Repubblica e Cantone Ticino
Dipartimento del territorio

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)

Annual report 2019-2020

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 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 SO_2 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 below 20 meq m^{-3} at all sites and sulphate depositions from 110 meq m^{-2} to below 30 meq m^{-2}. Concentrations and depositions of nitrate also decreased significantly at most sites (8 out of 9) and the most the pronounced decrease occurred 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 of 5 out 9 and depositions of 4 out of 9 sites). Consequently, during the last 30 years annual mean concentrations of Gran alkalinity increased significantly at all sites from values ranging from -54 to -11 meq/m^3 (1988-1992) to values ranging from -2 to 43 meq/m^3 (2016-2020) and deposition of potential acidity decreased from values ranging from 93 to 272 meq/m^2 to values ranging from 22 to 135 meq/m^2. Accordingly, yearly mean rainwater pH increased from values ranging from 4.3 to 4.8 between 1988-1992 to values ranging between 5.1 and 6.1 more recently (2016-2020).

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 aluminium also decreased, especially

after 2005, in the most acidic lakes (pH < 6) Lago Tomé (from 40 $\mu g\ l^{-1}$ to 20 $\mu g\ l^{-1}$), Lago del Starlaresc da Sgiof (from 80-100 $\mu g\ l^{-1}$ to 25-70 $\mu g\ l^{-1}$) and after 2012 in Laghetto Gardiscio (from 30-60 to 20-25 $\mu g\ l^{-1}$).

River chemistry also responded to emission reductions of sulphur and nitrogen. The time trend analysis revealed that from 2000 to 2020 concentrations of sulphate and nitrate decreased and Gran alkalinity increased in river Maggia, Vedeggio and Verzasca. The highest increase in concentrations of nitrate probably occurred after 2010.

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 SO_2, 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 inferiori a 20 meq m^{-3} in tutte le stazioni di campionamento e le deposizioni da 110 meq m^{-2} a valori inferiori a 30 meq m^{-2}. A causa della diminuzione delle emissioni di NO_x, anche le concentrazioni e le deposizioni di nitrato sono diminuite significativamente quasi ovunque (8 stazioni su 9), 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 4 stazione su 9 per le deposizioni). Conseguentemente, negli ultimi 30 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 -11 meq/m^3 a valori che oggi variano da -2 a 43 meq/m^3 (2016-2020) e le deposizioni di acidità potenziale sono dimuniute da valori che variavano da 93 a 272 meq/m^2 a valori che variano da 22 a 135 meq/m^2. Analogamente il pH medio annuo delle acque piovane è aumentato da valori che variavano da 4.3 a 4.8 tra il 1988 e il 1992 a valori che oggi variano tra 5.1 e 6.1 (2016-2020).

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 in modo significativo nei laghi maggiormente acidi (pH < 6): dopo il 2005 nel Lago di Tomé da valori medi annui di 40 a 20 $\mu g\ l^{-1}$ e nel Starlaresc da Sgiof da 80-100 $\mu g\ l^{-1}$ a 25-70 $\mu g\ l^{-1}$ e dopo il 2012 nel Laghetto Gardiscio da circa 30-60 a 20-25 $\mu g\ l^{-1}$.

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 e un aumento dell'alcalinità dei fiumi Maggia, Vedeggio e Verzasca dal 2000 al 2020. La diminuzione delle concentrazioni di nitrato sembra essere avvenuta principalmente dopo il 2010.

1 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 the Canton of Ticino.

1.1 Climatic parameters during 2019-2020

2019 has been the 5th warmest year and 2020 the overall warmest year (together with 2018) in Switzerland since the beginning of measurements in 1864. Annual precipitations in Southern Switzerland were slightly above the norm values in 2019 (on average 113% at the wet deposition sampling sites) and slightly below the norm values in 2020 (on average 89% at the wet deposition sampling sites). The wettest months were April 2019, October 2019, November 2019 and October 2020 and the driest January 2019, February 2019, January 2020, February 2020 and November 2020. Compared to the norm values January 2019, January 2020, February 2020, November 2020 were particularly dry (on average < 30%) and October 2019, November 2019, December 2019, October 2020 and December 2020 particularly wet (on average > 150%).

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 north-western part of the Canton of Ticino 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 lakes and 3 rivers and wet deposition has been monitored at 10 sampling sites distributed over all the Canton of Ticino. Macroinvertebrates as bioindicators were sampled in 4 lakes and 3 rivers at the beginning of their monitoring in 2000; afterwards the sampling sites were progressively reduced until 2019. From then on biologic sampling was limited to the 2 most acidic lakes.

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 lakes.

The geographic distribution of the sampling sites (wet deposition, rivers and lake sampling) 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)

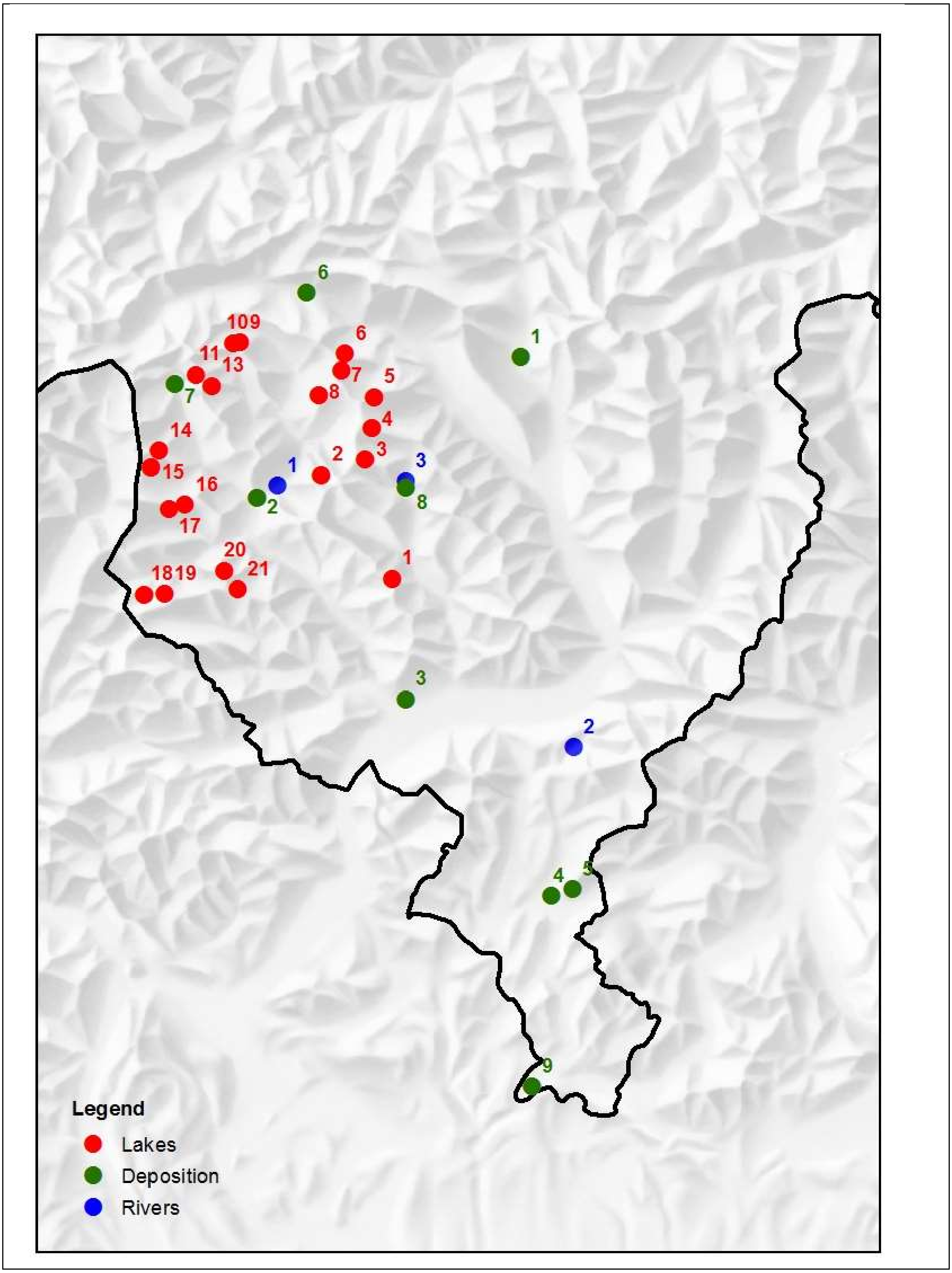


Table 2.1 Geographic and morphometric parameters of the wet deposition sampling sites

Sampling site number	Code	Sampling site	CH1903 LV03 (m)		WGS84		Altitude
			Longitude	Latitude	Longitude	Latitude	m a.s.l.
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	694930	152500	8°40'35"	46°31'7"	1007
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 rivers

River number	River code	River name	Sampling site	CH1903 LV03 (m)		WGS84		Altitude	Catchment area
				Longitude	Latitude	Longitude	Latitude	m a.s.l	km²
1	MAG	Maggia	Brontallo	692125	134375	8°38' 8"	46°21'16"	610	ca. 189
2	VED	Vedeggio	Isone	719900	109800	8°59'24"	46°07'45"	740	20
3	VER	Verzasca	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	Catchment area	Lake area	Max depth
			Longitude	Latitude	Longitude	Latitude	m a.s.l.	ha	ha	m
1	STA	Lago del Starlaresc da Sgiof	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 Porchieirsc	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'Orsalìa	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 north-western 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 aluminium 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 of acidification appear, when pH drops below 6 (Wright et al. 1975).

3.2 Sampling methods

Although 2020 has been a difficult year under many circumstances (lockdown in spring and autumn-winter 2020), monitoring occurred almost completely as planned.

In order to monitor and assess acidification of freshwaters in acid sensitive areas of the Canton of Ticino, wet deposition at 10 sites, water chemistry of 20 Alpine lakes and 3 rivers (Maggia, Vedeggio, Verzasca) have been monitored.

Rainwater has been sampled at weekly intervals with wet-only samplers. The first sampler of this type was installed at Locarno Monti in 1988. Other samplers followed in 1989 (Lugano), in 1990 (Acquarossa, Piotta, Stabio), in 1995 (Monte Brè), in 1996 (Robiei) in 2001 (Bignasco, Sonogno). 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 the Cristallina hut (2575 m). Because the hut is inhabited only periodically, up to now we have only data from a few months of 2017 and 2019. During 2020, because of the Covid-19 pandemia, sampling at the Cristallina hut could did not occur. For the same reason, during 2020 sampling at Monte Brè has been interrupted between mid March to mid June.

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 of the three rivers has been sampled monthly since 2000.

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	Filtration	Conservation	Method	Limit of quantification
pH	No	No	potentiometry	0.02
conductivity	No	No	potentiometry	1 μS cm^{-1}
Gran alkalinity	No	No	potentiometry	0.001 meq l^{-1}
Ca^{2+}	CA filter	PP bottle, 4°C	ion cromatography	0.06 mg l^{-1}
Mg^{2+}	CA filter	PP bottle, 4°C	ion cromatography	0.01 mg l^{-1}
Na^{+}	CA filter	PP bottle, 4°C	ion cromatography	0.01 mg l^{-1}
K^{+}	CA filter	PP bottle, 4°C	ion cromatography	0.08 mg l^{-1}
NH_4^{+}	CA filter	PP bottle, 4°C	ion chromatography (precipitations)	0.030 mg N l^{-1}
NH_4^{+}	CA/GF filter	PP bottle, 4°C	UV/VIS (lakes, rivers)	0.012 mg N l^{-1}
SO_4^{2-}	CA/GF filter	PP bottle, 4°C	ion cromatography	0.08 mg l^{-1}
NO_3^{-}	CA/GF filter	PP bottle, 4°C	ion cromatography	0.02 mg N l^{-1}
NO_2^{-}	CA/GF filter	PP bottle, 4°C	ion cromatography	0.2 μg N l^{-1}
Cl^{-}	CA/GF filter	PP bottle, 4°C	ion cromatography	0.1 mg l^{-1}
soluble reactive P	CA/GF filter	PP bottle, 4°C	ion cromatography	2 μg P l^{-1}
total P	No	glass bottle, persulphate mineralisation	UV/VIS	32 μg P l^{-1}
soluble reactive Si	CA/GF filter	PP bottle, 4°C	ICP-MS	0.06 mg SiO_2 l^{-1}
total N	No	glass bottle, persulphate mineralisation	UV/VIS	0.15 mg N l^{-1}
DOC	PC filter	brown glass bottle	IR-catalytic oxidation and combustion	0.05 mg C l^{-1}
soluble Al	PC filter	acid washed PP bottle, +HNO_3, 4°C	ICP-MS	1.0 μg l^{-1}
total Al	No	acid washed PP bottle, +HNO_3, 4°C	ICP-MS	1.0 μg l^{-1}
soluble Pb	PC filter	acid washed PP bottle, +HNO_3, 4°C	ICP-MS	0.1 μg l^{-1}
total Pb	No	acid washed PP bottle, +HNO_3, 4°C	ICP-MS	0.1 μg l^{-1}
soluble Cd	PC filter	acid washed PP bottle, +HNO_3, 4°C	ICP-MS	0.1 μg l^{-1}
total Cd	No	acid washed PP bottle, +HNO_3, 4°C	ICP-MS	0.1 μg l^{-1}
soluble Cu	PC filter	acid washed PP bottle, +HNO_3, 4°C	ICP-MS	0.1 μg l^{-1}
total Cu	No	acid washed PP bottle, +HNO_3, 4°C	ICP-MS	0.1 μg l^{-1}
soluble Zn	PC filter	acid washed PP bottle, +HNO_3, 4°C	ICP-MS	0.1 μg l^{-1}
total Zn	No	acid washed PP bottle, +HNO_3, 4°C	ICP-MS	0.1 μg l^{-1}
soluble Cr	PC filter	acid washed PP bottle, +HNO_3, 4°C	ICP-MS	0.1 μg l^{-1}
total Cr	No	acid washed PP bottle, +HNO_3, 4°C	ICP-MS	0.1 μg l^{-1}
soluble Ni	PC filter	acid washed PP bottle, +HNO_3, 4°C	ICP-MS	0.1 μg l^{-1}
total Ni	No	acid washed PP bottle, +HNO_3, 4°C	ICP-MS	0.1 μg l^{-1}
soluble Fe	PC filter	acid washed PP bottle, +HNO_3, 4°C	ICP-MS	1.0 μg l^{-1}
total Fe	No	acid washed PP bottle, +HNO_3, 4°C	ICP-MS	1.0 μg 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 (Acquarossa → Comprovasco, Locarno Monti → Locarno Monti, Lugano → Lugano, Monte Brè → Lugano, Piotta → Piotta, Robiei → Robiei, Stabio → Stabio) and of the Canton of Ticino (Bignasco → Cavergno, Sonogno → Sonogno) have been chosen.

Depositions of potential acidity were calculated subtracting depositions of base cations (calcium, magnesium, sodium, potassium) from the sum of acid anions (sulphate, nitrate, chloride) plus ammonium.

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 2019 and 2020 are shown in Tab. 3.2.

Table 3.2 Yearly mean rainwater concentrations and deposition rates in 2019 and 2020

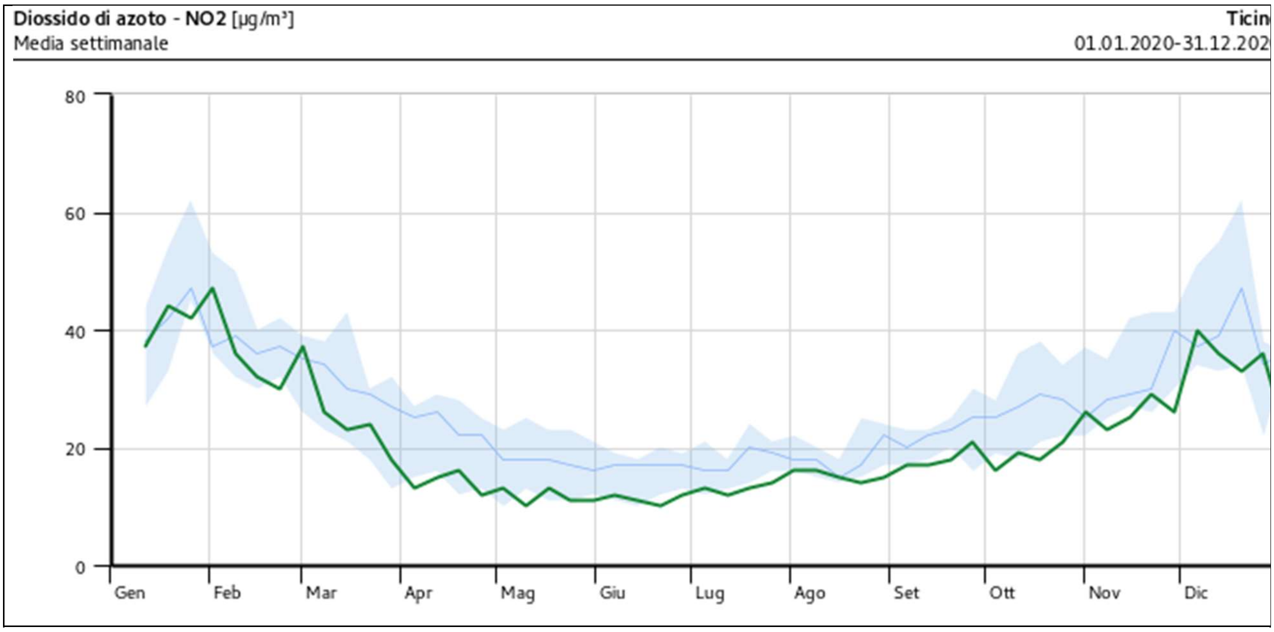
Sampling site	Year	Precipitation MeteoCH (mm)	Analysed precipitation (mm)	Cond 25°C (µS cm^{-1})	pH	Ca^{2+} Concentration (meq m^{-3})	Ca^{2+} Deposition (meq m^{-2})	Mg^{2+} Concentration (meq m^{-3})	Mg^{2+} Deposition (meq m^{-2})	Na^{+} Concentration (meq m^{-3})	Na^{+} Deposition (meq m^{-2})	K^{+} Concentration (meq m^{-3})	K^{+} Deposition (meq m^{-2})	NH_4^{+} Concentration (meq m^{-3})	NH_4^{+} Deposition (meq m^{-2})	HCO_3^{-} Concentration (meq m^{-3})	HCO_3^{-} Deposition (meq m^{-2})	SO_4^{2-} Concentration (meq m^{-3})	SO_4^{2-} Deposition (meq m^{-2})	NO_3^{-} Concentration (meq m^{-3})	NO_3^{-} Deposition (meq m^{-2})	Cl^{-} Concentration (meq m^{-3})	Cl^{-} Deposition (meq m^{-2})	Gran Alk Concentration (meq m^{-3})	Potential acidity Deposition (meq m^{-2})
ACQ	2019	1393	1335	10	5.8	24	33	3	5	5	7	2	3	36	51	32	45	15	21	21	29	5	7	32	58
	2020	1097	1055	6	5.7	12	14	2	2	4	4	2	2	21	23	17	19	8	8	12	13	4	5	16	29
BIG	2019	2271	2042	9	5.7	26	58	4	8	6	13	2	5	31	70	31	69	15	33	20	45	5	12	29	75
	2020	1558	1397	7	5.7	16	26	5	7	6	9	3	4	19	29	18	28	9	14	15	24	6	9	17	33
LOC	2019	1868	1729	9	5.5	17	32	4	8	7	13	2	4	28	53	20	38	14	27	20	38	6	12	17	73
	2020	1599	1435	7	5.7	14	22	3	4	7	11	1	2	25	39	18	29	10	15	15	24	6	9	17	53
LUG	2019	1675	1359	11	5.5	21	35	4	6	7	12	2	3	40	68	27	46	17	29	26	44	8	13	24	94
	2020	1543	1251	9	5.8	21	32	4	6	6	9	2	3	36	55	30	46	11	17	19	29	7	10	29	66
BRE	2019	1675	1566	10	5.6	20	33	3	6	9	14	2	4	32	54	22	38	15	25	24	41	9	15	20	74
	2020	1543	1020	7	5.7	14	22	3	5	6	9	1	2	27	41	20	31	8	13	17	26	7	10	19	54
PIO	2019	1843	1598	9	5.8	24	44	2	4	9	16	1	2	25	47	27	50	13	25	16	29	9	17	26	47
	2020	1306	1135	13	5.8	14	19	2	2	73	96	1	1	14	18	13	17	7	9	12	15	70	91	13	22
ROB	2019	3070	2180	8	5.4	17	51	2	8	3	10	2	5	18	54	10	30	10	31	22	66	4	11	6	92
	2020	1981	1367	5	5.5	11	21	2	3	4	7	1	2	10	20	6	13	6	11	15	30	3	6	5	33
SON	2019	2326	2138	8	5.8	18	42	2	6	4	9	1	3	28	66	24	56	12	27	18	41	4	9	21	80
	2020	1800	1434	6	5.7	11	20	2	3	3	6	1	3	20	36	16	28	7	12	13	23	3	6	13	47
STA	2019	1542	1300	13	5.5	22	34	6	10	11	16	4	6	46	71	31	48	17	26	31	47	12	18	29	97
	2020	1350	1243	11	5.8	26	35	5	6	8	11	2	3	44	60	40	55	12	17	22	30	9	12	39	67

In general, ion concentrations of anthropogenic origin (sulphate, nitrate, ammonia) still decrease with increasing latitude and altitude. The gradients, however, are not as pronounced as they were at the beginning of the measurements. In 2019 and 2020, the highest concentrations of the sum of sulphate, nitrate and ammonium were measured at Stabio and Lugano, the lowest at Robiei and Piotta. 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. Because of the low concentrations of base cations and ammonium lowest Gran alkalinity was measured at Robiei. In fact, Gran alkalinity can be approximated subtracting concentrations of acid anions from concentrations of acid anions plus ammonium.

Wet deposition of atmospheric pollutants depends on their concentration in and the amount of precipitation. Highest precipitation usually occurs in the north-western part of the Canton of 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 2019, highest deposition rates of the sum of ammonia, nitrate and sulphate occurred at Robiei and Bignasco and the lowest at Acquarossa and Piotta. In 2020, highest deposition rates of the sum of ammonia, nitrate and sulphate occurred at Stabio followed by Lugano and the lowest again at Acquarossa and Piotta. In both 2019 and 2020 highest annual mean deposition of potential acidity was measured at Stabio and Lugano; the lowest at Piotta.

Usually, years with higher average precipitations are characterized by slightly lower concentrations of the base cations calcium, magnesium and potassium and the ions of antropogenic origin sulphate, nitrate and ammonium. 2019 has been a relatively wet year, while precipitations in 2020 were average. Neverthless, mean concentrations of calcium, magnesium, potassium, sulphate, nitrate and ammonium were generally lower in 2020 compared to 2019. The reason might be related with the general reduction of the anthropogenic activities as a consequence of the Covid-19 pandemia. However, it is too soon to know this by certitude. Anyhow, at a local scale, concentrations of NO_2 in the air decreased by 50% between mid March and mid April 2020, after the introduction of the first national lock-down (see also press release of the 1.5.2020, https://www4.ti.ch/area-media/comunicati/dettaglio-comunicato/?NEWS_ID=187709) and remained in the range order of the 20th percentiles of the previous five years until the end of November 2020 (Fig. 3.1).

Figure 3.1 Weekly mean concentrations of NO_2 in Ticino during 2020 (green line) and between 2011 and 2019 (blue line) with their 10th and 90th percentiles (blue shadow).



Seasonal variation

Fig. 3.2 shows the amount of monthly precipitation at each sampling site during 2019 and 2020 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. 3.3.

Average monthly precipitation is normally low from December to March and higher from May to November. Compared to average values, precipitation was significantly higher in April, October, November 2019 and October, December 2020 and significantly lower in July, September, November 2020.

During 2011-2020 average sulphate concentrations were higher in summer and lower in winter. This follows the oxidation rate of SO_2 to SO_4^{2-} (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 nitrate during 2011-2020 were highest in March and lowest in November and December. The nitrate 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 ammonium during 2011-2020 was very similar to that of sulphate. Hedin et al. (1990) explained this similarity with a chemical coupling between ammonia and sulphate, with acidic sulphate aerosols acting as a vehicle for long-range transport of ammonia. Seasonal variations in ammonium concentrations at sites distant from major sources of ammonia emissions thus may be influenced strongly by the supply of sulphate aerosol and by seasonal variations in emissions and oxidation of SO_2.

As regards average rainwater concentrations of the base cations calcium, magnesium and potassium, during 2011-2020 they tended to be higher in spring and to be similar at all sites. Similar behaved concentrations of Gran alkalinity, indicating that concentrations of base cations heavily influence the seasonality of alkalinity. Rainwater pH is usually also higher in spring/summer.

In general, compared to the last decade, concentrations of sulphate and nitrate were in the same order of magnitude during 2019 and slightly lower during 2020, while concentrations of ammonium were comparable to those of the last decade in both 2019 and 2020. Single concentration peaks can often be attributed to small precipitation volumes (example: concentration peaks in January). Others, especially as regards base cation and Gran alkalinity peaks are related to alkaline rain events (deposition of Saharan dust). Alkaline rain events occurred at all sites during the first two weeks of June 2019 and at all sites with exception of Robiei during the third week of May 2020. The data also indicate that the pH of the rainwater samples during 2019 and 2020 was in general lower compared to the overall samples from the last decade. In fact, during 2019 and 2020 only 4% and 5%, respectively of the analysed rainwater samples had pH values below 5, while they were 9% between 2011 and 2020. Similarly, during 2019 and 2020 96% of the samples had pH values higher than 5.5 and 44% and 53%, respectively higher than 6.0. These percentages were only 90% and 39%, respectively during 2011-2020.

Monthly variations of wet depositions behave in general similar to monthly variations of concentrations, with the difference that precipitation amounts gain further importance (Fig. 3.4). Average (2011-2020) monthly depositions of sulphate, nitrate, ammonium, the sum of the base cations calcium, magnesium and potassium and potential acidity are normally higher during the warm months when both concentrations and precipitations are highest. Compared to these values. Depositions of sulphate, nitrate, ammonium, base cation, potential acidity were average during 2019, while the depositions of the same parameters measured during 2020 were lower because of the already discussed lower concentrations and the lower precipitation volumes.

Figure 3.2 Monthly precipitations

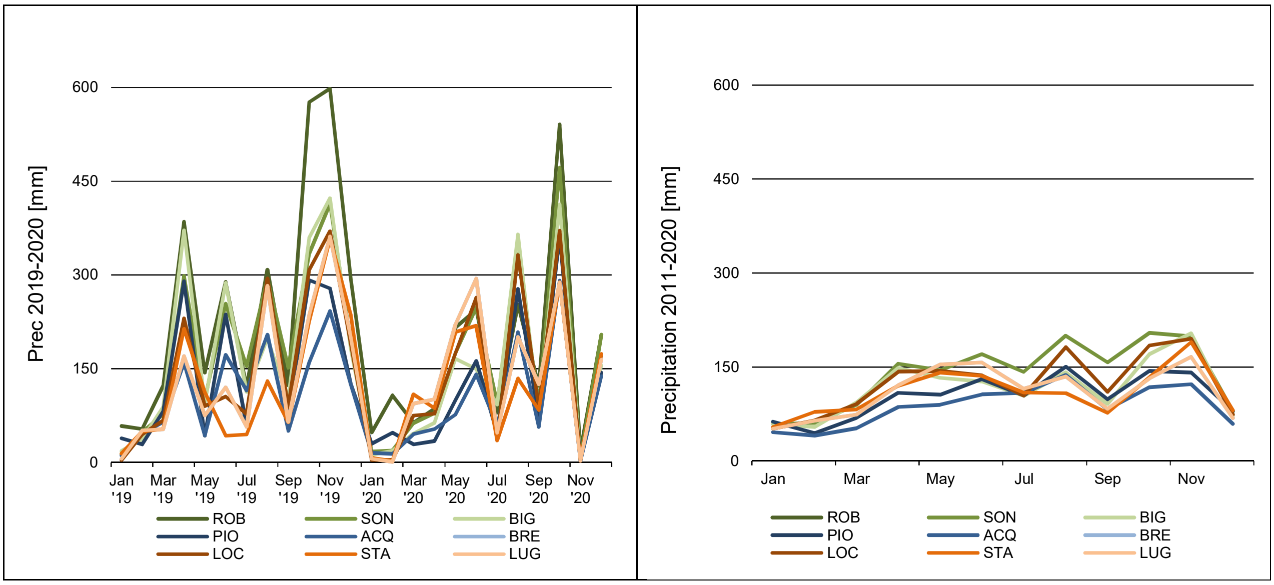
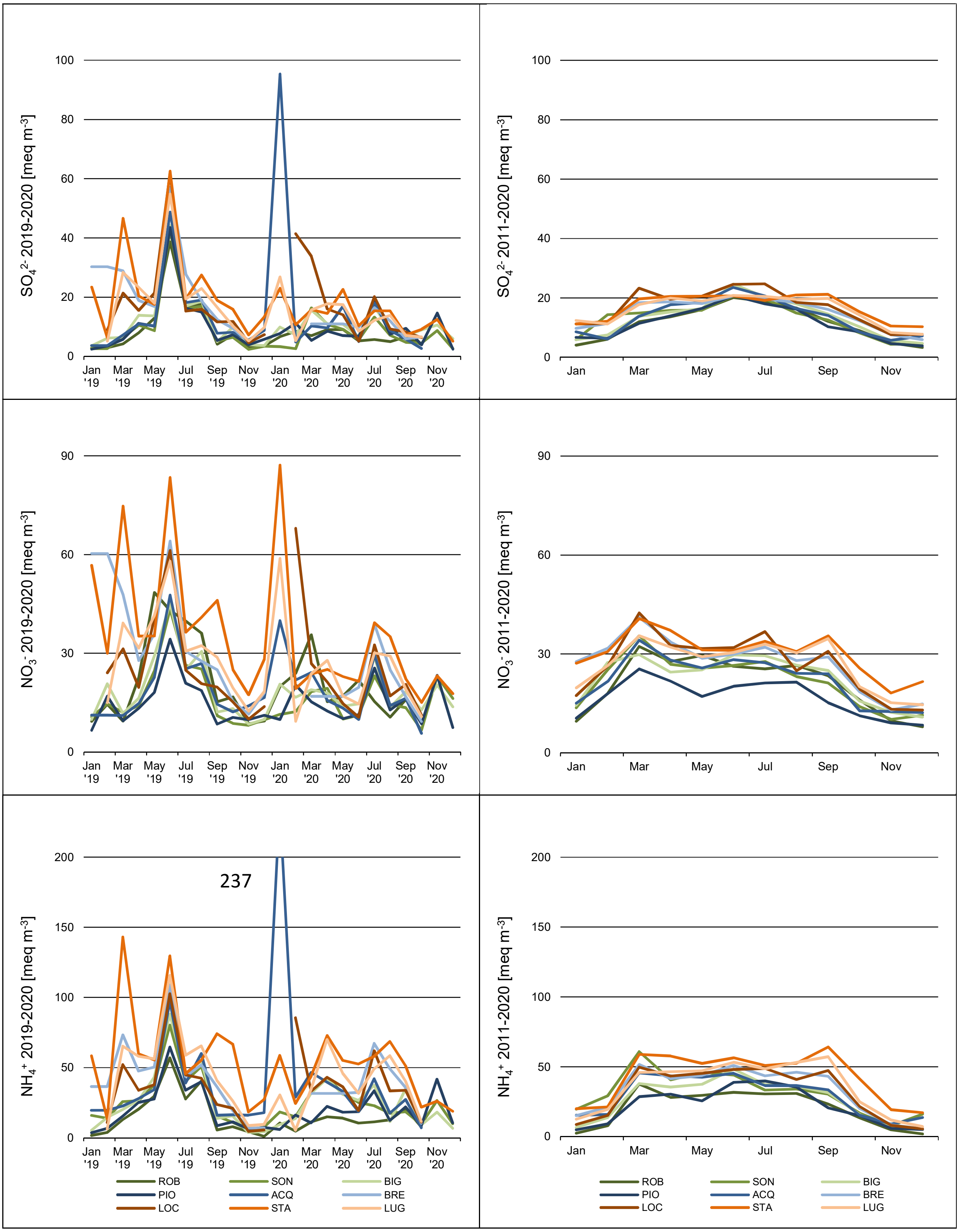


Figure 3.3 Seasonal variations of monthly average rainwater concentrations



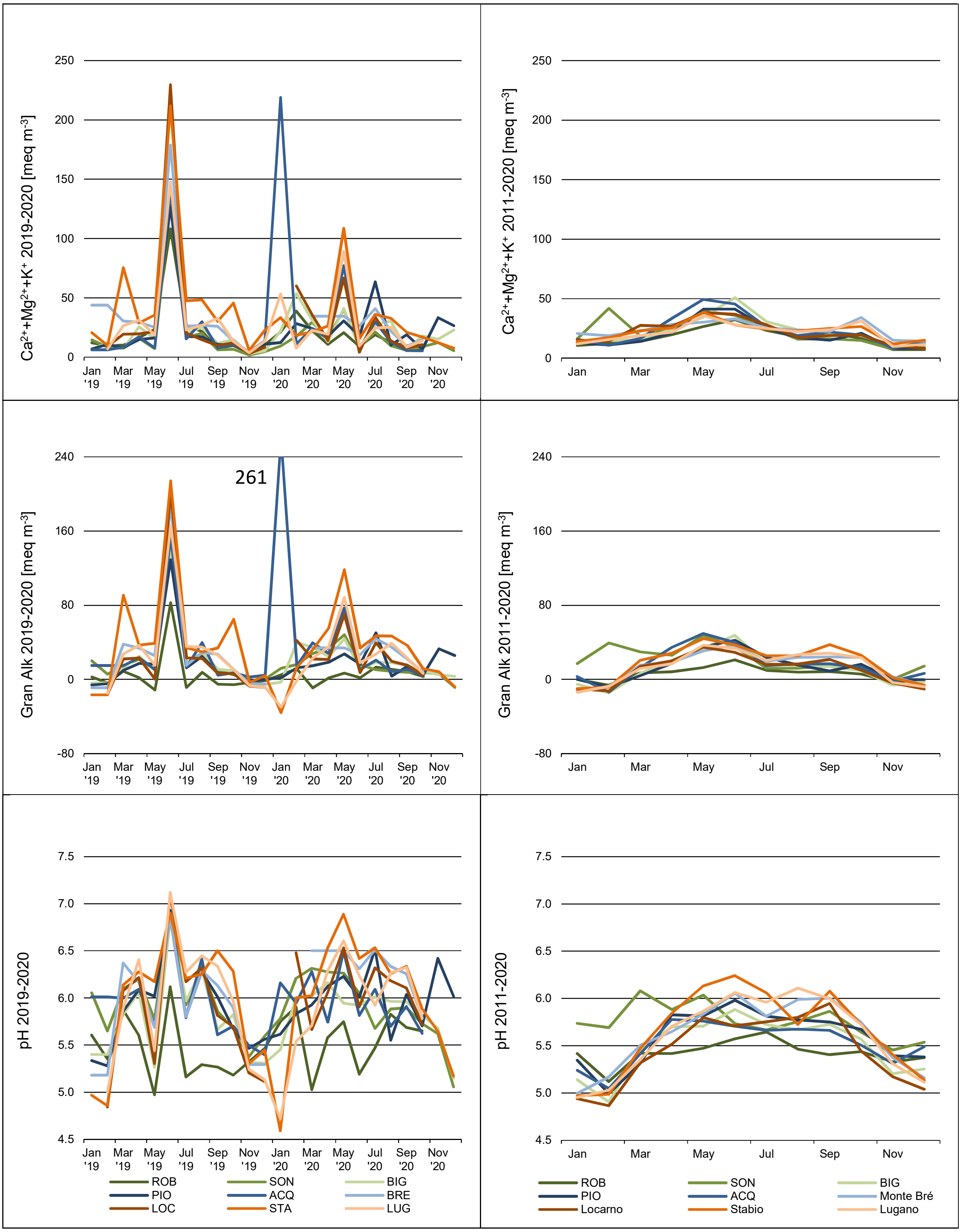
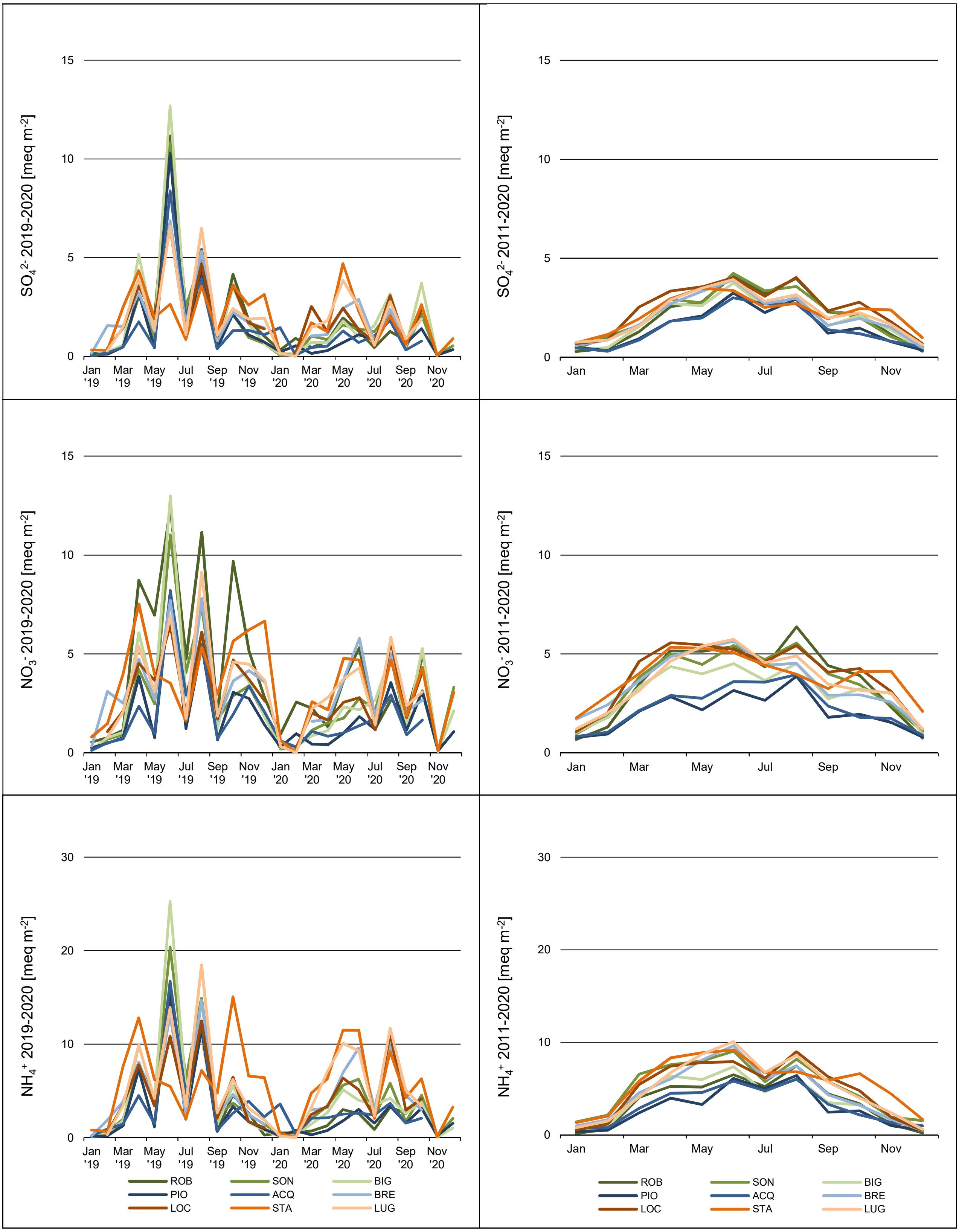
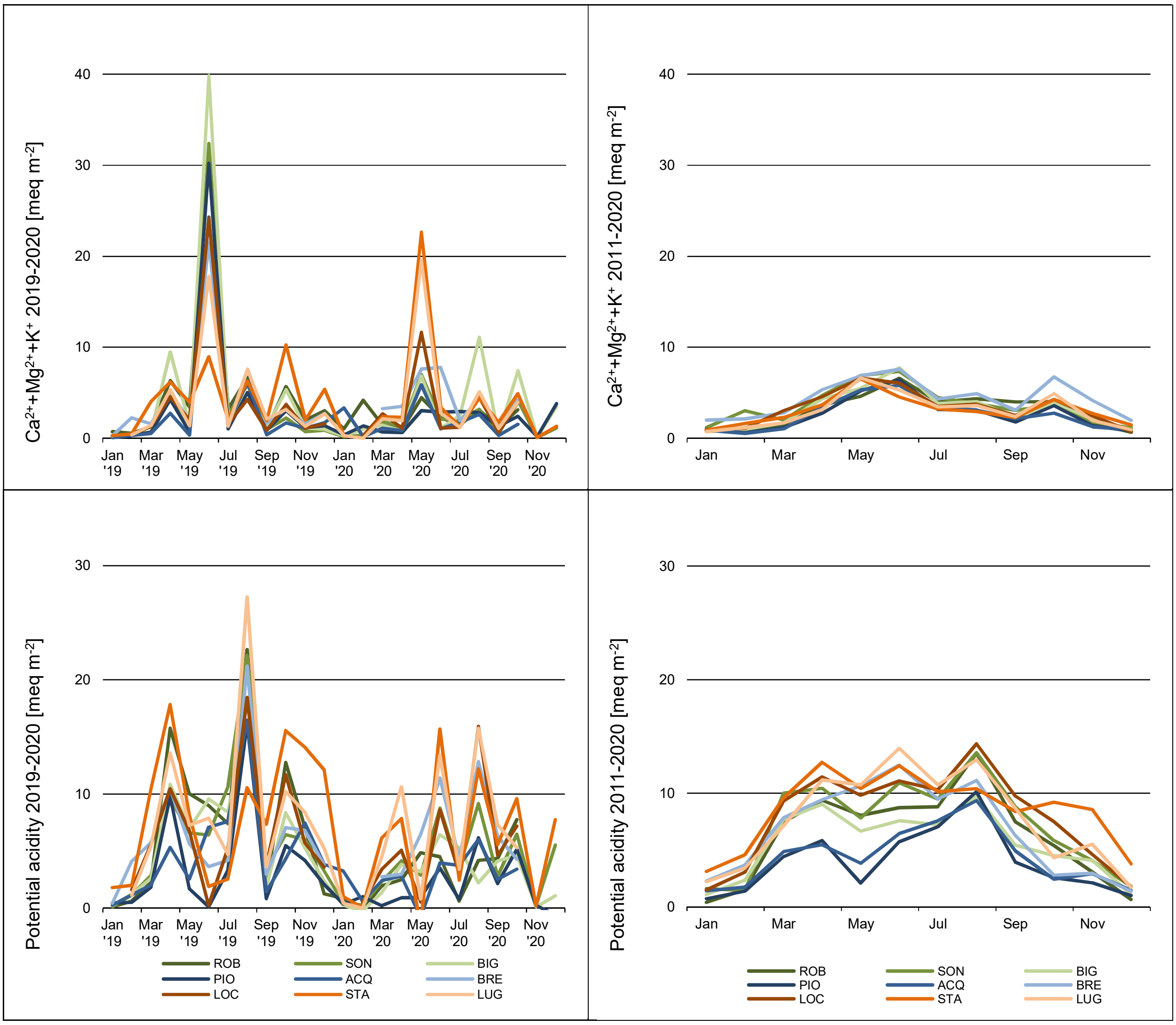

Ca²⁺+Mg²⁺+K⁺ 2019-2020 [meq m⁻³]
Ca²⁺+Mg²⁺+K⁺ 2011-2020 [meq m⁻³]
Gran Alk 2019-2020 [meq m⁻³]
261
Gran Alk 2011-2020 [meq m⁻³]
pH 2019-2020
pH 2011-2020
Jan '19 Mar '19 May '19 Jul '19 Sep '19 Nov '19 Jan '20 Mar '20 May '20 Jul '20 Sep '20 Nov '20
Jan Mar May Jul Sep Nov
ROB SON BIG
PIO ACQ BRE
LOC STA LUG
ROB SON BIG
PIO ACQ Monte Bré
Locarno Stabio Lugano

Figure 3.4 Seasonal variations of monthly wet deposition

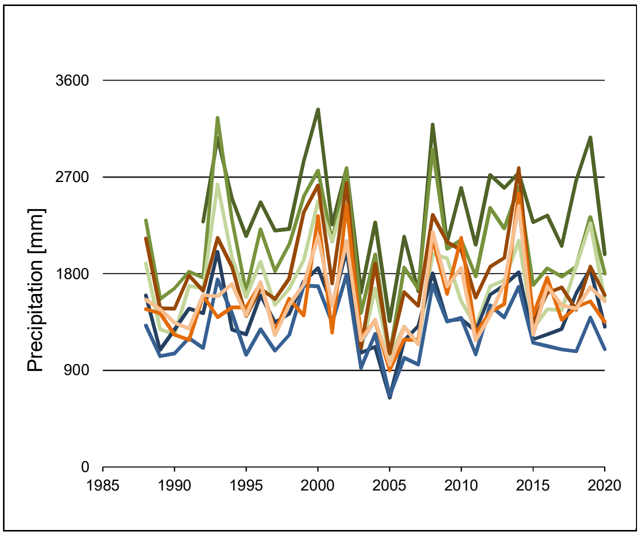



$Ca^{2+}+Mg^{2+}+K^{+}$ 2019-2020 [meq m^{-2}]
$Ca^{2+}+Mg^{2+}+K^{+}$ 2011-2020 [meq m^{-2}]
Potential acidity 2019-2020 [meq m^{-2}]
Potential acidity 2011-2020 [meq m^{-2}]
0
10
20
30
40
Jan '19
Mar '19
May '19
Jul '19
Sep '19
Nov '19
Jan '20
Mar '20
May '20
Jul '20
Sep '20
Nov '20
Jan
Mar
May
Jul
Sep
Nov
ROB
SON
BIG
PIO
ACQ
BRE
LOC
STA
LUG

Temporal variations

The amount of yearly precipitations at each sampling site is presented in Fig. 3.5. Yearly precipitation was higher than average during 2019 and average during 2020 at the usually "wet" sites (northwestern part of the Canton) Bignasco, Sonogno, Robiei but also at Piotta. At the southern sites Lugano, Monte Brè, Stabio but also at Acquarossa and at Locarno yearly precipitations during 2019 and 2020 were average. Annual mean rainwater concentrations and depositions of the main chemical parameters since 1988 are shown in Fig. 3.6.

Figure 3.5 Yearly precipitations



Temporal trends for some of the measured parameters are immediately visible. The most pronounced trend show concentrations and depositions of sulphate with a steep decrease after 1990 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 nitrate and even smaller for ammonium. Concentrations and depositions of the base cations calcium, magnesium and potassium also decreased and alkaline rain events became less frequent.

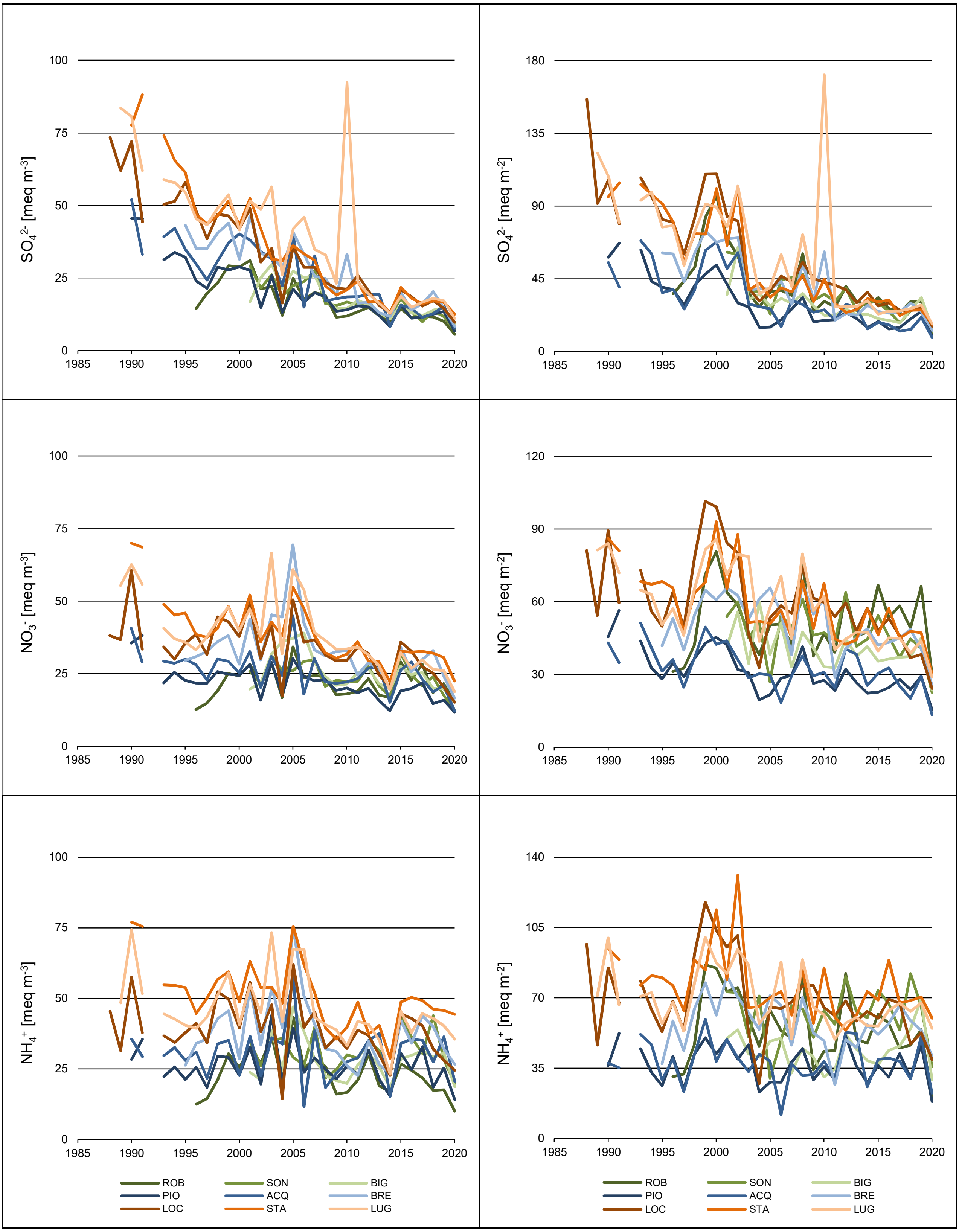
Concentrations of Gran alkalinity, that can be approximated by the difference of the sum of base cations plus ammonia and the acid anions, increased at most sites. In general, concentrations of Gran alkalinity increased from values around -40 and -30 meq m^{-3} to values around 20 meq m^{-3} with exception of the high altitude mountain site Robiei, where it stabilized around 5 meq m^{-3}. Consequently to the Gran alkalinity trend, average pH increased from values around 4.3 in the 1990's to values ranging between 5.6 and 5.8 at all sites except Robiei, that has an average pH over the last five years of 5.4.

Trends of rainwater concentrations were analysed for four different time periods: from 1988-1991 until 2020, from 1988-1991 until 2000, from 2000 until 2010, and from 2010 until 2020 (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.

Sulphate concentrations decreased significantly at all sites. The highest change in concentrations occurred at the most polluted sites Locarno Monti, Lugano and Stabio and during the first two analysed time periods (from 1988-1991 until 2000 and from 2000 until 2010). After 2010 concentrations of sulphate decreased less and significantly only at five sites. Concentrations of nitrate decreased significantly at all sites with exception of the high altitude mountain site Robiei. Similar to concentrations of sulphate, the decrease in concentrations of nitrate seems to be less pronounced in the more recent decade (2010-2020). Concentrations of ammonium decreased significantly at five sites and mainly between 2000 and 2010. The sum of calcium, magnesium and potassium also decreased significantly at five sites and for most of them mainly during 2000-2010. Also concentrations of hydrogen decreased significantly at all sites mainly at the beginning of the monitoring period (1980/1990-2000), but even during the last decade concentrations decreased significantly at six sites although less dramatically. Similar behaved concentrations of Gran alkalinity with a significant increase at all sites mainly at the beginning of monitoring but still pronounced during the last decade with a significant increase at five site.

Deposition of sulphate and potential acidity decreased significantly at all sites, deposition of nitrate and hydrogen ions at eight sites, deposition of ammonium and base cations at four sites

Figure 3.6 Temporal variations of annual mean rainwater concentrations, depositions and rainwater pH



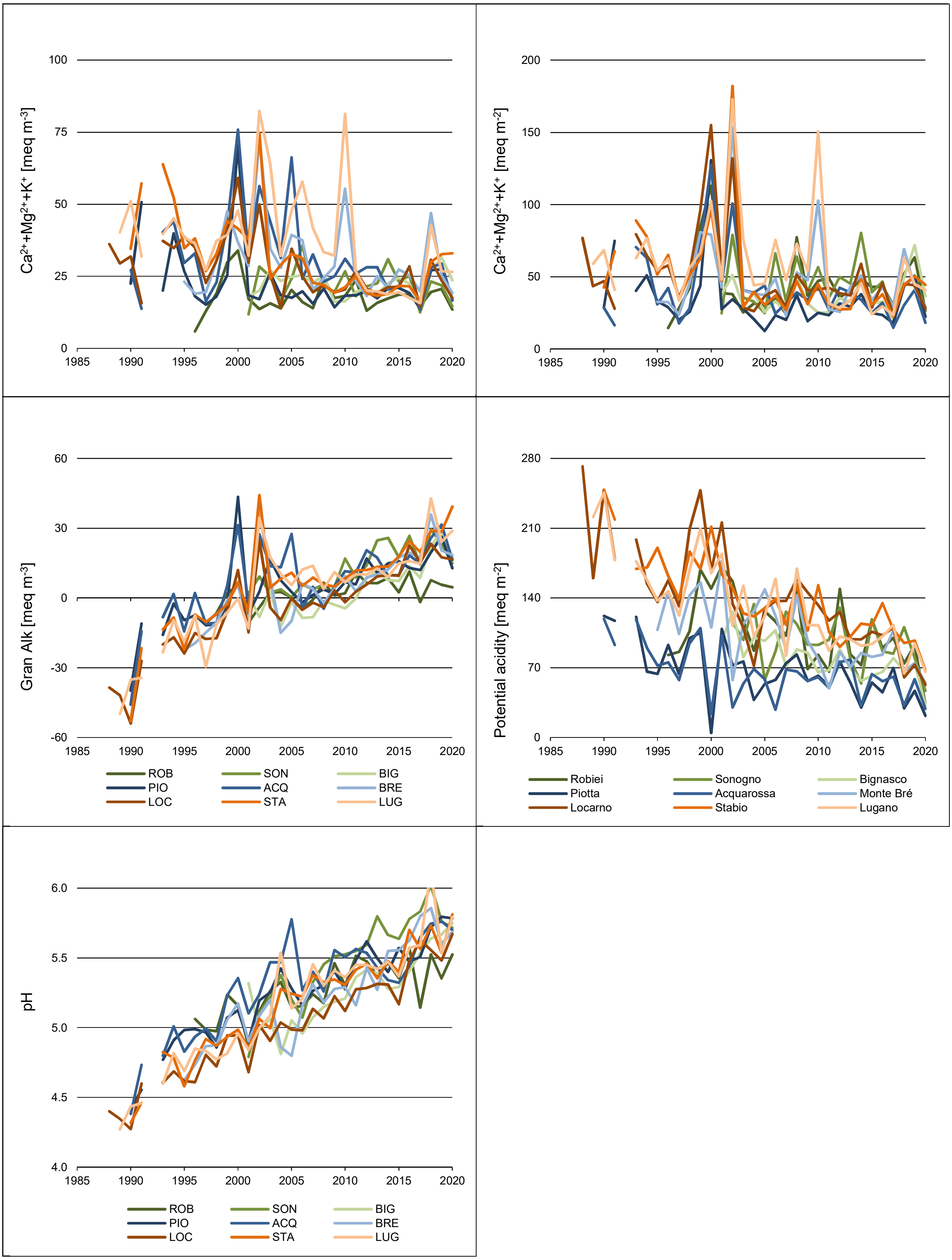

Ca2++Mg2++K+ [meq m-3]
Ca2++Mg2++K+ [meq m-2]
Gran Alk [meq m-3]
Potential acidity [meq m-2]
pH
ROB
PIO
LOC
SON
ACQ
STA
BIG
BRE
LUG
Robiei
Piotta
Locarno
Sonogno
Acquarossa
Stabio
Bignasco
Monte Bré
Lugano

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.

CONCENTRATIONS	Period	SO_4^{2-}	NO_3^-	NH_4^+	$Ca^{2+}+Mg^{2+}+K^+$	H^+	Gran Alk
(meq m^{-3} yr^{-1})		'80/'90-20	'80/'90-20	'80/'90-20	80/'90-20	80/'90-20	80/'90-20
ACQ	1990-2020	-1.17	-0.52	-0.19	-0.63	-0.34	1.26
BIG	2001-2020	-0.68	-0.66	-0.14	-0.07	-0.46	1.60
BRE	1995-2020	-1.16	-0.51	-0.16	-0.07	-0.53	1.92
LOC	1988-2020	-1.77	-0.83	-0.48	-0.47	-1.03	2.17
LUG	1989-2020	-1.89	-0.83	-0.46	-0.72	-0.65	1.96
PIO	1990-2020	-0.77	-0.52	-0.19	-0.35	-0.49	1.19
ROB	1996-2020	-0.62	-0.07	-0.25	-0.09	-0.22	0.53
SON	2001-2020	-0.61	-0.44	-0.07	-0.16	-0.21	1.27
STA	1990-2020	-1.86	-0.80	-0.40	-0.59	-0.52	2.03

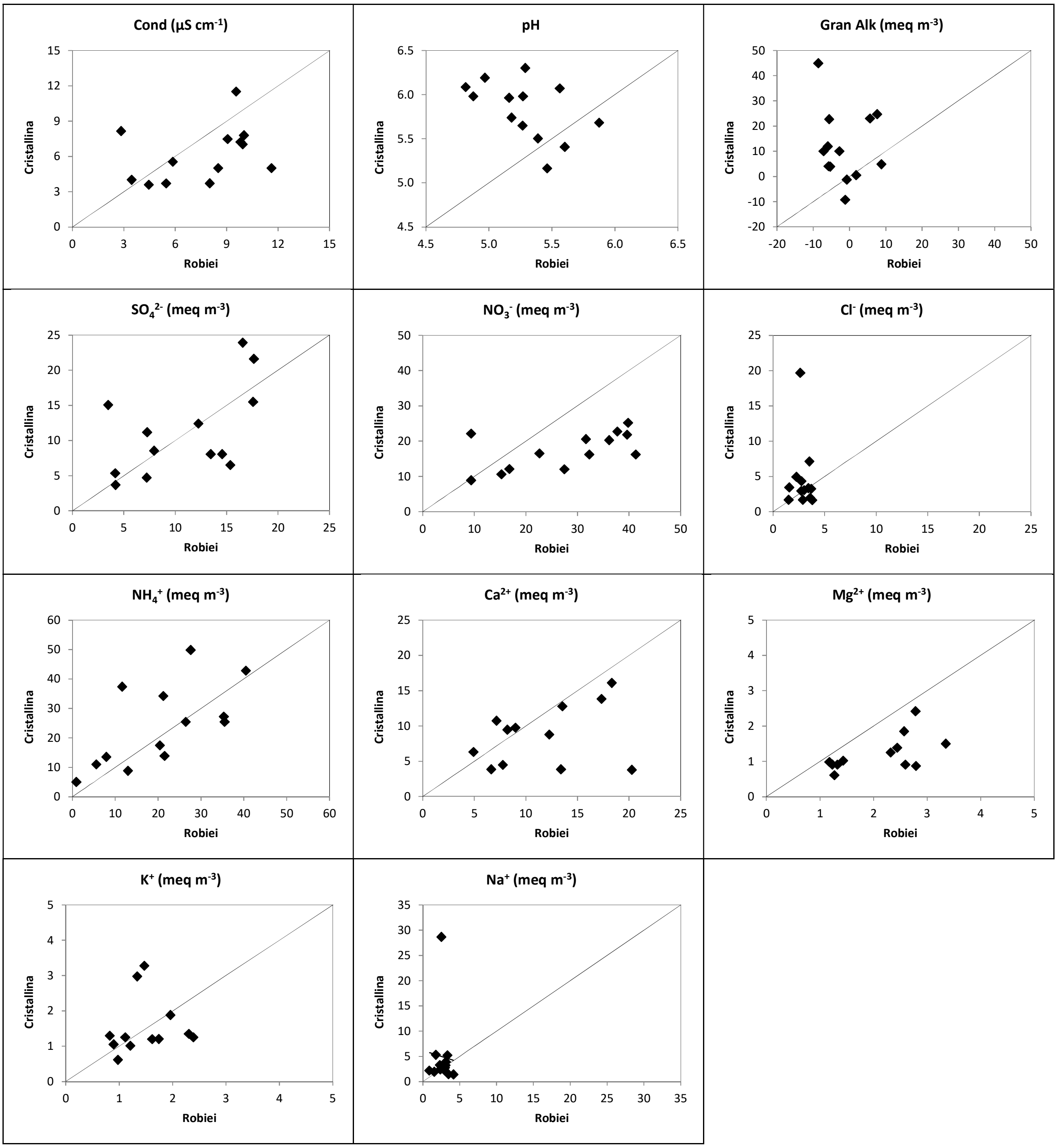
CONCENTRATIONS	Period	SO_4^{2-}			NO_3^-			NH_4^+			$Ca^{2+}+Mg^{2+}+K^+$			H^+			Gran Alk		
(meq m^{-3} yr^{-1})		'80/'90-00	'00-'10	'10-'20	'80/'90-00	'00-'10	'10-'20	'80/'90-00	'00-'10	'10-'20	80/'90-00	'00-'10	'10-'20	80/'90-00	'00-'10	'10-'20	80/'90-00	'00-'10	'10-'20
ACQ	1990-2020	-1.41	-2.14	-0.71	-1.04	-0.76	-0.49	-1.05	-0.93	0.13	-0.47	-2.09	-1.09	-2.29	-0.06	-0.14	4.61	-0.42	1.08
BIG	2001-2020		-1.27	-0.36		-1.19	-0.68		-1.20	0.09		-0.44	0.18		-0.56	-0.28		0.42	1.91
BRE	1995-2020		-1.65	-0.28		-0.63	-0.29		-0.77	0.78		-0.65	0.73		-0.48	-0.23		1.96	2.30
LOC	1988-2020	-2.40	-2.46	-0.70	-0.71	-1.58	-1.34	-0.53	-1.50	-0.25	-0.62	-1.25	-0.20	-3.48	-0.76	-0.27	2.56	0.98	1.96
LUG	1989-2020	-2.78	-3.07	-0.75	-1.22	-1.47	-0.75	-0.11	-1.69	0.26	0.09	-1.61	-0.20	-2.85	-0.42	-0.10	3.76	1.39	1.14
PIO	1990-2020	-1.43	-1.01	-0.27	-0.62	-0.58	-0.56	-0.11	-0.70	-0.09	-0.87	-0.89	0.44	-1.63	-0.31	-0.25	2.43	0.10	1.55
ROB	1996-2020		-1.17	-0.27		-0.43	0.12		-0.77	-0.30		-0.48	0.36		-0.28	-0.02		0.44	0.03
SON	2001-2020		-1.14	-0.49		-0.66	-0.55		-0.88	-0.22		-0.65	-0.19		-0.42	-0.08		0.57	0.74
STA	1990-2020	-3.44	-2.48	-0.26	-2.07	-1,11	-0.09	-0.85	-1.32	1.09	-2.17	-1.38	0.70	-2.65	-0.47	-0.08	4.30	1.72	1.94

DEPOSITIONS	Period	SO_4^{2-}	NO_3^-	NH_4^+	$Ca^{2+}+Mg^{2+}+K^+$	H^+	Potential acidity
(meq m^{-2} yr^{-1})		beginning-20	beginning-20	beginning-20	beginning-20	beginning-20	beginning-20
ACQ	1990-2020	-1.17	-0.66	-0.24	-0.54	-0.40	-1.46
BIG	2001-2020	-0.60	-0.50	-0.03	0.06	-0.43	-1.74
BRE	1995-2020	-1.30	-0.66	-0.20	-0.02	-0.69	-2.58
LOC	1988-2020	-2.34	-1.16	-0.56	-0.48	-1.45	-3.96
LUG	1989-2020	-2.35	-0.83	-0.27	-0.70	-0.94	-2.82
PIO	1990-2020	-0.68	-0.41	-0.12	-0.16	-0.48	-1.28
ROB	1996-2020	-1.20	-0.18	-0.37	-0.03	-0.40	-1.70
SON	2001-2020	-0.87	-0.77	-0.14	-0.14	-0.36	-1.74
STA	1990-2020	-2.29	-1.09	-0.40	-0.64	-0.73	-3.08

Comparison between the sampling sites Robiei and Cristallina hut

To have an idea how rainwater chemistry changes at altitudes above the until then highest sampling site Robiei (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.), aware that at this very isolated site sampling could be performed only intermittently, more precisely during the stay of the custodian. Fig. 3.7 shows the comparison between the monthly concentrations measured at the Cristallina hut and at Robiei from April 2017 to September 2017 and from April 2019 to December 2019. Concentrations of sulphate, ammonium, potassium, sodium and chloride were similar among the two sites, while concentrations of nitrate, calcium and magnesium were slightly lower at the more elevated Cristallina hut. Gran alkalinity and pH are often higher at the Cristallina hut.

Figure 3.7 Comparison between the rainwater chemistry collected at Robiei and at the Cristallina hut during 2017 and 2019.

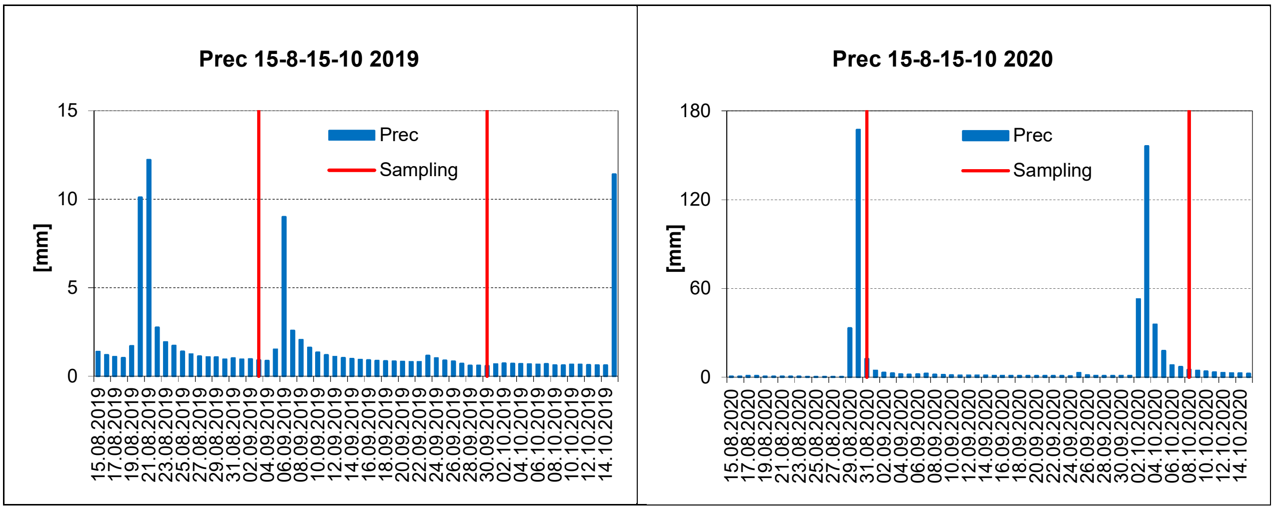


3.5.2 Alpine lakes

Spatial variations

During the last two years, lake sampling occurred on 3rd and 30th September 2019, 31th August 2020 and 8th October 2020. Fig. 3.8 shows the daily precipitation volumes at Robiei during the lake sampling periods. During 2019 both samplings were preceded by continuous light rainfalls, while during 2020 both samplings were immediately preceded by heavy rain events following a dry period.

Figure 3.8 Daily precipitation at Robiei during the sampling months in 2019 and 2020 <. Sampling dates are indicated with red bars.



Average autumn concentrations of the main chemical parameters measured in lake surface water are presented in Tab. 3.4. During 2019 conductivity at 25°C varied between 7 and 32 µS cm^{-1}, Gran alkalinity between -1 and 88 meq m^{-3}, pH between 5.6 and 7.2, calcium between 22 and 165 meq m^{-3}, sulphate between 12 and 213 meq m^{-3}, nitrate between 4 and 26 meq m^{-3}, dissolved organic carbon between 0.3 and 1.4 mg C l^{-1}, reactive dissolved silica between 0.9 and 2.9 mg SiO_2 l^{-1} and soluble aluminium between 3 and 25 µg l^{-1}. 15% of the autumn samples were characterized by total alkalinities below 20 meq m^{-3} and 13% by pH's below 6. During 2020 conductivity at 25°C varied between 7 and 25 µS cm^{-1}, Gran alkalinity between -1 and 82 meq m^{-3}, pH between 5.6 and 7.1, calcium between 18 and 149 meq m^{-3}, sulphate between 11 and 155 meq m^{-3}, nitrate between 6 and 28 meq m^{-3}, dissolved organic carbon between <0.2 and 1.2 mg C l^{-1}, reactive dissolved silica between 0.9 and 2.8 mg SiO_2 l^{-1} and soluble aluminium between 3 and 55 µg l^{-1}. 18% of the autumn samples were characterized by total alkalinities below 20 meq m^{-3} and 18% by pH's below 6. In general, concentrations of base cations, sulphate, nitrate were slightly lower and pH and metals higher during 2020 compared to 2019. The lower values are caused by dilution of the groundwater and lake water with rainwater, while the higher values are the consequence of soil leaching during the heavy rain event preceding sampling. Particularly interesting is the strong increase of total aluminium and total iron leaching after heavy rain events in lakes with rock glaciers in their catchment (LEI, MOR, MOG), suggesting accumulation of these metals in the catchment as a consequence of the oxidation of freshly exposed pyrite in the area of the melting rock glacier.

Table 3.4 Average lake surface water concentrations in autumn 2019 and 2020. 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
Cond 25°C (µS cm^{-1})	2019	7.1	7.9	22.9	8.9	7.6	31.8	14.1	20.0	8.1	8.0	15.8	13.9	12.8	7.0	9.3	11.6	8.6	8.8	8.5	15.1
	2020	7.0	6.9	22.7	8.5	6.9	24.5	13.4	16.2	9.0	7.8	17.1	10.7	12.1	6.9	9.0	9.2	7.1	9.1	8.5	14.3
pH	2019	5.8	6.0	7.0	6.4	5.6	6.5	6.7	7.2	6.7	6.7	6.9	7.0	7.1	6.5	6.7	6.7	6.8	6.5	6.3	7.0
	2020	5.6	5.9	6.7	6.3	5.6	6.3	6.5	6.5	6.7	6.7	6.9	6.6	7.1	6.6	6.7	6.5	6.3	6.6	5.9	6.8
Gran Alk (meq m^{-3})	2019	11	10	80	20	-1	33	50	73	33	35	71	66	79	30	43	53	50	37	27	88
	2020	3	20	70	21	-1	25	46	39	44	42	76	50	79	33	47	37	28	43	16	82
Ca^{2+} (meq m^{-3})	2019	23	39	158	54	22	165	84	116	51	52	107	104	96	46	65	81	51	56	44	98
	2020	18	31	149	51	19	115	75	85	56	50	111	77	88	44	62	57	38	57	36	88
Mg^{2+} (meq m^{-3})	2019	7	5	14	6	9	64	18	25	7	7	14	8	6	5	7	9	9	8	11	17
	2020	6	5	14	6	8	46	17	22	7	6	15	7	5	5	6	7	7	8	11	16
Na^{+} (meq m^{-3})	2019	12	12	21	11	7	23	15	27	10	10	15	12	18	10	13	14	16	15	14	20
	2020	10	10	20	10	7	18	14	19	12	10	16	10	17	11	13	12	12	16	12	19
K^{+} (meq m^{-3})	2019	4	3	11	5	5	14	12	12	6	6	10	6	6	3	4	6	4	3	7	11
	2020	4	3	12	4	5	12	11	11	7	6	11	5	5	4	4	6	5	3	7	11
NH_4^{+} (meq m^{-3})	2019	2	0	0	1	1	1	0	0	0	1	1	0	0	1	1	0	0	1	1	1
	2020	1	0	1	1	1	1	1	1	0	0	1	0	0	1	1	0	3	3	1	1
SO_4^{2-} (meq m^{-3})	2019	21	24	101	35	35	213	60	84	21	19	58	43	17	12	15	23	20	23	24	32
	2020	16	20	98	32	31	155	56	76	23	17	61	32	15	11	14	18	14	21	17	28
NO_3^{-} (meq m^{-3})	2019	17	23	16	16	11	13	13	16	15	15	11	15	20	17	23	26	4	15	18	18
	2020	16	17	14	12	8	11	12	12	8	6	7	9	14	13	17	19	13	11	28	12
NO_2^{-}-N (µg l^{-1})	2019	1	2	2	3	1	1	2	2	2	2	2	1	3	2	3	2	1	1	2	2
	2020	0	0	0	1	1	1	1	1	1	1	1	1	2	1	1	0	0	1	1	1
Cl^{-} (meq m^{-3})	2019	4	3	3	3	3	3	3	4	3	2	3	2	3	3	3	3	4	5	3	5
	2020	5	3	3	3	2	3	3	3	2	2	2	2	3	3	3	3	5	4	3	4
SRP (µg P l^{-1})	2019	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2
	2020	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2
P_{tot} (µg P l^{-1})	2019	<32	<32	<32	<32	<32	<32	<32	<32	<32	<32	<32	<32	<32	<32	<32	<32	<32	<32	<32	<32
	2020	<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})	2019	0.32	0.30	0.24	0.23	0.16	0.20	0.19	0.28	0.27	0.24	0.22	0.22	0.29	0.24	0.33	0.35	0.22	0.24	0.30	0.31
	2020	0.36	0.30	0.27	0.24	0.20	0.26	0.26	0.27	0.27	0.24	0.21	0.21	0.31	0.25	0.31	0.36	0.26	0.25	0.48	0.30
DOC (mg C l^{-1})	2019	1.4	0.6	0.4	0.4	0.3	0.5	0.4	0.5	0.6	0.6	0.4	0.5	0.5	0.4	0.4	0.5	1.0	0.7	0.9	0.7
	2020	1.2	0.6	0.3	0.3	<0.2	0.4	0.4	0.5	0.5	0.6	0.3	0.4	0.5	0.3	0.4	0.4	1.0	0.9	1.0	0.7
SiO_2 (mg l^{-1})	2019	1.8	1.8	2.9	1.3	0.9	2.2	1.9	2.7	1.2	1.2	1.9	1.5	2.5	1.5	1.6	2.1	2.3	1.9	1.8	2.7
	2020	1.4	1.5	2.8	1.3	0.9	1.7	1.7	2.1	1.4	1.2	2.0	1.1	2.3	1.5	1.5	1.9	1.9	1.9	1.9	2.6

Parameter	Year	STA	TOM	POR	BAR	GAR	LEI	MOR	MOG	INF	SUP	NER	FRO	ANT	CRO	ORS	SCH	POZ	SFI	SAS	ALZ
Al_{sol} (µg l^{-1})	2019	24.8	13.2	3.4	4.0	21.8	6.4	4.7	6.0	6.1	5.0	4.6	5.9	6.5	3.1	6.9	6.5	19.1	14.0	17.4	9.2
	2020	55.0	25.7	3.7	4.7	18.0	12.7	9.9	12.1	7.8	8.5	3.6	8.6	9.4	3.3	5.7	9.9	28.2	23.9	37.2	12.6
Al_{tot} (µg l^{-1})	2019	38.8	17.5	4.8	7.4	29.8	25.4	21.5	12.4	16.9	17.0	14.3	12.0	10.4	7.5	11.5	11.9	32.6	21.2	30.7	11.6
	2020	64.3	36.2	5.3	8.1	22.9	339.7	135.4	92.4	15.5	18.1	7.6	13.2	24.0	8.9	44.8	16.0	34.3	34.4	44.5	15.8
Pb_{sol} (µg l^{-1})	2019	<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
	2020	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
Pb_{tot} (µg l^{-1})	2019	<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
	2020	0.2	<0.1	<0.1	<0.1	<0.1	0.5	0.2	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
Cd_{sol} (µg l^{-1})	2019	<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
	2020	<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})	2019	<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
	2020	<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})	2019	0.2	<0.2	0.2	<0.1	0.2	0.3	0.3	0.3	0.1	0.1	0.1	0.1	<0.1	<0.1	<0.1	<0.1	0.1	<0.1	0.2	<0.1
	2020	0.3	0.3	0.2	<0.2	0.2	0.7	0.6	0.6	0.1	0.1	0.2	0.2	0.1	0.1	0.1	0.1	0.1	0.1	0.2	0.1
Cu_{tot} (µg l^{-1})	2019	0.2	0.2	0.2	<0.1	0.2	0.4	0.3	0.3	0.1	0.3	0.2	0.2	<0.1	<0.1	<0.1	<0.1	0.1	<0.1	0.2	<0.1
	2020	0.3	0.3	0.2	<0.2	0.3	2.0	1.0	1.0	0.2	0.2	0.2	0.2	<0.1	<0.1	<0.1	0.1	0.1	<0.1	0.2	<0.1
Zn_{sol} (µg l^{-1})	2019	1.5	1.2	0.4	0.5	1.4	0.9	0.6	0.5	0.5	0.5	0.4	0.5	0.3	0.6	0.5	0.8	0.5	1.0	1.1	0.5
	2020	1.9	0.8	0.3	0.4	1.1	1.1	0.5	0.8	0.3	0.4	0.3	0.6	<0.2	0.2	0.4	0.5	0.6	0.7	1.2	0.6
Zn_{tot} (µg l^{-1})	2019	1.5	1.8	0.5	0.6	1.5	1.1	0.7	0.7	0.7	0.6	0.5	0.5	0.4	0.6	0.7	1.0	1.2	1.8	1.6	1.1
	2020	2.0	0.9	0.3	0.4	1.2	2.2	1.0	1.3	0.4	0.5	0.3	0.7	0.3	0.3	0.5	0.5	0.7	0.9	1.3	0.5
Cr_{sol} (µg l^{-1})	2019	<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
	2020	<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	<0.1	<0.1	<0.1
Cr_{tot} (µg l^{-1})	2019	<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
	2020	<0.1	<0.1	<0.1	<0.1	<0.1	0.4	0.2	0.2	<0.1	<0.1	<0.1	<0.2	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Ni_{sol} (µg l^{-1})	2019	<0.2	<0.1	<0.1	0.1	1.3	8.1	0.4	0.6	<0.1	<0.1	0.2	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	0.2	<0.1
	2020	0.2	0.1	<0.1	<0.1	1.2	7.6	0.5	1.0	<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})	2019	0.2	0.1	<0.1	0.1	1.3	8.1	0.4	0.6	<0.1	<0.1	0.2	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	0.2	<0.1
	2020	0.2	0.1	<0.1	<0.1	1.2	8.2	0.7	1.1	<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})	2019	<2.0	<1.1	<1.0	<1.0	9.1	6.6	3.4	3.6	<1.0	<1.0	1.3	<1.1	<1.0	<1.0	<1.0	<1.0	2.7	1.9	8.1	1.3
	2020	12.3	1.7	<1.2	1.0	5.9	8.9	8.0	6.6	1.6	2.0	<1.1	3.4	<1.0	<1.0	1.5	<1.4	4.8	3.9	7.4	2.6
Fe_{tot} (µg l^{-1})	2019	10.4	2.9	1.2	2.6	11.3	23.9	28.4	16.8	6.2	9.3	7.5	5.0	2.9	2.3	3.4	4.3	8.1	4.0	20.4	2.9
	2020	21.5	7.0	<2.2	3.4	10.0	438.3	144.3	86.7	8.9	14.2	4.9	7.0	12.7	3.5	37.4	4.6	8.7	10.3	11.6	4.5

Fig. 3.9 compares the main parameters measured during 2019 and 2020 with their mean values from 2011 to 2020.

Highest concentrations of sulphate were measured in lakes which may have sulphur sources in their catchments (Lago della Capannina Leit, Lago dei Porchieirsc, Lago di Mognòla, Lago Nero, Lago di Morghirolo). Because deposition of sulphate does not differ greatly among lakes, concentrations of sulphate in the other lakes were similar to each other.

Similar as observed for sulphate, the marginal differences in nitrate concentrations in rainwater did not explain differences in lake nitrate concentrations. These are rather determined by the retention capacity of the lakes catchments.

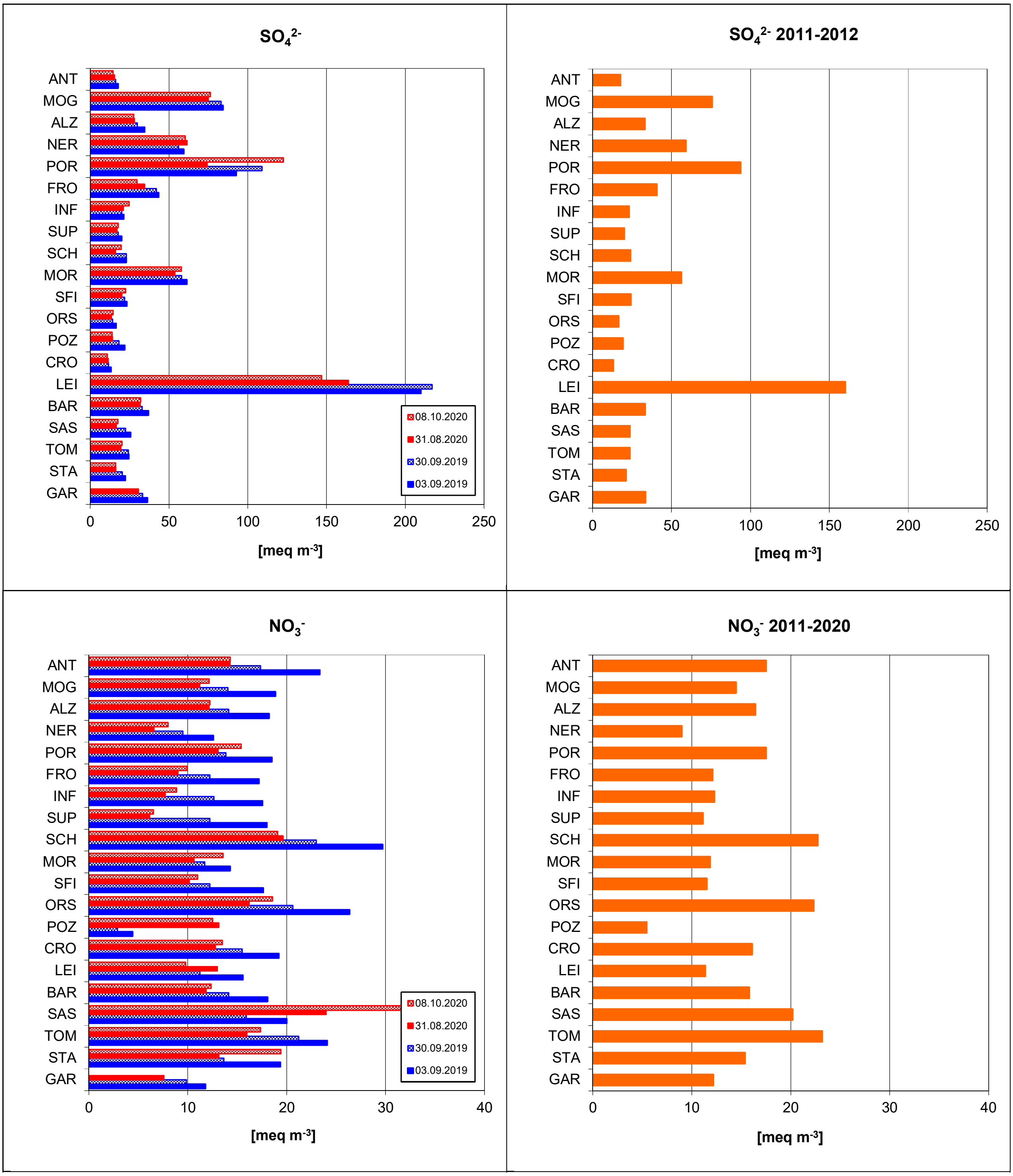
High concentrations of calcium and magnesium normally characterize lakes with elevated alkalinities and pH’s, as well. Lago Leit again differs from this tendency and has relatively high concentrations of calcium and magnesium compared to its alkalinity and pH.

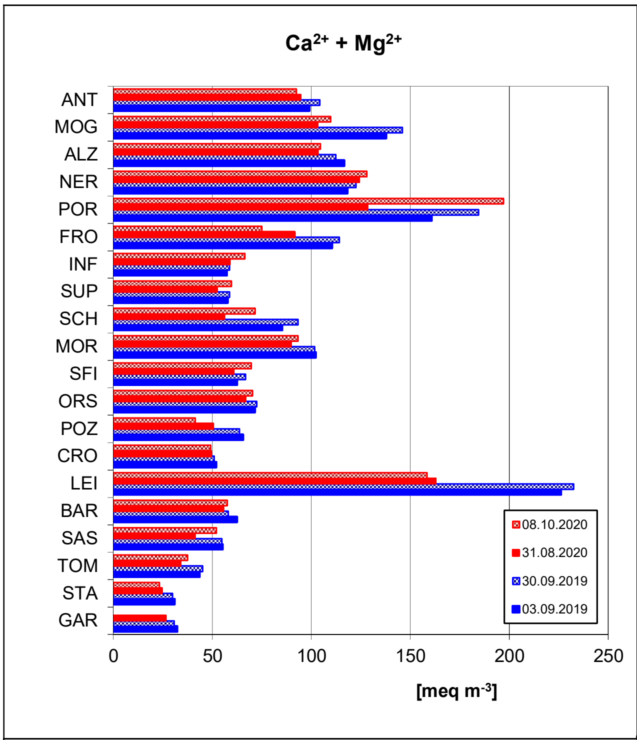
Only Laghetto Gardiscio and Lago del Starlaresc da Sgiof during one occasion had Gran alkalinities below 0 meq m^{-3}, while alkalinities constantly above 50 meq m^{-3} were measured only in Lago dei Porchieirsc, Laghetto d’Antabia, Lago d’Alzasca and Lago Nero. All other 16 lakes were at least temporary sensitive to acidification (0 < alkalinity < 50 meq m^{-3}).

In general, lakes with low pH’s are characterized by relatively high concentrations of aluminium (Lago del Starlaresc da Sgiof: 5-58 µg l^{-1}; Laghetto Gardiscio: 18-25 µg l^{-1}, Lago di Tomè: 8-28 µg l^{-1}, Lago Sascòla: 15-41 µg l^{-1}).

Concentrations of DOC were always low (< 1.5 mg C l^{-1}). Shallow lakes situated at lower altitudes are characterized by slightly higher values of DOC (Lago del Starlaresc da Sgiof, Lago dei Pozzöi, Lago Sascola.

Figure 3.9 Concentrations of the main chemical parameters in 20 Alpine lakes during 2019 and 2020 and their average autumn values between 2011 and 2020.




Ca²⁺ + Mg²⁺
ANT
MOG
ALZ
NER
POR
FRO
INF
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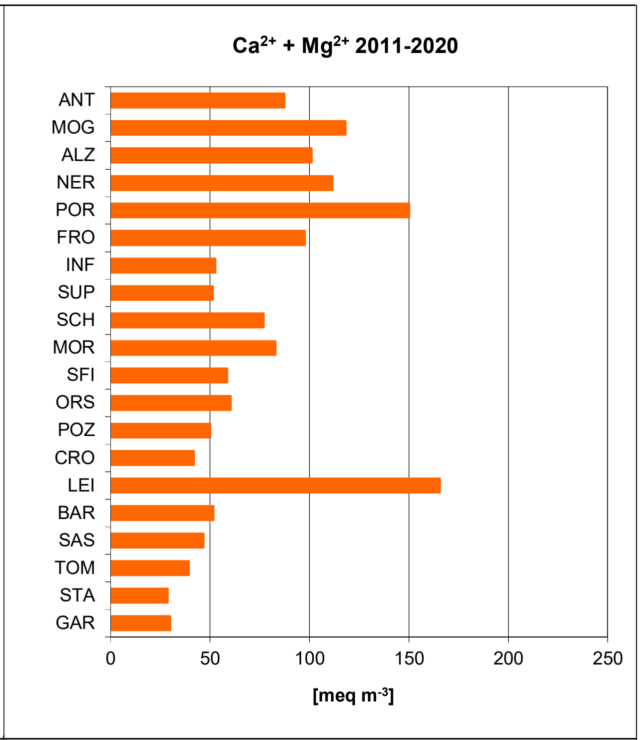
MOR
SFI
ORS
POZ
CRO
LEI
BAR
SAS
TOM
STA
GAR
0
50
100
150
200
250
[meq m⁻³]
08.10.2020
31.08.2020
30.09.2019
03.09.2019


Ca²⁺ + Mg²⁺ 2011-2020
ANT
MOG
ALZ
NER
POR
FRO
INF
SUP
SCH
MOR
SFI
ORS
POZ
CRO
LEI
BAR
SAS
TOM
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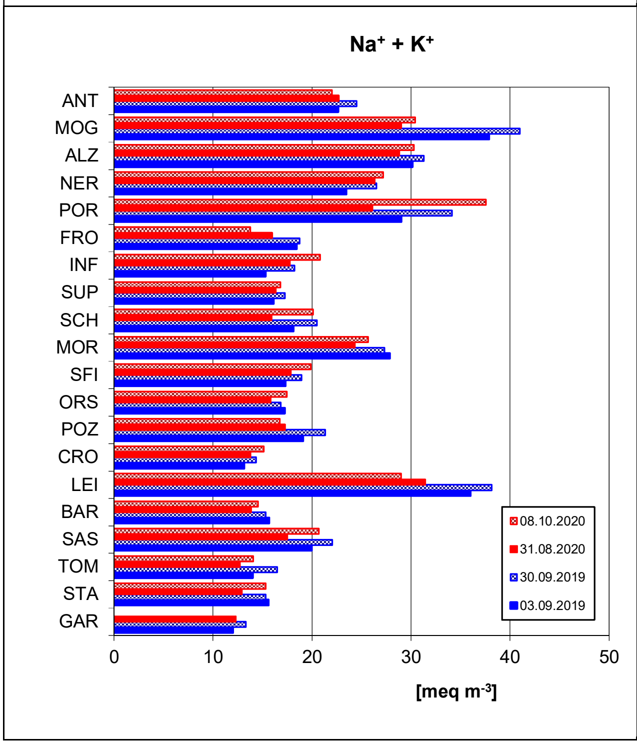
GAR
0
50
100
150
200
250
[meq m⁻³]


Na⁺ + K⁺
ANT
MOG
ALZ
NER
POR
FRO
INF
SUP
SCH
MOR
SFI
ORS
POZ
CRO
LEI
BAR
SAS
TOM
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GAR
0
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20
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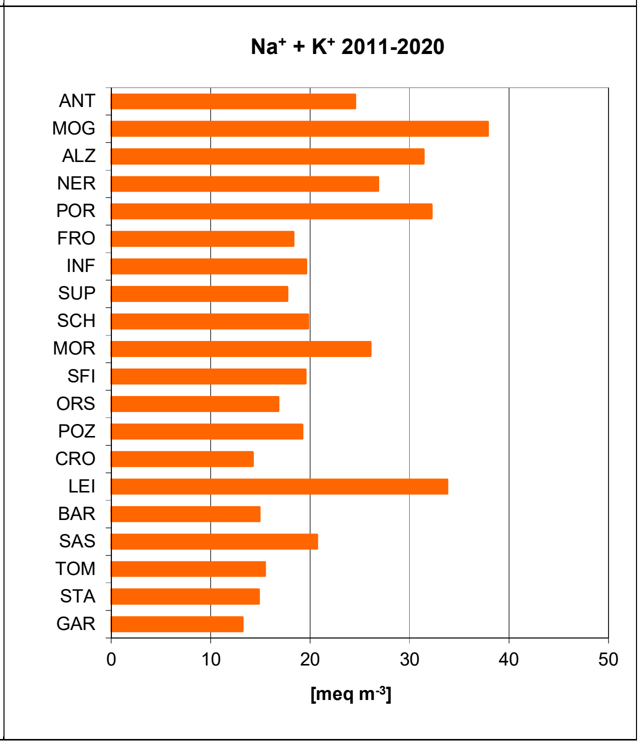
40
50
[meq m⁻³]
08.10.2020
31.08.2020
30.09.2019
03.09.2019


Na⁺ + K⁺ 2011-2020
ANT
MOG
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FRO
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MOR
SFI
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SAS
TOM
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GAR
0
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20
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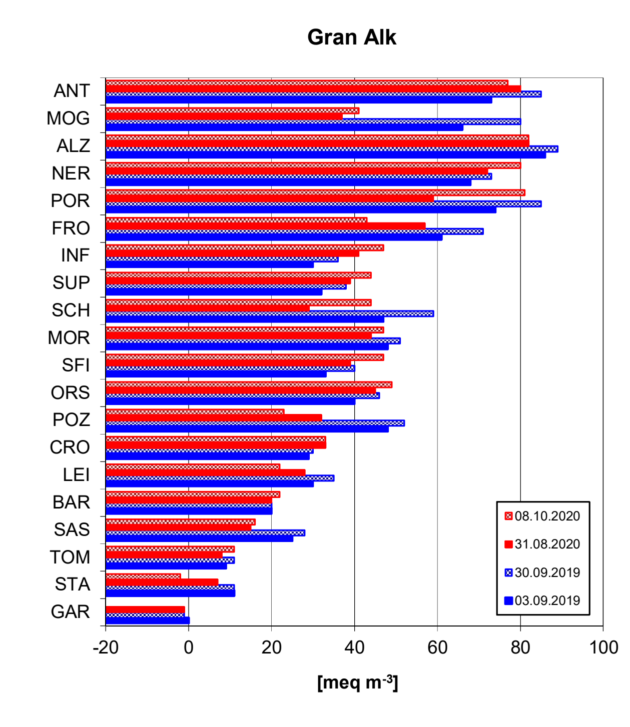
40
50
[meq m⁻³]


Gran Alk
ANT
MOG
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NER
POR
FRO
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ORS
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CRO
LEI
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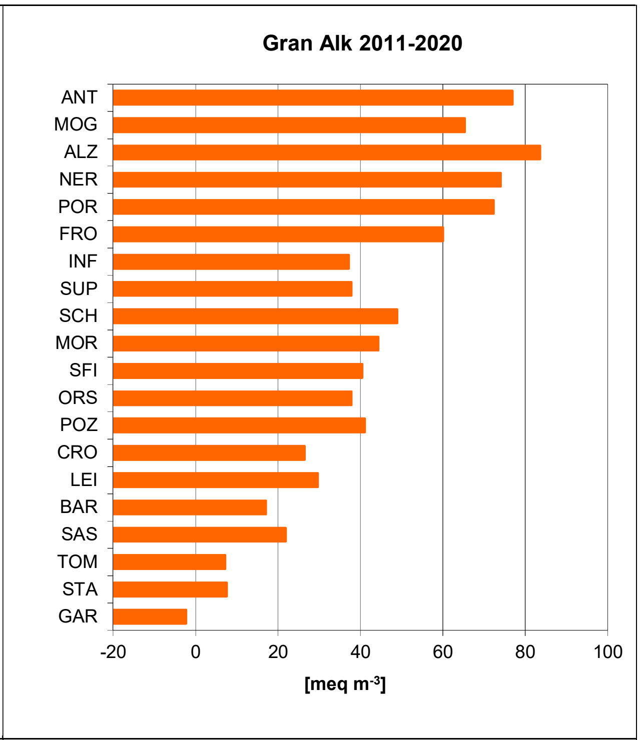
SAS
TOM
STA
GAR
08.10.2020
31.08.2020
30.09.2019
03.09.2019
-20
0
20
40
60
80
100
[meq m-3]


Gran Alk 2011-2020
ANT
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BAR
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GAR
-20
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20
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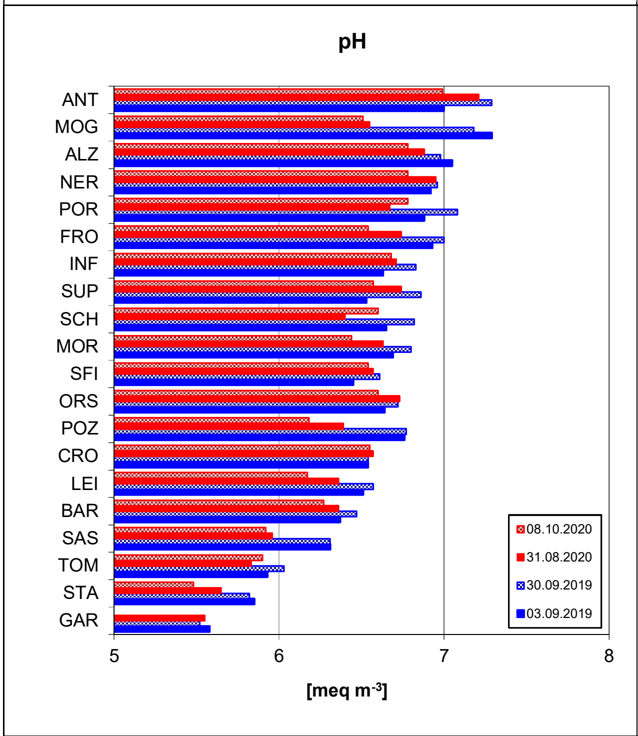
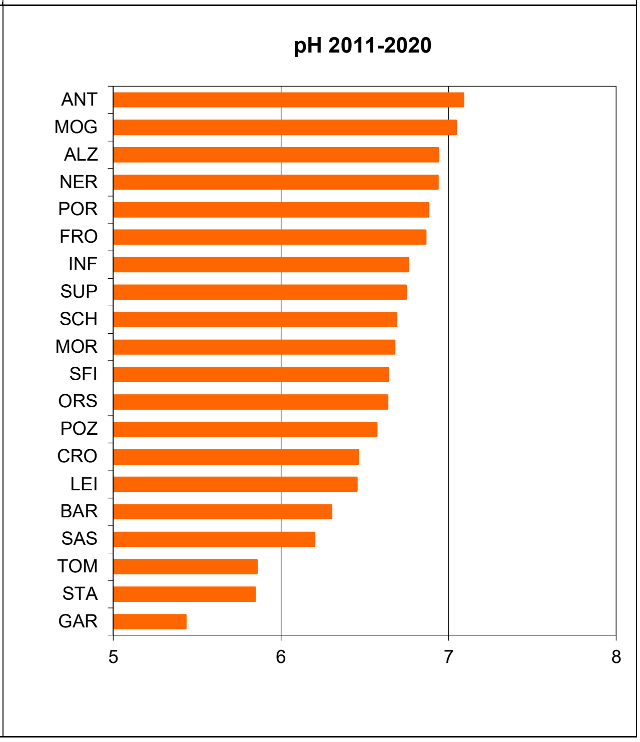
60
80
100
[meq m-3]


pH
ANT
MOG
ALZ
NER
POR
FRO
INF
SUP
SCH
MOR
SFI
ORS
POZ
CRO
LEI
BAR
SAS
TOM
STA
GAR
08.10.2020
31.08.2020
30.09.2019
03.09.2019
5
6
7
8
[meq m-3]


pH 2011-2020
ANT
MOG
ALZ
NER
POR
FRO
INF
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SCH
MOR
SFI
ORS
POZ
CRO
LEI
BAR
SAS
TOM
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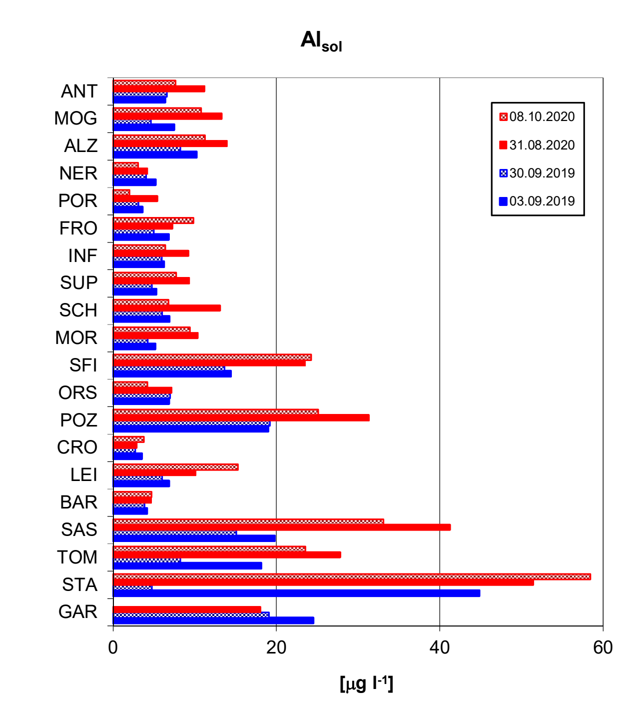
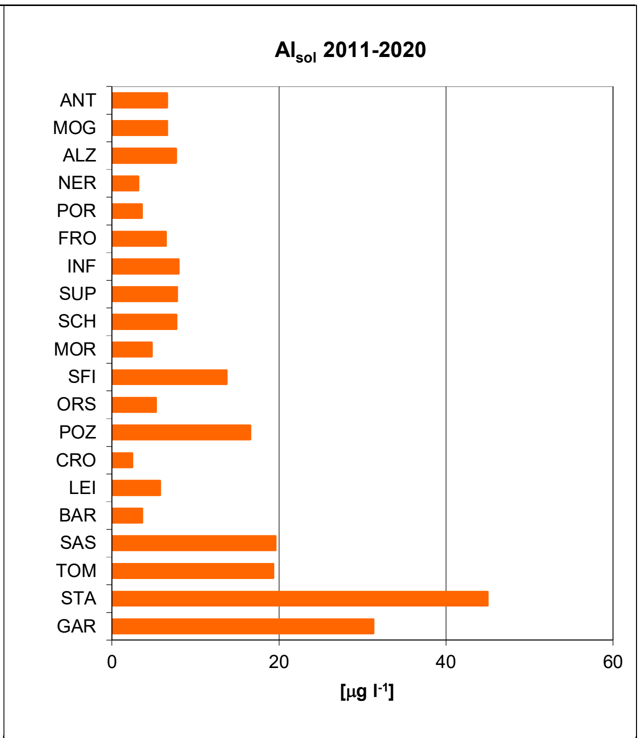

Al$_{sol}$
ANT
MOG
ALZ
NER
POR
FRO
INF
SUP
SCH
MOR
SFI
ORS
POZ
CRO
LEI
BAR
SAS
TOM
STA
GAR
08.10.2020
31.08.2020
30.09.2019
03.09.2019
0
20
40
60
[µg l-1]


Al$_{sol}$ 2011-2020
ANT
MOG
ALZ
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FRO
INF
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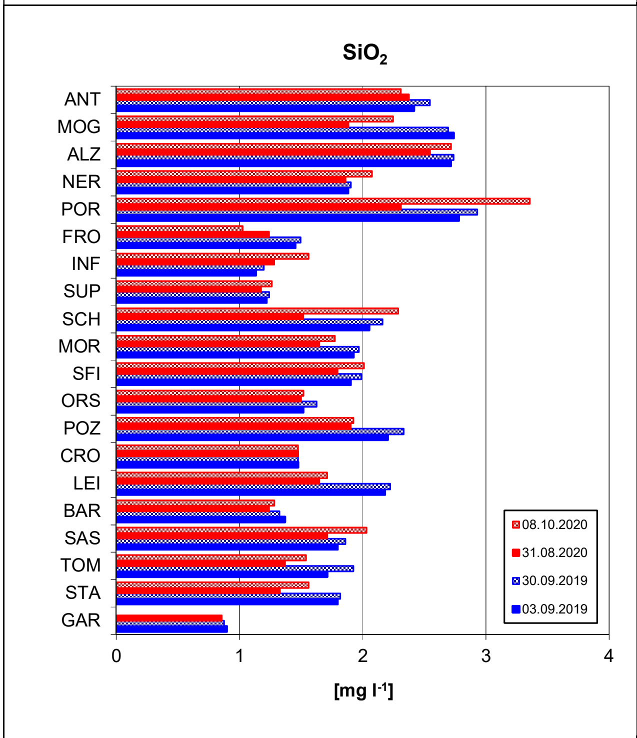
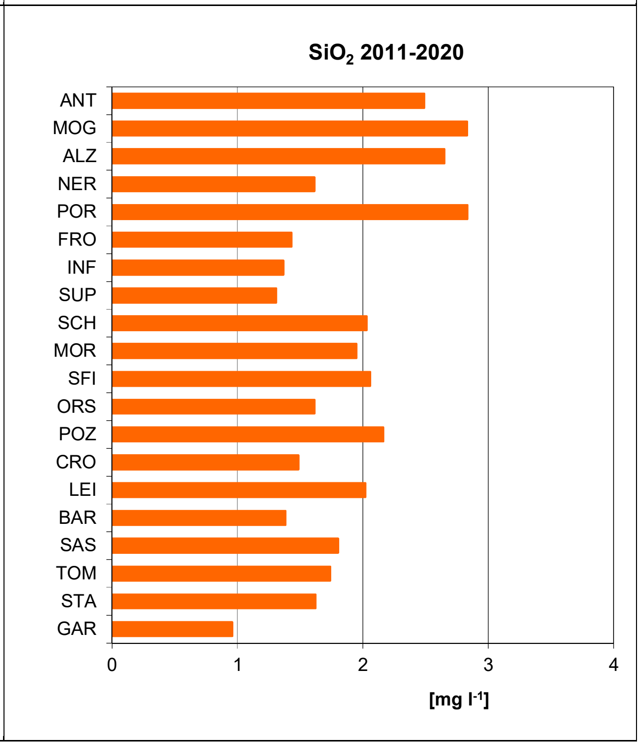
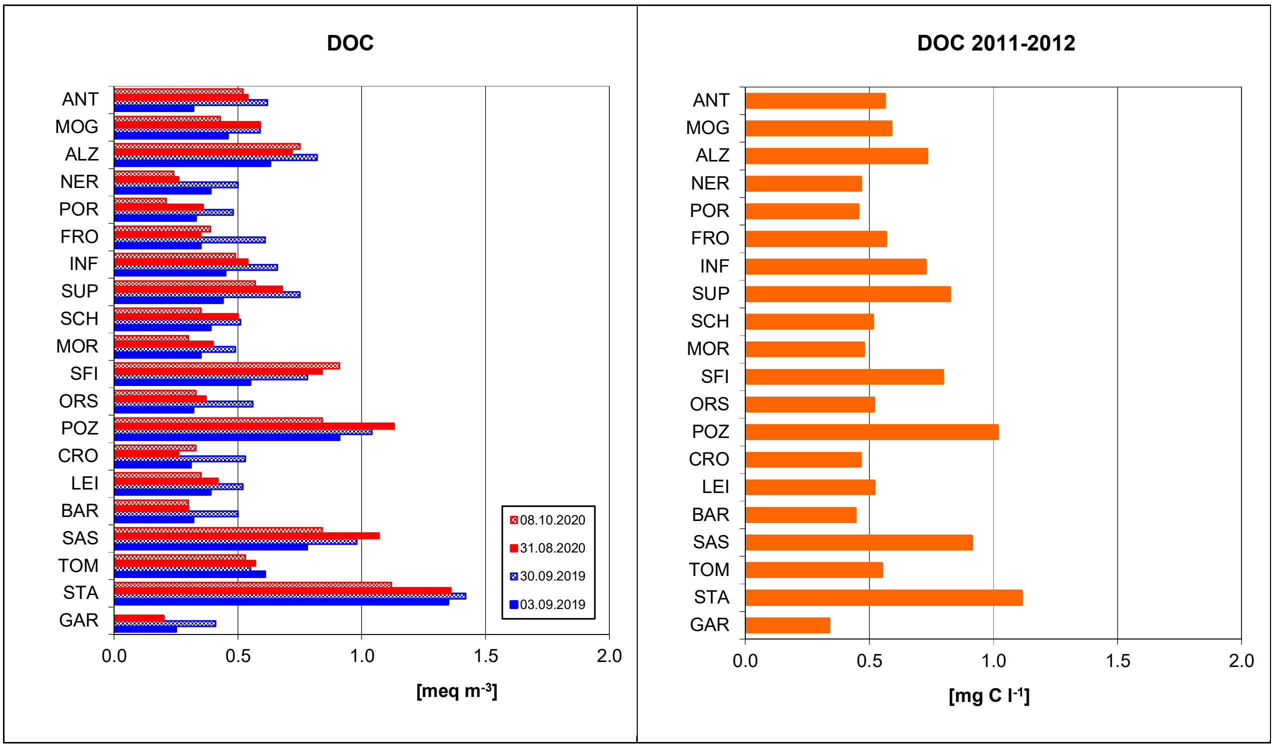
SCH
MOR
SFI
ORS
POZ
CRO
LEI
BAR
SAS
TOM
STA
GAR
0
20
40
60
[µg l-1]


SiO$_2$
ANT
MOG
ALZ
NER
POR
FRO
INF
SUP
SCH
MOR
SFI
ORS
POZ
CRO
LEI
BAR
SAS
TOM
STA
GAR
08.10.2020
31.08.2020
30.09.2019
03.09.2019
0
1
2
3
4
[mg l-1]


SiO$_2$ 2011-2020
ANT
MOG
ALZ
NER
POR
FRO
INF
SUP
SCH
MOR
SFI
ORS
POZ
CRO
LEI
BAR
SAS
TOM
STA
GAR
0
1
2
3
4
[mg l-1]



Temporal variations

In order to show temporal variations of lake water quality, autumn median values of pH, alkalinity and concentrations of base cations, sulphate and nitrate of all lakes and their corresponding boxplots are represented in Fig. 3.10. Only years, where all 20 Alpine lakes have been monitored are shown. After the 1980's, median sulphate concentrations decreased in most lakes. This can be attributed to reduced SO_x emissions and the associated decrease in sulphate depositions. Concentrations of nitrate also decreased because of reduced emissions of NO_x. As a consequence of decreasing sulphate and nitrate concentrations, concentrations of base cations decreased as well and alkalinity and pH increased.

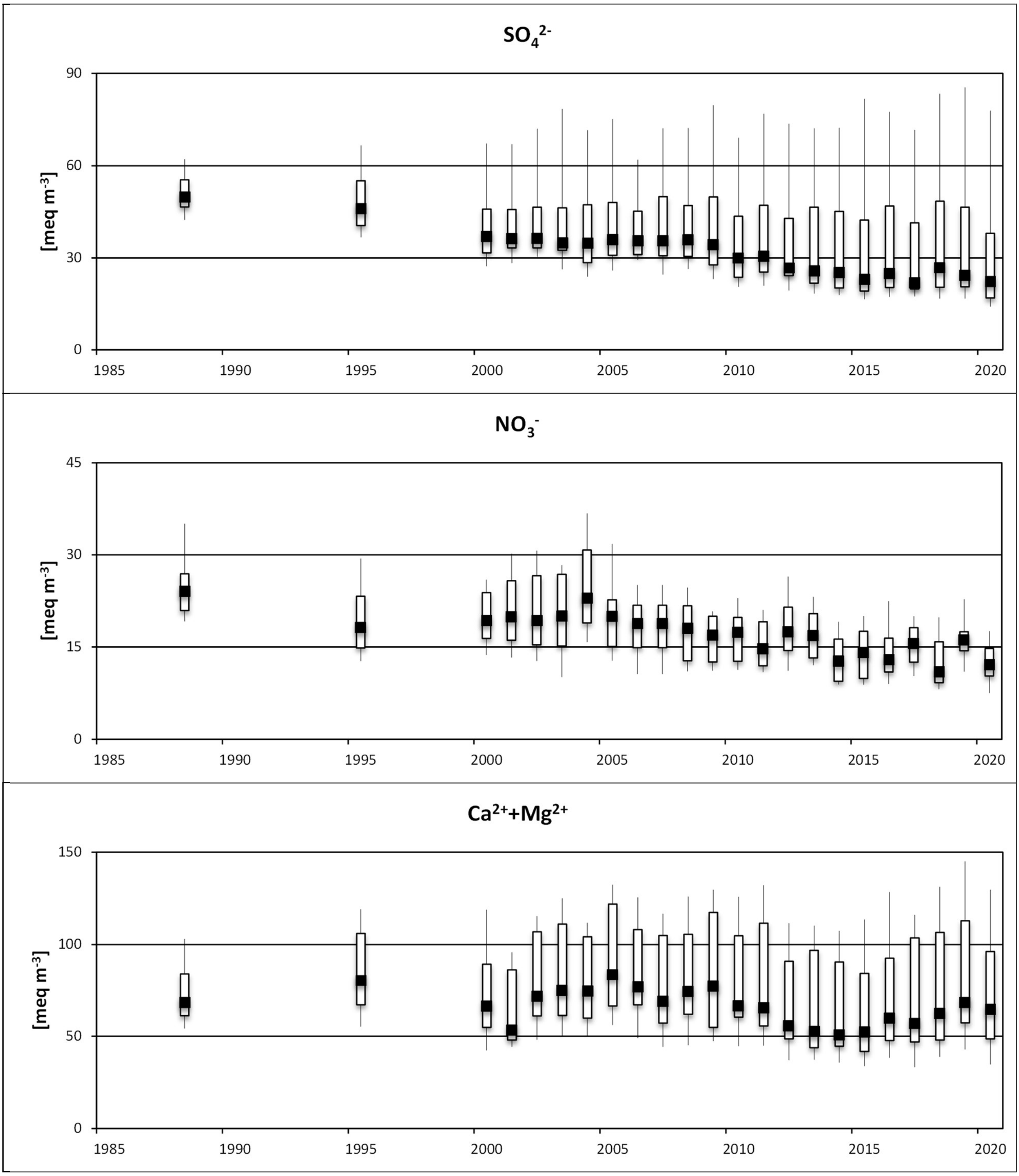
Aluminium concentrations of the three most acidic lakes are presented in Fig. 3.11. The most evident decrease in mean autumn concentrations occurred in Lago del Starlaresc da Sgiof from 80-100 to 25-70 μg l^{-1}. In Lago di Tomè concentrations decreased from about 40 to 15-25 μg l^{-1} and in Laghetto Gardiscio from 30-60 μg l^{-1} to 20-25 μg l^{-1}.

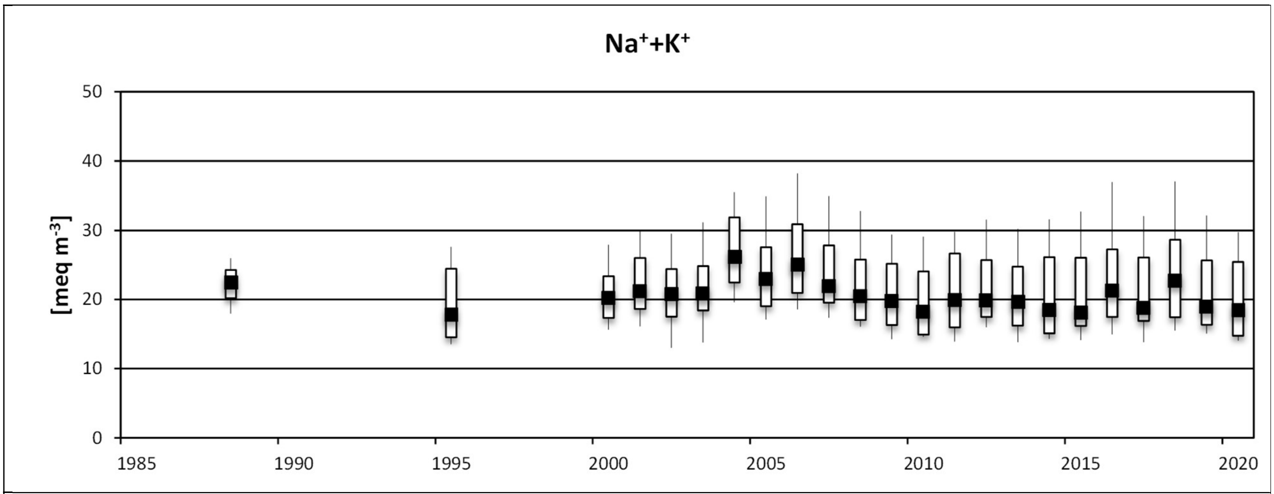
Results of a detailed trend analysis of the main parameters are presented in Tab. 3.5. Trends were calculated for the entire monitoring period and for the period since 2000 and since 2010 when sampling occurred more regularly and frequently. Since the 1980s, due to decreasing sulphate and nitrate depositions, concentrations of sulphate decreased significantly in 15 lakes and nitrate in 18 lakes. In most lakes with observed decreasing concentrations of sulphate, the trend slopes were higher at the beginning of the monitoring period. Differently, for most lakes trend slopes of nitrate were higher after 2000, indicating a more pronounced decrease more recently. Decreasing acidic depositions also caused a decrease of the lake concentrations of base cations (for the sum of calcium and magnesium it was significant in 10 lakes and for the sum of sodium and potassium significant in 7). Interestingly, after 2010 (more precisely after 2015, data not shown) in many lakes base cations seem to increase again. Statistically, this recent increase is not significant for most lakes. In order to can confirm this trend, we have to wait and observe what happens in the coming years.

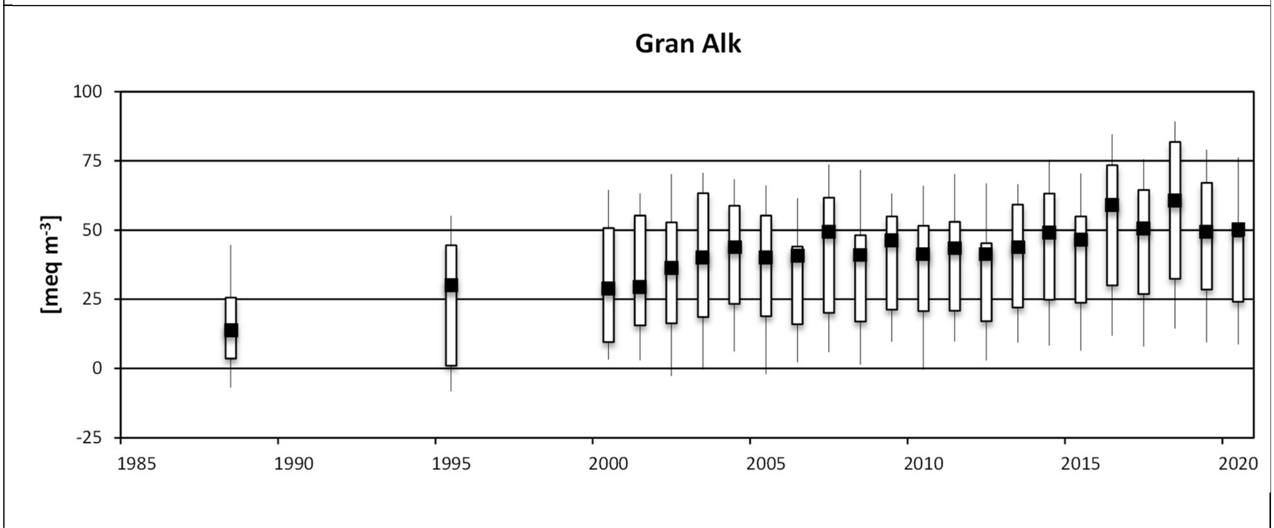
Interestingly, differently to most lakes, concentrations of sulphate increased significantly in five lakes (Lago dei Porchieirsc, Lago della Capannina Leit, Lago di Morghirolo, Lago di Mognòla). For Lago Leit and Lago Morghirolo this increase is higher after 2000 and for Lago Leit and Lago dei Porchieirsc even more pronounced after 2010. These increase in sulphate concentrations are often accompanied by an increase of the concentrations of 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) showed that in Lago Leit calcium, magnesium and sulphate originate from the dissolution of gypsum/anhydrite. They 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.

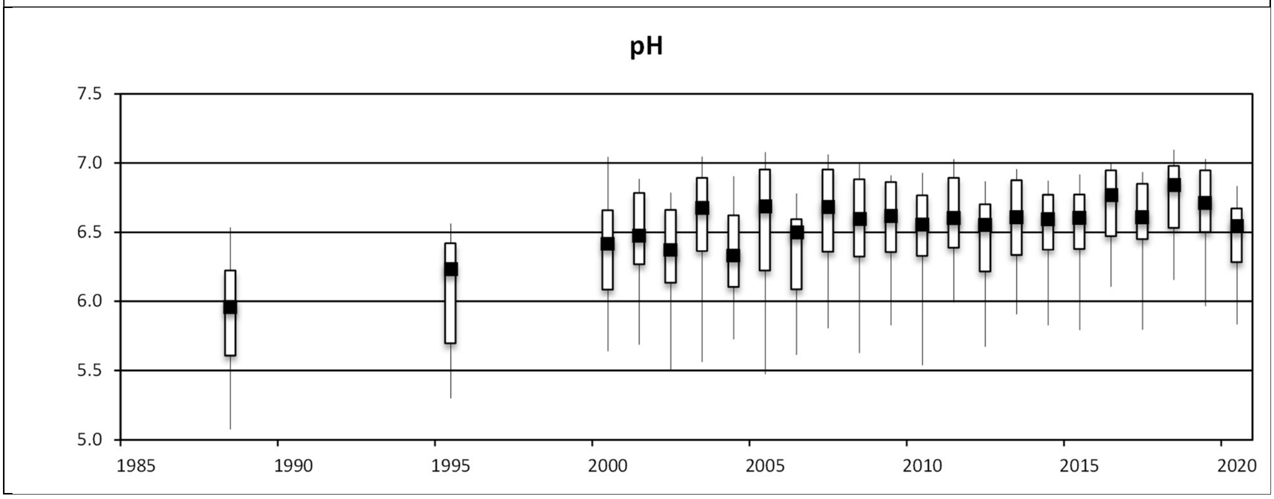
Gran alkalinity increased during the entire monitoring period significantly in 19 lakes. Following the base cation trend, the trend slope of alkalinity also started to increase further more recently (after 2010). As observed for base cations, this trend is statistically not yet significant. Hydrogen ions decreased significantly in 17 lakes. Between the 1980's and 2020 concentrations of aluminium decreased significantly in lakes with the highest concentrations (Lago del Starlaresc da Sgiof, in Lago di Tomè, in Lago Gardiscio). Surprisingly, after 2010 in many lakes concentrations of aluminium seem to increase again (significantly in 8 lakes). Three of this eight lakes have a rock glacier in their catchment (Leit, Morghirolo, Mognola) with probably melting permafrost in it and the increase in aluminium concentrations may be caused by the related increase of the weathering rate. However, concentrations of aluminium are increasing significantly also in other lakes (Antabia, Crosa, Orsalia, Pozzöi, Alzasca. Fig. 3.12 shows the temporal change of aluminium concentrations of these lakes after 2010. Again, it is too early to identify the causes. Possible explanations may be a general increase of the weathering rates caused by the more recent increase in temperature (see the increase of the temperature deviation from the average of the monitoring period (1992–2018) at the MeteoSwiss weather station at Robiei after 2010 in Fig. 3.13a) or by the recent increase of the intensity of rain events during the months of monitoring (see Fig. 3.13b).

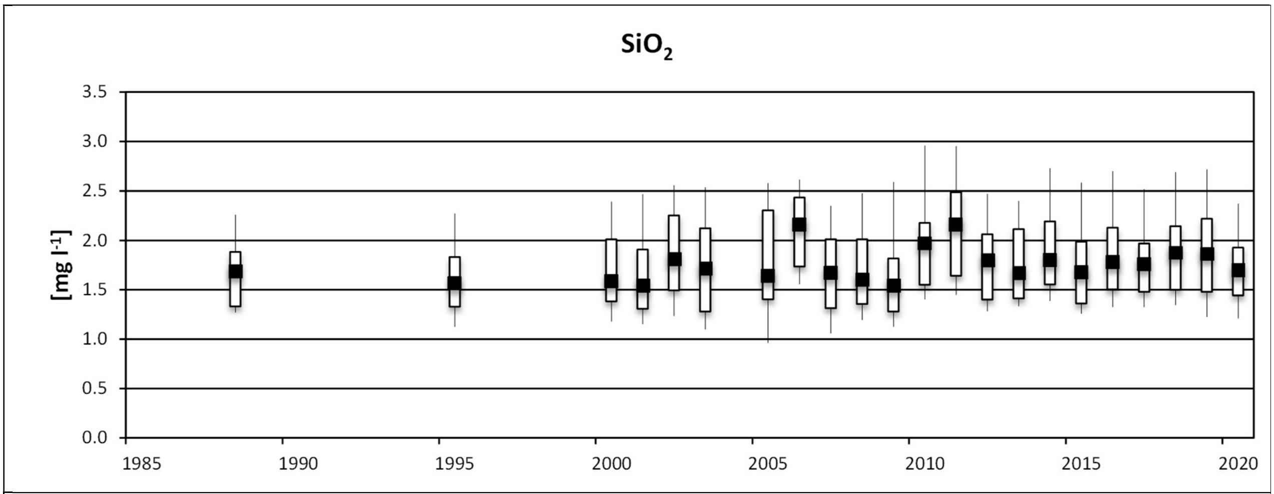
Figure 3.10 Temporal variations of parameters measured in 20 Alpine lakes from 1988 to 2020. Boxplots show the median and the 10th, 25th, 75th, 90th percentiles of autumn mean values.




Na⁺+K⁺
[meq m⁻³]
0
10
20
30
40
50
1985
1990
1995
2000
2005
2010
2015
2020


Gran Alk
[meq m⁻³]
-25
0
25
50
75
100
1985
1990
1995
2000
2005
2010
2015
2020


pH
5.0
5.5
6.0
6.5
7.0
7.5
1985
1990
1995
2000
2005
2010
2015
2020


SiO$_2$
[mg l^{-1}]
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
1985
1990
1995
2000
2005
2010
2015
2020

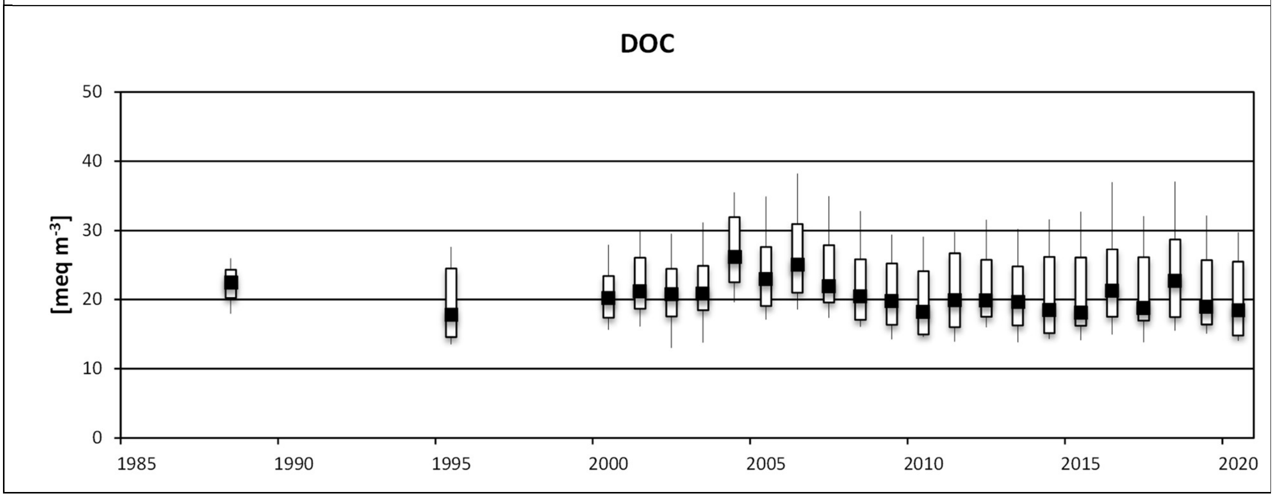

DOC
[meq m^{-3}]
50
40
30
20
10
0
1985
1990
1995
2000
2005
2010
2015
2020

Figure 3.11 Temporal variations of dissolved aluminium from 1988 to 2020 in the three most acidic lakes (mean autumn values).

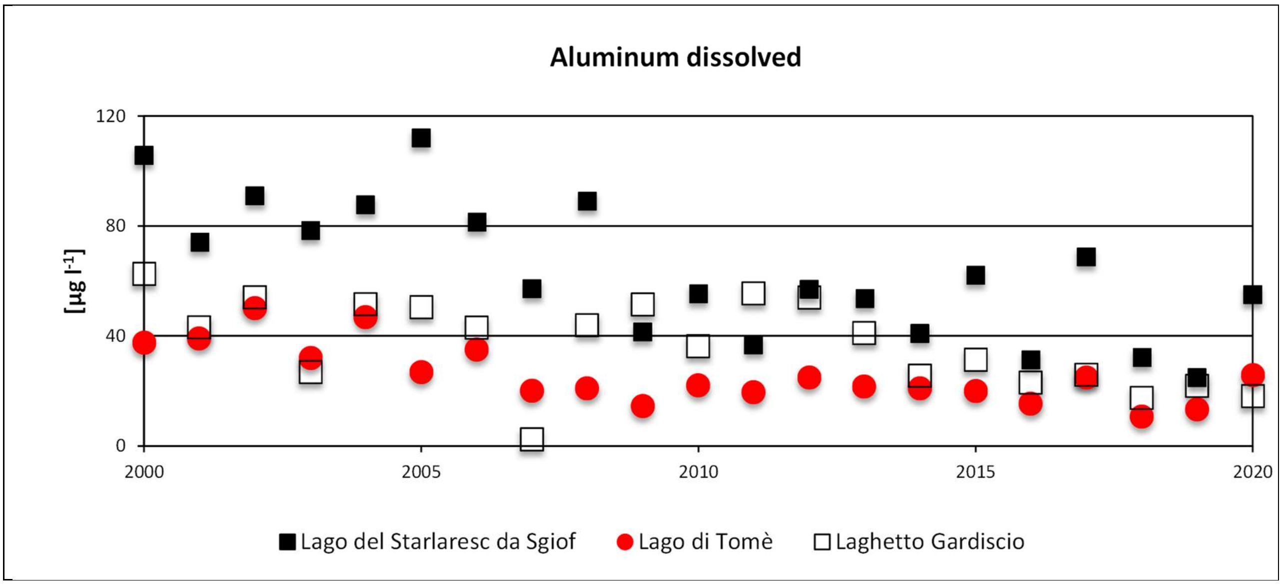


Table 3.5 Changes in lake water concentrations during the indicated time periods. Red values indicate significant trends. All changes are expressed in meq m^{-3} yr^{-1} with exceptions of SiO_2 and Al_{sol} that are expressed in mg l^{-1} yr^{-1} and µg l^{-1}, respectively.

Lake	SO_4^{2-}			NO_3^-			$Ca^{2+}+Mg^{2+}$			Na^++K^+			Gran Alk			H^+			SiO_2			Al_{dis}	
	'80-20	00-20	10-20	'80-20	00-20	10-20	'80-20	00-20	10-20	'80-20	00-20	10-20	'80-20	00-20	10-20	'80-20	00-20	10-20	'80-20	00-20	10-20	00-20	10-20
STA	-1.19	-1.08	-0.86	-0.56	-0.75	-0.38	-0.88	-0.94	-0.88	-0.29	-0.32	0.08	0.85	1.07	0.60	-3.5E1	-2.7E-1	-8.6E-2	0.010	0.009	0.012	-3.14	-1.09
TOM	-0.84	-0.75	-0.52	-0.52	-0.87	-0.96	-0.95	-1.21	-0.81	-0.10	-0.26	-0.13	0.40	0.35	1.00	-7.0E-2	-4.5E-2	-1.2E-1	-0.003	-0.013	-0.035	-1.24	-0.71
POR	0.77	0.73	2.51	-0.45	-0.52	-0.52	0.42	0.31	2.84	0.09	0.06	0.33	0.85	0.69	2.00	-3.5E-3	-1.4E-3	-3.3E-3	0.008	-0.006	-0.039	-0.27	0.03
BAR	-0.40	-0.35	-0.22	-0.33	-0.50	-0.54	-0.34	-0.44	-0.01	-0.06	-0.08	0.00	0.61	0.61	0.80	-3.4E-2	-2.1E-2	-2.9E-2	0.003	-0.001	-0.029	-0.24	0.12
GAR	-0.25	-0.22	-0.33	-0.29	-0.36	-0.54	-0.27	-0.44	-0.53	-0.16	-0.18	-0.17	0.28	0.25	0.31	-1.3E-1	-1.1E-1	-1.6E-1	0.002	0.001	-0.026	-1.94	-2.79
LEI	3.87	6.01	10.97	-0.21	-0.22	-0.07	3.31	5.23	11.32	0.41	0.55	0.93	0.50	0.38	0.60	-6.7E-3	-5.6E-18	-2.5E-3	0.018	0.020	-0.016	-0.13	0.69
MOR	0.35	0.66	0.86	-0.16	-0.20	-0.06	0.57	0.62	1.27	0.13	0.13	0.19	0.80	0.75	1.25	-3.8E-3	-2.4E-3	-7.0E-3	0.015	0.019	-0.030	-0.25	0.59
MOG	0.39	0.34	0.83	-0.23	-0.40	-0.56	0.23	-0.60	0.04	-0.10	-0.18	0.14	0.13	-0.07	1.44	-1.5E-3	0.0E00	-4.7E-3	0.004	-0.019	-0.065	-0.06	0.73
INF	-0.86	-0.77	-0.36	-0.45	-0.58	-0.49	-0.77	-0.89	0.80	-0.16	-0.18	-0.06	0.61	0.69	1.00	-7.4E-3	-7.1E-3	-4.4E-3	0.000	-0.008	-0.020	-0.22	-0.02
SUP	-0.80	-0.72	-0.51	-0.43	-0.72	-0.63	-0.32	-0.55	-0.32	-0.07	-0.11	-0.03	0.90	0.95	0.80	-1.2E-2	-9.0E-3	-7.5E-4	0.007	0.003	-0.010	-0.03	0.00
NER	0.08	0.25	0.58	-0.12	-0.18	-0.19	0.28	0.29	2.55	0.07	0.09	0.25	0.71	0.70	1.05	-1.6E-3	4.1E-4	2.0E-3	0.011	0.056	0.097	-0.15	0.11
FRO	-0.34	-0.35	-0.47	-0.23	-0.25	-0.15	0.29	0.20	0.21	-0.11	-0.07	0.16	0.85	0.67	1.93	-4.7E-3	-1.6E-3	-8.0E-4	0.003	0.000	-0.026	-0.22	0.31
ANT	-0.67	-0.68	-0.53	-0.33	-0.48	-0.32	-0.05	-0.48	0.78	-0.03	-0.06	0.03	0.79	0.74	2.00	-3.9E-3	-2.6E-3	-7.8E-3	0.012	0.006	-0.001	-0.03	0.66
CRO	-0.78	-0.74	-0.53	-0.19	-0.29	-0.33	-0.35	-0.53	0.43	0.02	0.04	0.22	0.80	0.86	1.33	-2.0E-2	-1.1E-2	-1.3E-2	0.005	0.001	-0.010	-0.19	0.20
ORS	-0.78	-0.78	-0.37	-0.19	-0.53	-0.12	-0.35	-0.28	1.05	0.02	-0.04	0.15	0.80	1.29	1.92	-2.0E-2	-1.2E-2	-9.8E-3	0.005	-0.001	-0.013	-0.24	0.31
SCH	-1.02	-0.98	-0.58	-0.25	-0.26	-0.22	-0.91	-1.11	-0.28	-0.13	-0.13	0.08	0.57	0.53	1.08	-5.8E-3	-3.3E-3	-4.4E-3	0.004	-0.004	-0.004	-0.35	0.17
POZ	-0.97	-0.91	-0.79	-0.16	-0.21	-0.36	-0.63	-0.94	0.02	-0.08	-0.07	0.01	0.42	0.34	1.25	-4.9E-3	-4.4E-3	-1.3E-2	0.010	0.001	-0.020	-0.02	1.34
SFI	-0.92	-0.82	-0.52	-0.19	-0.15	-0.09	-0.56	-0.52	0.70	-0.08	-0.11	-0.03	0.68	0.70	1.25	-9.3E-3	-4.1E-3	1.5E-3	0.010	0.001	-0.021	-0.16	0.49
SAS	-1.03	-1.02	-1.29	-0.35	-0.79	-0.81	-0.99	-1.44	-1.03	-0.17	-0.21	0.03	0.43	0.40	0.38	-1.6E-2	-1.1E-2	-2.4E-2	0.001	-0.010	-0.034	-0.09	1.37
ALZ	-0.96	-0.97	-1.08	-0.07	-0.11	0.18	-0.24	-1.02	-0.57	-0.08	-0.19	-0.03	0.89	0.85	1.25	-2.4E-3	3.0E-4	9.4E-4	0.019	0.014	-0.015	-0.08	0.54

Figure 3.12 Soluble aluminium concentrations in selected lakes between 2010 and 2020.

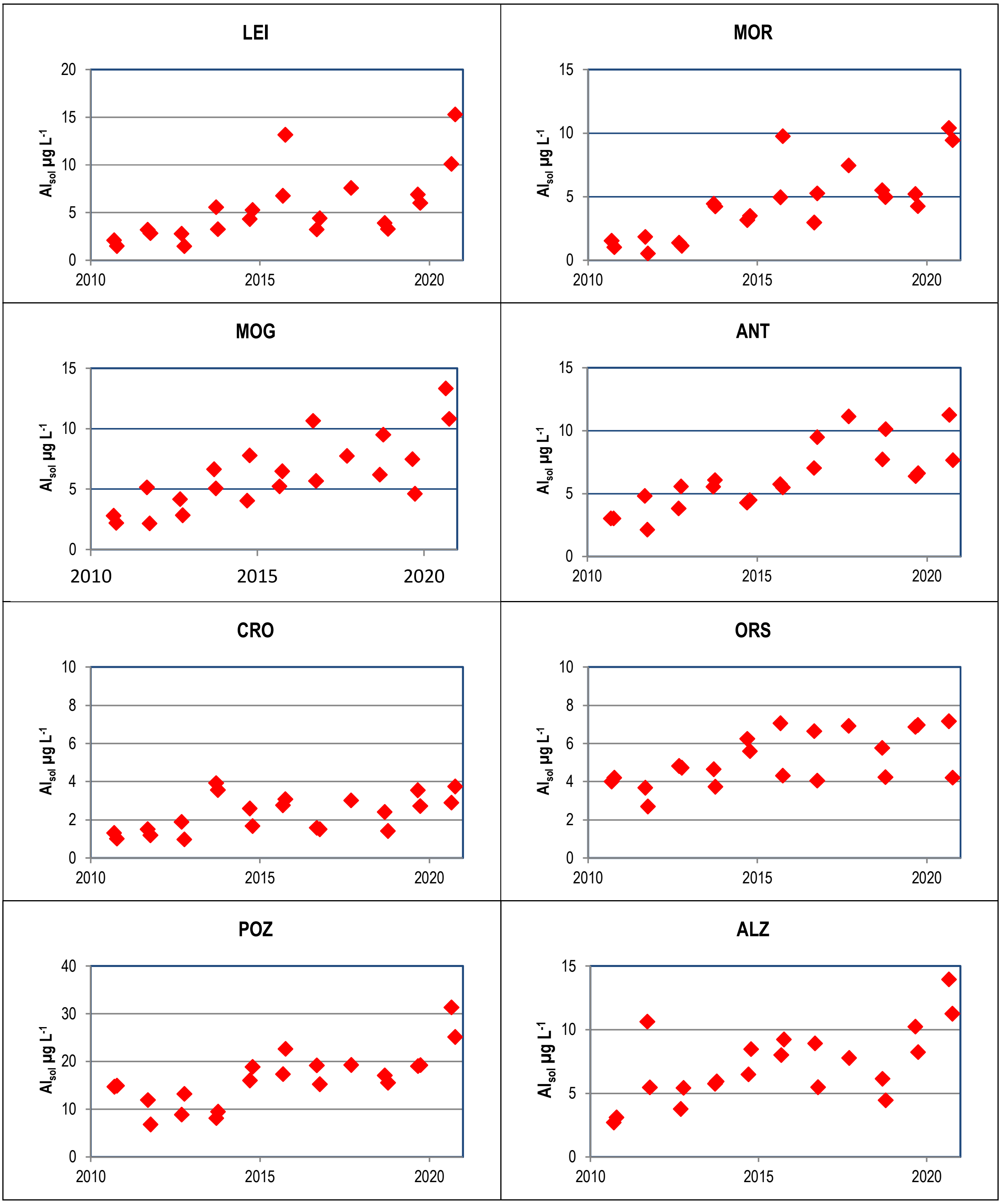
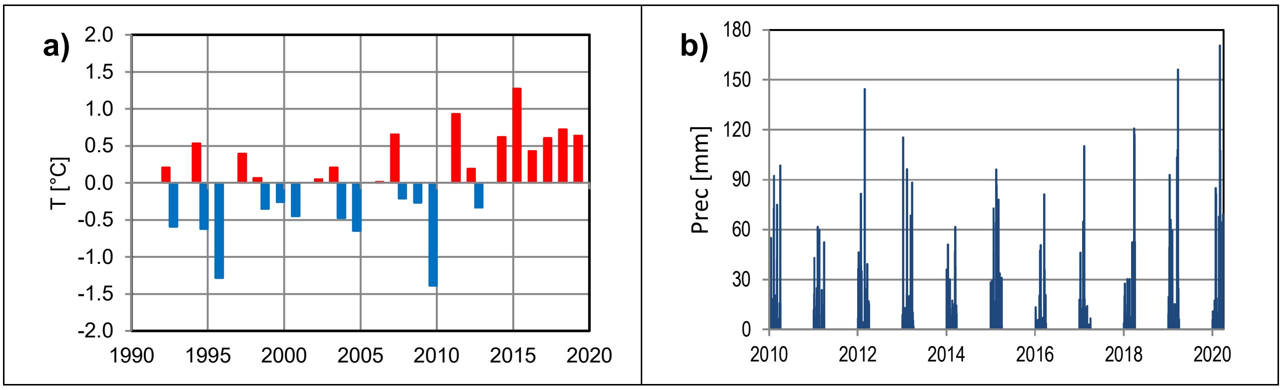


Figure 3.13 a) Temperature deviation from the average of the monitoring period (1992–2018) at the MeteoSwiss weather station at Robiei **b)** Daily precipitations measured at MeteoSwiss weather station at Robiei between August and October from 2010 to 2020.



3.5.3 Alpine rivers

Spatial variations

River water was sampled in 2019 and 2020 during the following days: 14.1.19, 1.2.19, 11.3.19, 8.4.19, 13.5.19, 3.6.19, 22.7.19, 26.8.19, 9.9.19, 7.10.19, 11.11.19, 9.12.19, 13.1.20, 10.2.20, 9.3.20, 20.4.20, 11.5.20, 8.6.20, 6.7.20, 3.8.20, 7.9.20, 12.10.20, 9.11.20, 30.11.20. Annual mean concentrations of the chemical parameters measured in river Maggia, Vedeggio and Verzasca during 2019 and 2020 are shown in Tab. 3.6. Conductivity, Gran alkalinity, concentrations of calcium, and sulphate were highest in river Maggia, followed by Vedeggio and Verzasca. 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 Maggia is 7 and 10 times larger than the watersheds of river Verzasca and Vedeggio, respectively, implying a longer average water residence time and higher average weathering. Differences in water chemistry of rivers Vedeggio and Verzasca are more related to their different catchment geology. Similarly to the catchment of river Maggia, the watersheds of river Vedeggio and Verzasca are very poor in carbonate containing rocks. But while the catchment of river Verzasca 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 Vedeggio 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 Vedeggio followed by river Verzasca and Maggia. This may be due to differences in average rainwater nitrogen concentrations and different nitrogen retention capacities of the watersheds. From 2013-2017, average nitrogen rainwater concentrations in the watershed of river Vedeggio, Verzasca and Maggia were 55, 39 and 36 meq m^{-3}, respectively and highest nitrogen retention during the same time period occurred in the larger river Verzasca (35%) followed by river Maggia (30%) and Vedeggio (29%).

During 2019 average Gran alkalinity was 328 meq m^{-3} in river Maggia, 184 meq m^{-3} in river Vedeggio and 77 meq m^{-3} in river Verzasca. During 2020 the same values were 301, 175 and 71 meq m^{-3}, for the rivers Maggia, Vedeggio and Verzasca, respectively. Based on these data river Verzasca and river Vedeggio have low alkalinities (50-200 meq m^{-3}), but no river is sensitive to acidification. The same is suggested by their minimum Gran alkalinities that were always > 0 meq m^{-3}. Average pH for the years 2019 and 2020 was 7.5 and 7.4 in river Maggia, 7.2 in river Vedeggio and 6.9 and 6.8 in river Verzasca. Their minimum pH’s were not much lower (Maggia: 7.0, Vedeggio: 6.8, Verzasca: 6.5).

Table 3.6 Average concentrations in river water during 2019 and 2020. Values based on at least one sample below the quantification limit were preceded with <.

Parameter	Year	MAG	VED	VER
Cond 25°C (µS cm^{-1})	2019	61	47	23
	2020	57	44	21
pH	2019	7.5	7.2	6.9
	2020	7.4	7.2	6.8
Gran Alk (meq m^{-3})	2019	328	184	77
	2020	301	175	71
Ca^{2+} (meq m^{-3})	2019	396	184	77
	2020	301	175	71
Mg^{2+} (meq m^{-3})	2019	53	75	16
	2020	53	76	17
Na^{+} (meq m^{-3})	2019	77	87	31
	2020	73	80	30
K^{+} (meq m^{-3})	2019	37	15	14
	2020	38	16	14
NH_4^{+} (meq m^{-3})	2019	0.5	0.4	0.3
	2020	0.6	0.3	0.6
SO_4^{2-} (meq m^{-3})	2019	172	121	65
	2020	163	112	61
NO_3^{-} (meq m^{-3})	2019	25	59	31
	2020	28	52	32
NO_2^{-}-N (µg l^{-1})	2019	0.5	0.5	0.4
	2020	0.5	0.3	0.3
Cl^{-} (meq m^{-3})	2019	33	42	10
	2020	30	32	9
SRP (µg P l^{-1})	2019	2.0	<2	<2
	2020	<2	<2	<2
N_{tot} (mg N l^{-1})	2019	0.5	1.0	0.5
	2020	0.5	0.8	0.6
DOC (mg C l^{-1})	2019	0.9	0.9	0.7
	2020	0.7	0.5	0.6
SiO_2 (mg l^{-1})	2019	5.3	7.6	4.1
	2020	4.6	7.2	3.7

Parameter	Year	MAG	VED	VER
Al_{sol} (µg l^{-1})	2019	10	9	8
	2020	15	8	13
Al_{tot} (µg l^{-1})	2019	12	14	9
	2020	21	41	17
Pb_{sol} (µg l^{-1})	2019	<0.1	<0.1	<0.1
	2020	<0.1	<0.1	<0.1
Pb_{tot} (µg l^{-1})	2019	<0.1	<0.1	<0.2
	2020	<0.1	<0.1	<0.1
Cd_{sol} (µg l^{-1})	2019	<0.1	<0.1	<0.1
	2020	<0.1	<0.1	<0.1
Cd_{tot} (µg l^{-1})	2019	<0.1	<0.1	<0.1
	2020	<0.1	<0.1	<0.1
Cu_{sol} (µg l^{-1})	2019	0.4	0.5	0.3
	2020	0.5	0.4	0.4
Cu_{tot} (µg l^{-1})	2019	0.4	0.5	0.3
	2020	0.5	0.5	0.4
Zn_{sol} (µg l^{-1})	2019	0.8	1.3	0.7
	2020	1.5	1.4	1.2
Zn_{tot} (µg l^{-1})	2019	1.0	1.5	0.7
	2020	1.9	1.7	1.5
Cr_{sol} (µg l^{-1})	2019	<0.1	<0.1	<0.1
	2020	<0.1	<0.1	<0.1
Cr_{tot} (µg l^{-1})	2019	<0.1	<0.1	<0.1
	2020	<0.1	<0.1	<0.1
Ni_{sol} (µg l^{-1})	2019	0.2	0.8	<0.1
	2020	0.2	0.8	<0.2
Ni_{tot} (µg l^{-1})	2019	0.2	0.9	<0.1
	2020	0.2	0.9	<0.2
Fe_{sol} (µg l^{-1})	2019	1.1	1.7	0.3
	2020	2.4	2.2	1.6
Fe_{tot} (µg l^{-1})	2019	2.2	5.4	1.4
	2020	7.3	31.8	4.5

Seasonal variations

Fig. 3.14 shows the daily mean discharges during 2019 and 2020 and average values of the last decade (2011-2020). Discharges are usually low during winter, high in spring because of frequent precipitation and snow melt, average during summer and higher again in autumn. Compared to 2019, 2020 characterized by lower discharges during August, November and December and consequently yearly average river discharges were lower during 2020 compared to 2019.

Concentrations of the main chemical parameters in river water during sampling days in 2019 and 2020 and their average values during 2011-2020 are shown in Fig. 3.15.

During 2011-2020 the seasonality was characterized by concentrations of sulphate, base cations, 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 sulphate, base cations, chloride and a combination of dilution and consumption of alkalinity occurs during rain events and/or snowmelt. River pH decreases during rain events because of rain acidity. Nitrate concentrations are higher in winter compared to summer and can, in addition, also 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 aluminium 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 chloride concentration in river Vedeggio and Maggia are caused by the use of road salt.

The main chemical parameters during 2019 and 2020 were in general in the same range as average values measured during 2011-2020. Only data from the sampling of the 13.5.2020 during a high discharge event were characterized by lower than usual concentrations of sulphate, base cations, Gran alkalinity and SiO_2 because of the dilution with rainwater, of pH because of the rainwater acidity and by positive peaks of soluble aluminium and DOC as consequence of soil leaching

Figure 3.14 Daily mean discharge during 2019 and 2020 of the rivers Maggia, Vedeggio and Verzasca, with the precipitation volumes in the area of the sampling site and average daily mean discharge during 2011-2020. Discharge of river Vedeggio at Isone and the precipitation volumes were measured by the Canton of Ticino (UCA, 2001-2021), discharge of river Verzasca at Sonogno was estimated by discharge values measured at Lavertezzo by BWG (2001-2004) and BAFU (2005-2021), discharge of river Maggia was measured at Brontallo by Ofima (discharge of days with no data were estimated from measurements at Bignasco by BWG (2001-2004) and BAFU (2005-2021)).

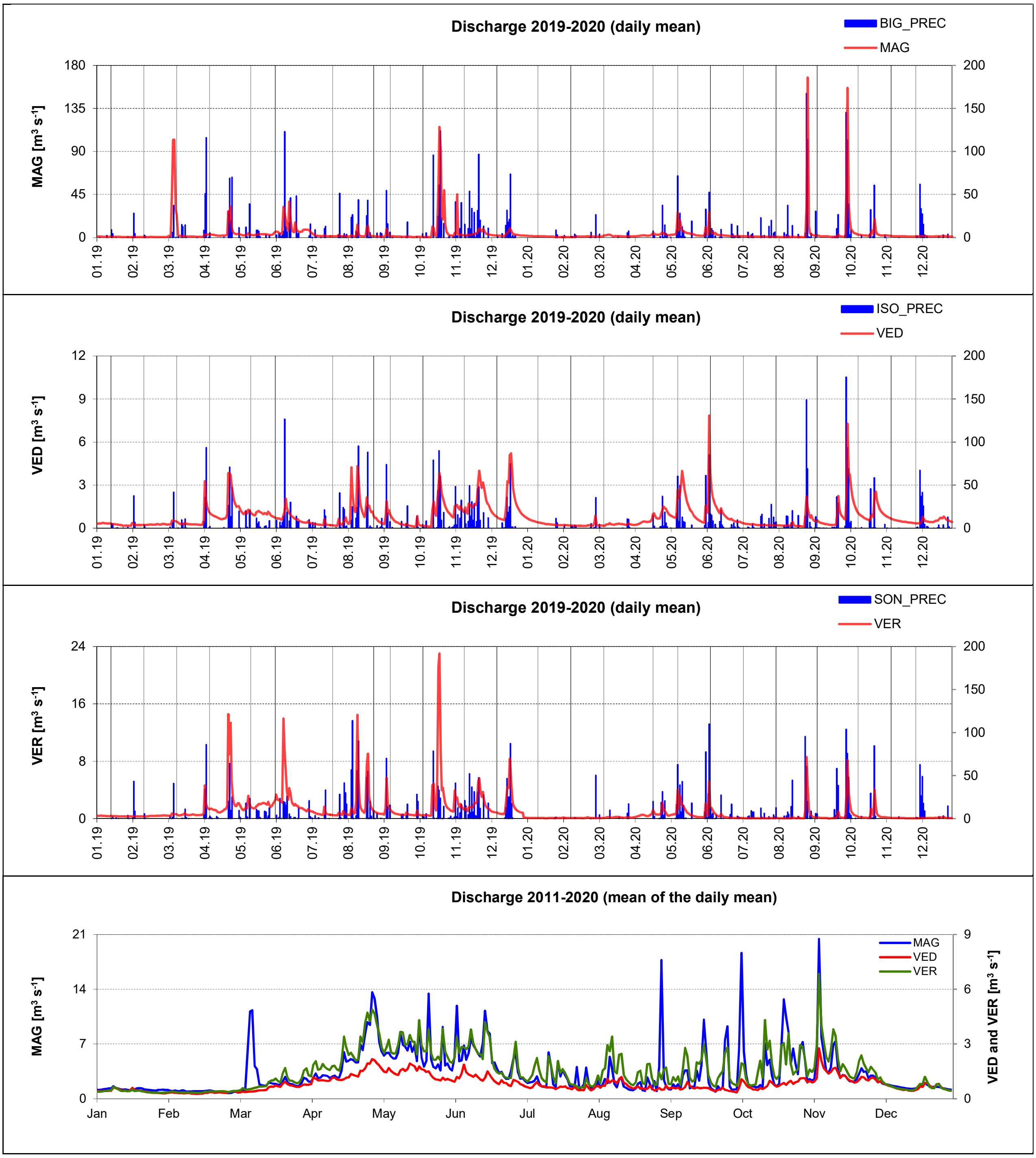
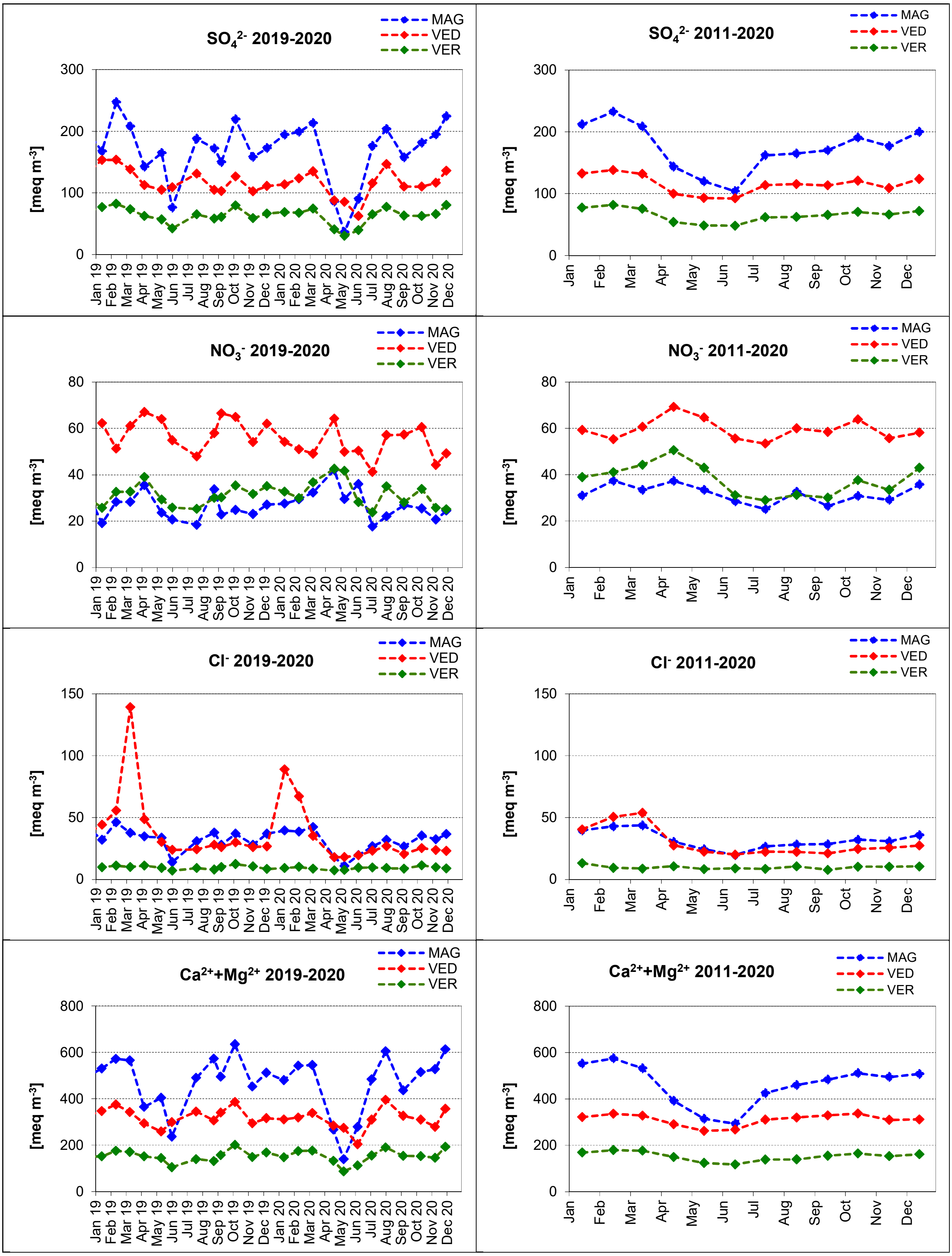
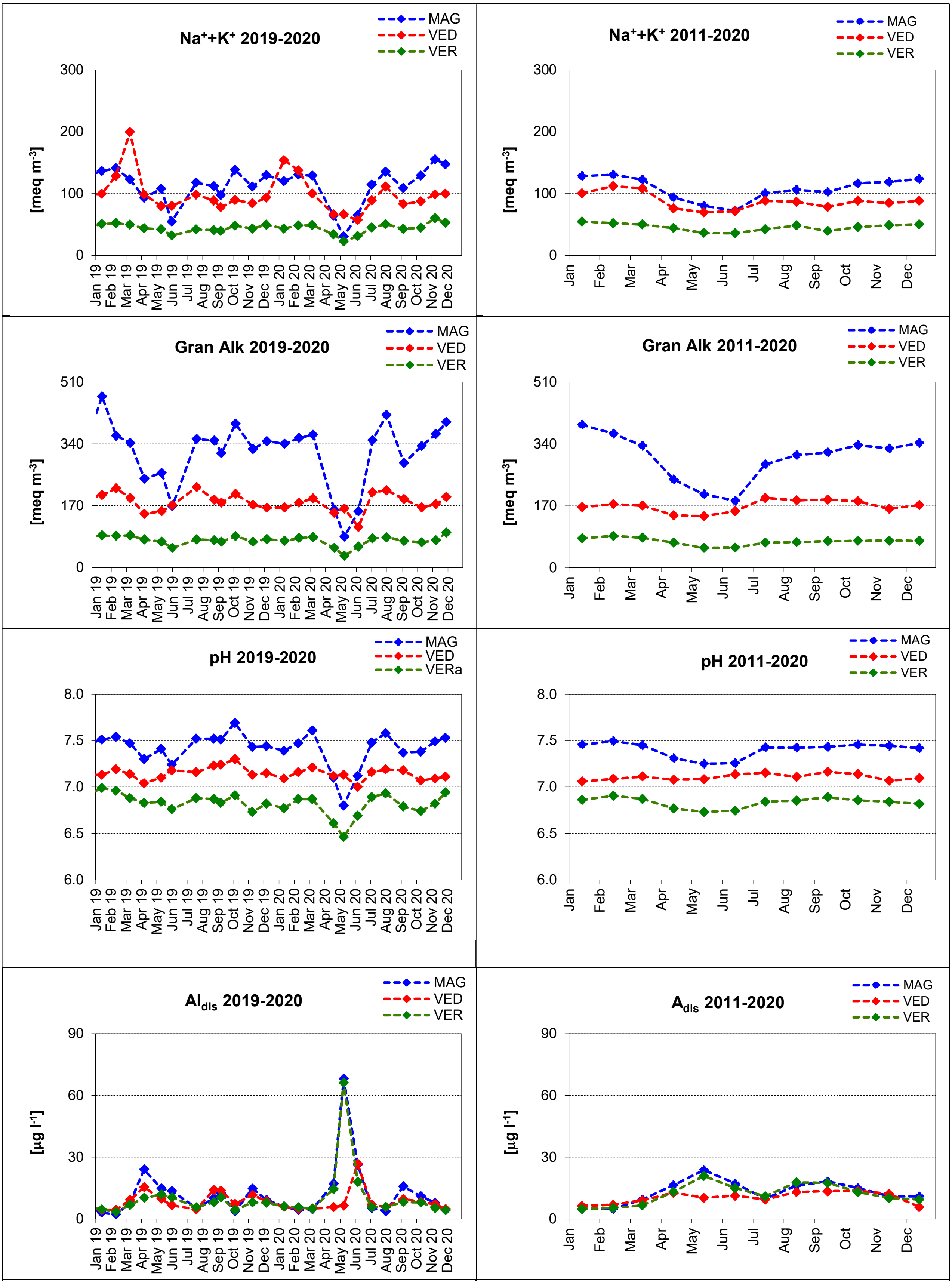
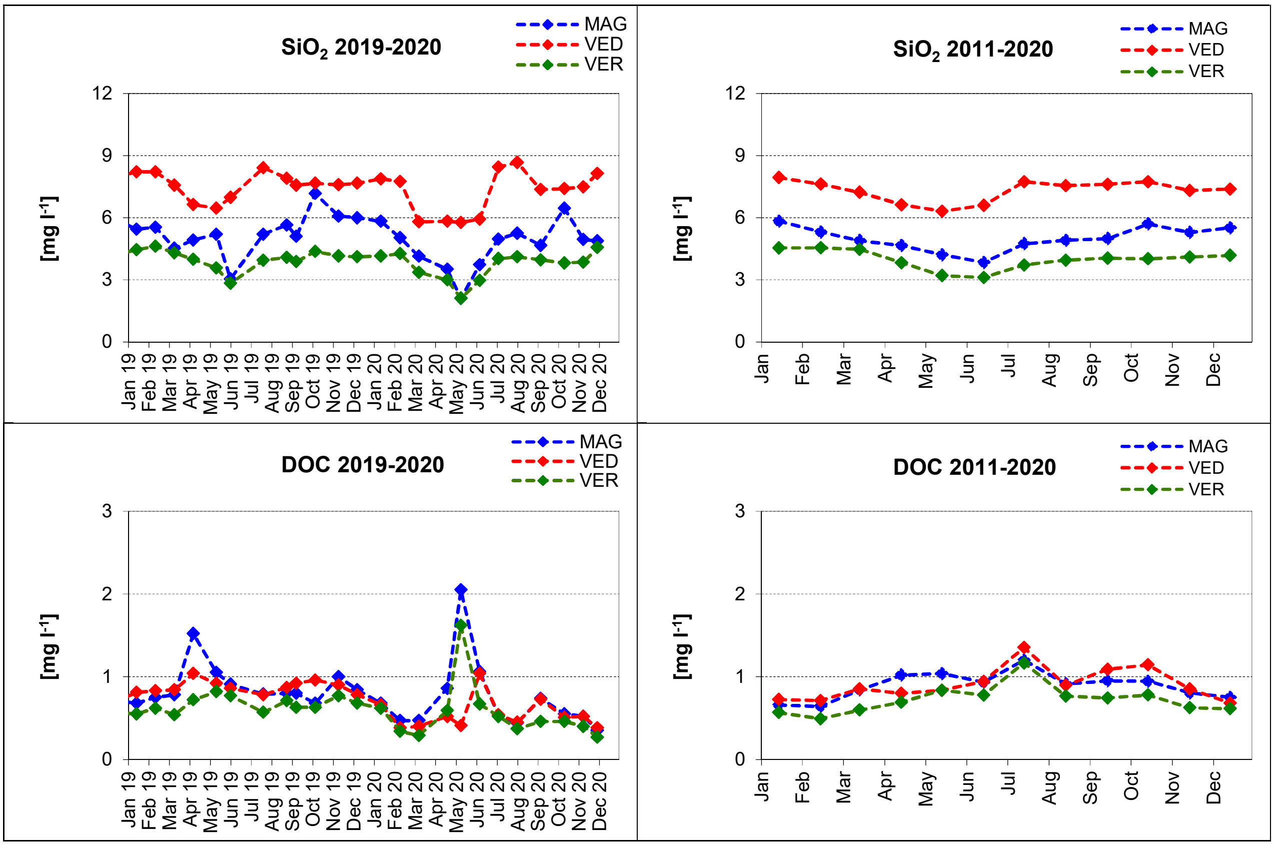


Figure 3.15 Concentrations of the main chemical parameters in river water during sampling days in 2019-2020 and their average values from 2011 to 2020.




Na⁺+K⁺ 2019-2020
MAG
VED
VER
[meq m⁻³]
300
200
100
0
Jan 19 Feb 19 Mar 19 Apr 19 May 19 Jun 19 Jul 19 Aug 19 Sep 19 Oct 19 Nov 19 Dec 19 Jan 20 Feb 20 Mar 20 Apr 20 May 20 Jun 20 Jul 20 Aug 20 Sep 20 Oct 20 Nov 20 Dec 20
Na⁺+K⁺ 2011-2020
MAG
VED
VER
[meq m⁻³]
Jan Feb Mar Apr May Jun Jul Aug Sep Oct Nov Dec
Gran Alk 2019-2020
MAG
VED
VER
[meq m⁻³]
510
340
170
0
Gran Alk 2011-2020
pH 2019-2020
MAG
VED
VERa
8.0
7.5
7.0
6.5
6.0
pH 2011-2020
MAG
VED
VER
Al_dis 2019-2020
MAG
VED
VER
[µg l⁻¹]
90
60
30
0
A_dis 2011-2020
MAG
VED
VER



<u>Temporal variations</u>

Variations of the monthly average discharges and concentrations of the chemical parameters from 2010 to 2020 are presented in Fig. 3.16 and 3.17, respectively.

Similar to the observations for lake chemistry, also in rivers, concentrations of sulphate, and during the last few years also of nitrate decreased. However, as described for seasonal variations in river chemistry, concentrations are very much related to the river discharge and a yearly trend in river chemistry is difficult to detect at a glance. We therefore performed a seasonal Mann-Kendall test for the entire monitoring period 2000-2020 and for the subperiods 2000-2010 and 2010-2020. Results of the trend analysis are shown in Tab. 3.7. Over the entire monitoring period concentrations of sulphate and nitrate decreased and Gran alkalinity increased significantly in all three rivers. As regards nitrate the highest increase in concentrations seems to have occurred after 2010.

Figure 3.16 Monthly mean discharge in river water from 2000 to 2020. Discharge of river Vedeggio at Isone was measured by the Canton of Ticino (UCA, 2001-2020), discharge of river Verzasca at Sonogno was estimated by discharge values measured at Lavertezzo by BWG (2001-2004) and BAFU (2005-2020), discharge of river Maggia at Brontallo was estimated from values measured at Brontallo by Ofima and at Bignasco by BWG (2001-2004) and BAFU (2005-2020).

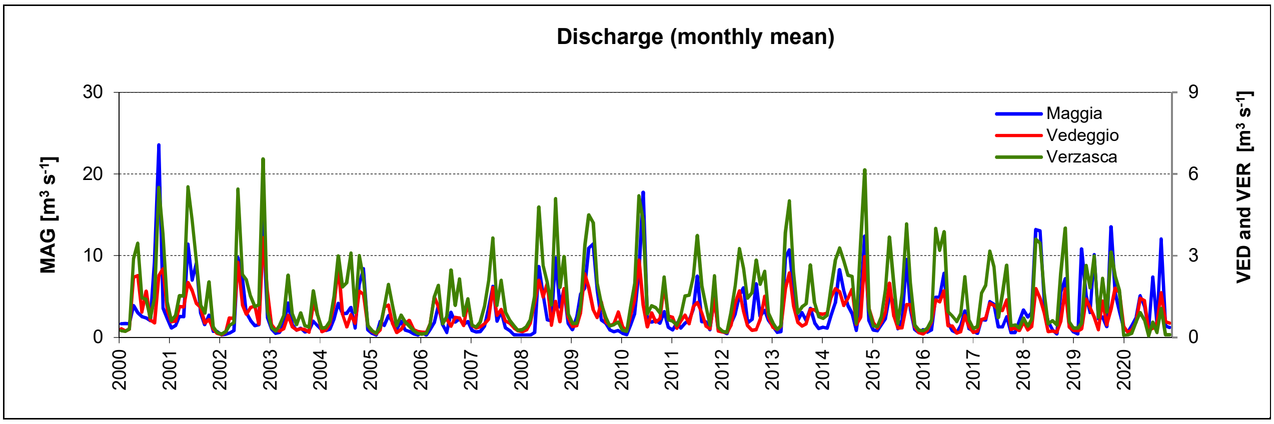
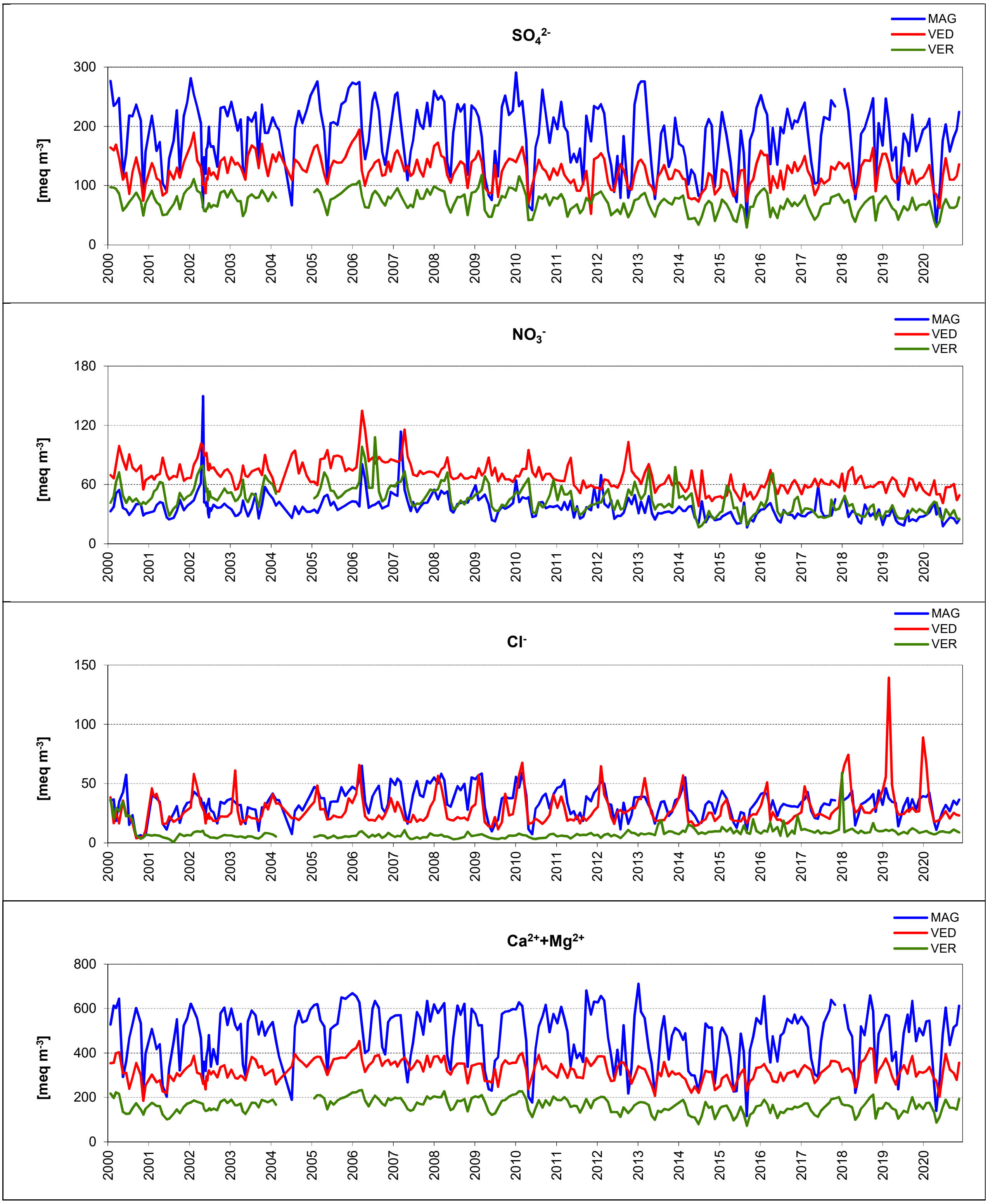
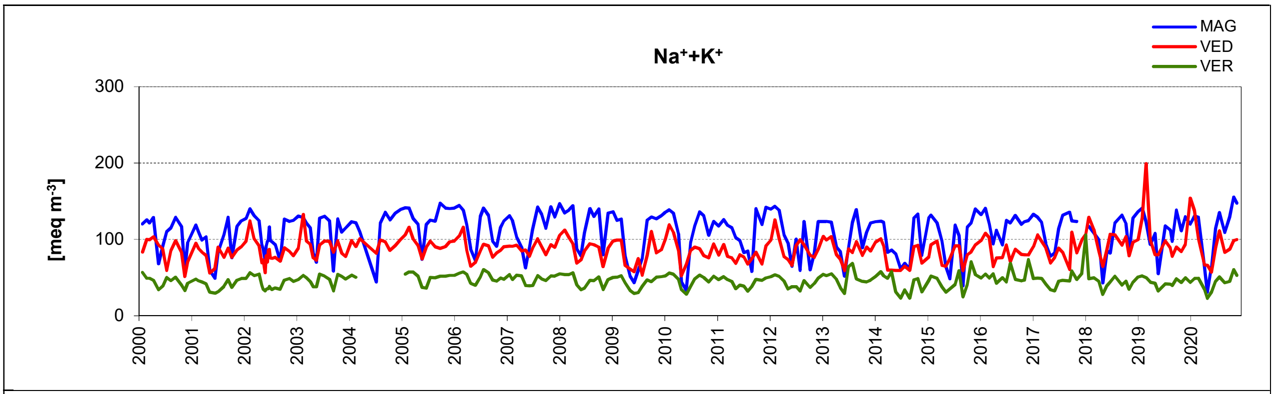
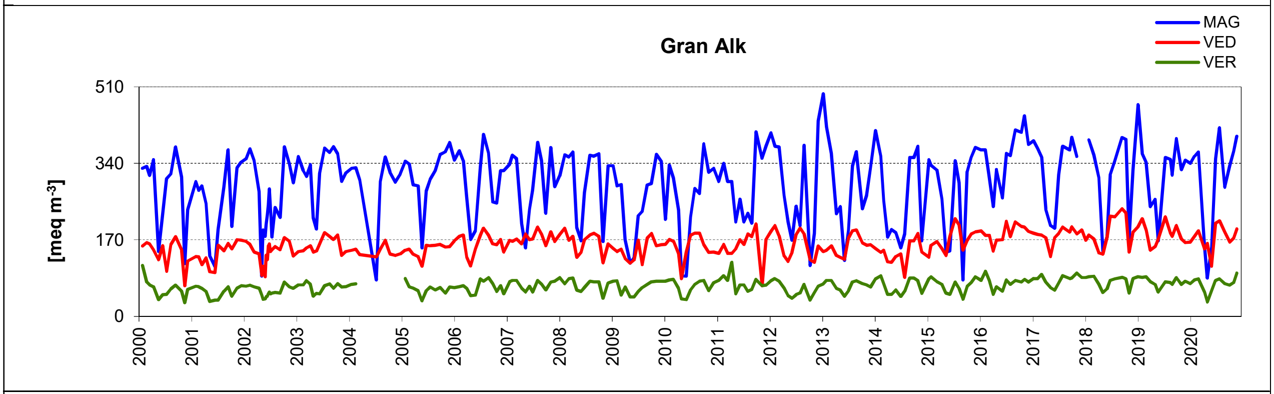
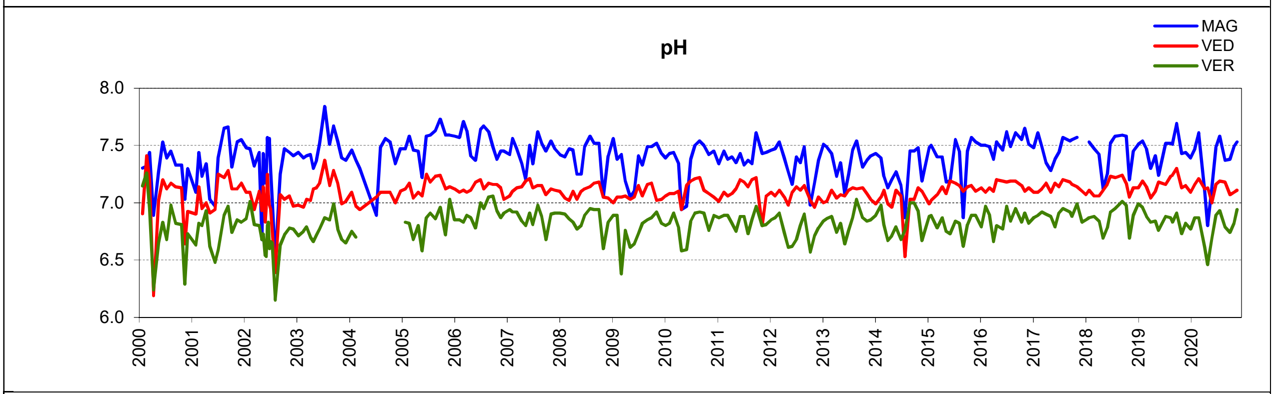


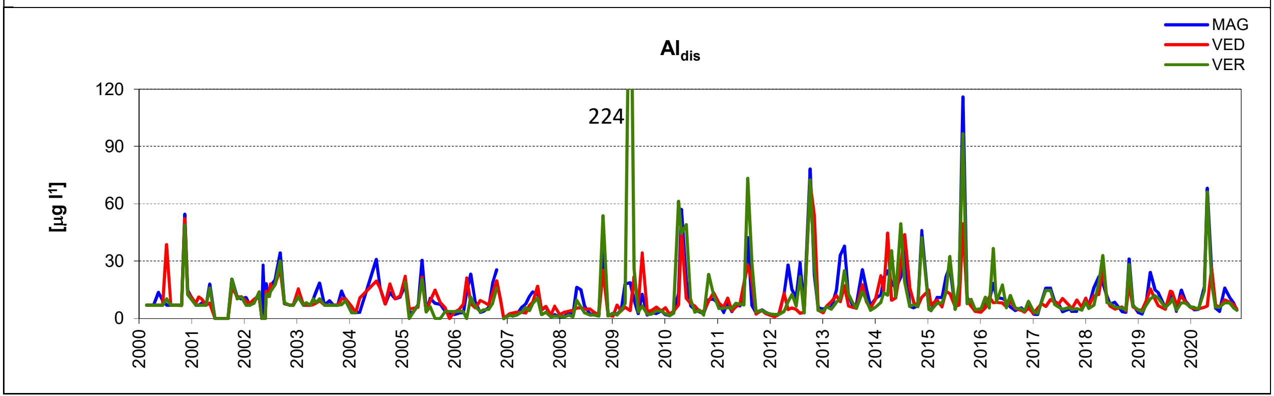
Figure 3.17 Concentrations of the main chemical parameters in river water from 2000 to 2020

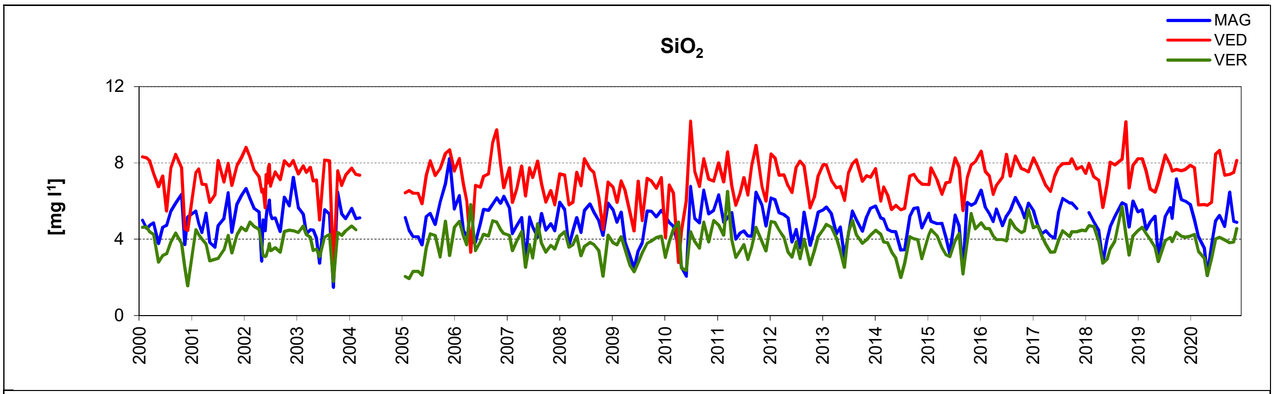



Na⁺+K⁺
MAG
VED
VER
[meq m-3]
300
200
100
0
2000 2001 2002 2003 2004 2005 2006 2007 2008 2009 2010 2011 2012 2013 2014 2015 2016 2017 2018 2019 2020


Gran Alk
MAG
VED
VER
[meq m-3]
510
340
170
0
2000 2001 2002 2003 2004 2005 2006 2007 2008 2009 2010 2011 2012 2013 2014 2015 2016 2017 2018 2019 2020


pH
MAG
VED
VER
8.0
7.5
7.0
6.5
6.0
2000 2001 2002 2003 2004 2005 2006 2007 2008 2009 2010 2011 2012 2013 2014 2015 2016 2017 2018 2019 2020


Al dis
MAG
VED
VER
[µg l-1]
120
90
60
30
0
224
2000 2001 2002 2003 2004 2005 2006 2007 2008 2009 2010 2011 2012 2013 2014 2015 2016 2017 2018 2019 2020


SiO2
MAG
VED
VER
[mg l-1]
0
4
8
12
2000
2001
2002
2003
2004
2005
2006
2007
2008
2009
2010
2011
2012
2013
2014
2015
2016
2017
2018
2019
2020

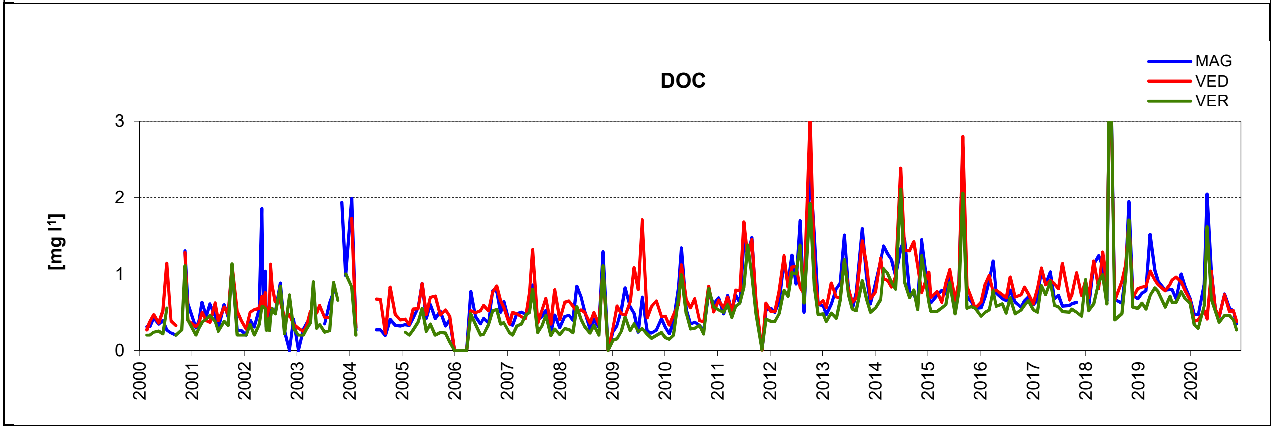

DOC
MAG
VED
VER
[mg l-1]
0
1
2
3
2000
2001
2002
2003
2004
2005
2006
2007
2008
2009
2010
2011
2012
2013
2014
2015
2016
2017
2018
2019
2020

Table 3.7 Changes in river water concentrations during the periods 2000-2020, 2000-2010 and 2010-2020 calculated with the Sens's slope. Red values indicate significant trends. All slopes are expressed in meq m^{-3} yr^{-1} with exception of Al_{sol} that is expressed in µg l^{-1}. Red values indicate significant trends.

River	SO_4^{2-}			NO_3^-			$Ca^{2+}+Mg^{2+}$			Na^++K^+			Gran Alk			H^+		
	00-20	00-10	10-20	00-20	00-10	10-20	00-20	00-10	10-20	00-20	00-10	10-20	00-20	00-10	10-20	00-20	00-10	10-20
MAG	-1.37	0.57	-0.37	-0.69	0.60	-1.13	-1.63	3.76	-2.02	0.03	0.98	0.26	1.70	-0.57	3.50	-2.0E-4	-2.5E-4	-7.2E-4
VED	-1.05	0.11	0.22	-1.18	-0.09	-1.05	-0.99	4.33	-0.27	0.14	0.22	1.11	1.86	2.00	3.00	-5.4E-4	-6.3E-4	-1.3E-3
VER	-0.95	0.30	-0.75	-1.11	-0.01	-1.43	-1.26	3.46	-1.83	-0.07	0.29	-0.18	1.00	1.20	1.18	-9.3E-4	-2.7E-3	-8.0E-4

River	SiO_2			Al_{sol}		
	00-20	00-10	10-20	00-20	00-10	10-20
MAG	0.000	-0.054	0.017	0.00	-0.60	0.07
VED	0.010	-0.099	0.060	-0.05	-0.49	0.10
VER	0.006	-0.031	0.003	0.02	-0.57	0.11

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Acknowledgments

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