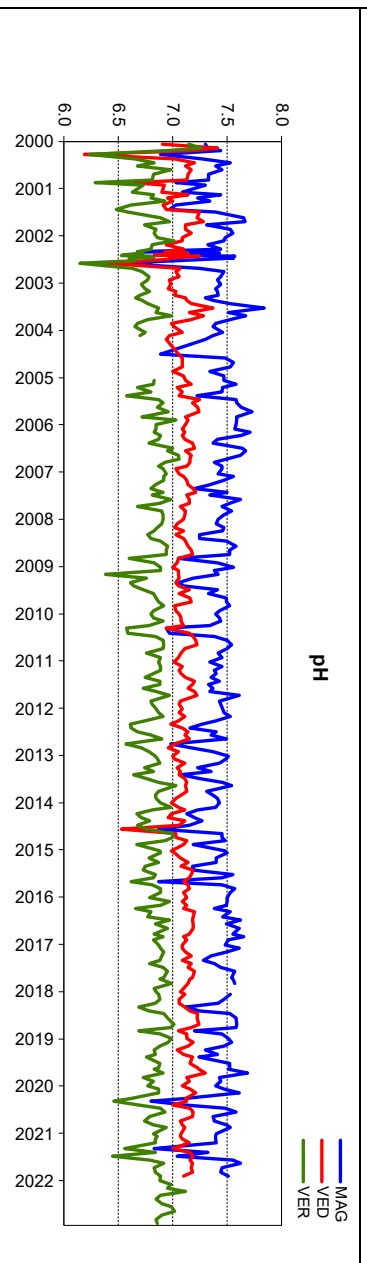
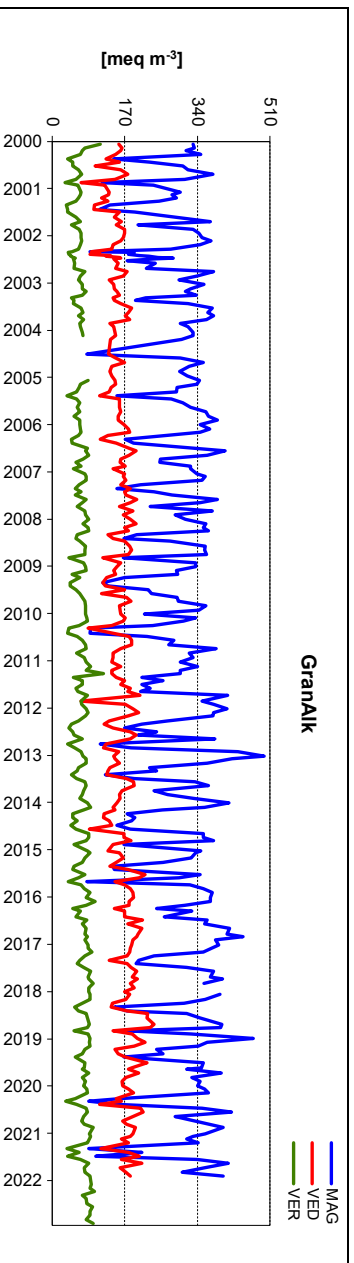


Figure 3.16 Concentrations of the main chemical parameters in river water from 2000 to 2022





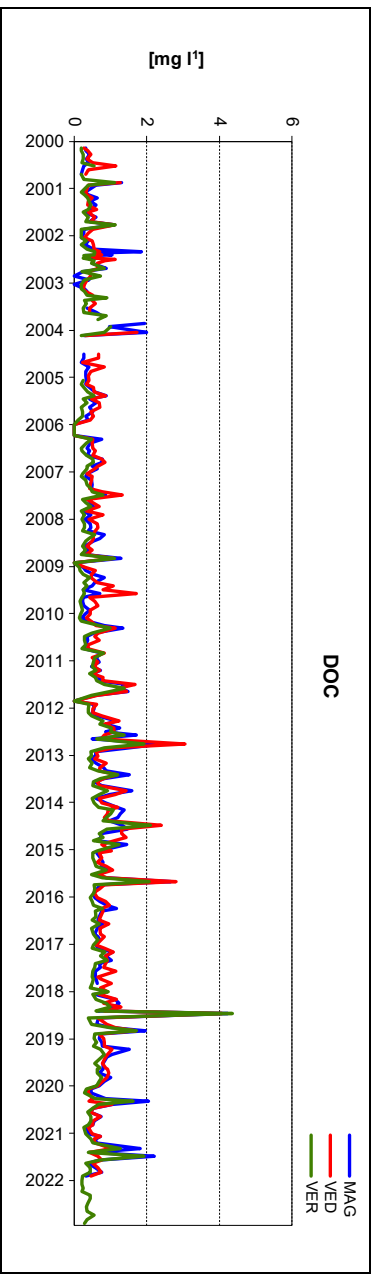


Table 3.8 Changes in river water concentrations during 2000-2021 for MAG and VED and during 2000-2021 for VER calculated with the Sens's slope. Red values indicate significant trends. All slopes are expressed in $\text{meq m}^{-3} \text{ yr}^{-1}$ with exception of SiO_2 that is expressed in $\text{mg l}^{-1} \text{ yr}^{-1}$ and Al_{sol} that is expressed in $\mu\text{g l}^{-1} \text{ yr}^{-1}$.

River	Period	SO ₄	NO ₃	Cl	Ca+Mg+K+Na	GranAlk	H ⁺	SiO ₂	DOC
MAG	2000-2021	-1.50	-0.63	0.00	-2.01	1.53	-1.4E-4	0.00	0.02
VED	2000-2021	-1.04	-1.03	0.24	-0.41	1.76	-5.0E-4	0.01	0.02
VER	2000-2022	-0.70	-0.89	0.19	-0.71	1.00	-1.0E-3	0.01	0.01

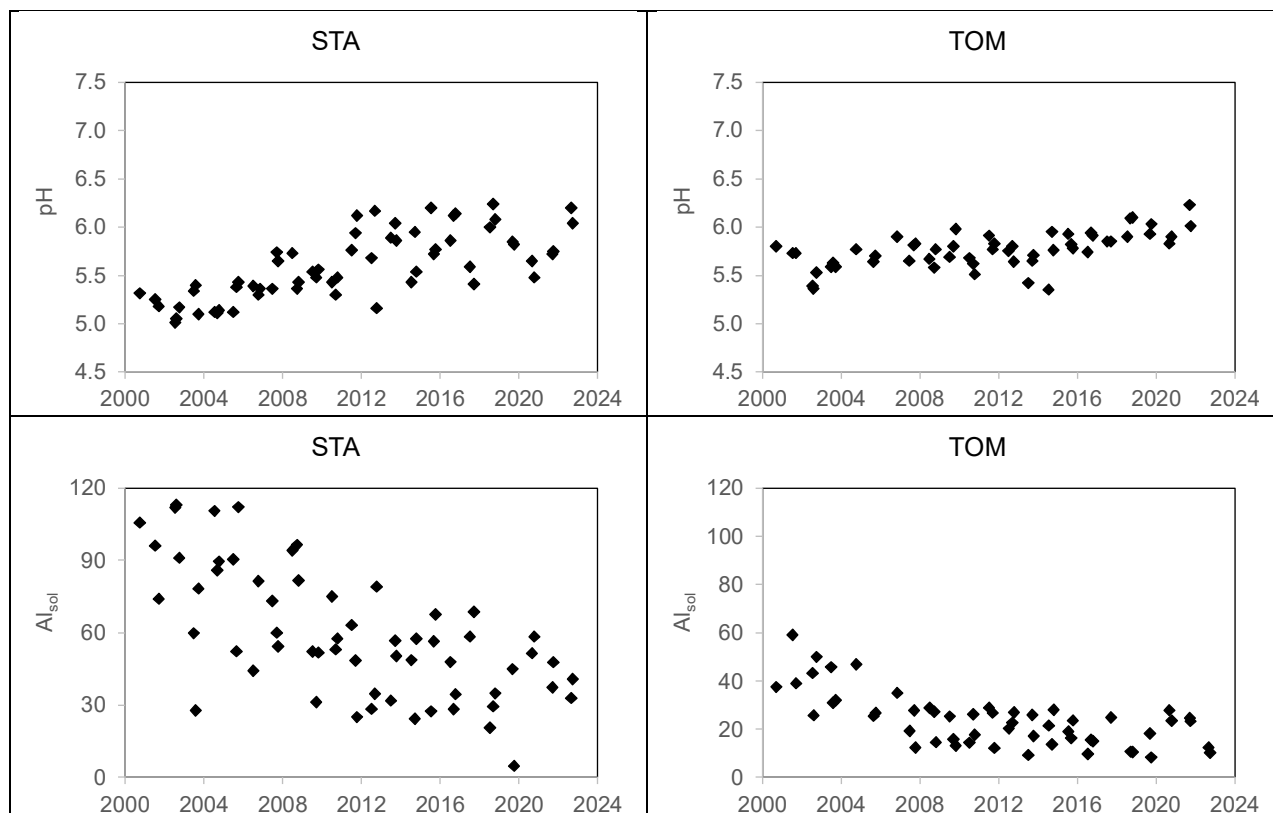
4 Macroinvertebrates as bioindicators

4.1 Introduction

The ultimate goal of emission control programmes is biological recovery (for example the return of acid sensitive species that have disappeared) and the restoration of biological functions that have been impaired during the course of acidification. Since concentrations of soluble aluminum start to increase below a pH of ca. 6.3, it is generally assumed that first signs of changes in the biological communities due to acidification appear, when pH drops below 6 (Wright et al. 1975). To study biological recovery at sites with acidification problems, macroinvertebrates were included as bioindicators in the monitoring programme. Between 2000 and 2011 the macroinvertebrates were regularly monitored in four lakes (INF, SUP, TOM, STA) and three rivers (MAG, VED, VER). From 2012 to 2018, because of financial restrictions, monitoring of macroinvertebrates was limited to the most acid sensitive sites (INF, SUP, TOM, STA, VER). Afterwards macroinvertebrates were sampled yearly in spring and autumn only in the most acidic lakes TOM and STA and determined only every third year (2021, 2024, ...).

During 2021, the average autumn lake pH was 5.7 in STA and 6.1 in TOM. Concentrations of Al_{sol} were $43 \mu g l^{-1}$ in STA and $12 \mu g l^{-1}$ in TOM. The concentrations of Al_{tot} ($58 \mu g l^{-1}$) exceeded the critical value proposed by US EPA ($\sim 47 \mu g l^{-1}$) in STA. Autumn pH and GranAlk increased significantly STA and TOM during the macroinvertebrate monitoring period (from 2000 to present) from about 5.2 and $-10 \mu eq l^{-1}$ to 5.9 and $10 \mu eq l^{-1}$ in STA and from about 5.7 and $3 \mu eq l^{-1}$ to 6.0 and $11 \mu eq l^{-1}$ in TOM. Concentrations Al_{sol} decreased significantly also in both lakes: from about 87 to $38 \mu g l^{-1}$ in STA and from 41 to $17 \mu eq l^{-1}$ in TOM (mean 2000-2004 and mean 2018-2022). See Fig. 4.1.

Figure 4.1 pH and soluble aluminum (in $\mu\text{g l}^{-1}$) in TOM and STA



4.2 Methods

4.2.1 Sampling

Macroinvertebrate samples were collected by “kicksampling” according to the ICP Waters Manual (ICP Waters Programme Centre 2010). Until 2013 lake samples were collected from the littoral and the emissary 2-3 times a year. From 2014 because of financial reasons only emissaries have been sampled. Emissaries were preferred to littorals because they are known to be more often inhabited by indicator species for acidity (Steingruber et al. 2013). In fact, many of these species were determined for rivers and are therefore current loving. Usually, for each site samples from fine and coarse substrates were collected separately. Before 2012 for each site a mixed sample from different substrates was sampled. Macroinvertebrates were conserved in 70% ethanol. During the first 2 years (2000-2001) mixed littoral and outlet samples were taken. Because the results of these samples are difficult to compare with those after 2002, when littoral and outlet samples were collected separately, they were omitted in the temporal analysis. Instead, we used results from samples taken in the outlets of TOM and STA for EMERGE in 2000 (European Mountain lake Ecosystems: Regionalisation, diagnostic & socio-economic Evaluation).

4.2.2 Assessment approach

In Switzerland the assessment of invertebrate river samples is based on the standardized calculation of the IBCH quality index (BAFU 2019), that is itself based on the taxonomic diversity (VT) and the indicator group (GI) and is characterized by values ranging between 0 and 1. For its calculation the semi-quantitative sampled invertebrates are determined mainly at the family taxonomic level or at coarser taxonomic levels (e.g. oligochaetes). The

Swiss Macroinvertebrate Index IBCH_2019 permits to roughly determine the biological condition of the watercourse and to assign one of the following five condition classes: very good ($IBCH \geq 0.8$), good ($0.6 \leq IBCH < 0.8$), moderate ($0.4 \leq IBCH < 0.6$), insufficient ($0.2 \leq IBCH < 0.4$), bad (< 0.2). It is indicative of deficits in water quality and in the structural habitat diversity. The calculation of the IBCH_2019 index for the here studied lakes has shown that it cannot describe the differences in the invertebrate population among high-altitude Alpine lakes with different pH (Steingruber, in prep). A more specific indicator for acidification does not exist in Switzerland.

However, Steingruber et al. (2007) observed a good overlap between the pH of river MAG, VED and VER and the German acidification classes developed for mountain streams of average altitude (400-1500 m a.s.l.) by Braukmann and Biss (2004). Their scale consists of the following five acidification classes: 1 continuously neutral (pH 6.5 to >7.0 , never below 6.0); 2 predominantly neutral to episodically acidic (pH 6.5 to 7.0, rarely below 5.5); 3 periodically critically acidic (pH 5.5 to 6.5, sometimes below); 4 periodically strongly acidic (pH around 5.5, periodically below); 5 continuously extremely acidic (pH 4.3 to 5.5, often below). Not surprisingly, these classes do not suit to assess the acidity of the high-altitude lake outlets. In fact, the lake outlets are characterized by low invertebrate taxa diversity and by very low relative abundances of EPT taxa (Ephemeroptera, Plecoptera, Trichoptera) and high relative abundances of chironomids independently of the water acidity (Boggero and Lencioni 2006, Füreder et al. 2006, Steingruber et al. 2013). A decrease of the EPT species richness with increasing elevation and decreasing catchment areas has also been reported by Altermatt et al. (2013). Nonetheless, the method proposed by Braukmann and Biss (2004) could be adapted to high-altitude outlets of mountain lakes. In the original version, to determine the acidification class, the indicator taxa are sorted first by the indicator value (from 1 (acid sensitive organisms) to 5 (very acid-resistant organisms)) and then by the relative abundance (from the highest to the lowest). Afterwards the relative abundances are cumulatively added up to a dominance of 10%. The indicator value of the last added taxa corresponds then to the acidification class. We saw that the resulting acidification classes fit quite well with the lake pH of high-altitude lake outlets if the abundances are added up to a dominance of 1% instead of 10% (Steingruber et al. 2013). Next to the indicator taxa, also more general invertebrate indicators like the total number of taxa and the number of EPT taxa (especially mayflies and stoneflies) and the relative abundance of the EPT taxa have been shown to correlate positively with the pH of the lake outlets (Steingruber et al. 2013).

Changes in the taxonomic composition through time were also analysed. In order to avoid differences in the taxa number caused by different identification levels used through time, we defined an identification level for each taxonomic group and ignored information beyond this level. The identification levels were the following: Annelida -> class, Arachnida -> subcohort, Coleoptera -> genus, Diptera -> family (except Chironomidae -> species) (except Chironomidae -> species), Ephemeroptera -> genus, Heteroptera -> genus, Megaloptera -> genus, Odonata -> genus, Trichoptera -> genus, Mollusca -> class, Plathelminthes -> family. Moreover, since the sample sizes varied greatly from year to year and it is known that the number of taxa/species increases with the number of individuals, the number of total and EPT taxa were standardized. For each sampling site a linear regression was calculated between the logarithm of the yearly number of total and EPT taxa and the number of individuals sampled in a year. With this function for each year the taxa numbers were standardized to a sample size of 1000 individuals.

The identification of the chironomids is not foreseen in the ICP waters manual (ICP Waters Programme Centre, 2010) because they are generally not considered to be acid sensitive and they are challenging to identify. Nevertheless, we decided to identify the chironomids in order to gain more information regarding the taxonomic composition of the invertebrates. In fact, the high altitude Alpine lakes are generally very poor in invertebrate species and the chironomids are often the most important taxonomic group. In addition, there are insights that during recovery from acidification the taxonomic composition of the chironomid population (Orendt et al. 1999, Ruse 2011) also changes and that the number of the chironomid taxa might increase (Pinder and Morley 1995, Steingruber 2013).

4.3 Results and discussion

The sample size and the relative abundance of the identified taxa and taxa groups (EPT) with the most important taxa numbers (total, EPT) in the lake outlets of TOM and STA during 2021 are shown in Tab. 4.1 and 4.2, respectively. In TOM the most abundant taxonomic groups were Diptera (Chironomidae), Nematelminthes, Plecoptera (Leuctridae) and Hydracarina and in STA Nematelminthes, Diptera (Chironomidae) and Hydracarina. Other relevant groups (> 1%) were Oligochaeta and Simuliidae in TOM and Ceratopogonidae, Oligochaeta, Plecoptera, Heteroptera (Corixidae), Odonata and Simuliidae in STA. The generally acid sensitive Ephemeroptera were absent in both lakes. As regards Plecoptera and Trichoptera in TOM only the very acid resistant *Leuctra sp.*, Nemouridae (probably *Nemoura sp.*), the acid resistant *Limnephilus sp.*, *Odontocerum albicorne*, *Ryacophyla hirticornis*, *Ryacophila sp.* and the acid tolerant *Isoperla carbonaria*, *Isoperla sp.* were identified. Similarly, in STA we found only the very acid resistant *Nemoura cinerea*, *Nemoura sp.*, *Plectrocnemia conspersa* and *Plectrocnemia sp.* Odonata, Corixidae and Ceratopogonidae were found only in STA and are probably related to the wetland character of this lake (small, shallow lake, with wetland vegetation). Nematelminthes and Oligochaeta were more abundant on fine substrates and Plecoptera and Trichoptera more on coarse substrates.

As regards the relative abundances of the chironomid subfamilies, Chironominae (Tanytarsini) dominated in the outlet of STA, followed by Orthoclaadiinae (Tanypodinae were not frequent). A similar fauna composition was found in warm Alpine lakes by Boggero and Lencioni (2006). Other publications (<https://www.landcareresearch.co.nz/tools-and-resources/identification/freshwater-invertebrates-guide/identification-guide-what-freshwater-invertebrate-is-this/no-jointed-legs/true-fly-larvae/midges/chironomid-midge-tanytarsini/>) indicate the abundance of Tanytarsini together with the presence of abundant algae or other aquatic plants. Indeed, because of its low depth (max. depth: 6 m) and its relatively low altitude (1865 m a.s.l.) STA is characterized by high summer surface temperatures (up to 21°C, July 2015) and aquatic vegetation. In the outlet of TOM Chironominae (Chironomini), Orthoclaadiinae and Tanypodinae were about equally abundant. High abundances of Tanypodinae and Chironomini are reported to occur at warmer temperatures, while Orthoclaadiinae and Diamesinae seem to be more common in cold waters (Eggermont and Heiri 2012). High abundance of Tanypodinae were also related to low altitude and high nitrate concentrations (Boggero and Lencioni 2006). In fact, the deep lake TOM (max. depth 38 m) is situated at low altitude (1692 m a.s.l.) and has, compared to lake STA significantly higher NO₃ concentrations, probably related to a lower N retention capacity of the catchment (less vegetation).

The total, the EPT and the chironomid taxa numbers were slightly higher in TOM than in STA (56 vs. 45, 12 vs. 8 and 24 vs. 14, respectively). The relative abundance of EPT taxa was also significantly higher in TOM. Similarly, the mean of the calculated acidification class of the samples is slightly lower in TOM indicative of the presence of slightly more acid sensitive taxa in this lake. Indeed, despite the recently similar mean pH of the two lakes (~6), in TOM the short term variations of the yearly autumn pH were much smaller (± 0.4 versus ± 0.2) and the concentrations of the toxic Al_{sol} were also lower ($\sim 20 \mu g l^{-1}$ in TOM and in $40 \mu g l^{-1}$ STA (see Fig. 4.1)

Table 4.1 Lake sample sizes during 2018

LAKE OUTLETS	MONTH	Fine substrate	Coarse substrate
TOM	July (2.7.2021)	579	667
	September (28.09.2021)	1420	1961
STA	July (30.6.2021)	1363	1258
	September (30.09.2021)	1653	3958

Table 4.2 Relative abundance and number of taxa in lake outlets on different substrates during 2021. 0.0% indicate values >0.0% but < 0.05%.

TAXA	TOM		STA		TOM	STA
	Fine	Coarse	Fine	Coarse		
OLIGOCHAETA	4.7%	0.4%	10.3%	2.9%	2.6%	6.6%
Eiseniella tetraedra	0.4%				0.2%	
Enchitraeidae	0.1%	0.2%	0.7%	0.8%	0.1%	0.7%
Lunbricidae	1.7%	0.2%	0.1%		1.0%	0.0%
Lumbriculidae	0.2%		0.2%		0.1%	0.1%
Naididae			0.1%	0.2%		0.1%
Tubificidae		0.0%			0.0%	
Other	2.3%	0.0%	9.3%	1.9%	5.6%	1.1%
HYDRACARINA	19.9%	6.7%	16.9%	27.6%	13.3%	22.2%
COLEOPTERA	0.2%	0.2%		0.2%	0.2%	0.1%
Agabus sp.		0.0%		0.2%	0.0%	0.1%
Cucurculionidae.				0.0%		0.0%
Dytiscidae	0.1%			0.0%	0.1%	0.1%
Helophorus sp.		0.1%			0.0%	
Other	0.0%	0.1%			0.0%	
DIPTERA (Chironomidae)	27.6%	54.9%	17.3%	23.4%	41.3%	20.3%
Polypedilum nubeculosum-Gr.	3.8%	36.4%			20.1%	
Cladotanytarsus sp.			0.0%			0.0%
Micropsectra aristata		0.0%		0.2%	0.0%	0.1%
Micropsectra atrofasciata	0.2%				0.1%	
Micropsectra radialis	0.1%				0.0%	
Micropsectra sp.	0.3%		0.0%		0.2%	0.0%
Neozavrelia fuldensis/luteola			0.6%	2.3%		1.5%
Paratanytarsus austriacus	0.2%				0.1%	
Paratanytarsus sp.	2.1%	0.6%	1.3%	0.9%	1.4%	1.1%
Tanytarsini			5.5%	9.0%		7.2%
Corynoneura lobata		0.0%			0.0%	
Corynoneura scutellata	2.7%	0.1%	2.2%	4.4%	1.4%	3.3%
Corynoneura sp.		1.9%	0.1%	0.0%	1.0%	0.0%
Cricotopus bicinctus-Gr.	0.0%	0.2%			0.1%	
Cricotopus intersectus-Gr.	0.1%				0.0%	
Cricotopus sp.	1.8%				0.9%	
Heterotanytarsus apicalis	0.2%				0.1%	
Heterotanytarsus marcidus			0.1%			0.0%
Limnophyes sp.		0.0%	0.0%	0.0%	0.0%	0.0%
Parametrioctenus sp.	0.1%				0.0%	
Psectrocladius limbatellus-Gr.	8.4%	1.1%	7.3%	5.6%	4.8%	6.4%
Psectrocladius octomaculatus	0.2%				0.1%	
Psectrocladius sordidellus-Gr.	2.5%		0.2%	0.1%	1.3%	0.1%
Orthoclaadiinae	1.0%			0.6%	0.5%	0.3%
Trissopelopia longimana	1.6%	0.1%			0.8%	
Trissopelopia sp.		14.1%			7.0%	
Zavrelimyia sp.	2.4%		0.1%	0.2%	1.2%	0.1%
Tanypodinae		0.2%			0.1%	
DIPTERA (Other)	0.1%	5.5%	9.8%	8.7%	2.8%	9.2%
Ceratopogonidae	0.1%		9.2%	6.6%	0.0%	7.8%
Empididae		0.1%			0.0%	
Miscidae			0.1%	0.0%		0.1%
Simuliidae	0.0%	5.2%	0.4%	2.4%	2.6%	1.4%
Other	0.0%	0.2%			0.1%	
HETEROPTETA			0.1%	6.7%		3.4%
Corixidae			0.1%	6.7%		3.4%
MEGALOPTERA	0.1%	0.0%			0.0%	
Sialis sp.	0.1%	0.0%			0.0%	

ODONATA			2.3%	2.1%		2.2%
<i>Aeshna caerulea</i>			0.1%	0.0%		0.0%
<i>Aeshna juncea</i>			0.1%	0.1%		0.1%
<i>Aeshna sp.</i>			0.8%	0.3%		0.5%
Aeshnidae			1.0%	1.7%		1.3%
<i>Coenagrion sp.</i>			0.0%	0.0%		0.0%
<i>Orthetrum sp.</i>						
Cordulidae			0.2%	0.1%		
<i>Somatochlora sp.</i>			0.1%			0.1%
Corduliidae			0.1%	0.1%		
Cordulidae						0.1%
PLECOPTERA	9.4%	22.6%	0.4%	7.0%	16.0%	3.7%
<i>Leuctra sp.</i>	1.3%	7.6%			4.5%	
Leuctridae	4.6%	7.0%			5.8%	
<i>Nemoura cinerea</i>				0.0%		0.0%
<i>Nemoura sp.</i>			0.0%	1.2%		0.6%
Nemuridae		0.2%	0.4%	0.0%	0.1%	0.2%
<i>Isoperla carbonaria</i>		0.1%			0.0%	
<i>Isoperla sp.</i>		0.0%			0.0%	
Perlodidae		0.0%			0.0%	
Other	3.5%	7.8%		5.7%	5.6%	2.9%
TRICHOPTERA	0.0%	0.4%	0.1%	1.2%	0.2%	0.6%
Limnephilidae		0.2%		0.0%	0.1%	0.0%
<i>Odontocerum albicorne</i>		0.0%			0.0%	
<i>Plectrocnemia conspersa</i>				0.2%		0.1%
<i>Plectrocnemia sp.</i>				0.1%		0.0%
Policentropodidae			0.1%	1.0%		0.5%
<i>Rhyacophila (Rhyacophila) sp.</i>						
<i>Rhyacophila praemorsa</i>						
<i>Rhyacophila dorsalis</i>						
<i>Rhyacophila hirticornis</i>		0.0%			0.0%	
<i>Rhyacophila sp.</i>		0.2%			0.1%	
Other	0.0%				0.0%	
NEMATHELMINTHES	37.9%	9.3%	42.8%	20.1%	23.6%	31.4%
TURBELLARIA	0.1%		0.1%	0.1%	0.0%	0.1%
Planariidae	0.1%		0.1%	0.1%	0.0%	0.1%
Rel. abundance EPT taxa	9.4%	23.0%	0.5%	8.2%	16.2%	4.3%
Number total taxa	37	36	35	38	56	45
Number EPT taxa	4	11	3	8	12	8
Mean acidification class	4.0	3.5	4.5	4.5	3.8	4.5

The temporal changes of the relative abundances of the main taxa and taxa groups (EPT) and the most important taxa numbers (total (without the chironomids), EPT) and the acidification classes calculated with the modified Braukmann and Biss index are presented in Tab. 4.3-4.4. The temporal changes of the relative abundances of the chironomid subfamilies and tribes and their total taxa numbers are shown in Tab. 4.5. A change toward more acid sensitive taxa/species cannot be observed.

Table 4.3 Temporal variations of the relative abundances and the number of taxa in the outlet of TOM.
0% indicates values between 0% and < 0.5%

PARAMETER	2000	2002	2003	2004	2005	2006	2007	2008	2009	2011	2012	2013	2014	2015	2016	2017	2018	2021
Sampling times	1	2	2	1	1	2	2	2	2	2	2	2	2	2	2	2	2	2
Individuals	11	156	331	337	2128	2983	3975	4407	3726	230	866	319	4133	372	981	977	729	4489
Rel. abundance OLIGOCHAETA		7%	1%	0%	0%	0%	0%	1%	1%	42%	4%	1%	15%					4%
Rel. abundance HYDRACARINA			1%	1%	0%	2%	1%	0%	0%		1%							20%
Rel. abundance COLEOPTERA		1%	3%		0%	0%	0%	0%	0%	1%	1%		1%	1%	0%	0%	1%	0%
<i>Rel. abundance DYTISCIDAE</i>		1%	2%		0%	0%	0%	0%	0%	1%				1%	0%	0%	1%	0%
<i>Rel. abundance ELMIDAE</i>				1%														
<i>Rel. abundance HELOPHORIDAW</i>				1%														0%
Rel. abundance DIPTERA	36%	28%	34%	40%	84%	58%	64%	90%	87%	53%	77%	72%	70%	67%	76%	78%	69%	55%
<i>Rel. abundance Athericidae</i>															0%	0%	0%	0%
<i>Rel. abundance CERATOPOGONIDAE</i>								0%						1%		0%	0%	0%
<i>Rel. abundance CHIRONOMIDAE</i>	36%	14%	33%	37%	75%	38%	57%	61%	65%	26%	40%	68%	19%	50%	46%	49%	23%	52%
<i>Rel. abundance EMPIDIDAE</i>					0%	0%	0%	0%					0%					0%
<i>Rel. abundance LIMONIIDAE</i>						0%												
<i>Rel. abundance PSYCHODIDAE</i>								0%		0%								
<i>Rel. abundance SIMULIDAE</i>		14%	1%	3%	9%	20%	6%	29%	22%	26%	36%	5%	51%	16%	30%	29%	46%	3%
Rel. abundance HETEROPTERA			0%		0%	0%							1%					
<i>Rel. abundance MESOVELIIDAE</i>													1%					
Rel. abundance MEGALOPTERA	18%	2%	1%	1%	0%		0%	0%	0%									0%
<i>Rel. abundance SIALIDAE</i>	18%	2%	1%	1%	0%		0%	0%	0%									0%
Rel. abundance PLECOPTERA	36%	60%	57%	58%	13%	37%	34%	8%	10%	3%	14%	27%	10%	28%	18%		19%	20%
<i>Rel. abundance LEUCTRIDAE</i>	36%	57%	55%	58%	12%	35%	34%	1%	9%	3%	10%	13%	4%	23%	16%	12%	16%	13%
<i>Rel. abundance NEMOURIDAE</i>		3%	2%		2%	1%	0%	1%	1%		4%	13%	6%	4%	3%	2%	3%	0%
<i>Rel. abundance PERLODIDAE</i>								0%										0%
Rel. abundance TRICHOPTERA	9%	2%	4%	1%	2%	2%	1%	1%	1%	1%	1%	1%	3%	6%	4%		9%	0%
<i>Rel. abundance LIMNEPHILIDAE</i>		1%	1%		1%	1%		0%	1%				3%	1%	0%	0%	1%	0%
<i>Rel. abundance ODONTOCERIDAE</i>						0%	0%		0%									0%
<i>Rel. abundance PHILOPOTAMIDAE</i>	9%																	
<i>Rel. abundance POLYCENTROPODIDAE</i>		1%	3%	0%	0%	0%	0%	0%	0%	1%	1%	1%						
<i>Rel. abundance RHYACOPHILIDAE</i>			1%	1%	0%	1%	1%	0%	0%				0%	5%	3%	5%	9%	0%
Rel. abundance TURBELLARIA						1%	0%	0%	0%		3%		0%		1%	1%	1%	0%
<i>Rel. abundance PLANARIIDAE</i>						1%	0%	0%	0%		3%		0%		1%	1%	1%	0%
Rel. abundance EPT taxa	45%	62%	61%	59%	15%	39%	35%	9%	12%	4%	15%	27%	13%	33%	22%	20%	29%	21%
Number of total taxa	4	10	15	8	17	18	17	22	20	7	10	7	13	8	9	10	10	25
Standardized number of total taxa	5	12	17	9	13	12	9	10	11	8	10	8	6	9	9	10	11	11
Number of EPT taxa	2	5	6	3	9	9	8	12	11	2	4	4	5	4	4	4	4	10
Standardized number of EPT taxa	3	6	7	4	7	5	4	5	6	2	4	5	2	5	4	4	4	4
Mean acidification class	3.0	4.5	3.0	4.0	4.0	4.0	4.0	4.0	4.0	5.0	5.0	5.0	4.3	4.0	4.0	4.0	4.0	4.0

Table 4.4 Temporal variations of the relative abundances and the number of taxa in the outlet of STA.
0% indicates values between 0% and < 0.5%

PARAMETER	2000	2002	2003	2004	2005	2006	2007	2008	2009	2011	2012	2013	2014	2015	2016	2017	2018	2021
Sampling times	1	2	2	1	2	2	2	2	2	2	2	2	2	2	2	2	2	2
Individuals	21	706	808	478	2634	6223	3451	3935	2846	604	774	929	1512	1493	976	898	770	8186
Rel. abundance OLIGOCHAETA			1%	3%	3%	1%	0%	2%	10%		6%	6%		4%	4%	4%	5%	11%
Rel. abundance HYDRACARINA			1%	1%		0%	0%	1%	2%		6%	7%	0%					33%
Rel. abundance COLEOPTERA	14%	2%	0%	0%	0%	0%	0%	0%	0%	1%	0%		0%	0%		1%	1%	0%
<i>Rel. abundance CHRYSOMELIDAE</i>								0%										
<i>Rel. abundance CURCULIONIDAE</i>																		0%
<i>Rel. abundance DYTISCIDAE</i>	14%	2%	0%		0%	0%	0%	0%	0%	1%			0%	0%		0%		0%
<i>Rel. abundance ELMIDAE</i>														0%		1%	1%	
Rel. abundance DIPTERA	29%	85%	91%	66%	89%	96%	85%	87%	74%	95%	69%	87%	73%	86%	83%	82%	79%	48%
<i>Rel. abundance ATHERICIDAE</i>					0%					25%								
<i>Rel. abundance CERATOPOGONIDAE</i>		16%	5%	10%	14%	3%	5%	14%	13%	7%	20%	15%	8%	12%	30%	33%	40%	13%
<i>Rel. abundance CHIRONOMIDAE</i>	29%	69%	85%	56%	75%	93%	79%	71%	56%	63%	35%	59%	16%	73%	53%	47%	36%	29%
<i>Rel. abundance LIMONIIDAE</i>							0%											
<i>Rel. abundance PSYCHIDIDAE</i>					0%					0%								0%
<i>Rel. abundance SIMULIDAE</i>				0%	0%	0%	1%	2%	4%	0%	15%	13%	49%	1%		2%	3%	4%
<i>Rel. abundance TABANIDAE</i>																		2%
Rel. abundance EPHEMEROPTERA								0%										
<i>Rel. abundance BAETIDAE</i>								0%										
Rel. abundance HETEROPTERA			1%	11%	0%	0%	0%	0%	0%	0%	0%	0%						0%
<i>Rel. abundance CORIXIDAE</i>			0%	11%	0%	0%	0%	0%	0%									0%
<i>Rel. abundance GERRIDAE</i>			0%							0%	0%	0%						
Rel. abundance MEGALOPTERA									0%									
<i>Rel. abundance SIALIDAE</i>									0%									
Rel. abundance ODONATA		6%	0%	13%	5%	1%	3%	2%	2%	2%	3%	0%	1%	1%	1%	2%	2%	4%
<i>Rel. abundance AESHNIDAE</i>		5%	0%	12%	4%	1%	3%	1%	1%	1%	2%	0%	0%	1%	1%	2%	1%	3%
<i>Rel. abundance COENAGRIONIDAE</i>				1%	1%	0%	0%	0%	0%	1%								
<i>Rel. abundance CORDULIDAE</i>																		0%
<i>Rel. abundance LIBELLULIDAE</i>		1%									1%		0%	0%	1%	0%	0%	0%
Rel. abundance PLECOPTERA	24%	2%	2%	5%	1%	1%	9%	8%	12%	1%	16%		26%	8%	12%	11%	13%	4%
<i>Rel. abundance NEMOURIDAE</i>	24%	2%	2%	5%	1%	1%	9%	8%	12%	1%	16%		26%	8%	12%	11%	13%	1%
Rel. abundance TRICHOPTERA	33%	5%	4%		0%	0%	1%	1%	1%				0%	1%		0%		1%
<i>Rel. abundance LIMNEPHLIDAE</i>			0%		0%	0%	0%	0%	0%									0%
<i>Rel. abundance PHRYGANEIDAE</i>	33%	5%	4%		0%	0%	1%	0%	0%				0%					
<i>Rel. abundance POLYCENTROPODIDAE</i>					0%	0%	0%	0%	1%					0%		0%		1%
Rel. abundance PLATHELMINTHES																		0%
<i>Rel. abundance PLANARIIDAE</i>																		0%
Rel. abundance EPT taxa	57%	7%	6%	5%	2%	1%	10%	9%	13%	1%	16%		26%	9%	12%	11%	13%	5%
Number of total taxa	4	8	13	11	16	16	19	23	18	12	10	7	9	12	8	12	8	25
Standardized number of total taxa	5	9	14	13	13	7	13	15	13	13	10	7	8	11	8	12	8	8
Number of EPT taxa	2	3	3	1	4	6	6	8	6	1	1	0	2	2	1	2	1	6
Standardized number of EPT taxa	3	3	3	1	3	2	3	4	4	1	1	0	2	2	1	2	1	1
Mean acidification class	5.0	4.0	4.0	5.0	4.0	4.0	4.0	4.0	4.0	5.0	5.0		4.8	5.0	5.0	5.0	5.0	5.0

Table 4.5 Temporal variations of the relative abundances and the number of taxa of Chironomidae in TOM and STA. 0% indicates values between 0% and < 0.5%

LAKE	PARAMETER	2002	2003	2004	2005	2006	2007	2008	2009	2011	2012	2013	2014	2015	2016	2017	2018	2021	
TOM	Sampling times		2	1	2	2	2	2	2		2		1	2	2	2	2	2	
	Individuals		64	115	1035	943	1845	2956	2606		132		544	193	428	445	101	729	
	Rel. abundance CHIRONOMINAE		16%	5%	67%	20%	45%	64%	69%		54%		93%	46%	45%	44%	34%	38%	
	Rel. abundance Chirnonomini		14%		63%	17%	42%	63%	65%		54%		93%	42%	42%	43%	31%	31%	
	Rel. abundance Tanytarsini		2%	5%	4%	3%	2%	2%	4%					4%	2%	1%	3%	7%	
	el. abundance DIAMESINAE							0%				1%							
	Rel. abundance Diamesini							0%				1%							
	Rel. abundance ORTHOCLADIINAE		26%	77%	16%	51%	36%	29%	22%		45%			4%	18%	15%	29%	17%	37%
	Rel. abundance PRODIAMESINAE																		
	Rel. abundance TANYPODINAE		58%	18%	15%	30%	16%	7%	4%					2%	36%	40%	27%	49%	25%
	Rel. abundance Macropelopiini																		
	R Rel. abundance Pentaneurini		58%	18%	15%	30%	16%	7%	4%					2%	36%	40%	27%	49%	25%
	R R Rel. abundance Procladiini																		
	Rel. abundance NOT DETERMINED							4%		1%									
Number of total taxa			7	9	12	14	24	19	14		14		9	12	15	14	17	25	
Standardized number of total taxa			8	10	10	11	17	13	10		14		6	13	15	14	18	16	
STA	Sampling times		2	1	2	2	2	2	2		1		1	2	2	2	2	2	
	Individuals		625	211	1462	5641	1768	2842	1532		74		270	952	667	330	156	2583	
	Rel. abundance CHIRONOMINAE		81%	32%	58%	64%	46%	44%	60%		50%		90%	72%	62%	33%	3%	45%	
	Rel. abundance Chirnonomini		32%	9%	2%	0%	1%	0%	0%				0%	1%	0%	2%			
	Rel. abundance Tanytarsini		49%	23%	55%	63%	44%	43%	60%		50%		90%	71%	61%	31%	5%	45%	
	el. abundance DIAMESINAE				0%	0%		0%	1%										
	Rel. abundance Diamesini				0%	0%			1%										
	Rel. abundance ORTHOCLADIINAE		10%	48%	37%	31%	43%	54%	36%		14%			9%	28%	37%	64%	95%	54%
	Rel. abundance PRODIAMESINAE																		
	Rel. abundance TANYPODINAE		8%	18%	5%	5%	10%	2%	3%		36%			1%	0%	1%	4%	2%	0%
	Rel. abundance Macropelopiini		1%		0%	4%	0%	0%											
	R Rel. abundance Pentaneurini		7%	18%	5%	1%	9%	1%	2%		1%			1%	0%	1%	4%	2%	0%
	R R Rel. abundance Procladiini		0%		0%	0%	0%		0%										
	Rel. abundance NOT DETERMINED		1%	2%				2%		1%									
Number total taxa			12	10	16	18	20	16	14		12		8	15	17	13	8	4	
tandardized number of total taxa			12	10	16	18	20	16	14		12		8	15	17	13	8	4	

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