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 2018

Ufficio dell'aria, del clima e delle energie rinnovabili
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Content

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 yearly reports.

2018 has been the warmest year in Switzerland since the beginning of measurements in 1864. As regards precipitations in Southern Switzerland, annual volumes were close to the norm values, while monthly volumes were characterized by seasonal extremes. After a wet winter (December 2017/January 2018) with heavy snow at high altitudes, followed a dry February, an average wet spring (March-May), a very dry summer (June-mid of October) and abundant precipitations in autumn (mid of October, end of November).

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 before 2000. 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}. After 2000, concentrations and depositions of nitrate also decreased significantly at most sites (7 out of 9 for concentrations and 6 out of 9 for depositions). This can mainly be attributed to the reduction of NO_x emissions. During the last 5 years (2014-2018) annual mean nitrate concentrations ranged from 12 to 36 meq m^{-3} and annual mean nitrate depositions from 20 to 67 meq m^{-2}. Concentrations and depositions of ammonium also slightly decreased at some sites after 2000 (concentrations of 4 out 9 and depositions of 1 out of 9 sites).

Consequently, during the last 30 years annual mean concentrations of total acidity decreased significantly at all sites from values ranging from 8 to 40 meq/m^3 (1988-1992) to values ranging from -42 to 5 meq/m^3 (2014-2018) and deposition of potential acidity decreased from values ranging from 93 to 272 meq/m^2 to values ranging from 29 to 135 meq/m^2. Accordingly, yearly mean rainwater pH increased from values around 4.3 in the 1990's to values ranging between 5.1 and 6.1 today.

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 at almost constant rates since the 1980's, concentration of nitrate decreased at higher rates after 2000. Lake water concentrations of aluminum also decreased, especially after 2005, in the most acidic lakes ($pH < 6$) Lago Tomé (from 40 μg l^{-1} to 20 μg l^{-1}), Lago del Starlaresc da Sgiof (from 80-100 μg l^{-1} to 30-70 μg l^{-1}) and Laghetto Gardiscio (from 30-60 to 20-30 μg l^{-1}).

As regards the this year autumn lake water samples, their chemistry was heavily influenced by the dry summer and early autumn. In fact, concentrations of parameters that normally get diluted with precipitations (sulphate, base cations, alkalinity, pH, SiO_2) were significantly higher than the last decade averages, while nitrate and dissolved aluminium, that normally increase with precipitation, were lower than average.

Similarly, than observed for lakes, river concentrations of sulphate, base cations, silica, alkalinity and pH were higher than average from June to October because of the lower than average discharge, while they were lower than average in May and in November because of the higher than average discharge. Concentrations of nitrate did not deviate from average values, while concentrations of aluminium peaked in May and November, the months with the highest discharge during sampling.

River chemistry also responded to emission reductions of sulphur and nitrogen. The time trend analysis revealed that from 2000 to 2018 concentrations of nitrate decreased significantly in all three rivers, while the decrease of sulphate and the increase of alkalinity was significant in the two less alkaline rivers 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 four lakes.

In the four monitored lakes, the macroinvertebrate population changed with lake pH and aluminum concentrations. Numbers of total, EPT (Ephemeroptera, Plecoptera, Trichoptera), acid sensitive and chironomid taxa were lower at sites with higher aluminum concentrations. The same rank order was observed for the relative abundance of acid sensitive taxa. As regards temporal changes, almost no trend can be observed. The only early sign of recovery seems to be the reappearance of *Crenobia alpina* in Lago di Tomè after 2006.

Overall, despite the significant decrease in deposition of acidifying pollutants and the significant increase of alkalinity in most lakes and rivers, the most sensitive surface waters did still not completely recover. A further decrease in emissions, especially for nitrogen oxides and ammonia is needed.

Analysis of POP's and metals in homogenized fish muscle sample from two high altitude alpine lakes (Laghetto Inferiore and Superiore) showed that all concentrations were below the edibility limits fixed by the Swiss legislation. In addition, concentrations of total DDT, the sum of indicator PCB, Al, Cd, Cr, Ni and Pb decreased significantly since the beginning of measurements in 2000, while concentrations of Cu, Hg and Zn remained rather constant.

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 rapporti annuali.

Il 2018 è stato l'anno più caldo in Svizzera dall'inizio delle misurazioni nel 1864. Le precipitazioni totali annue al sud della Svizzera sono state nella norma, i volumi mensili invece sono stati caratterizzati da estremi stagionali Dopo un inverno piovoso con abbondanti precipitazioni e neve in alta quota (dicembre 2017/gennaio 2018), è seguito un febbraio asciutto, una primavera con precipitazioni nella norma (marzo-maggio), un' estate molto secca (giugno-metà ottobre) e precipitazioni abbondanti in autunno (metà ottobre-fine novembre).

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 del 2000. 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, dopo il 2000 le concentrazioni e le deposizioni di nitrato sono diminuite significativamente quasi ovunque (7 stazioni su 9 per le concentrazioni e 6 stazioni su 9 per le deposizioni). Durante gli ultimi 5 anni (2014-2018) le concentrazioni medie annue variavano da un minimo di 12 a un massimo di 36 meq m^{-3} e le deposizioni da un minimo di 20 a un massimo di 67 meq m^{-2}. Le concentrazioni e le deposizioni di ammonio sono anche diminuite leggermente in alcuni punti dopo il 2000 (4 stazioni su 9 per le concentrazioni e 1 stazione su 9 per le deposizioni). Conseguentemente, negli ultimi 30 anni le concentrazioni di acidità sono

diminuite in modo significativo in tutti i punti di monitoraggio da valori medi annui che potevano variare da 8 a 40 meq/m^3 a valori che oggi possono variare da -42 a 5 meq/m^3 (2014-2018) e le deposizioni di acidità da valori che variavano da 93 a 272 meq/m^2 a valori che variano da 29 a 135 meq/m^2. Analogamente il pH medio annuo delle acque piovane è aumentato da valori medi annui attorno il 4.3 negli anni 1990 a valori che oggi variano tra 5.1 e 6.1.

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 in pressoché ugual misura durante i 2 periodo temporali analizzati (1980's-2015 and 2000-2016), 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 μg l^{-1} e nel Starlaresc da Sgiof da 80-100 μg l^{-1} a 30-70 μg l^{-1} e dopo il 2012 nel Laghetto Gardiscio da circa 30-60 a 20-30 μg l^{-1}.

Per quanto riguarda i campioni autunnali dei laghi di quest'anno, la loro chimica è stata fortemente influenzata da un'estate e da un inizio autunno particolarmente secchi. Infatti, le concentrazioni di parametri che normalmente sono diluiti dalle precipitazioni (solfato, cationi basici, alcalinità, pH, SiO_2) sono state significativamente superiori rispetto alla loro media dell'ultimo decennio, al contrario le concentrazioni di nitrato e di alluminio disciolto che normalmente aumentano con le precipitazioni, sono state inferiori.

Similmente a quanto osservato per i laghi, nei fiumi, a causa della lunga siccità, da giugno a ottobre le concentrazioni di solfato, cationi basici, SiO_2 alcalinità e pH sono state inferiori alla media, mentre sono state superiori alla media in maggio e novembre caratterizzati da portate elevate. Le concentrazioni di nitrato non sono deviate dalla media, mentre le concentrazioni di alluminio disciolto sono state superiori alla media in maggio e in novembre, i mesi con le portate più elevate durante il campionamento.

La riduzione delle emissioni di zolfo e azoto si riflette anche nella chimica dei fiumi. L'analisi delle tendente temporali ha mostrato una diminuzione delle concentrazioni di nitrato in tutti e 3 i fiumi monitorati dal 2000 al 2018, mentre la diminuzione del solfato e l'aumento dell'alcalinità è stato significativo nei 2 fiumi con minore alcalinità (Vedeggio, Verzasca).

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 4 laghi.

Nei 4 laghi monitorati la popolazione di macroinvertebrati varia con il pH e le concentrazioni di alluminio. I numeri di taxa totale, taxa EPT (Efemerotteri, Plecotteri, Tricotteri) e taxa sensibili all'acidificazione e di chironomidi diminuiscono con l'aumentare delle concentrazioni di alluminio e con il diminuire del pH. L'abbondanza relativa di taxa sensibili all’acidificazione segue la stessa graduatoria. Per quanto riguarda l’evoluzione temporale, non si è osservato praticamente alcuna tendenza. L’unico primo segno di recupero sembra essere il ritorno di *Crenobia alpina* nel Lago di Tomè dopo il 2006.

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.

Le analisi di POP e metalli in campioni oomogeneizzati di muscolo di pesce pescati in 2 laghetti alpini di alta quota (Laghetto Inferiore and Superiore) hanno mostrato che le concentrazioni di tutti i parametri sono state inferiori dei limiti di edibilità fissati dalla legislazione Svizzera. Inoltre, le concentrazioni del DDT totale, della somma dei PCB indicatori, di Al, Cd, Cr, Ni and Pb sono diminuite significativamente dall’inizio delle misurazioni nel 2000, mentre sono rimaste piuttosto invariate le concentrazioni di Cu, Hg e Zn.

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 2018

2018 has been the warmest year in Switzerland since the beginning of measurements in 1864 and after 2012, 2014 and 2015, it has been the fourth year in a short period with average temperatures exceeding the norm value (1981-2000). As regards annual precipitation, in Southern Switzerland they did not vary greatly from the norm values: they were slightly higher in the northwestern part of the Canton Ticino and slightly lower in the southeastern part. However, monthly precipitations differed significantly from the norm values. After a wet winter (December 2017/January 2018) with heavy snow at high altitudes (at Robiei precipitations were 140% of the norm values in December and 270% in January), followed a dry February, an average wet spring (March-May), a very dry summer (June-September) and a very dry autumn (October, November). In summer precipitations varied between 30% and 50% of the norm values and in autumn between 75% at the normally wettest sites (northwest) and 150% at the normally driest sites (northeast). (MeteoSvizzera, 2019)

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. In 2018, macroinvertebrates have been sampled in four lakes. In addition, wet deposition has been monitored at 9 sampling sites distributed over all the Canton of Ticino.

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)

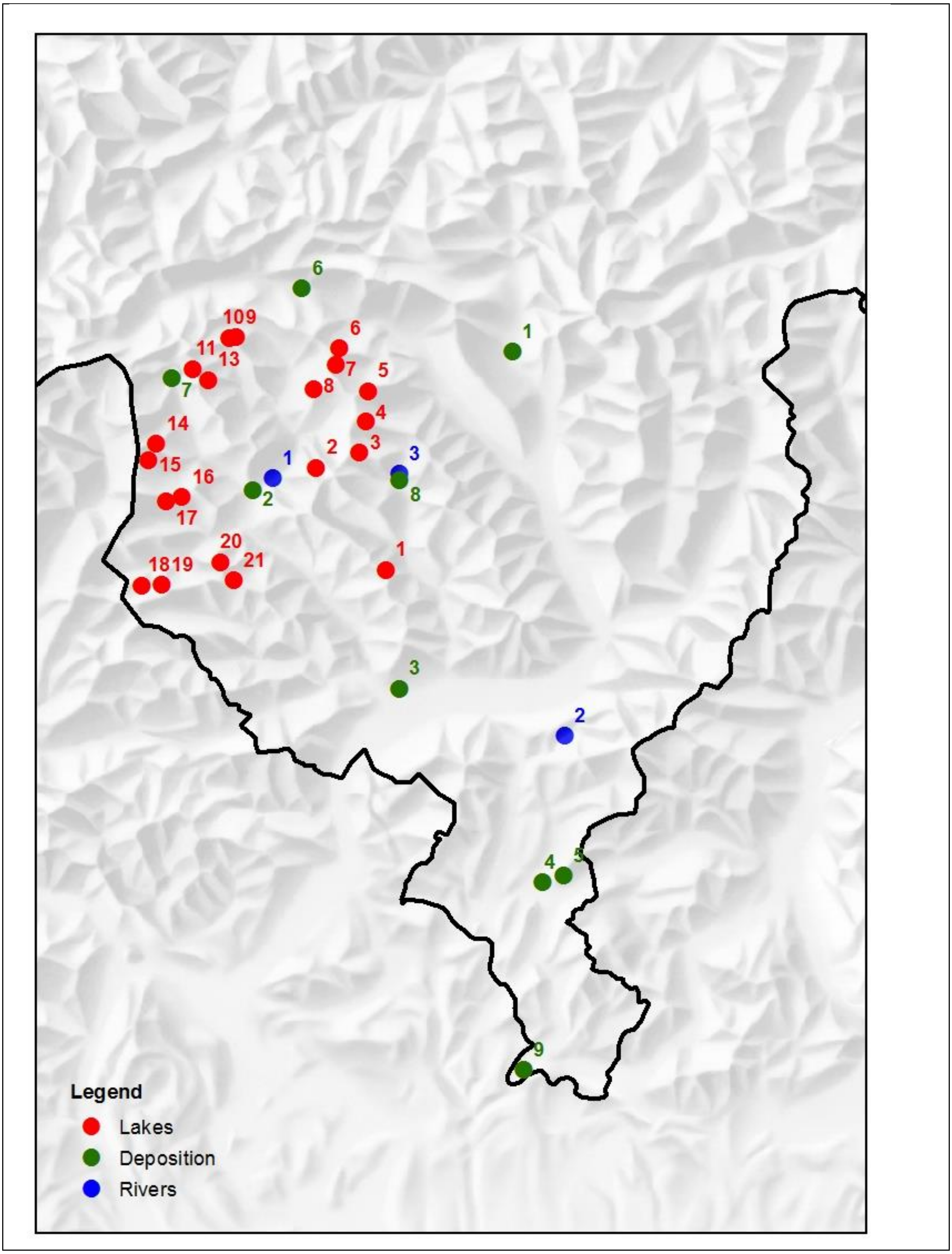

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Table 2.1 Geographic and morphometric parameters of the wet deposition sampling sites

Sampling site number	Sampling site	CH1903 LV03 (m)		WGS84		Altitude
		Longitude	Latitude	Longitude	Latitude	m a.s.l.
1	Acquarossa	714998	146440	8°56’12”	46°27’41”	575
2	Bignasco	690205	132257	8°59’17”	46°00’32”	443
3	Locarno Monti	704160	114350	8°47’17”	46°10’27”	366
4	Lugano	717880	95870	8°57’18”	46°00’24”	273
5	Monte Brè	719900	96470	8°59’17”	46°00’32”	925
6	Piotta	694930	152500	8°40’35”	46°31’7”	1007
7	Robiei	682540	143984	8°30’51”	46°26’43”	1890
8	Sonogno	704250	134150	8°47’14”	46°21’05”	918
9	Stabio	716040	77970	8°55’52”	45°51’36”	353
10	Cristallina	683526	147305	8°31’34”	46°28’19”	2575

Table 2.2 Geographic and morphometric parameters of the studied rivers

River number	River name	Sampling site	CH1903 LV03 (m)		WGS84		Altitude	Catchment area
			Longitude	Latitude	Longitude	Latitude	m a.s.l	km^2
1	Maggia	Brontallo	692125	134375	8°38’ 8”	46°21’16”	610	ca. 189
2	Vedeggio	Isone	719900	109800	8°59’24”	46°07’45”	740	20
3	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 name	CH1903 LV03 (m)		WGS84		Altitude	Catchment area	Lake area	Max depth
		Longitude	Latitude	Longitude	Latitude	m a.s.l.	ha	ha	m
1	Lago del Starlaresc da Sgiof	702905	125605	8°46’25”	46°16’26”	1875	23	1.1	6
2	Lago di Tomè	696280	135398	8°41’23”	46°21’47”	1692	294	5.8	38
3	Lago dei Porchieirsc	700450	136888	8°44’39”	46°22’33”	2190	43	1.5	7
4	Lago Barone	700975	139813	8°45’06”	46°24’07”	2391	51	6.6	56
5	Laghetto Gardiscio	701275	142675	8°45’22”	46°45’22”	2580	12	1.1	10
6	Lago della Capannina Leit	698525	146800	8°43’17”	46°27’55”	2260	52	2.7	13
7	Lago di Morghirolo	698200	145175	8°43’00”	46°27’03”	2264	166	11.9	28
8	Lago di Mognòla	696075	142875	8°41’19”	46°25’49”	2003	197	5.4	11
9	Laghetto Inferiore	688627	147855	8°35’34”	46°28’34”	2074	182	5.6	33
10	Laghetto Superiore	688020	147835	8°35’05”	46°28’34”	2128	125	8.3	29
11	Lago Nero	684588	144813	8°32’22”	46°26’58”	2387	72	12.7	68
13	Lago della Froda	686025	143788	8°33’29”	46°26’24”	2363	67	2.0	17
14	Laghetto d'Antabia	681038	137675	8°29’32”	46°23’08”	2189	82	6.8	16
15	Lago della Crosa	680375	136050	8°28’60”	46°22’16”	2153	194	16.9	70
16	Lago d'Orsalìa	683513	132613	8°31’24”	46°20’23”	2143	41	2.6	16
17	Schwarzsee	681963	132188	8°30’11”	46°20’10”	2315	24	0.3	7
18	Laghi dei Pozzöi	679613	124200	8°28’17”	46°15’52”	1955	33	1.1	4
19	Lago di Sfille	681525	124213	8°29’46”	46°15’52”	1909	63	2.8	12
20	Lago di Sascòla	687175	126413	8°34’11”	46°17’01”	1740	90	3.2	5
21	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 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 of acidification appear, when pH drops below 6 (Wright et al. 1975).

3.2 Sampling methods

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 is 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. Because of the renovation works at the Ritom hydropower station, the sampling site of Piotta had to be moved during 2018. The new site is located at about one kilometer from the old site and is close to the meteorological station of MeteoSwiss at Piotta. To verify the representativeness of the new site, from June to November samples at both sites were collected.

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), from 2006 three times a year (once at the beginning of summer, 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, accuracy and quantification limits. CA, PC, GF, PP stay for cellulose acetate, polycarbonate, glass fibre and polypropylene, respectively and ICP-OES for inductively coupled plasma atomic-emission spectroscopy.

Parameter	Filtration	Conservation	Method	Accuracy
pH	No	No	potentiometry	0.02
conductivity	No	No	Kolrausch bridge (20°C)	1 μS cm^{-1}
alkalinity	No	No	potentiometric Gran titration	0.001 meq l^{-1}
				Quantification limit
Ca^{2+}	CA filter	PP bottle, 4°C	ion cromatography	0.16 mg l^{-1}
Mg^{2+}	CA filter	PP bottle, 4°C	ion cromatography	0.03 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	spectrophotometry	30 μg N l^{-1}
SO$_4^{2-}$	CA filter	PP bottle, 4°C	ion cromatography	0.05 mg l^{-1}
NO$_3^-$	CA filter	PP bottle, 4°C	ion cromatography	0.02 mg N l^{-1}
NO$_2^-$	CA filter	PP bottle, 4°C	spectrophotometry	6 μg N l^{-1}
Cl$^-$	CA filter	PP bottle, 4°C	ion cromatography	0.002 mg l^{-1}
soluble reactive P	CA filter	PP bottle, 4°C	spectrophotometry	11 μg P l^{-1}
total P	No	glass bottle, immediate mineralisation	persulphate digestion, spectrophotometry	32 μg P l^{-1}
soluble reactive Si	CA filter	PP bottle, 4°C	ICP-OES with ultrasonic nebulizer	0.09 mg SiO$_2$ l^{-1}
total N	No	glass bottle, immediate mineralisation	persulphate digestion, spectrophotometry	
DOC	PC filter	brown glass bottle, + H$_3$PO$_4$	UV-persulfate	0.2 mg C l^{-1}
soluble Al	PC filter	acid washed PP bottle, +HNO$_3$, 4°C	Adsorptive Stripping Voltammetry (AdSV)	1.0 μg l^{-1}
total Al	No	acid washed PP bottle, +HNO$_3$, 4°C	Adsorptive Stripping Voltammetry (AdSV)	1.0 μg l^{-1}
soluble Pb	PC filter	acid washed PP bottle, +HNO$_3$, 4°C	Adsorptive Stripping Voltammetry (AdSV)	0.1 μg l^{-1}
total Pb	No	acid washed PP bottle, +HNO$_3$, 4°C	Adsorptive Stripping Voltammetry (AdSV)	0.1 μg l^{-1}
soluble Cd	PC filter	acid washed PP bottle, +HNO$_3$, 4°C	Adsorptive Stripping Voltammetry (AdSV)	0.1 μg l^{-1}
total Cd	No	acid washed PP bottle, +HNO$_3$, 4°C	Adsorptive Stripping Voltammetry (AdSV)	0.1 μg l^{-1}
soluble Cu	PC filter	acid washed PP bottle, +HNO$_3$, 4°C	Adsorptive Stripping Voltammetry (AdSV)	0.1 μg l^{-1}
total Cu	No	acid washed PP bottle, +HNO$_3$, 4°C	Adsorptive Stripping Voltammetry (AdSV)	0.1 μg l^{-1}
soluble Zn	PC filter	acid washed PP bottle, +HNO$_3$, 4°C	Adsorptive Stripping Voltammetry (AdSV)	0.1 μg l^{-1}
total Zn	No	acid washed PP bottle, +HNO$_3$, 4°C	Adsorptive Stripping Voltammetry (AdSV)	0.1 μg l^{-1}
soluble Cr	PC filter	acid washed PP bottle, +HNO$_3$, 4°C	Adsorptive Stripping Voltammetry (AdSV)	0.1 μg l^{-1}
total Cr	No	acid washed PP bottle, +HNO$_3$, 4°C	Adsorptive Stripping Voltammetry (AdSV)	0.1 μg l^{-1}
soluble Ni	PC filter	acid washed PP bottle, +HNO$_3$, 4°C	Adsorptive Stripping Voltammetry (AdSV)	0.1 μg l^{-1}
total Ni	No	acid washed PP bottle, +HNO$_3$, 4°C	Adsorptive Stripping Voltammetry (AdSV)	0.1 μg l^{-1}
soluble Fe	PC filter	acid washed PP bottle, +HNO$_3$, 4°C	Adsorptive Stripping Voltammetry (AdSV)	1.0 μg l^{-1}
total Fe	No	acid washed PP bottle, +HNO$_3$, 4°C	Adsorptive Stripping Voltammetry (AdSV)	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.

For river and lake water data analysis, concentrations of calcium, magnesium, potassium and sodium were summed up and presented as base cations. For rainwater data analysis only concentrations of calcium, magnesium and potassium were summed and presented as base cations, because sodium originates almost entirely from sea salt (or road salt in winter at Piotta) and does not affect deposition of acidity. Concentrations of total acidity were calculated subtracting concentrations and depositions of positive alkalinity from concentrations and depositions of hydrogen ion calculated from the measured pH's. Depositions of potential acidity were calculated subtracting depositions of base cations 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 2018 are shown in Tab. 3.2.

Table 3.2 Yearly mean rainwater concentrations and deposition rates in 2018

Sampling site	Precipitation MeteoCH (mm)	Analysed precipitation (mm)	Cond 25°C (µS cm^{-1})	pH	Ca^{2+}		Mg^{2+}		Na^{+}		K^{+}		NH_4^{+}		HCO_3^{-}		SO_4^{2-}		NO_3^{-}		Cl^{-}		Total acidity	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})
Acquarossa	1077	1101	9	5.7	23	25	3	4	6	6	2	2	28	30	27	29	13	14	19	20	6	7	-15	32
Bignasco	1869	1781	9	5.6	21	39	4	7	8	16	2	3	31	55	25	46	14	26	20	37	9	17	-23	67
Locarno Monti	1467	1340	11	5.6	25	36	5	7	10	15	2	2	32	47	26	38	17	25	25	37	10	15	-23	60
Lugano	1474	739	12	6.1	35	47	5	6	8	13	3	4	43	73	43	49	18	30	26	55	9	15	-42	64
Monte Brè	1474	1158	13	5.9	35	52	6	12	12	18	4	6	40	59	36	54	20	30	33	49	12	18	-35	66
Piotta	1617	1374	8	5.7	23	37	3	5	9	14	1	2	19	30	21	34	12	20	15	24	9	14	-19	29
Robiei	2665	1986	7	5.5	15	41	3	7	4	11	1	4	17	46	10	27	12	31	18	49	5	12	-7	74
Sonogno	1867	1278	10	6.0	17	32	3	6	8	14	3	6	44	81	29	54	14	26	24	45	8	14	-28	111
Stabio	1489	1335	12	5.7	23	34	4	6	8	12	3	4	46	69	31	45	17	25	32	48	9	13	-29	95

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 measurements. In 2018, the highest concentrations of the sum of sulphate, nitrate and ammonia were measured at Monte Brè and Stabio, the lowest at Piotta and Robiei. 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 highest annual mean rainwater acidity was measured at Robiei. In fact, concentrations of acidity can be approximated subtracting concentrations of base cations and ammonium from concentrations of acid anions.

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 2018, highest deposition rates of the sum of ammonia, nitrate and sulphate occurred at Sonogno and the lowest at Acquarossa. Highest annual mean deposition of potential acidity was measured at Sonogno and Stabio; the lowest at Acquarossa and Piotta.

Seasonal variation

Fig. 3.1 shows the amount of monthly precipitation at each sampling site during 2018 and the average values during the previous decade 2008-2017. 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 from May to November. Highest precipitation volumes usually occur in May and November. Compared to average values, precipitation of 2018 was significantly higher in January, October and November and significantly lower in June and July.

During 2008-2017 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 2008-2017 were highest in March and lowest from November to January. 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 2008-2017 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 base cations, during 2008-2017 they tended to be higher in spring and to be similar at all sites. In winter, variations in concentrations among the different sites were more pronounced: especially at Sonogno and Piotta they tended to be higher from December to February maybe because of the higher local wood combustion. Acid deposition showed an opposite behaviour with the lowest monthly concentrations during spring, indicating that concentrations of base cations heavily influence the seasonality of acidity. Similarly, rainwater pH is usually higher in spring/summer.

In general, compared to the last decade, concentrations of sulphate were slightly lower, while concentrations of nitrate and ammonium were in the same range of order. Single concentration peaks can often be attributed to an increase due to small precipitation volumes. Examples are the sulphate peaks in February and July at Monte Bré and in December at Lugano, all combined with base cations peaks and the nitrate and ammonium peaks in February and September at almost all sites. Concentrations of base cations were in general higher in part due to small precipitation volumes (February, June, September and July and December at Monte Bré and Lugano, respectively) and in part due to alkaline rain events (January, October, November). As a result concentrations of total acidity were also often lower and pH higher compared to average values of the last decade. In fact, during 2018 only 4% of the analyzed rainwater samples had pH values below 5, while they were 13% between 2008 and 2017. Similarly, during the last year 96% and 49% of the samples had pH values higher than 5.5 and 6.0, respectively. These percentages were only 86% and 32%, respectively during 2008-2017.

Monthly variations of wet depositions behave in general similar to monthly variations of concentrations, with the difference that precipitation amounts gain further importance (Fig. 3.3). Average (2007-2018) monthly depositions of sulphate, nitrate, ammonium, base cations and potential acidity are normally higher during the warm months when both concentrations and precipitations are highest. Because of the last year drier than usual summer (June and August) and wetter than usual January and autumn (September and October), monthly depositions varied from the last decade average values. Depositions of especially sulphate and base cations but also of nitrate and ammonium were in general lower in summer and higher in autumn. In accordance with the monthly variation of the precipitation volume, in 2018 deposition peaks occurred in January, March-May, August and October-November. Deposition of potential acidity was higher than average in the precipitation rich January at Monte Brè and lower than average in the dry month June and July at all sites. During the rainy autumn months (October, November), at Robiei and Sonogno deposition of potential acidity was higher than average, while at the same time it was lower at most other sampling sites.

Figure 3.1 Monthly precipitations

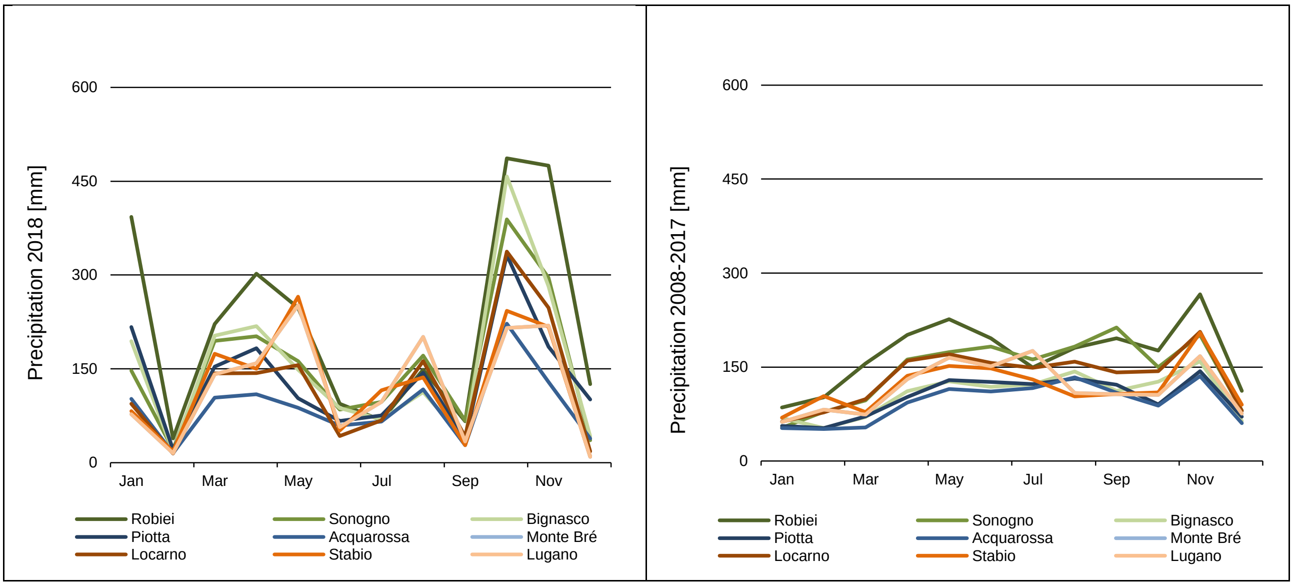
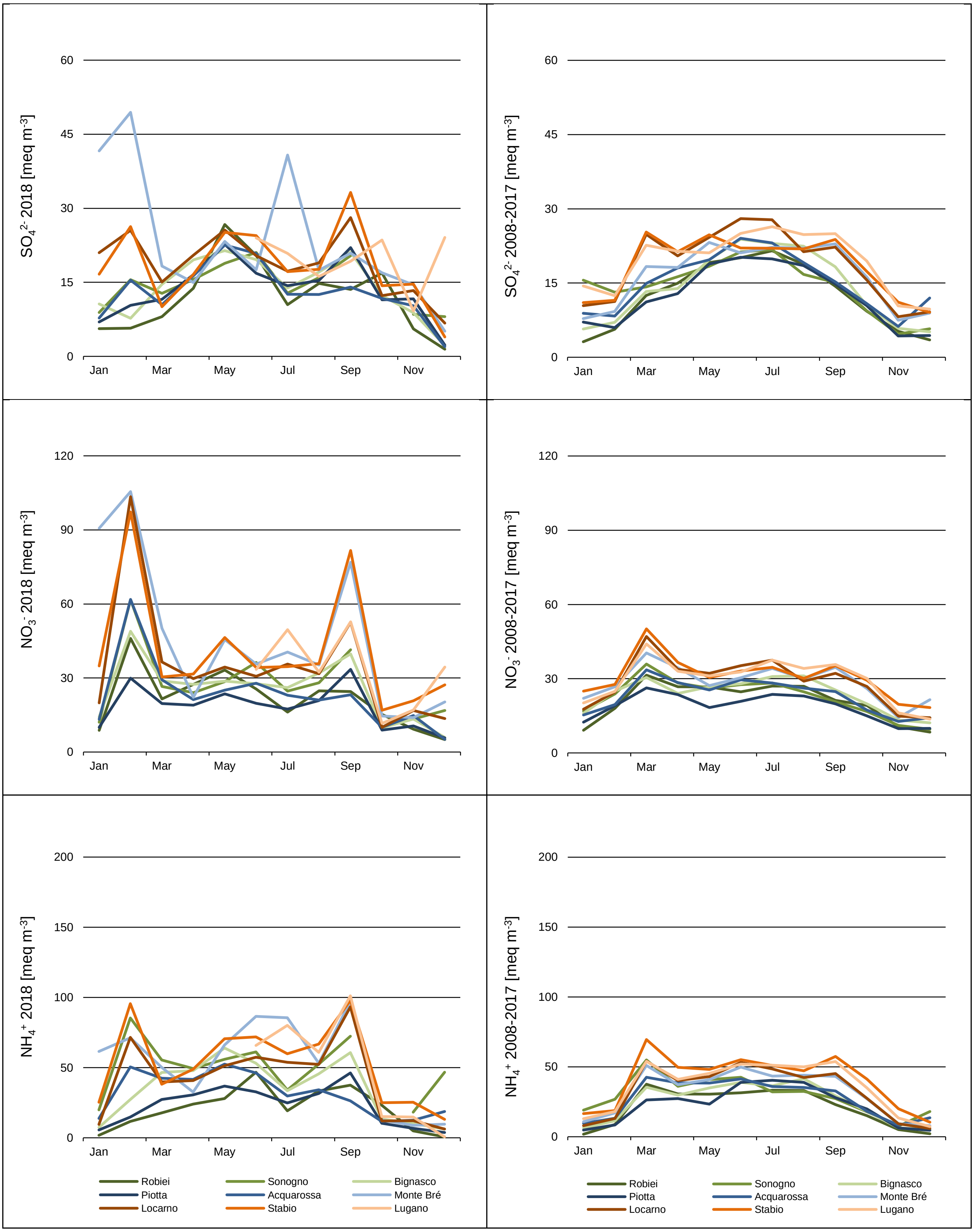


Figure 3.2 Seasonal variations of monthly average rainwater concentrations



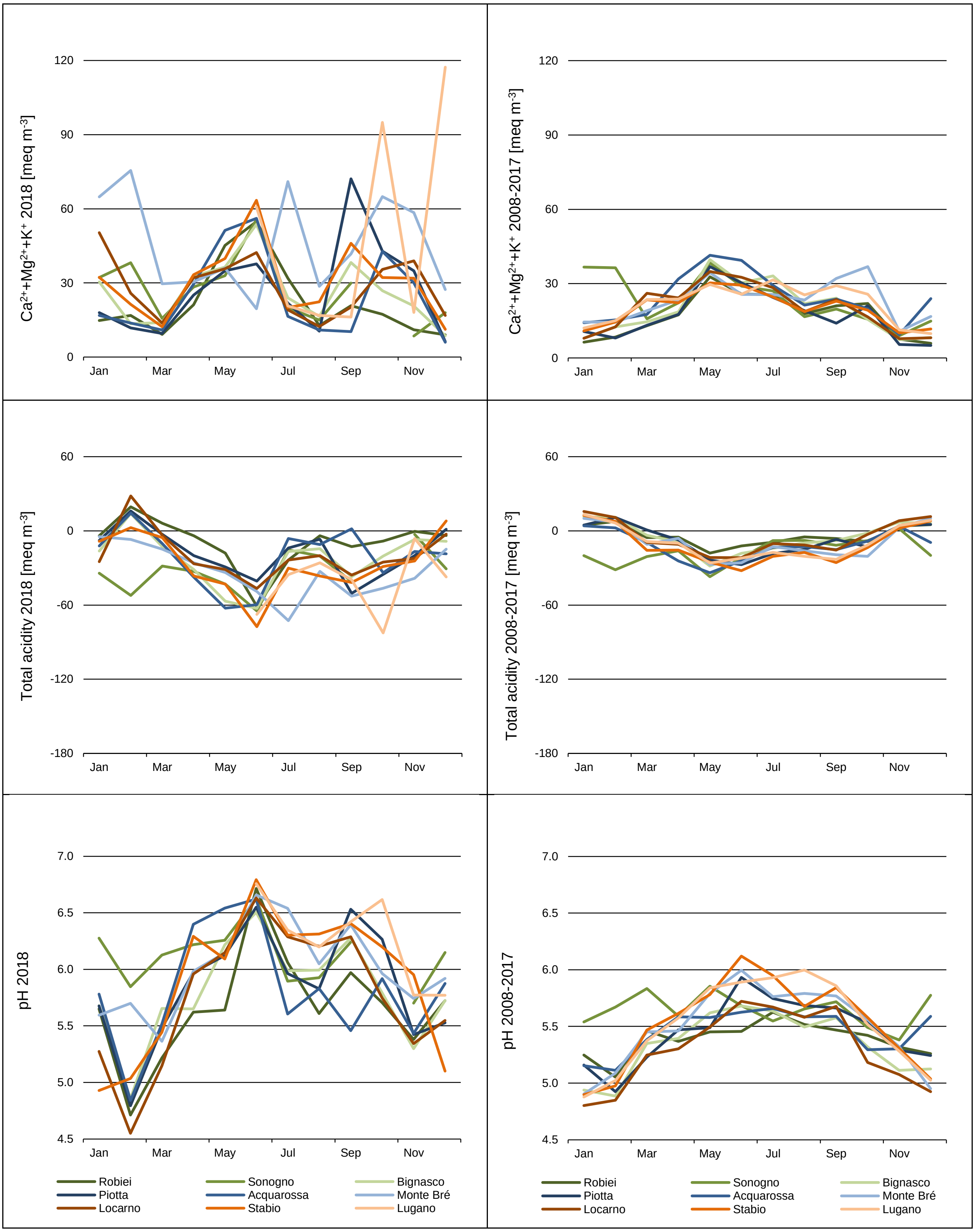
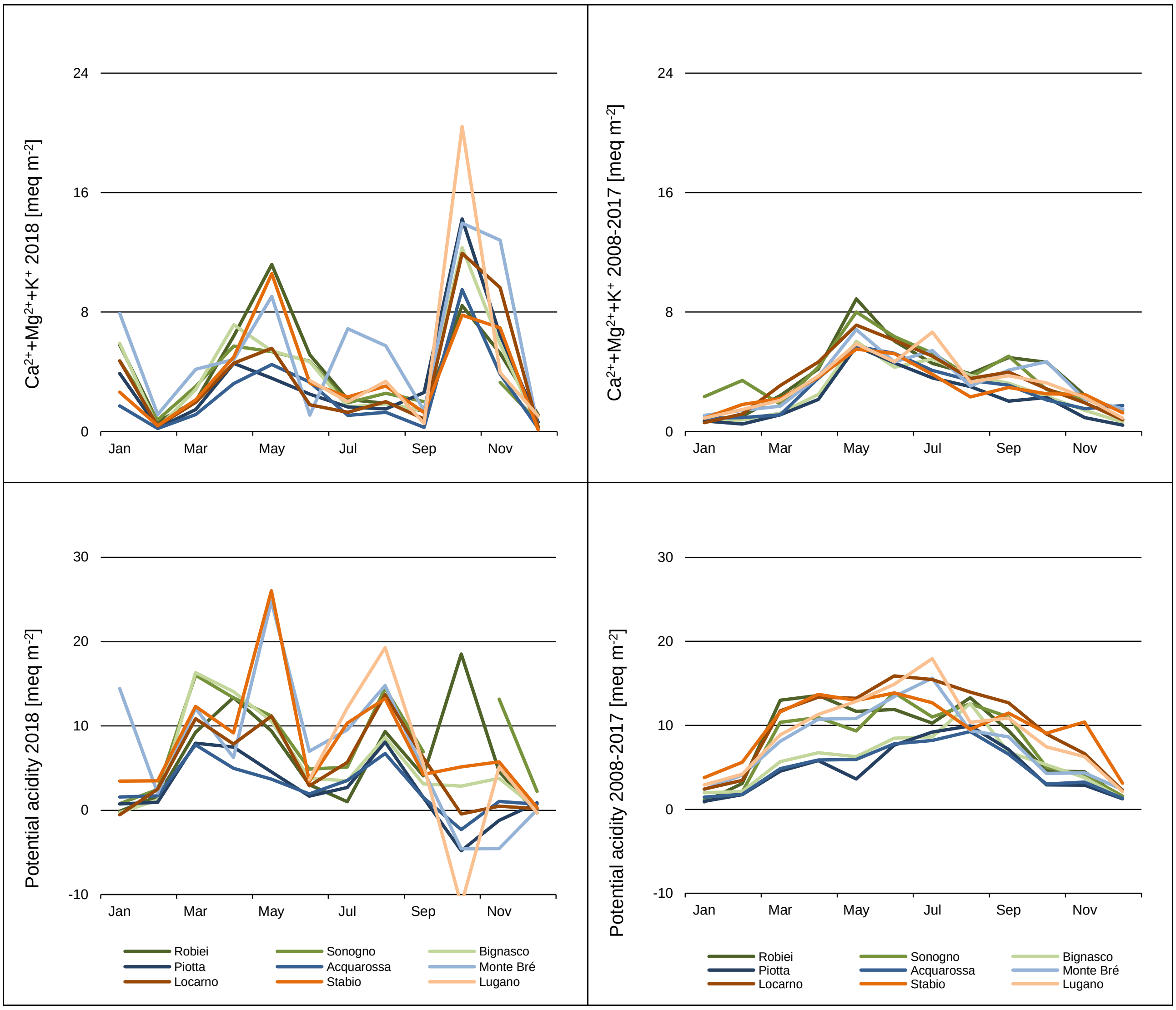

Ca²⁺+Mg²⁺+K⁺ 2018 [meq m⁻³]
Ca²⁺+Mg²⁺+K⁺ 2008-2017 [meq m⁻³]
Total acidity 2018 [meq m⁻³]
Total acidity 2008-2017 [meq m⁻³]
pH 2018
pH 2008-2017
0
30
60
90
120
-180
-120
-60
0
60
4.5
5.0
5.5
6.0
6.5
7.0
Jan
Mar
May
Jul
Sep
Nov
Robiei
Sonogno
Bignasco
Piotta
Acquarossa
Monte Bré
Locarno
Stabio
Lugano

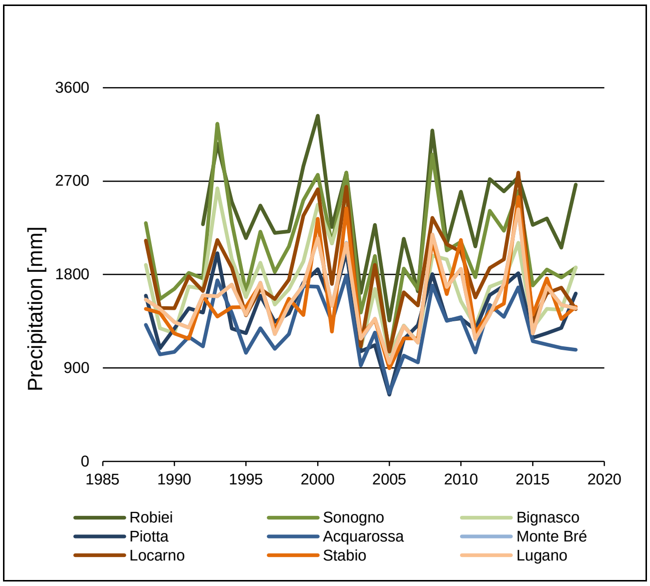
Figure 3.3 Seasonal variations of monthly wet deposition


Ca2++Mg2++K+ 2018 [meq m-2]
Ca2++Mg2++K+ 2008-2017 [meq m-2]
Potential acidity 2018 [meq m-2]
Potential acidity 2008-2017 [meq m-2]
0
8
16
24
-10
0
10
20
30
Jan
Mar
May
Jul
Sep
Nov
Robiei
Sonogno
Bignasco
Piotta
Acquarossa
Monte Bré
Locarno
Stabio
Lugano

Temporal variations

The amount of yearly precipitations at each sampling site is presented in Fig. 3.4. As regards precipitations, 2018 was characterized not only by seasonal extremes but also by extremes among the different sampling sites. At normally wet sites precipitations were higher than average (e.g. Robiei: 110% of the norm value) and at drier sites precipitations were lower than average (e.g. Acquarossa: 82% of the norm value). 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 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 base cations also decreased and alkaline rain events became less frequent.

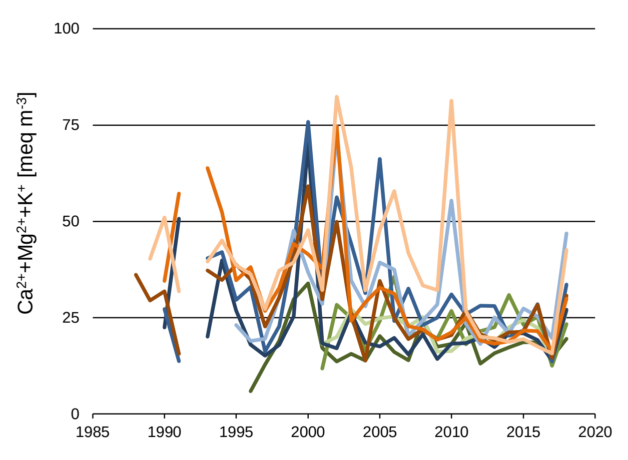
Concentrations of total acidity, that also corresponds to the difference between acid anions and base cations and ammonia, decreased significantly at most sites. In general, concentrations of total acidity decreased from values around 30-40 meq/m^3 to values around -15 meq/m^3 on average over the last 30 years. Last year, with exception of Robiei, because of the higher depositions of base cations especially in autumn, average concentrations of total acidity was even lower. As a consequence of the total acidity concentration trend, average pH increased from values around 4.3 in the 1990’s to values ranging between 5.3 and 5.7 today.

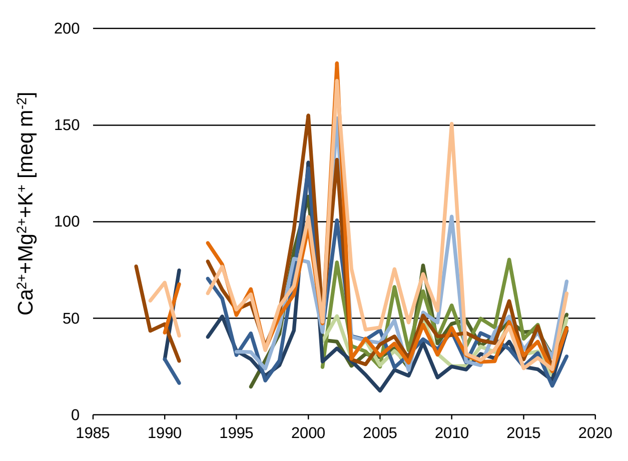
Trends of rainwater concentrations were analyzed for two different time periods: from 1988-1991 until 2000 and from 2000 until 2018 (Tab. 3.4). Since trends of depositions are “disturbed” by the precipitation volumes that vary irregularly through time, trends in depositions were calculated only for the entire monitoring period in order to level out as much as possible the influence of rainwater volume.

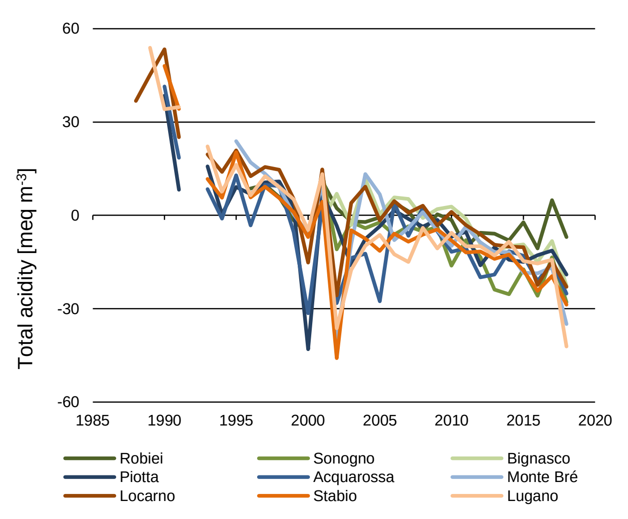
Sulphate concentrations decreased at all sites and changes in concentrations were higher before 2000, except for Acquarossa. In contrast, nitrate and ammonium started to decrease significantly only after 2000 (7 out of 9 for nitrate and 4 out of 9 for ammonium). Before 2000 a significant decrease could only be observed at Stabio. Because of the decrease in sulphate and nitrate concentrations, concentrations of hydrogen ions and total acidity decreased significantly at all sites, although the changes in concentrations were higher before 2000.

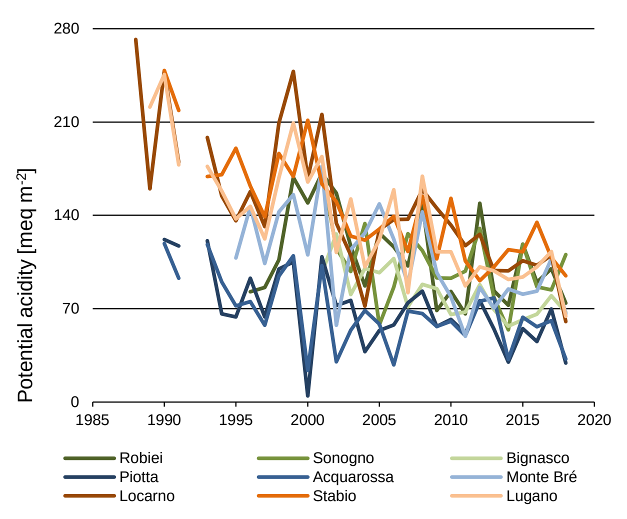
Trends in depositions are similar but less pronounced. The decrease in depositions of sulphate was significant at all sites. Depositions of nitrate decreased significantly at Acquarossa, Locarno Monti, Lugano, Monte Brè, Piotta, Stabio. Trends were smaller for depositions of ammonium and significant only at Locarno Monti. Similar to concentrations, depositions of hydrogen ions also decreased significantly at all sites. Deposition of potential acidity decreased at almost all sites.

Figure 3.5 Temporal variations of annual mean rainwater concentrations, depositions and rainwater pH


Ca^{2+}+Mg^{2+}+K^{+} [meq m^{-3}]
100
75
50
25
0
1985
1990
1995
2000
2005
2010
2015
2020


Ca^{2+}+Mg^{2+}+K^{+} [meq m^{-2}]
200
150
100
50
0
1985
1990
1995
2000
2005
2010
2015
2020


Total acidity [meq m^{-3}]
60
30
0
-30
-60
1985
1990
1995
2000
2005
2010
2015
2020
Robiei
Sonogno
Bignasco
Piotta
Acquarossa
Monte Bré
Locarno
Stabio
Lugano


Potential acidity [meq m^{-2}]
280
210
140
70
0
1985
1990
1995
2000
2005
2010
2015
2020
Robiei
Sonogno
Bignasco
Piotta
Acquarossa
Monte Bré
Locarno
Stabio
Lugano

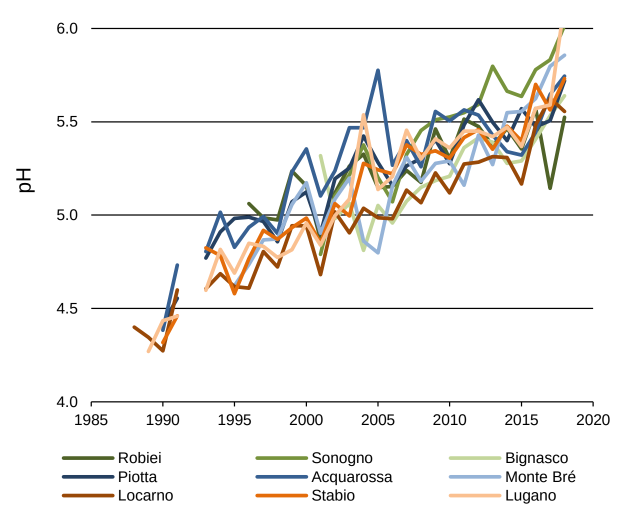

pH
6.0
5.5
5.0
4.5
4.0
1985
1990
1995
2000
2005
2010
2015
2020
Robiei
Sonogno
Bignasco
Piotta
Acquarossa
Monte Bré
Locarno
Stabio
Lugano

Table 3.4 Changes in rainwater concentrations and depositions during the indicated time periods. Red rates indicate significant trends.

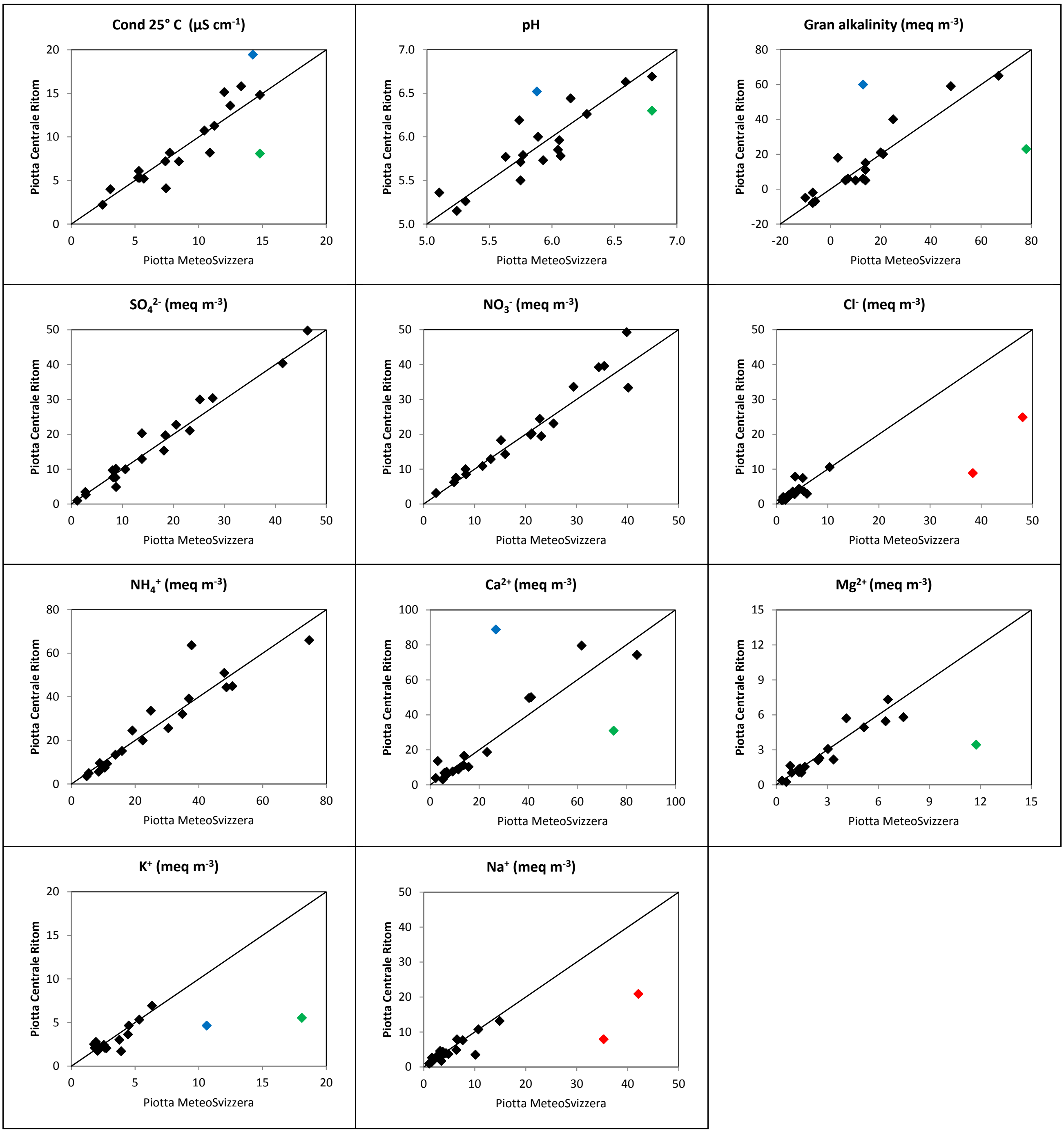
CONCENTRATIONS	**SO_4^{2-}**		**NO_3^-**		**NH_4^+**		**Cl^-**		**Base cations**		**H^+**		**Total acidity**	
(meq m^{-3} yr^{-1})	'80/'90-00	'00-18	'90-00	'00-18	'90-00	'00-18	'90-00	'00-18	'90-00	'00-18	'90-00	'00-18	'90-00	'00-18
Acquarossa	-1.41	-1.41	-1.04	-0.45	-1.04	-0.15	-0.83	-0.03	-0.46	-1.68	-2.29	-0.04	-4.53	-0.22
Bignasco		-0.73		-0.56		-0.09		-0.01		-0.08		-0.48		-1.45
Monte Brè		-1.22		-0.64		-0.36		0.04		-0.17		-0.45		-1.68
Locarno Monti	-3.20	-1.35	-0.78	-1.01	-0.54	-0.54	-0.61	0.01	0.07	-0.45	-3.48	-0.58	-4.38	-1.52
Lugano	-2.79	-2.13	-1.22	-1.36	-0.10	-1.00	-0.70	-0.22	0.08	-1.57	-2.85	-0.22	-4.28	-1.07
Piotta	-1.43	-0.58	-0.62	-0.50	-0.11	-0.28	-0.43	-0.04	-0.88	-0.21	-1.63	-0.25	-2.14	-0.70
Robiei		-0.66		-0.17		-0.39		0.00		-0.06		-0.21		-0.46
Sonogno		-0.52		-0.23		0.17		0.07		0.02		-0.26		-1.44
Stabio	-3.44	-1.54	-2.08	-0.84	-0.85	-0.59	-0.98	-0.06	-2.16	-0.53	-2.65	-0.23	-3.83	-1.43

DEPOSITIONS	**SO_4^{2-}**	**NO_3^-**	**NH_4^+**	**Cl^-**	**Base cations**	**H^+**	**Potential acidity**
(meq m^{-2} yr^{-1})	beginning-18	beginning-18	beginning-18	beginning-18	beginning-18	beginning-18	beginning-18
Acquarossa	-1.00	-0.58	-0.20	-0.11	-0.46	-0.45	-1.38
Bignasco	-0.67	-0.35	0.12	0.07	0.06	-0.46	-1.47
Monte Brè	-1.32	-0.57	-0.17	0.12	-0.02	-0.76	-2.47
Locarno Monti	-2.38	-0.92	-0.48	-0.25	-0.47	-1.59	-3.72
Lugano	-2.45	-0.68	-0.20	-0.18	-0.68	-1.08	-2.68
Piotta	-0.70	-0.38	-0.10	-0.08	-0.20	-0.51	-0.95
Robiei	-1.18	-0.12	-0.30	0.00	0.05	-0.46	-1.30
Sonogno	-0.80	-0.39	0.29	0.11	0.20	-0.42	-1.07
Stabio	-2.42	-0.98	-0.38	-0.17	-0.77	-0.79	-2.91

Comparison between old and new sampling site at Piotta

Fig. 3.6 compares the measured concentrations of sulphate, nitrate, chloride, ammonium, base cations, alkalinity and pH in weekly samples between July and December 2018 at the two sampling sites at Piotta. Concentrations of sulphate, nitrate and ammonium correlated very well at the two sites. Concentrations of chloride and sodium correlated well from June to October, but varied considerably after November when the use of road salt at the highway close by started (see red points in the graph): at both sites rainwater chemistry is influenced by road salt, but at the new site the influence is greater because situated closer to the highway. However, this does not cause any particular problem, because concentrations of chloride and sodium are not used to model acid deposition. Concentrations of base cations and alkalinity also varied considerably among the two sites in two occasions. In samples from the first week of July (2.7.18-9.7.18, green point) concentrations were considerably higher at the new site, probably because of the influence of a heap of earth nearby. In samples from the second week of October (8.10.18-15.10.18, blue point) concentrations were higher at the old site. We don’t know exactly why. At all other sites with similar latitude (Bignasco, Robiei, Sonogno) concentrations of base cations and alkalinity were not particularly high during this week, therefore a local source can be supposed, maybe the construction area of the new Ritom hydropower station. However, for most samples base cations and alkalinity measured at the two sites corresponded well, wherefore we accepted to continue to monitor at the new site and abandoned the old one.

Figure 3.6 Comparision between the rainwater chemistry collected at the old (Centrale Ritom) and new (MeteoSwiss) sampling site at Piotta.



3.5.2 Alpine lakes

Spatial variations

In 2018, lake sampling occurred on 11th July, 10th September and 16th October. Average autumn concentrations of the main chemical parameters measured in lake surface water are presented in Tab. 3.5. Conductivity at 25°C varied between 6 and 32 $\mu S\ cm^{-1}$, total alkalinity between -1 and 96 $meq\ m^{-3}$, pH between 5.5 and 7.4, calcium between 19 and 151 $meq\ m^{-3}$, sulphate between 12 and 216 $meq\ m^{-3}$, nitrate between 3 and 24 $meq\ m^{-3}$, dissolved organic carbon between 0.3 and 1.2 $mg\ C\ l^{-1}$, reactive dissolved silica between 0.8 and 3.3 $mg\ SiO_2\ l^{-1}$ and dissolved aluminum between 2 and 32 $\mu g\ l^{-1}$. 35% of the autumn samples were characterized by total alkalinities below 20 $meq\ m^{-3}$ and 10% by pH's below 6.

Table 3.5 Lake surface water concentrations in autumn 2018. Values below the quantification limit were preceded with <.

Lake name	Lago del Starlaresc da Sgiof	Lago di Tomè	Lago dei Porchieirsc	Lago Barone	Laghetto Gardiscio	Lago della Capannina Leit	Lago di Morghirolo	Lago di Mognòla	Laghetto Inferiore	Laghetto Superiore	Lago Nero	Lago della Froda	Lago d’Antabia	Lago della Crosa	Lago d'Orsalia	Schwarzsee	Lago dei Pozzöi	Lago di Sfille	Lago di Sascòla	Lago d'Alzasca
Cond 25°C (µS cm^{-1})	6.3	8.3	24.4	8.8	7.5	31.7	14.3	20.9	9.3	8.1	17.9	15.4	13.9	7.1	9.1	13.6	9.1	11.2	9.0	16.7
pH	6.2	6.1	7.1	6.4	5.5	6.6	6.8	7.4	6.9	7.0	7.0	7.0	7.4	6.6	6.8	6.9	6.8	6.9	6.4	7.0
Total Alkalinity (meq m^{-3})	16	13	88	20	-1	37	52	89	47	45	85	81	92	32	43	71	51	57	33	96
Ca^{2+} (meq m^{-3})	19	35	148	43	20	151	69	103	47	43	102	98	85	36	49	83	45	61	37	89
Mg^{2+} (meq m^{-3})	8	5	15	6	7	60	17	24	7	7	15	9	6	5	6	9	8	9	11	18
Na^{+} (meq m^{-3})	13	14	23	11	7	23	16	30	14	12	17	14	12	11	13	16	16	18	14	21
K^{+} (meq m^{-3})	4	4	14	4	5	16	13	14	9	7	13	8	8	4	5	8	5	4	10	13
NH_4^{+} (meq m^{-3})	2	1	0	1	2	1	1	0	0	0	0	0	0	0	0	0	0	1	1	1
SO_4^{2-} (meq m^{-3})	20	24	107	33	33	216	57	81	24	20	64	46	17	12	15	27	20	27	23	34
NO_3^{-} (meq m^{-3})	8	24	15	16	10	9	10	9	9	6	9	10	16	15	20	21	3	11	14	19
NO_2^{-}-N (µg l^{-1})	0.8	2.1	1.2	1.9	0.9	0.9	1.1	1.9	0.8	0.7	1.1	0.8	2.3	1.9	2.7	1.3	0.9	0.8	0.8	2.6
Cl^{-} (meq m^{-3})	5	3	3	3	3	3	3	3	3	3	2	2	3	3	3	3	5	4	4	5
SRP (µg P l^{-1})	0.8	0.9	0.8	0.7	0.6	0.4	0.4	0.4	0.5	0.2	0.8	0.3	0.5	0.2	0.3	0.2	0.4	0.4	0.4	0.4
P_{tot} (µg P l^{-1})	3.6	1.7	2.7	2.2	1.5	3.3	2.3	6.4	3.7	3.5	1.7	2.9	2.2	1.4	4.8	2.6	4.5	2.5	3.1	2.4
N_{tot} (mg N l^{-1})	0.32	0.54	0.44	0.33	0.24	0.28	0.48	0.36	0.31	0.30	0.30	0.38	0.40	0.37	0.52	0.44	0.22	0.28	0.42	0.45
DOC (mg C l^{-1})	1.1	0.5	0.5	0.5	0.3	0.5	0.5	0.6	1.0	1.1	0.5	0.7	0.8	0.4	0.5	0.5	1.2	0.8	1.1	0.6
SiO_2 (mg l^{-1})	1.9	2.0	2.8	1.4	0.8	2.2	2.1	3.3	1.5	1.4	2.2	1.7	3.0	1.6	1.7	2.3	2.4	2.4	1.6	3.0
$Al_{dissolved}$ (µg l^{-1})	32.1	10.6	3.1	3.3	17.4	3.6	5.2	7.8	6.0	8.1	2.8	5.6	8.9	1.9	5.0	6.4	16.3	8.5	13.3	5.3
Al_{tot} (µg l^{-1})	55.8	14.6	5.6	6.3	20.9	7.1	20.4	12.3	12.8	18.0	6.3	10.1	12.2	4.6	9.5	13.4	26.7	13.4	25.2	6.8
$Pb_{dissolved}$ (µg l^{-1})	<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_{total} (µg l^{-1})	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	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
$Cd_{dissolved}$ (µg l^{-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	<0.1
Cd_{total} (µg l^{-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	<0.1
$Cu_{dissolved}$ (µg l^{-1})	0.2	0.1	0.2	<0.1	0.3	0.3	0.4	0.4	0.1	0.1	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	0.1	<0.1	0.2	<0.1
Cu_{tot} (µg l^{-1})	0.3	0.1	0.2	0.1	0.3	0.3	0.4	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
$Zn_{dissolved}$ (µg l^{-1})	1.5	1.0	0.4	0.8	1.4	0.6	0.6	0.4	0.5	0.3	1.2	0.3	1.0	0.3	0.7	0.6	0.5	0.5	0.8	0.3
Zn_{total} (µg l^{-1})	1.6	1.2	0.5	0.8	1.5	0.6	0.8	0.5	0.7	0.4	1.2	0.4	1.1	0.4	0.7	0.7	0.6	0.6	0.8	0.5
$Cr_{dissolved}$ (µg l^{-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	<0.1
Cr_{total} (µg l^{-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	<0.1
$Ni_{dissolved}$ (µg l^{-1})	0.1	0.1	<0.1	0.1	1.3	5.0	0.4	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
Ni_{total} (µg l^{-1})	0.1	0.1	<0.1	0.1	1.2	5.2	0.4	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
$Fe_{dissolved}$ (µg l^{-1})	14.9	<1.1	<1.0	<1.1	9.5	5.5	4.6	2.6	<1.0	<1.0	1.4	<1.4	<1.0	<1.0	<1.0	2.0	4.1	<1.1	13.1	1.2
Fe_{total} (µg l^{-1})	31.5	3.7	2.2	3.2	12.1	10.3	21.6	21.6	5.7	11.4	4.9	11.4	3.4	2.1	3.2	7.6	10.1	4.9	34.1	2.8

In order to better compare chemistry of lakes with low alkalinities, values of the main parameters measured during 2018 and their mean values from 2008 to 2017 are shown graphically in Fig. 3.7.

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.

As regards base cations, highest concentrations normally characterize lakes with highest alkalinities and pH's. Lago Leit again differs from this tendency and has relatively high concentrations of base cations compared to its alkalinity and pH.

Only Laghetto Gardiscio had 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}).

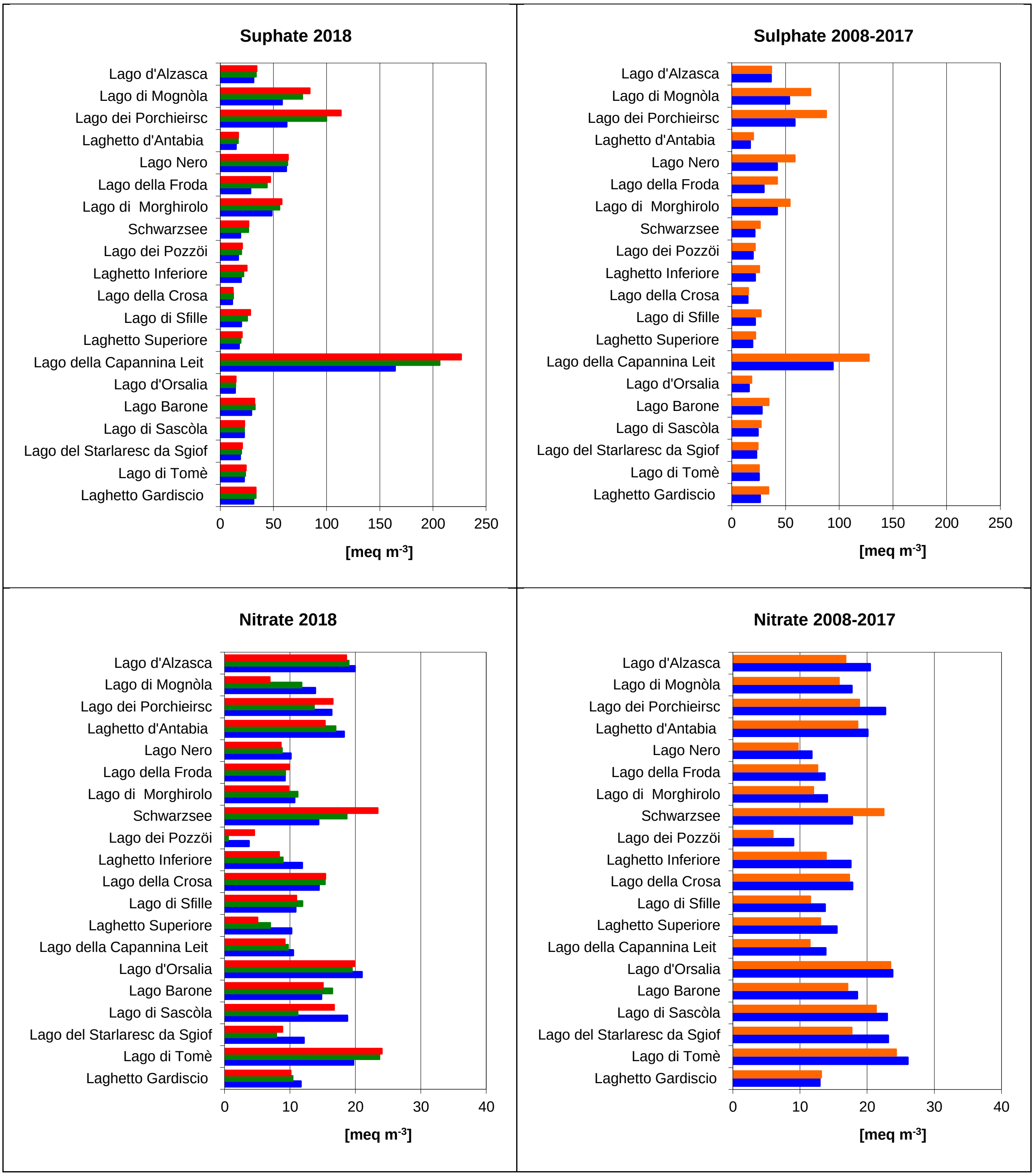
In general, lakes with low pH's are characterized by relatively high concentrations of aluminum (Lago del Starlaresc da Sgiof: 21-35 µg l^{-1}; Laghetto Gardiscio: 16-29 µg l^{-1}, Lago di Tomè: 10-11 µg l^{-1}, Lago Sascòla: 9-18 µg l^{-1}).

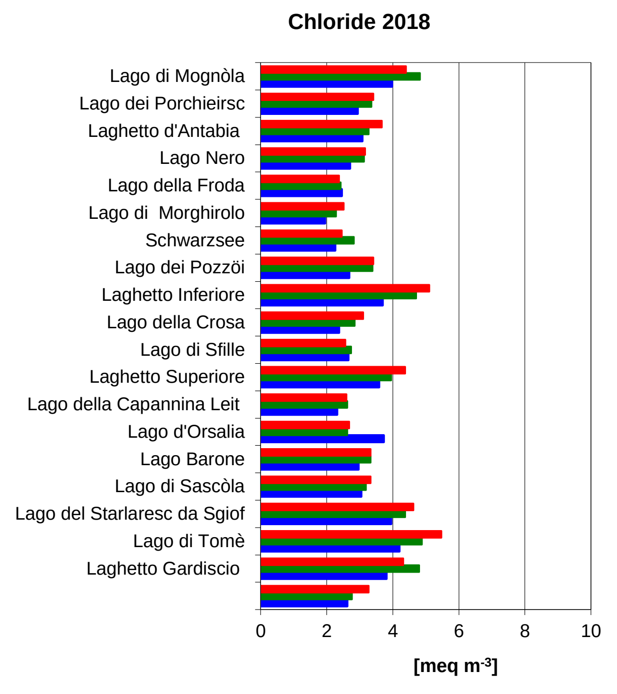
Seasonal variations

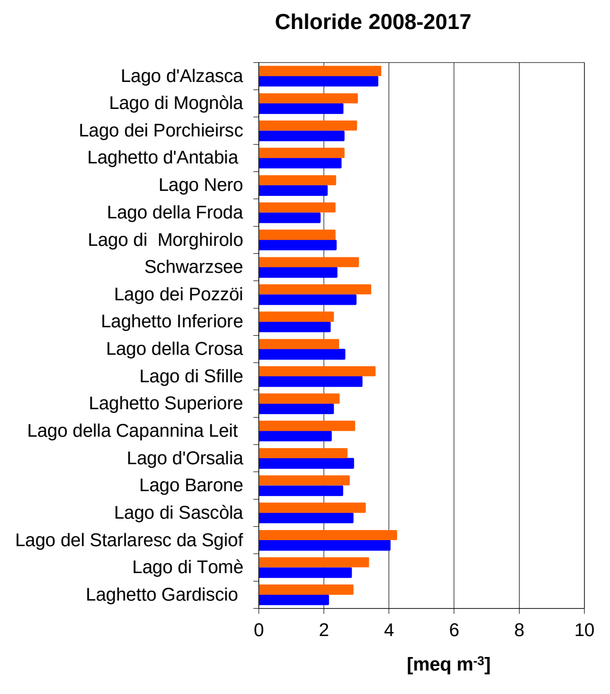
Fig. 3.6 also shows some seasonal differences. In most lakes alkalinity, pH and concentrations of sulphate and base cations tend to be lower in summer than in fall. The reason is the elevated discharge (precipitation and snow melt) in spring that causes a dilution of sulphate, base cations and a combination of dilution and consumption of alkalinity. Differently, concentrations of nitrate are often higher at the beginning of the summer compared to fall and may be caused by a combination of increased nitrate leaching during high discharge in spring and by increased assimilation and, eventually, also denitrification both in the catchment and in the lake itself during the warmer summer months.

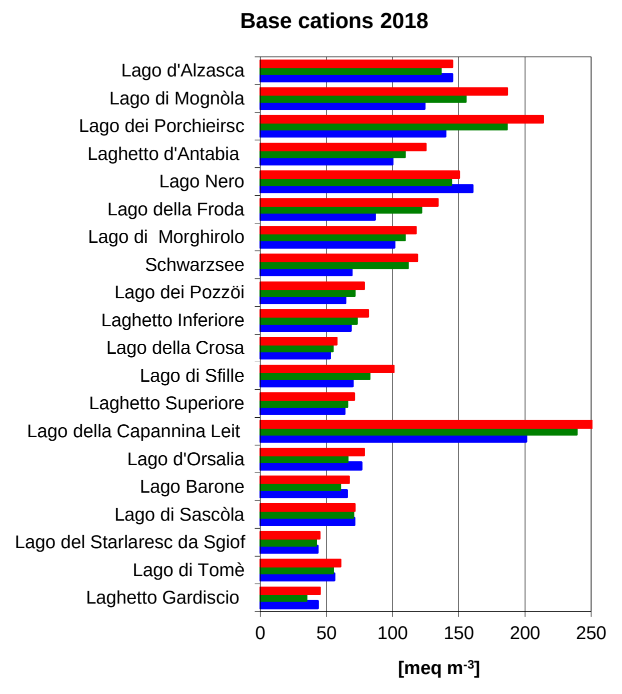
As regards the this year autumn values, they were heavily influenced by the dry summer and early autumn. In fact, concentrations of parameters that normally get diluted with precipitations (sulphate, base cations, alkalinity, pH, SiO_2) were significantly higher than the last decade averages, while nitrate and dissolved aluminium, that normally increase with precipitation, were lower than average.

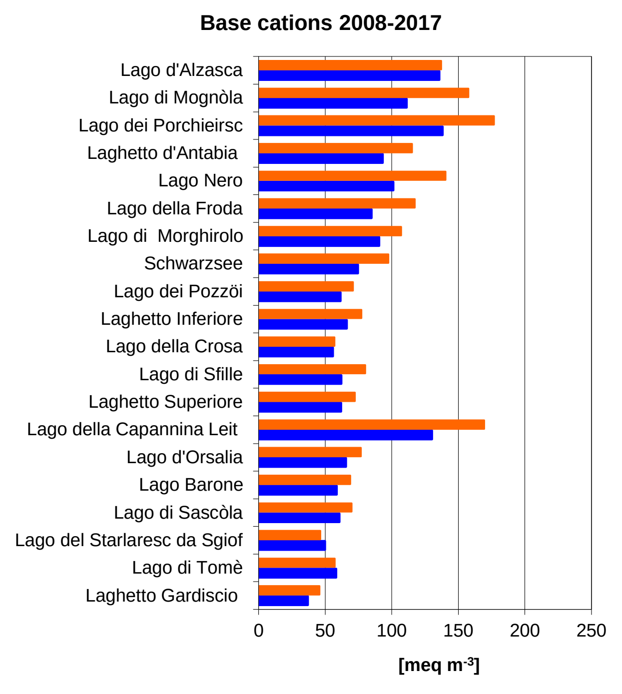
Figure 3.7 Concentrations of the main chemical parameters in 20 Alpine lakes during 2018 and their average values between 2008 and 2017. Blue columns represent summer, green early autumn, red late autumn and orange mean autumn values.

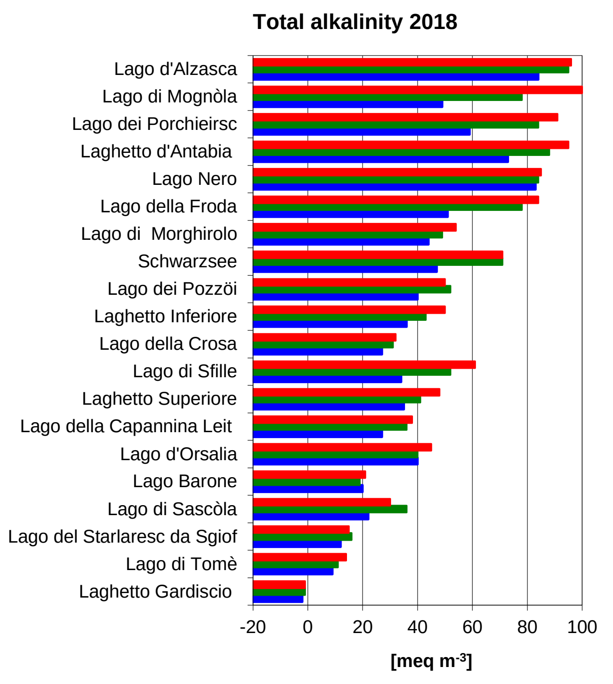


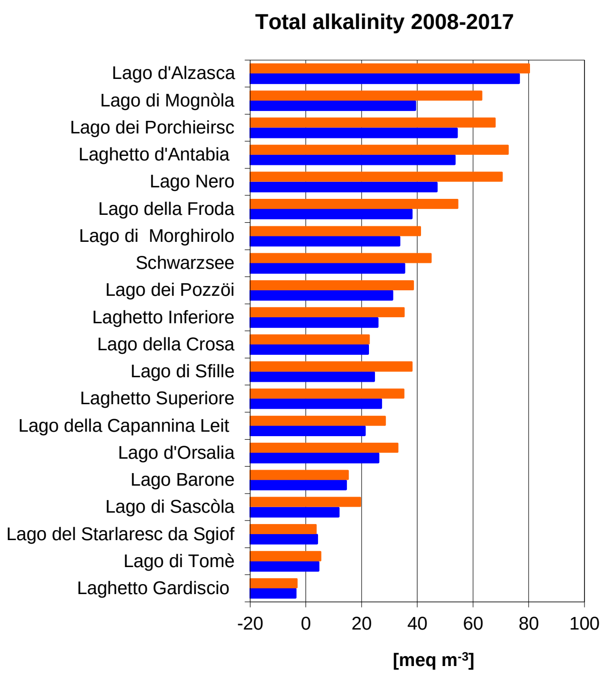

Chloride 2018
Lago di Mognòla
Lago dei Porchieirsc
Laghetto d'Antabia
Lago Nero
Lago della Froda
Lago di Morghirolo
Schwarzsee
Lago dei Pozzöi
Laghetto Inferiore
Lago della Crosa
Lago di Sfille
Laghetto Superiore
Lago della Capannina Leit
Lago d'Orsalia
Lago Barone
Lago di Sascòla
Lago del Starlaresc da Sgiof
Lago di Tomè
Laghetto Gardiscio
0
2
4
6
8
10
[meq m-3]

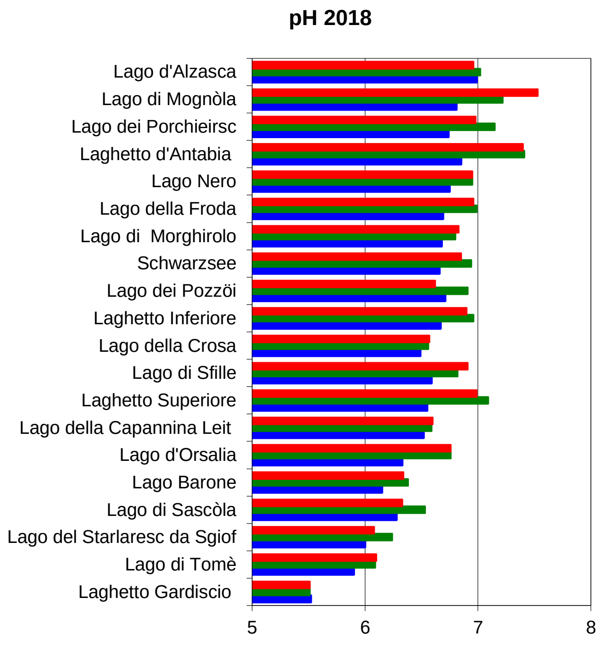

Chloride 2008-2017
Lago d'Alzasca
Lago di Mognòla
Lago dei Porchieirsc
Laghetto d'Antabia
Lago Nero
Lago della Froda
Lago di Morghirolo
Schwarzsee
Lago dei Pozzöi
Laghetto Inferiore
Lago della Crosa
Lago di Sfille
Laghetto Superiore
Lago della Capannina Leit
Lago d'Orsalia
Lago Barone
Lago di Sascòla
Lago del Starlaresc da Sgiof
Lago di Tomè
Laghetto Gardiscio
0
2
4
6
8
10
[meq m-3]

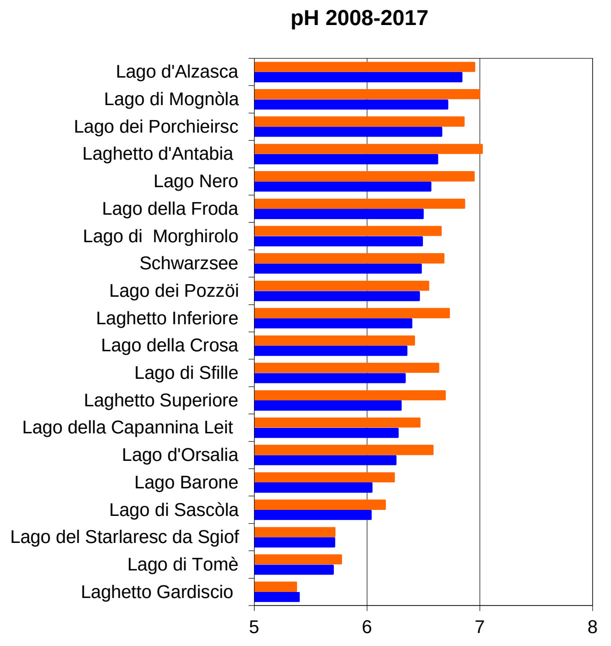

Base cations 2018
Lago d'Alzasca
Lago di Mognòla
Lago dei Porchieirsc
Laghetto d'Antabia
Lago Nero
Lago della Froda
Lago di Morghirolo
Schwarzsee
Lago dei Pozzöi
Laghetto Inferiore
Lago della Crosa
Lago di Sfille
Laghetto Superiore
Lago della Capannina Leit
Lago d'Orsalia
Lago Barone
Lago di Sascòla
Lago del Starlaresc da Sgiof
Lago di Tomè
Laghetto Gardiscio
0
50
100
150
200
250
[meq m-3]

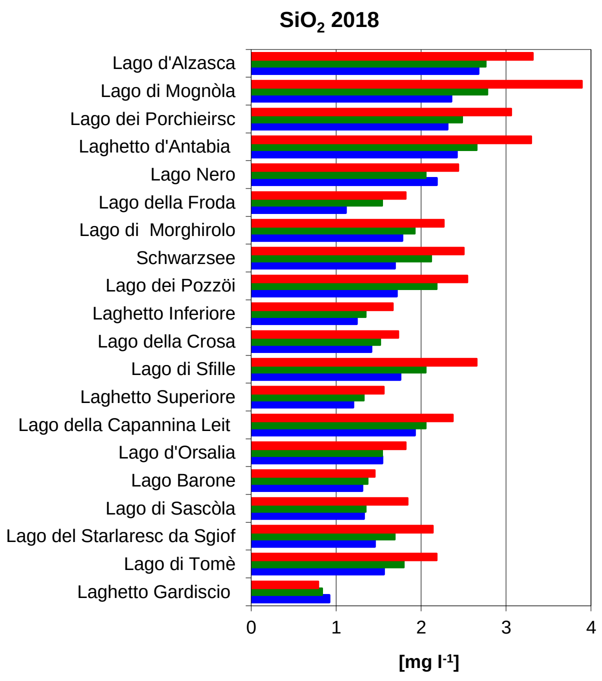

Base cations 2008-2017
Lago d'Alzasca
Lago di Mognòla
Lago dei Porchieirsc
Laghetto d'Antabia
Lago Nero
Lago della Froda
Lago di Morghirolo
Schwarzsee
Lago dei Pozzöi
Laghetto Inferiore
Lago della Crosa
Lago di Sfille
Laghetto Superiore
Lago della Capannina Leit
Lago d'Orsalia
Lago Barone
Lago di Sascòla
Lago del Starlaresc da Sgiof
Lago di Tomè
Laghetto Gardiscio
0
50
100
150
200
250
[meq m-3]

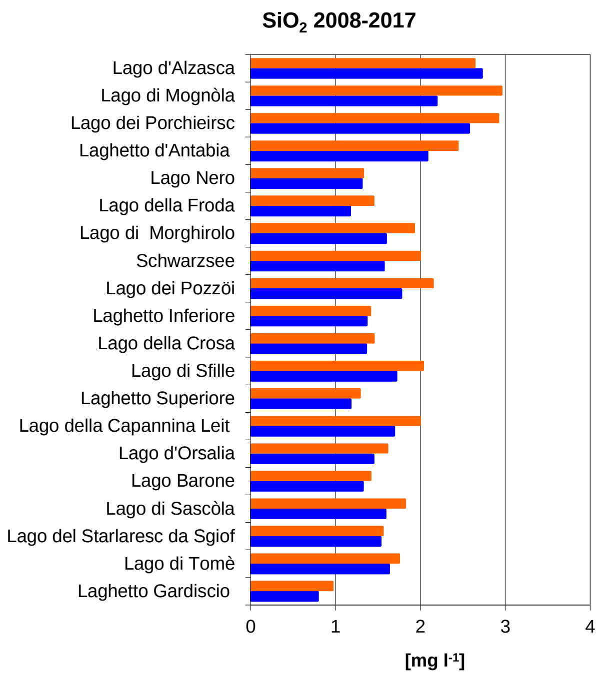

Total alkalinity 2018

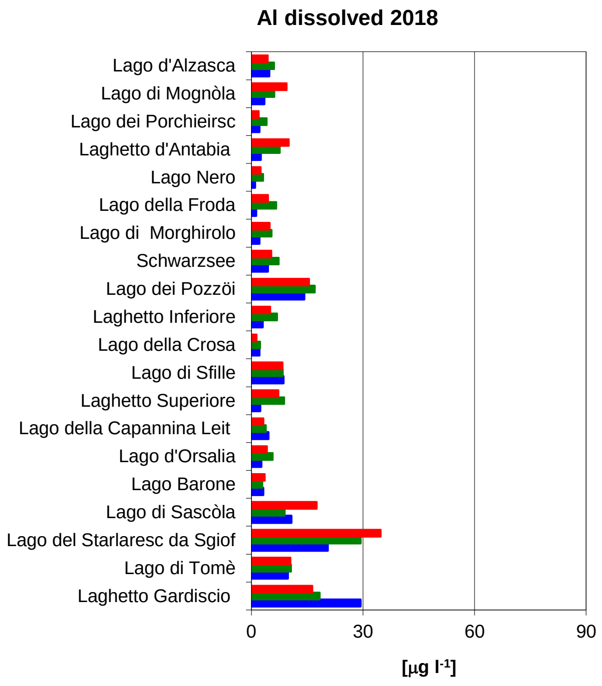

Total alkalinity 2008-2017

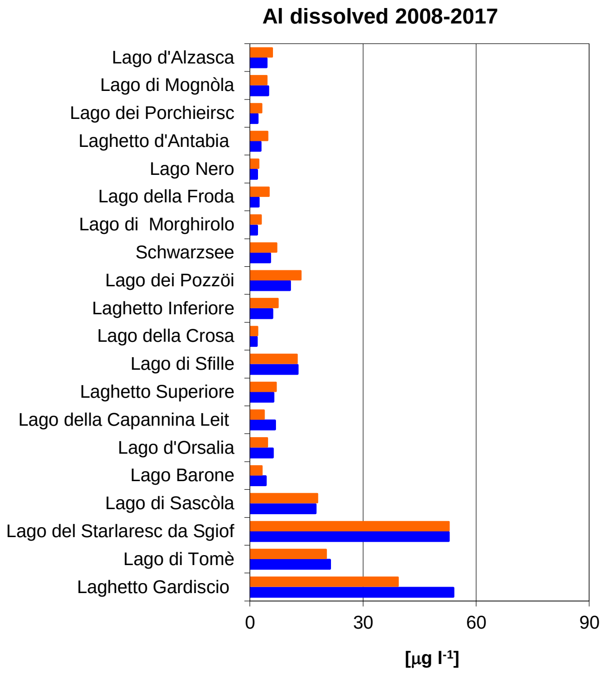

pH 2018


pH 2008-2017


SiO$_2$ 2018
Lago d'Alzasca
Lago di Mognòla
Lago dei Porchieirsc
Laghetto d'Antabia
Lago Nero
Lago della Froda
Lago di Morghirolo
Schwarzsee
Lago dei Pozzöi
Laghetto Inferiore
Lago della Crosa
Lago di Sfille
Laghetto Superiore
Lago della Capannina Leit
Lago d'Orsalia
Lago Barone
Lago di Sascòla
Lago del Starlaresc da Sgiof
Lago di Tomè
Laghetto Gardiscio
0
1
2
3
4
[mg l-1]


SiO$_2$ 2008-2017
Lago d'Alzasca
Lago di Mognòla
Lago dei Porchieirsc
Laghetto d'Antabia
Lago Nero
Lago della Froda
Lago di Morghirolo
Schwarzsee
Lago dei Pozzöi
Laghetto Inferiore
Lago della Crosa
Lago di Sfille
Laghetto Superiore
Lago della Capannina Leit
Lago d'Orsalia
Lago Barone
Lago di Sascòla
Lago del Starlaresc da Sgiof
Lago di Tomè
Laghetto Gardiscio
0
1
2
3
4
[mg l-1]


Al dissolved 2018
Lago d'Alzasca
Lago di Mognòla
Lago dei Porchieirsc
Laghetto d'Antabia
Lago Nero
Lago della Froda
Lago di Morghirolo
Schwarzsee
Lago dei Pozzöi
Laghetto Inferiore
Lago della Crosa
Lago di Sfille
Laghetto Superiore
Lago della Capannina Leit
Lago d'Orsalia
Lago Barone
Lago di Sascòla
Lago del Starlaresc da Sgiof
Lago di Tomè
Laghetto Gardiscio
0
30
60
90
[µg l-1]


Al dissolved 2008-2017
Lago d'Alzasca
Lago di Mognòla
Lago dei Porchieirsc
Laghetto d'Antabia
Lago Nero
Lago della Froda
Lago di Morghirolo
Schwarzsee
Lago dei Pozzöi
Laghetto Inferiore
Lago della Crosa
Lago di Sfille
Laghetto Superiore
Lago della Capannina Leit
Lago d'Orsalia
Lago Barone
Lago di Sascòla
Lago del Starlaresc da Sgiof
Lago di Tomè
Laghetto Gardiscio
0
30
60
90
[µg 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. 3.8. Only years, where all 20 Alpine lakes have been monitored are shown. After the 1980's, 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. However, contrary to this general trend, in some lakes concentrations of sulphate and base cations are not decreasing (Porchieirsc, Nero), in some they are even increasing (Leit, Morghirolo, Mognola), that's why 90th percentiles are not decreasing like median values.

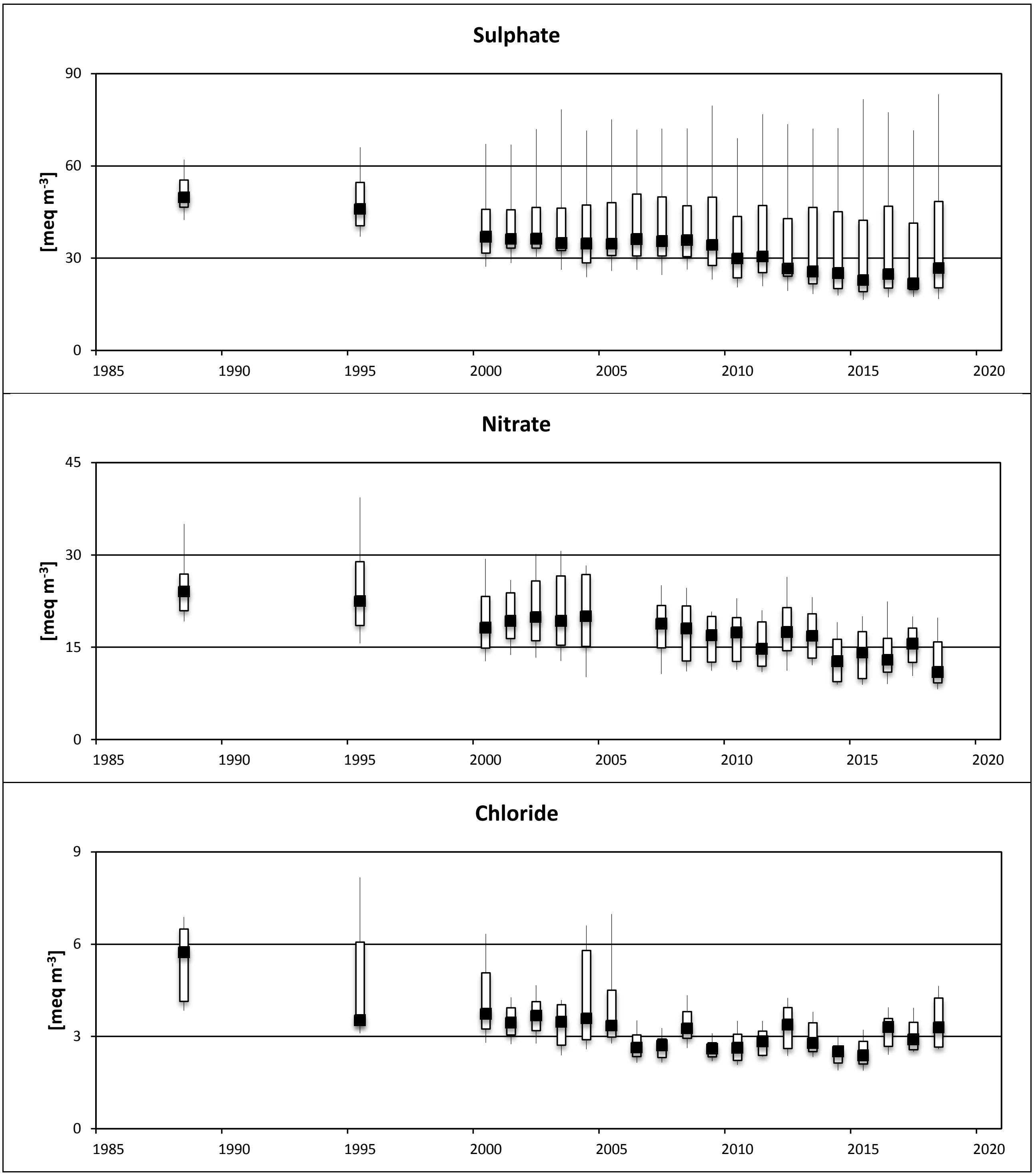
Aluminum concentrations of the three most acidic lakes are presented in Fig. 3.9 (see also trends in Tab. 3.6). The most evident decrease in concentrations occurred in Lago del Starlaresc da Sgiof from 80-100 to 30-70 µg l^{-1}. In Lago di Tomè concentrations decreased from about 40 to 15-25 µg l^{-1} and in Laghetto Gardiscio from 30-60 µg l^{-1} to 23-31 µg l^{-1}.

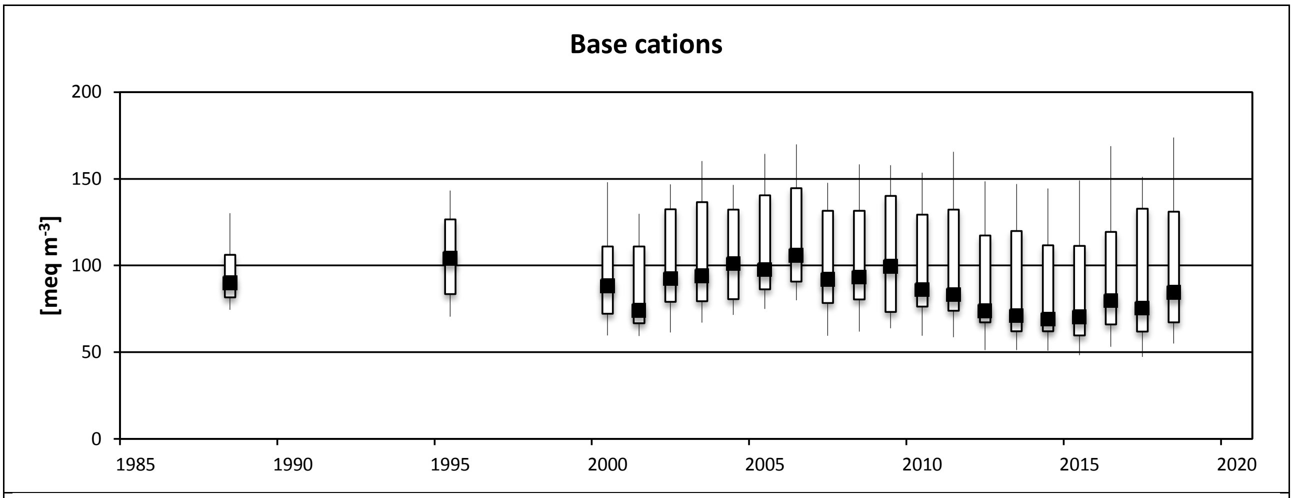
As already discussed, compared to the last years values, the this year higher median autumn concentrations of sulphate, chloride, base cations, total alkalinity, pH and lower concentrations of nitrate and dissolved aluminium are a consequence of the particularly dry summer and early autumn.

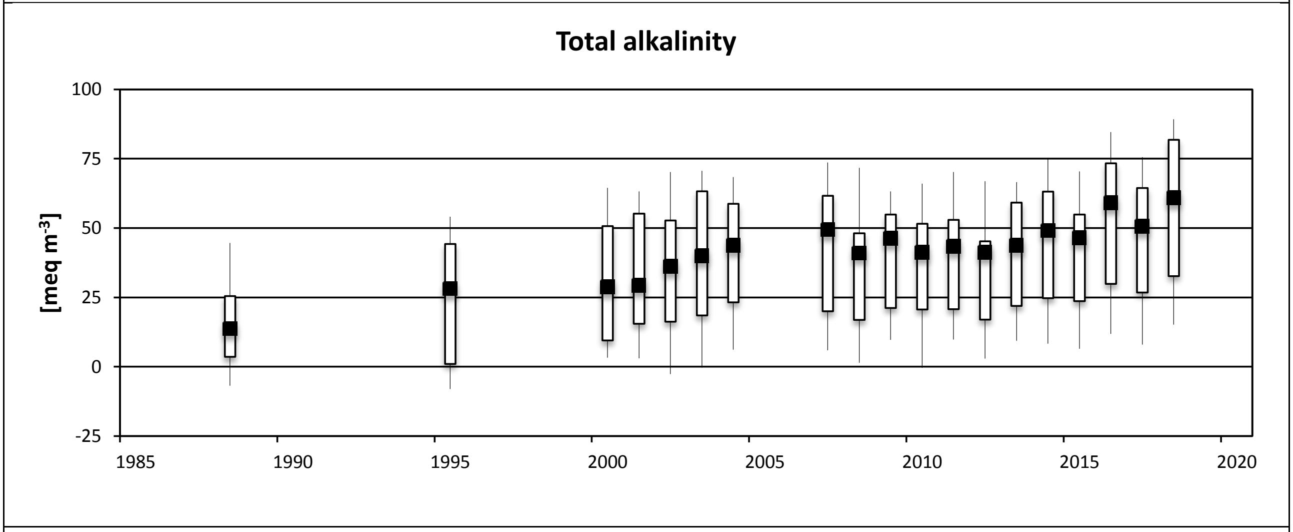
Results of a detailed trend analysis of the main parameters are presented in Tab. 3.6. Trends were calculated for the entire monitoring period and for the period since 2000, when sampling occurred more regularly and frequently. Since the 1980s, due to decreasing sulphate and nitrate depositions, concentrations of sulphate and nitrate decreased significantly in 15 and 16 lakes, respectively. While the decrease of sulphate was similar for the two analysed time periods, decrease of nitrate was higher after 2000, indicating a more pronounced decrease more recently. Decreases in anthropogenic sulphate and nitrate also caused decreasing concentrations of base cations (significant in 11 lakes), hydrogen ions (significant in 17 lakes) and increasing concentrations of total alkalinity (significant in 19 lakes). Concentrations of aluminum decreased significantly in lakes with the highest concentrations (Lago del Starlaresc da Sgiof, in Lago di Tomè, in Lago Gardiscio) but also in Lago dei Porchieirsc, Lago Nero and Lago d'Orsalìa.

Interestingly, differently to most lakes, concentrations of sulphate increased significantly in three lakes (Lago della Capannina Leit, Lago di Morghirolo and Lago di Mognòla). For Lago Leit and Lago Morghirolo this increase is higher after 2000 and for Lago Leit even more pronounced after 2010 (13.3 meq m^{-3} yr^{-1}, data not shown). A sulphur budget analysis of the catchments revealed that in the two lakes with constant sulphate concentrations (Porchieirsc, Nero), sulphur release from the catchments is significantly increasing (data not shown). Climate change leading to melting of permafrost and rock glaciers (Scapozza and Mari, 2010) might be the reason for the release of sulphur (Thies et al. 2007).

Figure 3.8 Temporal variations of parameters measured in 20 Alpine lakes from 1988 to 2018. Boxplots show the median and the 10th, 25th, 75th, 90th percentiles of autumn mean values.




Base cations
[meq m-3]
200
150
100
50
0
1985
1990
1995
2000
2005
2010
2015
2020


Total alkalinity
[meq m-3]
100
75
50
25
0
-25
1985
1990
1995
2000
2005
2010
2015
2020

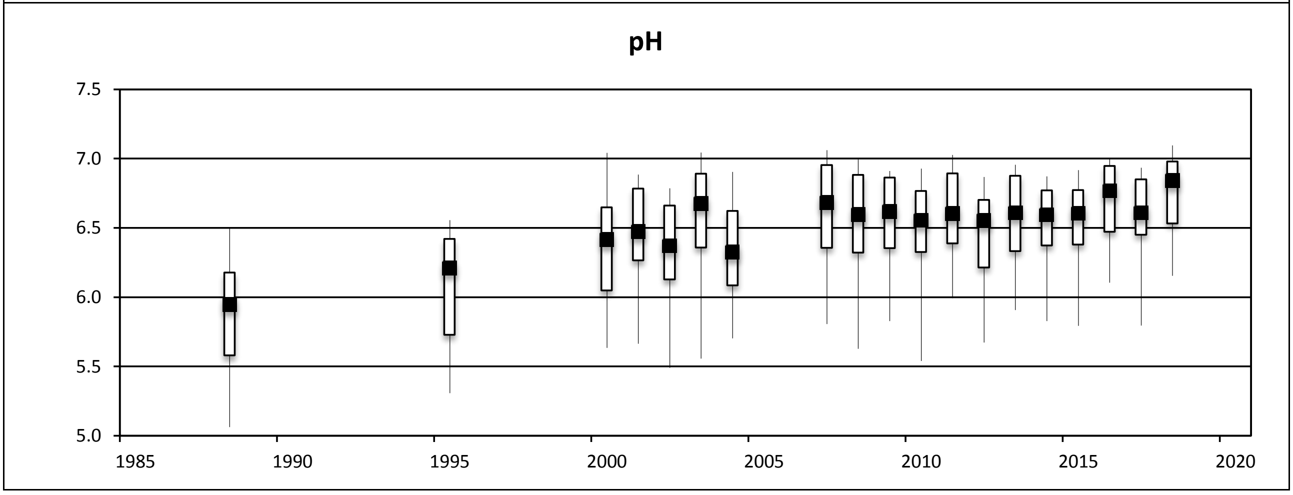

pH
7.5
7.0
6.5
6.0
5.5
5.0
1985
1990
1995
2000
2005
2010
2015
2020

Figure 3.9 Temporal variations of dissolved aluminum from 1988 to 2018 in the three most acidic lakes (mean autumn values).

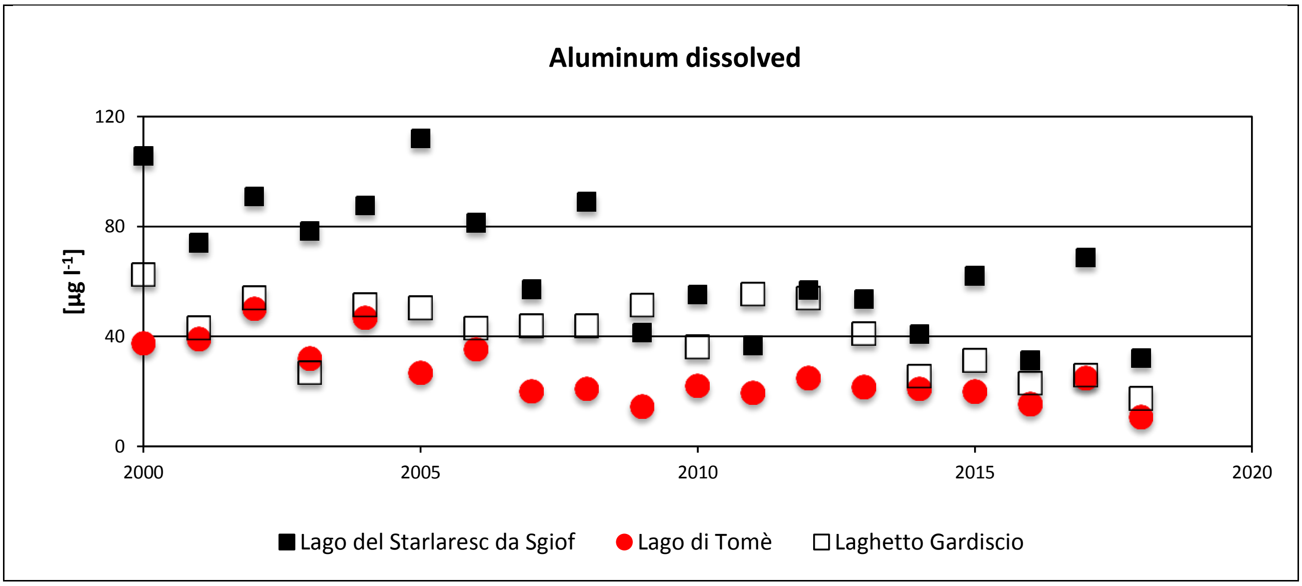


Table 3.6 Changes in lake water concentrations during the indicated time periods. Red values indicate significant trends.

Lake	SO_4^{2-}		NO_3^-		Cl^-		Base cations		H^+		Total alkalinity		Al_{dis}
	’80-18	00-18	’80-16	00-18	’80-18	00-18	’80-18	00-18	’80-18	00-18	’80-18	00-18	00-18
Lago del Starlaresc da Sgiof	-1.25	-1.15	-0.63	-0.90	-0.09	-0.09	-1.10	-1.38	-4.0E-1	-3.2E-1	0.93	1.23	-3.41
Lago di Tomè	-0.88	-0.75	-0.44	-0.84	-0.04	-0.03	-1.32	-1.86	-7.3E-2	-4.8E-2	0.42	0.40	-1.28
Lago dei Porchieirsc	0.68	0.61	-0.41	-0.51	-0.03	-0.04	-0.14	-1.01	-4.4E-3	-1.3E-3	0.93	0.64	-0.52
Lago Barone	-0.43	-0.38	-0.29	-0.46	-0.06	-0.05	-0.59	-1.04	-3.5E-2	-1.9E-2	0.62	0.63	-0.33
Laghetto Gardiscio	-0.27	-0.23	-0.24	-0.31	-0.05	-0.04	-0.51	-0.58	-1.1E-1	-1.0E-1	0.31	0.31	-1.83
Lago Leit	3.58	6.74	-0.24	-0.28	-0.04	0.01	3.40	5.52	-8.2E-3	-1.0E-3	0.56	0.46	-0.29
Lago di Morghirolo	0.35	0.67	-0.18	-0.26	-0.04	-0.02	0.46	-0.06	-5.2E-3	-3.0E-3	0.86	0.82	-0.48
Lago di Mognòla	0.35	0.27	-0.23	-0.45	-0.03	-0.02	0.06	-1.20	-1.8E-3	2.7E-1	0.25	0.00	-0.16
Laghetto Inferiore	-0.90	-0.84	-0.47	-0.62	-0.07	-0.04	-1.25	-1.78	-9.0E-3	-9.7E-3	0.67	0.83	-0.30
Laghetto Superiore	-0.81	-0.78	-0.45	-0.76	-0.05	-0.03	-0.65	-1.23	-1.5E-2	-1.2E-2	0.99	1.13	-0.21
Lago Nero	0.08	0.30	-0.12	-0.18	-0.05	-0.03	0.12	-0.23	-2.3E-3	-2.1E-4	0.76	0.90	-0.35
Lago della Froda	-0.32	-0.31	-0.25	-0.29	-0.02	-0.01	0.20	0.16	-5.6E-3	-2.3E-3	0.91	0.88	-0.30
Lago d'Antabia	-0.70	-0.72	-0.35	-0.49	-0.07	-0.06	-0.61	-1.72	-4.5E-3	-3.0E-3	0.95	0.97	-0.17
Lago della Crosa	-0.80	-0.76	-0.19	-0.30	-0.06	-0.06	-0.65	-1.05	-2.3E-2	-1.2E-2	0.79	0.85	-0.34
Lago d'Orsalìa	-0.88	-0.82	-0.23	-0.52	-0.06	-0.05	-0.31	-0.98	-3.5E-2	-1.3E-2	1.14	1.29	-0.32
Schwarzsee	-1.06	-1.02	-0.26	-0.26	-0.05	-0.06	-1.26	-1.69	-7.4E-3	-5.3E-3	0.62	0.69	-0.54
Laghi dei Pozzöi	-1.03	-0.94	-0.21	-0.28	-0.06	-0.02	-0.90	-1.56	-5.3E-3	-6.4E-3	0.44	0.50	-0.33
Lago di Sfille	-0.93	-0.88	-0.21	-0.22	-0.05	-0.04	-0.87	-1.22	-1.0E-2	-8.2E-3	0.80	0.88	-0.65
Lago di Sascòla	-1.03	-1.02	-0.42	-0.93	-0.08	-0.06	-1.51	-2.33	-1.9E-2	-1.2E-2	0.47	0.43	-0.34
Lago d'Alzasca	-0.96	-0.97	-0.05	-0.05	-0.08	-0.08	-0.60	-1.79	-2.6E-3	-5.0E-4	0.94	0.94	-0.21

3.5.3 Alpine rivers

Spatial variations

During 2018 river water was sampled at the following days: 15.1, 5.2, 12.3, 16.4, 14.5, 11.6, 3.7, 6.8, 24.9, 22.10, 12.11, 10.12. Annual mean concentrations of the chemical parameters measured in river Maggia, Vedeggio and Verzasca during 2018 are shown in Tab. 3.7. Conductivity, 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 2008-2012, average nitrogen rainwater concentrations in the watershed of river Vedeggio, Verzasca and Maggia were 61, 41 and 37 meq m^{-3}, respectively and highest nitrogen retention during the same time period occurred in the larger river Maggia (36%) followed by river Vedeggio (31%) and Verzasca (29%).

During 2018 average alkalinity was 303 meq m^{-3} in river Maggia, 185 meq m^{-3} in river Vedeggio and 76 meq m^{-3} in river Verzasca. 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 alkalinities that were always > 0 meq m^{-3}. Average pH was 7.4 in river Maggia, 7.1 in river Vedeggio and 6.9 in river Verzasca. Their minimum pH’s were not much lower (Maggia: 7.1, Vedeggio: 7.1, Verzasca: 6.7).

Table 3.7 Average concentrations in river water during 2018. Values based on at least one sample below the quantification limit were preceded with <.

River name	pH	Cond 25°C (µS cm^{-1})	Alkalinity (µeq l^{-1})	Ca^{2+} (meq m^{-3})	Mg^{2+} (meq m^{-3})	Na^+ (meq m^{-3})	K^+ (meq m^{-3})	SO_4^{2-} (meq m^{-3})	NO_3^- (meq m^{-3})	Cl^- (meq m^{-3})	SRP (µg P l^{-1})	DOC (mg C l^{-1})	SiO_2 (mg l^{-1})	$Al_{dissolved}$ (µg l^{-1})	Al_{tot} (µg l^{-1})	$Pb_{dissolved}$ (µg l^{-1})	Pb_{tot} (µg l^{-1})	$Cd_{dissolved}$ (µg l^{-1})	Cd_{total} (µg l^{-1})	$Cu_{dissolved}$ (µg l^{-1})	Cu_{tot} (µg l^{-1})	$Zn_{dissolved}$ (µg l^{-1})	Zn_{total} (µg l^{-1})	$Cr_{dissolved}$ (µg l^{-1})	Cr_{total} (µg l^{-1})	$Ni_{dissolved}$ (µg l^{-1})	Ni_{total} (µg l^{-1})
Maggia	7.1	60	303	378	55	69	33	182	31	34	<2	1.3	5.2	13	15	<0.1	<0.1	<0.1	<0.1	0.4	0.4	2.1	2.5	<0.1	<0.1	0.2	0.2
Vedeggio	7.1	47	185	238	78	82	15	124	64	38	<2	1.2	7.8	10	16	<0.1	<0.2	<0.1	<0.1	0.5	0.5	1.6	1.9	<0.1	<0.2	1.0	1.1
Verzasca	6.9	23	76	124	18	34	14	64	35	14	<2	1.1	4.2	12	13	<0.1	<0.1	<0.1	<0.1	0.4	0.4	1.6	1.9	<0.1	<0.1	<0.2	<0.2

Seasonal variations

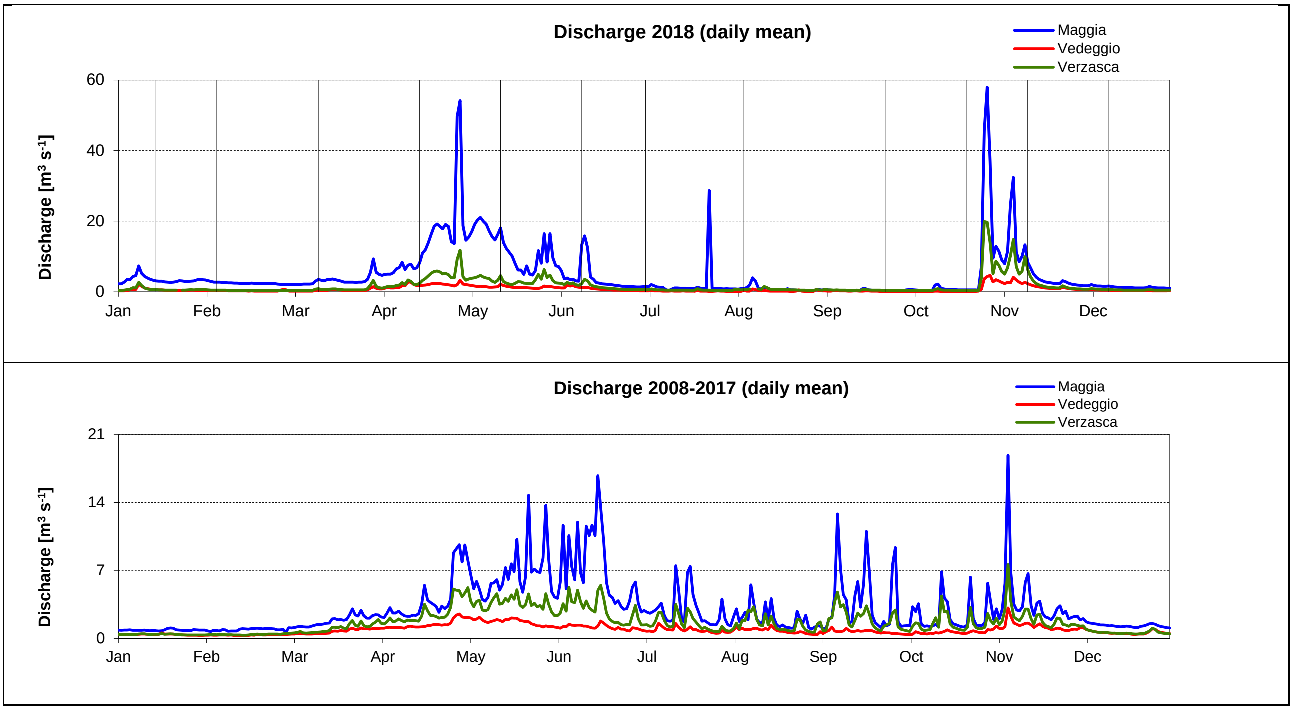
Fig. 3.10 shows the daily mean discharges during 2018 and average values of the previous decade (2008-2017). Discharges are usually low during winter, high in spring because of frequent precipitation and snow melt, average during summer and higher again in autumn. 2018 was characterized by typical low discharges during winter, high values during spring particularly in April and May, a very dry summer and early spring followed by high discharges at the end of October and November.

Concentrations of the main chemical parameters in river water during sampling days in 2018 and their average values during 2008-2017 are shown in Fig. 3.11.

During 2008-2017 the seasonality was characterized by concentrations of sulphate, base cations, alkalinity, SiO_2 and pH that are normally lower from spring to autumn 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 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 chloride concentration in river Vedeggio and Maggia are caused by the use of road salt.

The main chemical parameters during 2018 were in general in the same range as average values measured during 2007-2016. However, lower values of sulphate, base cations, silica, alkalinity and pH occurred in May and in November because of the higher than average discharges and higher values than average were measured from June to October because of the lower than average discharge. Concentrations of nitrate did not deviate from average values, while concentrations of aluminium peaked in May and November, the months with the highest discharges.

Figure 3.10 Daily mean discharge during 2018 and average daily mean discharge during 2008-2017. Discharge of river Vedeggio at Isone was measured by the Canton of Ticino (UCA, 2001-2019), discharge of river Verzasca at Sonogno was estimated by discharge values measured at Lavertezzo by BWG (2001-2004) and BAFU (2005-2019), 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 (2005-2019)).



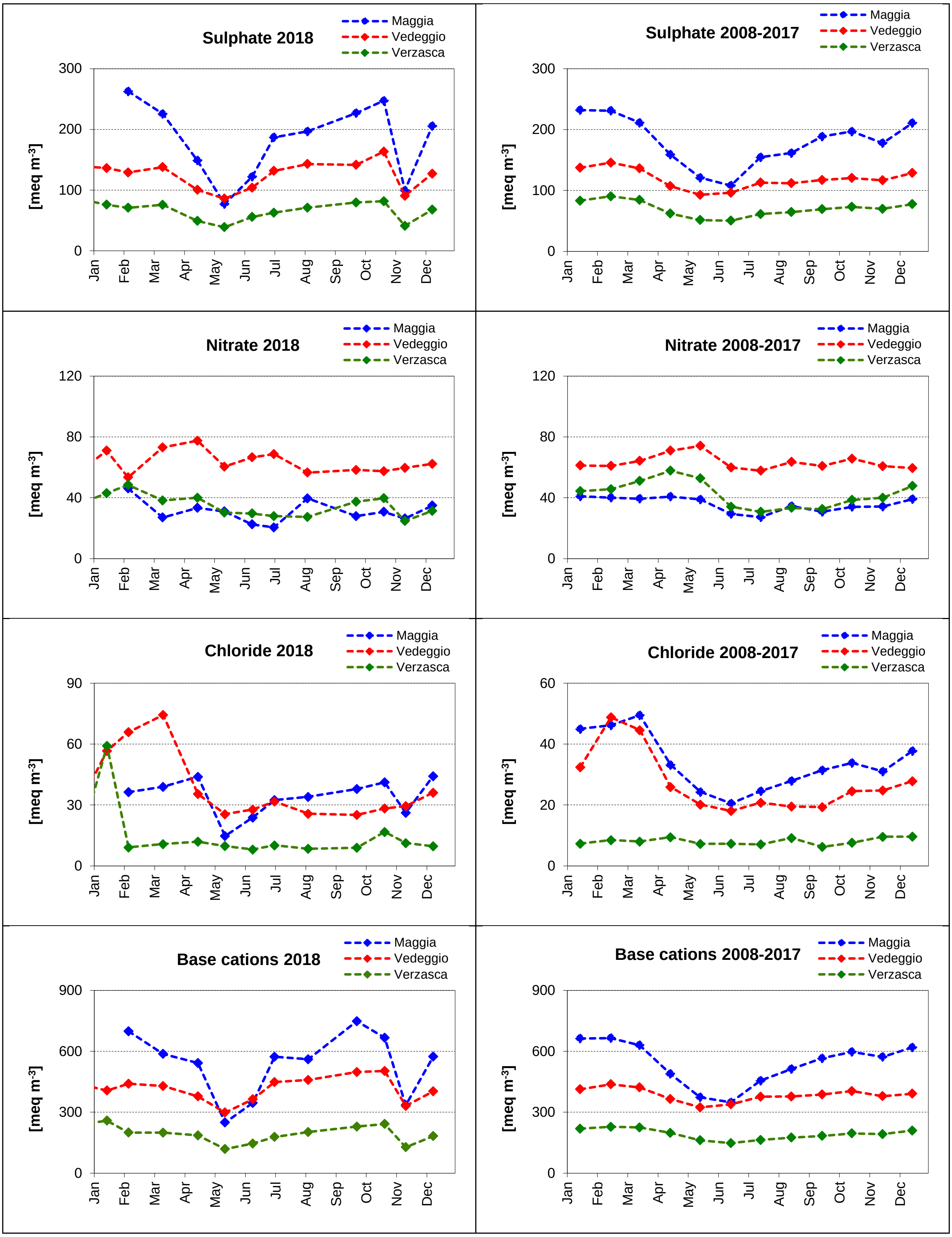
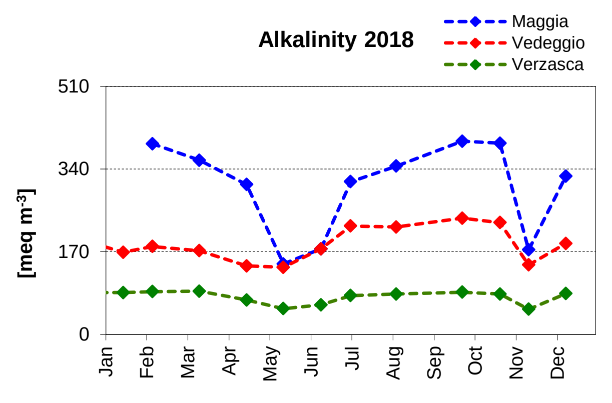
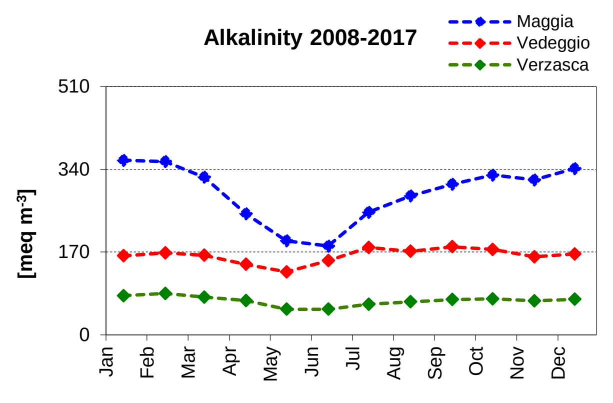
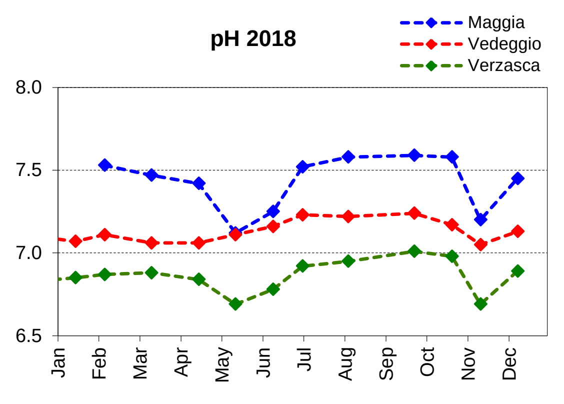
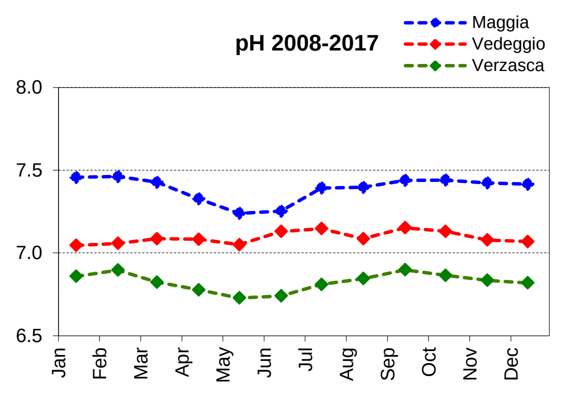


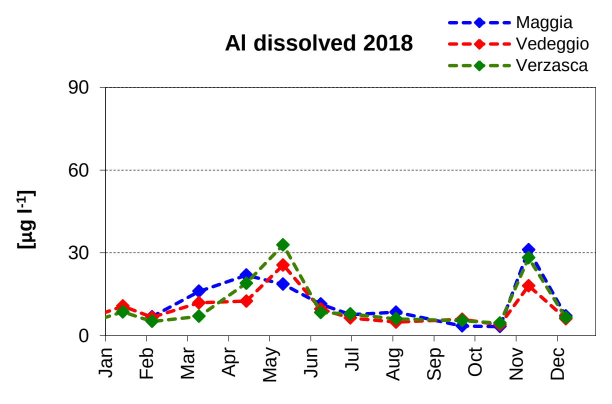
Figure 3.11 Concentrations of the main chemical parameters in river water during sampling days in 2018 and their average values from 2008 to 2017.

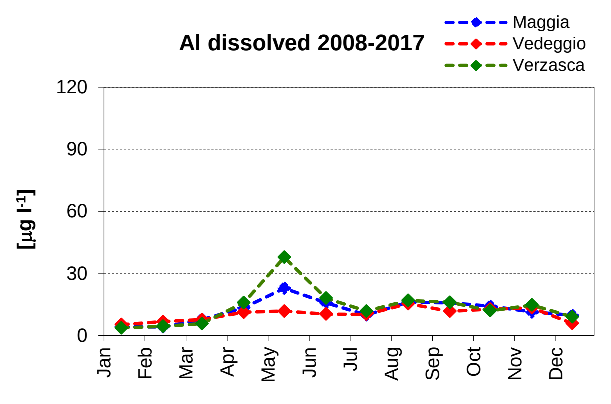

Alkalinity 2018

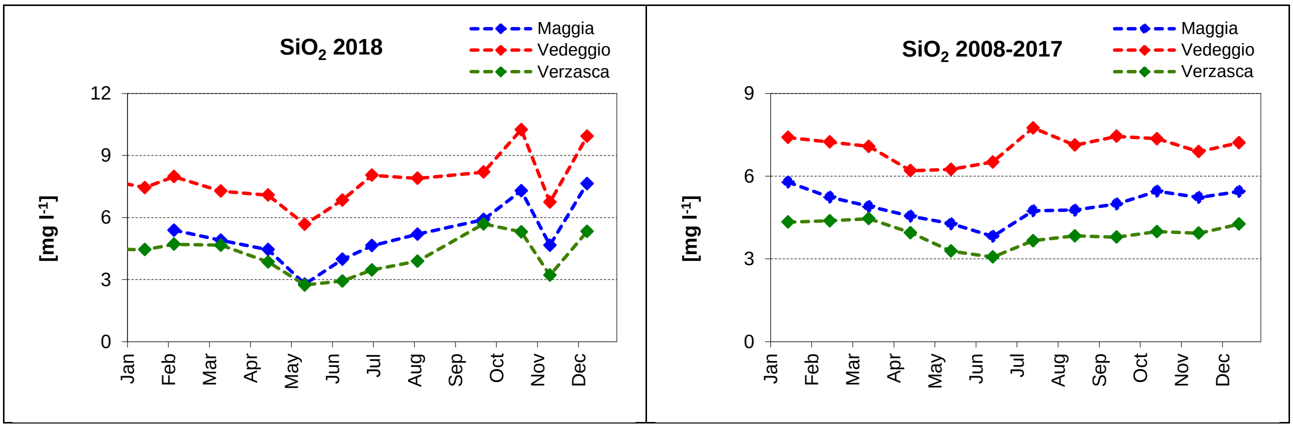

Alkalinity 2008-2017


pH 2018


pH 2008-2017


Al dissolved 2018


Al dissolved 2008-2017



Temporal variations

Variations of monthly average discharges and concentrations of chemical parameters from 2000 to 2018 are presented in Fig. 3.12 and 3.13, 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 period 2000-2017. Results of the trend analysis are shown in Tab. 3.8. Concentrations of nitrate decreased significantly in all three rivers, while concentrations of sulphate decreased significantly only in rivers Vedeggio and Verzasca. During the same time concentrations of sulphate in river Maggia decreased significantly at Solduno (28.7 km downstream). Interestingly, concentrations of sulphate are also significantly lower at Solduno (mean 2000-2017: 139 meq m^{-3}) compared to Brontallo (189 meq m^{-3}). Sources of geogenic sulphur may be responsible for the missing decrease in sulphate in the upper river stretch (already discussed in the lake chapter). No significant trend can be observed for base cations and pH, while for alkalinity significant increasing trends were detected in river Vedeggio and Verzasca.

Figure 3.12 Monthly mean discharge in river water from 2000 to 2018. Discharge of river Vedeggio at Isone was measured by the Canton of Ticino (UCA, 2001-2019), discharge of river Verzasca at Sonogno was estimated by discharge values measured at Lavertezzo by BWG (2001-2004) and BAFU (2005-2019), discharge of river Maggia at Brontallo was estimated from values measured at Brontallo by Ofima and at Bignasco by BWG (2001-2004) and BAFU (2005-2019).

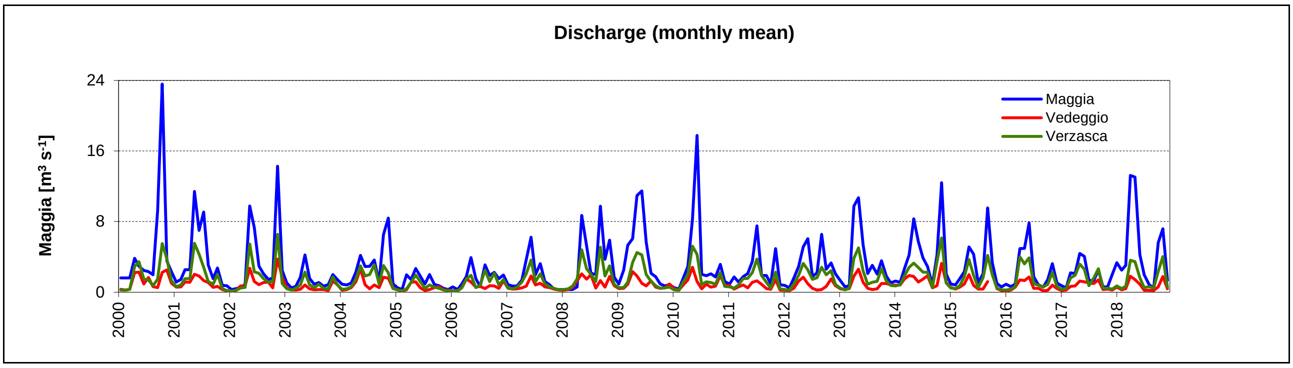
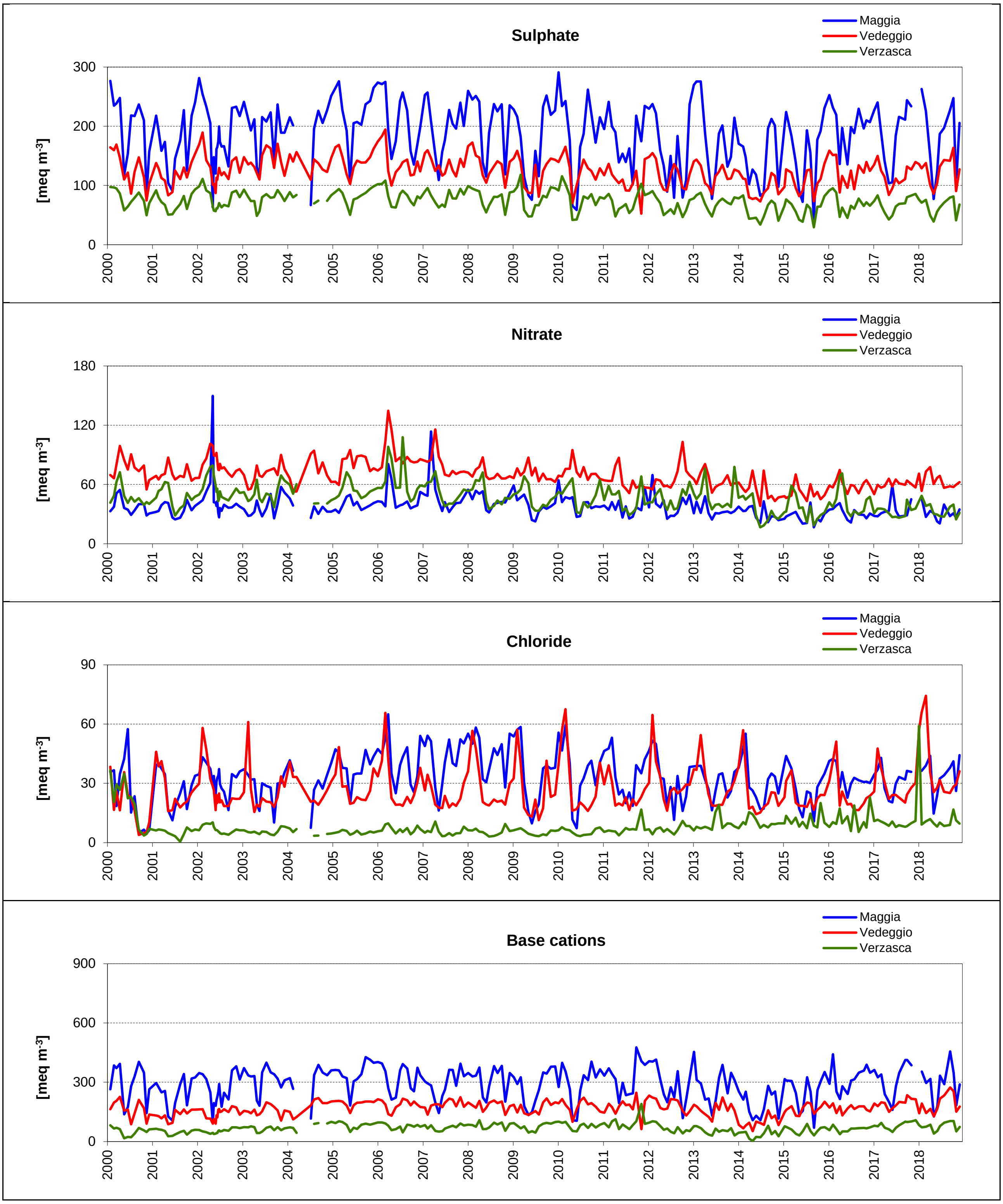
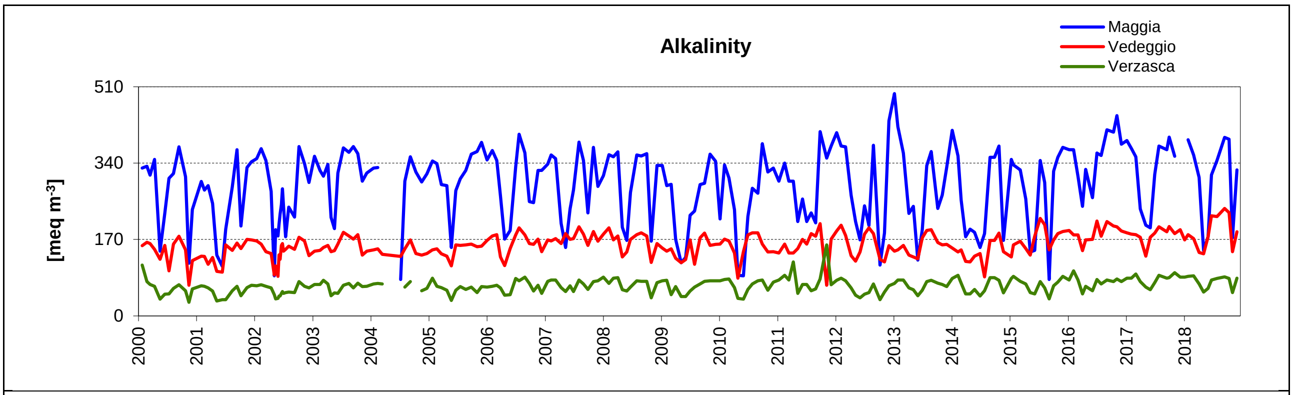
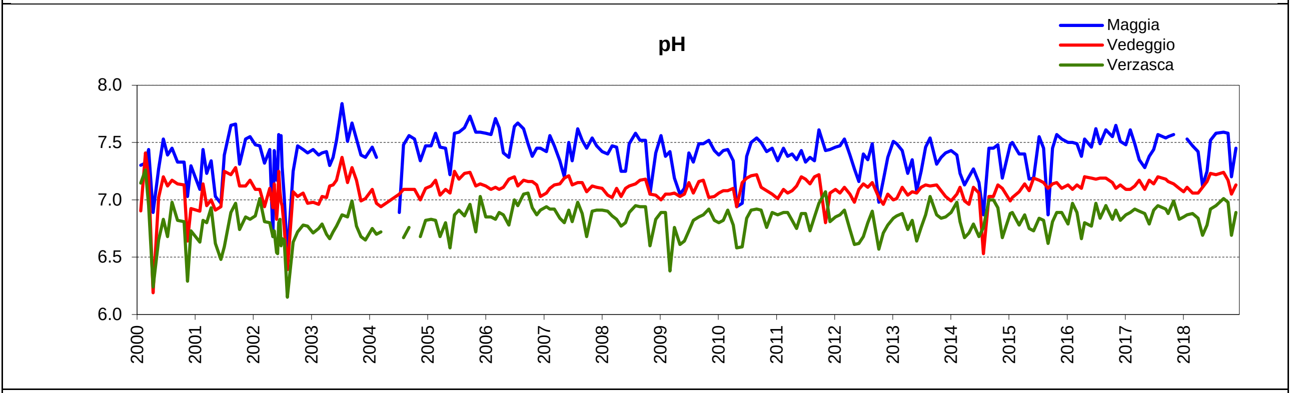
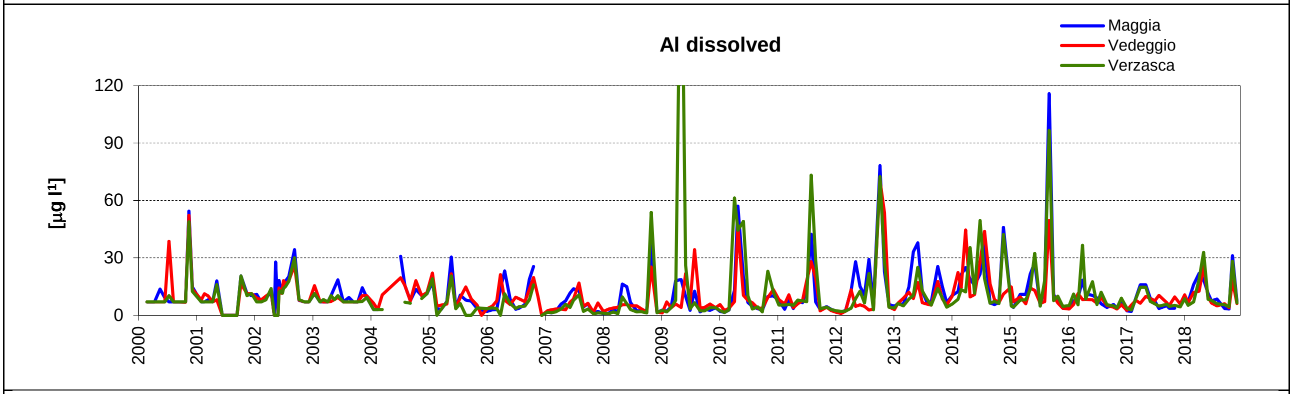


Figure 3.13 Concentrations of the main chemical parameters in river water from 2000 to 2018




Alkalinity
Maggia
Vedeggio
Verzasca
[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


pH
Maggia
Vedeggio
Verzasca
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


Al dissolved
Maggia
Vedeggio
Verzasca
[µg l-1]
120
90
60
30
0
2000
2001
2002
2003
2004
2005
2006
2007
2008
2009
2010
2011
2012
2013
2014
2015
2016
2017
2018

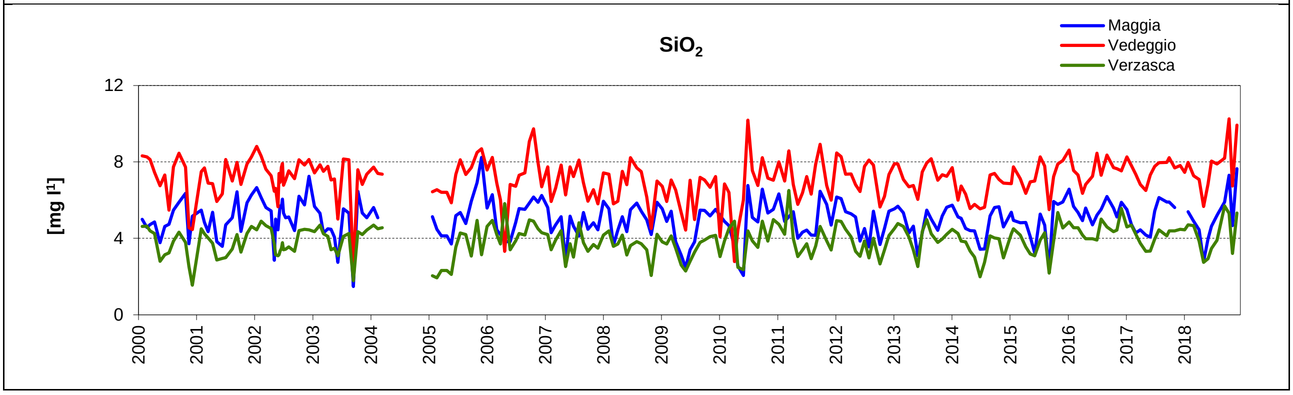

SiO2
Maggia
Vedeggio
Verzasca
[mg l-1]
12
8
4
0
2000
2001
2002
2003
2004
2005
2006
2007
2008
2009
2010
2011
2012
2013
2014
2015
2016
2017
2018

Table 3.8 The probability level obtained with the seasonal Mann-Kendall test (p) and the changes in river water concentrations during the period 2000-2018 expressed in (meq m^{-3} yr^{-1}) calculated with the Sens's slope. Red values indicate significant trends.

River	SO_4^{2-}		NO_3^-		Cl^-		Base cations		H^+		Alkalinity	
	p	slope	p	slope	p	slope	p	slope	p	slope	p	slope
Maggia	0.166	-1.11	0.011	-0.56	0.582	0.09	0.576	-1.25	0.347	2.1E-4	0.068	1.67
Vedeggio	0.018	-1.13	0.001	-1.20	0.127	0.17	0.457	-1.07	0.144	-4.1E-4	0.002	1.87
Verzasca	0.004	-0.93	0.001	-1.06	0.002	0.26	0.202	-1.12	0.132	-1.2E-3	0.000	1.00

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 of 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 macroinvertebrates were regularly monitored in four lakes (Laghetto Inferiore, Laghetto Superiore, Lago di Tomè, Lago del Starlaresc da Sgiof) and three rivers (Maggia, Vedeggio, Verzasca). To facilitate a better interpretation of results from Alpine lakes, the alkaline lake Lago Bianco was added to the monitoring list from 2006 to 2011. After 2012, because of financial restrictions, monitoring of macroinvertebrates was limited to the most acid sensitive sites (Laghetto Inferiore, Laghetto Superiore, Lago di Tomè, Lago del Starlaresc da Sgiof, river Verzasca). During 2018, we decided not to monitor river Verzasca, in order to have enough financial resources to measure POP’s and metals in fish muscle from Laghetto Superiore and Laghetto Inferiore after eight years of interval.

During 2018, spring and average autumn lake pH’s were 6.7 and 6.9 in Laghetto Inferiore, 6.6 and 7.0 in Laghetto Superiore, 6.0 and 6.2 in Lago del Starlaresc da Sgiof and 5.9 and 6.1 in Lago di Tomè. Concentrations of aluminum were 3 and 6 µg l^{-1} in Laghetto Inferiore, 2 and 8 µg l^{-1} and in Laghetto Superiore, 10 and 11 µg l^{-1} in Lago di Tomè and 21 and 32 µg l^{-1} in Lago del Starlaresc da Sgiof. Compared to Alpine lakes, river Verzasca is situated at much lower altitudes, having therefore a larger catchments area, which is responsible for higher average weathering rates. As a consequence river Verzasca is characterized by higher salinity and higher pH. During 2018, pH values ranged between 6.7 and 7.0 and aluminum between 5 and 33 µg l^{-1}.

From the beginning of the 1980’s autumn pH and alkalinity increased significantly in all four lakes. During the macroinvertebrate monitoring period (from 2000 to present) autumn pH and alkalinity increased significantly only in lakes Laghetto Inferiore, Laghetto Superiore and Lago del Starlaresc da Sgiof. In Laghetto Inferiore pH and alkalinity increased from about 6.5 and 28 µeq l^{-1} (average 2000-2003) to 6.9 and 41 µeq l^{-1} (average 2015-2018), in Laghetto Superiore from 6.4 and 24 µeq l^{-1} to 6.8 and 41 µeq l^{-1}, in Lago del Starlaresc da Sgiof from 5.2 and -9 µeq l^{-1} to 5.9 and 8 µeq l^{-1} and in Lago di Tomè from 5.7 and 2 µeq l^{-1} to 5.9 and 8 µeq l^{-1}. Concentrations of dissolved aluminum decreased significantly only in the more acidic Lago del Starlaresc da Sgiof and Lago di Tomè. Values decreased from about 90 to 50 µg l^{-1} in the first and from 40 to 20 µeq l^{-1} in the second.

4.2 Methods

Macroinvertebrate samples were collected by “kicksampling” according to the ICP Waters Manual (ICP Waters Programme Centre, 2010). Until 2013 lake samples (Laghetto Inferiore, Laghetto Superiore, Lago di Tomè, Lago del Starlaresc da Sgiof) 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 littorals and the outlets of Laghetto Inferiore and Superiore by the Institute for Ecosystem Studies in Pallanza during 1991 and results from samples taken in the littoral and the outlets of Laghetto Inferiore, Laghetto Superiore, Lago di Tomè, Lago del Starlaresc da Sgiof for EMERGE in 2000 (European Mountain lake Ecosystems: Regionalisation, diaGnostic & socio-economic Evaluation).

To show temporal trends, the relative abundances of the main taxonomic groups are shown (average values). In addition, the total number of taxa, the number of taxa belonging to the orders of Ephemeroptera, Plecoptera and Trichoptera (EPT taxa), considered particularly sensitive to pollution, and the number of acid sensitive taxa (AS taxa) according to literature are presented. In order to avoid differences in the taxa number that are caused by different levels of identification used for different surveys, for each taxonomic group a taxonomic identification level was defined and the results were filtered accordingly. The identification levels are the following: Annelida → class, Arachnida → subcohort, Coleoptera → genus, Diptera → family, 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 yearly numbers of taxa were standardized. For each sampling site linear regressions were calculated between the logarithm of the yearly number of taxa (total, EPT, AS) and the total number of sampled individuals. If statistically significant, this relations were used to standardize the yearly number of taxa (total, EPT, AS) to a sample size of 1000 individuals for total taxa.

In high altitude lakes, chironomids are often the most important taxonomic group. In order to gain more information regarding the taxonomic composition of invertebrates, determination of chironomids from past samples down to the species level was started. Since their identification required supplementary expertizes and therefore additional financial resources, this work was done irregularly when financing was available. Since from 2014 only emissaries were sampled, during backwards identification of chironomids priority was given to outlet samples, so that this year we could complete their time series. Only exceptions were samples from 2002, 2011 and 2013, that were lost. Since chironomids were determined in a second step, the number of identified individuals was mostly not identical to that determined during the general invertebrate identification done previously, because of counting errors or losses or damages of individuals in between. In addition, as already mentioned, not for all invertebrate samples identification of chironomids has been possible. For these reason we decided to analyse the chironomid data separately from the other invertebrates. As done for the general invertebrate analysis, also for chironomids, we calculated total taxa numbers normalized to the total numbers of chironomids in the samples.

4.3 Results and discussion

Sample size and the relative abundance of identified taxa and taxa groups (EPT, AS) with the most important taxa numbers (total, EPT, AS) in lake outlets during 2018 are shown in Tab. 4.1 and 4.2, respectively. At all sites Diptera was the most abundant taxonomic group, mainly represented by Chironomidae, but also by the current loving Simuliidae in Laghetto Inferiore, Laghetto Superiore, Lago di Tomè and by Ceratopogonidae in Lago del Starlaresc da Sgiof, probably because of the presence of wetland vegetation.

Other quantitatively important taxonomic groups were Oligochaeta (Naididae) and Turbellaria (Planariidae, probably the acid sensitive *Crenobia sp.*) in Laghetto Inferiore and Superiore. Another abundant order was Plecoptera. In Laghetto Inferiore, Laghetto Superiore and Lago di Tomè prevailed *Leuctra sp.* and *Nemoura sp.*, in Laghetto Inferiore, and Laghetto Superiore also *Protonemoura sp.* and in Lago del Staraleresc da Sgiof only *Nemoura sp*. Trichopterians were also present in Laghetto Inferiore, Laghetto Superiore and Lago di Tomè but with lower abundance. The more acid sensitive Ephemeroptera were found only in Laghetto Inferiore and Laghetto Superiore (*Ecdyonurus sp.*), while Odonata (*Aeshna sp., Libellula sp., Orthetrum sp.*), that are common in wetlands, were observed only in Lago del Starlaresc da Sgiof. In general, relative abundances of invertebrates sampled on fine and coarse substrates did no differ greatly.

As regards total taxa numbers (chironomids not included), highest values were found in Laghetto Inferiore (16) and Laghetto Superiore (16) followed by Lago di Tomè (12) and Lago del Starlaresc da Sgiof (9). The highest number of EPT taxa was identified in Laghetto Inferiore and in Laghetto Superiore (11), followed by Lago di Tomè (6) and at last in Lago del Starlaresc da Sgiof (1), while the highest number of AS taxa was determined in Laghetto Superiore (4), followed by Laghetto Inferiore (3), Lago di Tomè (1) and Lago del Starlaresc da Sgiof (0). As regards the relative abundance of EPT taxa, the highest percentage was registered in the acidic Lago di Tome (29%) because of the high abundance of *Leuctra sp.*, followed by Laghetto Superiore (22%), Laghetto Inferiore (13%) and Lago del Starlaresc da Sgiof (13%). The relative abundance of AS taxa decreased as follows: Laghetto Inferiore (25%), Laghetto Superiore (20%), Lago di Tomé (1%), Lago del Starlaresc da Sgiof (0%). These abundances were mainly determined by the presence of Planariidae (probably *Crenobia alpina*). Relative abundances of other AS species were low (Laghetto Inferiore: 1.4% *Ecdyonurus sp.,* 0.2% *Protonemoura nimborum*; Laghetto Superiore: 1.5% *Ecdyonurus sp.,* 0.04% *Protonemoura nimborum,* 0.2% *Perlodes intricatus*). In Lago del Starlaresc da Sgiof acid sensitive taxa were absent. In general the number of total and AS taxa and the relative abundance of AS taxa decreased in the following lake order Laghetto Inferiore/Laghetto Superiore, Lago di Tomè and Lago del

Starlaresc da Sgiof. This is well reflecting the increasing aluminum concentrations of these lakes (see par. 4.1). Also, pH's of both Lago di Tomè and Lago del Starlaresc da Sgiof are still, at least occasionally, below 6.

As regards chironomids (Tab. 4.7-4.10) the total number of taxa in the outlets was higher than in the littorals, which is not surprising since in the prior, species typical for both running and standing waters can be found. Among lakes the number of chironomid taxa followed the same rank order than observed for all other macroinvertebrates without the determination to species of chironomids: Laghetto Superiore (outlet: 60, littoral: 41), Laghetto Inferiore (outlet: 58, littoral: 38), Lago di Tomè (outlet: 48, littoral: 25), followed by Lago del Starlaresc da Sgiof (outlet: 43, littoral: 23). This indicates that the number of chironomid taxa may also decrease with increasing acidity. As regards the taxa number of chironomid subfamilies, Orthocladiinae dominated outlets and littorals of Laghetto Superiore, Laghetto Inferiore and Lago di Tomè. In the species poorer Lago del Starlaresc da Sgiof the number of taxa in the three subfamilies Chironominae, Orthocladiinae and Tanypodinae did not vary much. In terms of relative abundances, as expected from Alpine lakes (Füreder et al. 2006), Orthocladiinae was the dominant subfamily in the outlets of Laghetto Inferiore and Laghetto Superiore. In the littorals of these lakes, next to Orthocladiinae, Tanypodinae and Chironominae (Tanytarsini) were also abundant. Differently, Chironominae (Tanytarsini) dominated in both the outlet and littoral of Lago del Starlaresc da Sgiof. A similar fauna composition was found in warm Alpine lakes by Boggero and Lencioni (2006). Other publications[1] indicate 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.) Lago del Starlaresc da Sgiof is characterized by high summer surface temperatures (up to 21°C, July 2015) and aquatic vegetation. In the littoral of Lago di Tomè, Tanypodinae were most abundant followed by Orthocladiinae and Chironominae (Tanytarsini). In the outlet of Lago di Tomè Chironominae (Chironomini) was the most abundant subfamily followed by Orthocladiinae and Tanypodinae. High abundances of Tanypodinae and Chironomini are reported to occur at warmer temperatures, while Orthocladiinae 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, deep lake Lago di Tomè (max. depth 38 m) is situated at low altitude (1692 m a.s.l.) and has, compared to most other studied lakes, high nitrate concentrations and relatively high summer surface temperatures (up to 18°C, August 2003).

[1] (http://www.landcareresearch.co.nz/resources/identification/animals/freshwater-invertebrates/guide/no-jointed-legs2/true-fly-larvae/midges/chironomid-midge13)

Table 4.1 Lake sample sizes during 2018

LAKE OUTLETS	MONTH	Fine substrate	Coarse substrate
INF	**June (28.6.2018)**	537	451
	September (8.9.2018)	317	324
SUP	**June (28.6.2018)**	594	334
	September (8.9.2018)	250	190
TOM	**July (11.7.2018)**	339	250
	September (10.09.2018)	58	82
STA	**July (11.7.2018)**	65	120
	September (10.09.2018)	397	188

Temporal changes of the relative abundances of the main taxa and taxa groups (EPT, AS) and most important taxa numbers (total, EPT, AS) are presented in Tab. 4.4-4.6. There is no evidence for biological recovery from acidification. The in terms of chemistry and biology very similar Laghetto Inferiore and Laghetto Superiore are inhabited only by a few AS taxa: Laghetto Superiore by *Ecdyonurus sp.*, *Protonemoura nimborum*, *Perlodes intricatus, Isoperla grandis, Planariidae and Laghetto Inferiore by Ecdyonurus sp.*, *Protonemoura nimborum*, *Planariidae*). With exception of Planariidae (probably *Crenobia alpina*), that seemed to have slightly increased during the last four years (the reason is not clear), the relative abundance of the other taxa remained relatively unchanged. The number of AS species did also not increase over the years. Other typical AS taxa occurring in mountain streams like species of *Baetis sp.*, *Rhithrogena sp.*, *Perla sp.*, *Philopotamus sp.* are still missing. As regards Lago di Tomè, since 2006 the acid sensitive taxa Panariidae is found in this lake. No AS taxa is still found in Lago del Starlaresc da Sgiof.

Table 4.2 Relative abundance and number of taxa in lake outlets on different substrates during 2018. ***0.0% indicate values >0.0% but < 0.05%.***

TAXA	INF		SUP		TOM		STA		INF	SUP	TOM	STA
	Fine	Coarse	Fine	Coarse	Fine	Coarse	Fine	Coarse				
OLIGOCHAETA	**17.0%**	**12.2%**	**18.7%**	**23.2%**			**10.0%**		**14.6%**	**20.9%**		**5.0%**
Naididae	17.0%	12.2%	18.7%	23.3%					14.6%	20.9%		
COLEOPTERA			**0.2%**		**0.9%**	**0.6%**	**2.3%**			**0.1%**	**0.7%**	**1.2%**
Agabus sp.			0.2%		0.9%	0.6%				0.1%	0.5%	0.2%
Potamophilus sp.							2.3%					0.8%
DIPTERA	**52.0%**	**47.2%**	**49.7%**	**28.1%**	**64.5%**	**74.5%**	**61.2%**	**97.3%**	**49.6%**	**38.9%**	**69.5%**	**79.3%**
Athericidae					0.1%						0.1%	
Ceratopogonidae	0.3%					0.6%	15.8%	63.8%	0.2%		0.3%	39.8%
Chironomidae	32.7%	44.8%	34.3%	23.4%	17.2%	28.8%	39.8%	33.0%	38.7%	28.9%	23.0%	36.4%
Simuliidae	19.0%	2.4%	15.4%	4.7%	47.2%	45.1%	5.6%	0.4%	10.7%	10.1%	46.2%	3.0%
EPHEMEROPTERA	**1.7%**	**1.2%**	**0.3%**	**2.8%**					**1.4%**	**1.5%**		
Ecdyonurus sp.	1.7%	1.2%	0.3%	2.8%					1.4%	1.5%		
ODONATA							**2.5%**	**1.1%**				**1.8%**
Aeshna affinis							0.5%					0.2%
Aeshna sp.							1.9%	0.4%				1.5%
Libellula sp.							0.1%	0.7%				0.2%
Orthetrum sp.												0.1%
Libellulidae												0.1%
PLECOPTERA	**7.2%**	**10.3%**	**14.6%**	**20.1%**	**28.1%**	**10.5%**	**23.9%**	**1.6%**	**8.7%**	**17.4%**	**19.3%**	**12.8%**
Leuctra sp.	2.1%	0.6%	3.2%	2.8%	25.5%	6.6%			0.9%	2.8%	12.2%	
Nemoura minima			0.2%	0.3%						0.1%		
Nemoura mortoni	0.1%	0.1%							0.1%		0.4%	
Nemoura sp.	1.5%	8.3%	9.4%	8.3%	2.6%	3.8%	23.9%	1.6%	6.2%	9.8%	1.9%	11.1%
Protonemoura nimborum.		0.2%	0.1%						0.2%	0.0%		
Protonemoura sp.	3.5%	1.0%	1.3%	8.7%					3.2%	4.7%		
Isoperla grammatica										0.2%		
Perlodes intricatus			0.4%							0.2%		
TRICHOPTERA	**2.6%**	**2.2%**	**0.5%**	**5.6%**	**4.0%**	**14.4%**			**2.4%**	**3.0%**	**9.2%**	
Limnephilus sp.					1.0%				0.1%		0.4%	
Plectrocnemia conspersa				0.3%								
Plectrocnemia sp.			0.3%							0.3%		
Policentropodidae	0.9%								0.5%			
Rhyacophila (Rhyacophila) sp.	1.2%		0.3%	5.0%	2.0%	3.4%			0.6%	2.7%	1.9%	
Rhyacophila praemorsa	0.4%	0.3%			0.9%	7.3%			0.4%	0.8%	0.4%	
Rhyacophila sp.		0.4%		0.3%	0.1%	3.7%			0.2%		2.5%	
Rhyacophlidae		1.5%							0.9%			0.1%
TURBELLARIA	**19.7%**	**26.9%**	**16.1%**	**20.3%**	**2.5%**				**23.3%**	**18.2%**	**1.3%**	
Planariidae	19.7%	26.9%	16.1%	20.3%	2.5%				23.3%	18.2%	1.3%	
Rel. abundance EPT taxa	11.4%	13.7%	15.3%	28.5%	32.1%	24.9%	23.9%	1.6%	12.6%	21.9%	28.5%	12.8%
Rel. abundance AS taxa	21.3%	28.3%	16.9%	23.0%	2.5%				24.8%	19.9%	1.3%	
Number total taxa	13	13	14	12	11	9	9	6	16	16	12	9
Number EPT taxa	8	9	9	8	6	5	1	1	11	11	6	1
Number AS taxa	2	3	4	2	1	0	0	0	3	4	1	0

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

PARAMETER	1991	2000	2002	2003	2004	2005	2006	2007	2008	2009	2011	2012	2013	2014	2015	2016	2017	2018
Sampling times	1	3	3	3	3	3	3	2	2	2	2	2	2	2	2	2	2	2
Individuals	64	80	293	1224	2003	8353		7712	10507	5250	958	5170	4587	4587	1222	1669	1183	1629
Rel. abundance OLIGOCHAETA	22%	6%	11%	25%	36%	30%		30%	23%	23%		0%	1%	7%	10%	17%	16%	15%
Rel. abundance HYDRACARINA			1%	0%	0%	0%		0%	0%	0%	1%	0%	0%					
Rel. abundance COLEOPTERA				0%	0%	0%					0%							
Rel. abundance ELMIDAE				*0%*	*0%*													
Rel. abundance HYDROPHILIDAE						*0%*												
Rel. abundance DIPTERA	47%	25%	44%	45%	33%	45%		58%	52%	60%	92%	91%	92%	81%	63%	47%	41%	50%
Rel. abundance ATHERICIDAE		*8%*		*7%*	*5%*	*2%*		*1%*	*1%*	*1%*	*3%*							
Rel. abundance CERATOPOGONIDAE																	*0%*	*0%*
Rel. abundance CHIRONOMIDAE	*38%*	*13%*	*17%*	*29%*	*23%*	*18%*		*39%*	*46%*	*51%*	*86%*	*50%*	*70%*	*54%*	*55%*	*45%*	*25%*	*39%*
Rel. abundance EMPIDIDAE						*0%*		*0%*	*0%*									
Rel. abundance LIMONIIDAE			*1%*	*1%*	*0%*				*0%*		*0%*	*0%*	*0%*	*0%*				
Rel. abundance PEDICIIDAE	*9%*																	
Rel. abundance SIMULIDAE (%)		*5%*	*26%*	*8%*	*5%*	*25%*		*18%*	*6%*	*8%*	*2%*	*22%*	*22%*	*22%*	*9%*	*2%*	*15%*	*11%*
Rel. abundance EPHEMEROPTERA				2%	2%	1%		1%	1%	0%	0%	0%	0%	0%	1%	2%	1%	1%
Rel. abundance BAETIDAE						*0%*												
Rel. abundance HEPTAGENIIDAE				*2%*	*2%*	*1%*		*1%*	*1%*	*0%*	*0%*	*0%*	*0%*	*0%*	*1%*	*2%*	*1%*	*1%*
Rel. abundance HETEROPTERA														0%				
Rel. abundance PLECOPTERA	27%	56%	33%	23%	16%	12%		5%	5%	6%	6%	2%	1%	7%	10%	9%	11%	9%
Rel. abundance LEUCTRIDAE	*2%*		*0%*	*1%*	*0%*	*1%*		*0%*	*0%*	*0%*		*0%*	*1%*	*1%*	*0%*	*0%*	*1%*	*1%*
Rel. abundance NEMOURIDAE	*25%*	*56%*	*33%*	*22%*	*15%*	*11%*		*5%*	*4%*	*6%*	*6%*	*2%*	*1%*	*7%*	*10%*	*9%*	*10%*	*7%*
Rel. abundance PERLODIDAE				*0%*	*0%*	*0%*		*0%*	*0%*	*0%*								
Rel. abundance TAENIOPTERIGYDAE						*0%*												
Rel. abundance TRICHOPTERA		8%	1%	3%	3%	3%		0%	1%	1%	1%	0%	0%	1%	2%	2%	3%	2%
Rel. abundance LEPIDOSTOMATIDAE				*0%*							*0%*							
Rel. abundance LIMNEPHILIDAE				*1%*	*0%*	*1%*		*0%*		*0%*				*0%*			*0%*	
Rel. abundance PHILOPOTAMIDAE				*0%*	*1%*	*1%*					*0%*							
Rel. abundancePOLYCENTROPODIDAE				*0%*	*0%*	*0%*		*0%*	*0%*	*0%*	*0%*			*0%*	*0%*	*1%*	*0%*	*0%*
Rel. abundance RHYACOPHILIDAE		*8%*	*1%*	*2%*	*2%*	*0%*		*0%*	*1%*	*1%*		*0%*	*0%*	*1%*	*1%*	*1%*	*2%*	*2%*
Rel. abundance BIVALVIA											0%							
Rel. abundance TURBELLARIA	5%	5%	11%	2%	10%	8%		5%	18%	9%	1%	6%	4%	4%	14%	23%	29%	23%
Rel. abundance	*5%*	*5%*	*11%*	*2%*	*10%*	*8%*		*5%*	*18%*	*9%*	*1%*	*6%*	*4%*	*4%*	*14%*	*23%*	*29%*	*23%*
Rel. abundance EPT taxa	27%	64%	34%	28%	21%	16%		7%	6%	8%	6%	2%	2%	9%	13%	13%	15%	13%
Rel. abundance AS taxa	5%	5%	11%	5%	14%	11%		6%	19%	9%	1%	6%	5%	4%	15%	25%	31%	25%
Number of total taxa	8	8	11	21	18	23	15	21	20	17	13	11	11	12	11	11	13	12
Standardized number of total taxa	9	9	12	21	17	14	16	13	11	13	13	8	9	9	11	11	13	12
Number of EPT taxa	4	3	5	12	10	15	7	14	12	11	5	5	5	7	7	7	8	7
Standardized number of EPT taxa	4	3	5	12	9	8	8	8	5	8	5	3	4	5	7	7	8	7
Number of AS taxa	1	1	1	5	5	7	5	6	4	3	3	2	2	2	2	2	2	2

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

PARAMETER	1991	2000	2002	2003	2004	2005	2006	2007	2008	2009	2011	2012	2013	2014	2015	2016	2017	2018
Sampling times	1	3	3	3	3	3	3	2	2	2	2	2	2	2	2	2	2	2
Individuals	49	34	150	1528	1744	6624	5736	5347	4977	5469	963	6725	1711	1249	1094	1177	1231	1368
Rel. abundance OLIGOCHAETA	6%	3%	6%	21%	20%	38%	50%	64%	43%	29%	1%	24%	7%	26%	17%	18%	21%	21%
Rel. abundance HYDRACARINA					0%	0%	0%	0%	0%	0%								
Rel. abundance COLEOPTERA				0%		0%			0%	0%	0%				0%		0%	0%
Rel. abundance DRYOPIDAE				*0%*														
Rel. abundance DYTISCIDAE									*0%*						*0%*		*0%*	*0%*
Rel. abundance HELOPHORIDAE											*0%*							
Rel. abundance HYDROPHILIDAE						*0%*												
Rel. abundance DIPTERA	63%	6%	50%	35%	49%	47%	38%	30%	49%	49%	81%	65%	88%	56%	43%	45%	35%	39%
Rel. abundance CHIRONOMIDAE	*59%*	*6%*	*42%*	*30%*	*36%*	*31%*	*27%*	*19%*	*44%*	*43%*	*65%*	*63%*	*83%*	*38%*	*30%*	*41%*	*24%*	*29%*
Rel. abundance EMPIDIDAE					*0%*	*0%*	*0%*											
Rel. abundance LIMONIIDAE			*3%*	*0%*	*0%*	*0%*	*0%*	*0%*		*0%*								
Rel. abundance PEDICIIDAE									*0%*									
Rel. abundance PSYCHIDIDAE									*0%*									
Rel. abundance PTYCHOPTERIDAE									*0%*									
Rel. abundance SIMULIDAE	*4%*		*5%*	*5%*	*13%*	*16%*	*11%*	*11%*	*5%*	*6%*	*16%*	*3%*	*4%*	*18%*	*12%*	*4%*	*10%*	*10%*
Rel. abundance EPHEMEROPTERA				9%	7%	1%	0%	0%	0%	0%	1%		1%	0%	0%	2%	2%	2%
Rel. abundance BAETIDAE				*2%*	*0%*	*0%*	*0%*											
Rel. abundance HEPTAGENIIDAE				*6%*	*7%*	*1%*	*0%*	*0%*	*0%*	*0%*	*1%*		*1%*	*0%*	*0%*	*2%*	*2%*	*2%*
Rel. abundance HETEROPTERA					0%									0%				
Rel. abundance CORIXIDAE					*0%*									*0%*				
Rel. abundance PLECOPTERA	18%	68%	38%	29%	17%	11%	10%	3%	6%	21%	13%	7%	2%	12%	18%	19%	18%	17%
Rel. abundance LEUCTRIDAE	*14%*	*9%*	*6%*	*12%*	*5%*	*5%*	*6%*	*1%*	*1%*	*2%*	*5%*	*2%*	*1%*	*3%*	*3%*	*3%*	*3%*	*3%*
Rel. abundance NEMOURIDAE	*4%*	*59%*	*32%*	*17%*	*11%*	*6%*	*5%*	*2%*	*4%*	*2%*	*8%*	*5%*	*1%*	*9%*	*15%*	*16%*	*15%*	*14%*
Rel. abundance PERLODIDAE				*0%*	*1%*	*0%*	*0%*	*0%*	*0%*		*0%*				*0%*	*0%*	*0%*	*0%*
Rel. abundance TRICHOPTERA		24%	1%	4%	3%	1%	1%	1%	1%	1%	2%	1%	0%	0%	3%	2%	4%	3%
Rel. abundance LIMNEOHILIDAE		*6%*		*0%*		*0%*	*0%*	*0%*				*0%*	*0%*					
Rel. abundance PHILOPOTAMIDAE		*6%*		*0%*	*0%*													
Rel. abundance POLYCENTROPODIDAE		*6%*	*1%*	*2%*	*1%*	*0%*	*0%*	*0%*	*0%*	*0%*	*0%*	*1%*	*0%*		*0%*	*0%*	*0%*	*0%*
Rel. abundance PSYCHO;YIIDAE		*3%*																
Rel. abundance RHYACOPHILIDAE		*3%*		*2%*	*3%*	*1%*	*0%*	*0%*	*0%*	*1%*	*1%*	*0%*	*0%*	*0%*	*3%*	*2%*	*4%*	*3%*
Rel. abundance TURBELLARIA	12%		5%	1%	4%	1%	1%	2%	1%	1%	3%	2%	1%	5%	19%	15%	21%	18%
Rel. abundance PLANORBIDAE	*12%*		*5%*	*1%*	*4%*	*1%*	*1%*	*2%*	*1%*	*1%*	*3%*	*2%*	*1%*	*5%*	*19%*	*15%*	*21%*	*18%*
Rel. abundance EPT taxa	18%	91%	39%	43%	27%	13%	11%	4%	7%	21%	15%	8%	3%	13%	21%	22%	24%	22%
Rel. abundance AS taxa	12%	3%	5%	11%	12%	2%	1%	3%	1%	1%	4%	2%	2%	5%	20%	17%	23%	20%
Number of total taxa	6	11	10	19	22	20	18	20	24	17	14	10	11	9	13	11	13	12
Standardized number of total taxa	6	12	11	18	21	13	12	14	17	12	14	6	10	9	13	11	13	12
Number of EPT taxa	2	9	5	13	14	11	11	14	12	10	8	6	7	5	8	7	8	7
Standardized number of EPT taxa	2	10	5	12	13	7	7	10	8	7	8	4	7	5	8	7	8	7
Number of AS taxa	1	1	1	6	8	5	5	3	3	2	3	1	2	2	4	3	4	3

Table 4.5 Temporal variations of the relative abundances and the number of taxa in the outlet of Lago di Tomè. ***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
Sampling times	1	2	2	1	1	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
Rel. abundance OLIGOCHAETA		7%	1%	0%	0%	0%	0%	1%	1%	42%	4%	1%	15%				
Rel. abundance HYDRACARINA			1%	1%	0%	2%	1%	0%	0%		1%						
Rel. abundance COLEOPTERA		1%	3%		0%	0%	0%	0%	0%	1%	1%		1%	1%	0%	0%	1%
Rel. abundance DYTISCIDAE		1%	2%		0%	0%	0%	0%	0%	1%				1%	0%	0%	1%
Rel. abundance ELMIDAE			1%														
Rel. abundance DIPTERA	36%	28%	34%	40%	84%	58%	64%	90%	87%	53%	77%	72%	70%	67%	76%	78%	69%
Rel. abundance Athericidae															0%	0%	0%
Rel. abundance CERATOPOGONIDAE								0%						1%		0%	0%
Rel. abundance CHIRONOMIDAE	36%	14%	33%	37%	75%	38%	57%	61%	65%	26%	40%	68%	19%	50%	46%	49%	23%
Rel. abundance EMPIDIDAE					0%	0%	0%	0%					0%				
Rel. abundance LIMONIIDAE						0%											
Rel. abundance PSYCHODIDAE								0%		0%							
Rel. abundance SIMULIDAE		14%	1%	3%	9%	20%	6%	29%	22%	26%	36%	5%	51%	16%	30%	29%	46%
Rel. abundance HETEROPTERA			0%		0%	0%							1%				
Rel. abundance MESOVELIIDAE													1%				
Rel. abundance MEGALOPTERA	18%	2%	1%	1%	0%		0%	0%	0%								
Rel. abundance SIALIDAE	18%	2%	1%	1%	0%		0%	0%	0%								
Rel. abundance PLECOPTERA	36%	60%	57%	58%	13%	37%	34%	8%	10%	3%	14%	27%	10%	28%	18%		19%
Rel. abundance LEUCTRIDAE	36%	57%	55%	58%	12%	35%	34%	1%	9%	3%	10%	13%	4%	23%	16%	12%	16%
Rel. abundance NEMOURIDAE		3%	2%		2%	1%	0%	1%	1%		4%	13%	6%	4%	3%	2%	3%
Rel. abundance PERLODIDAE								0%									
Rel. abundance TRICHOPTERA	9%	2%	4%	1%	2%	2%	1%	1%	1%	1%	1%	1%	3%	6%	4%		9%
Rel. abundance LIMNEPHILIDAE		1%	1%		1%	1%		0%	1%				3%	1%	0%	0%	1%
Rel. abundance ODONTOCERIDAE						0%	0%		0%								
Rel. abundance PHILOPOTAMIDAE	9%																
Rel. abundance POLYCENTROPODIDAE		1%	3%	0%	0%	0%	0%	0%	0%	1%	1%	1%					
Rel. abundance RHYACOPHILIDAE			1%	1%	0%	1%	1%	0%	0%				0%	5%	3%	5%	9%
Rel. abundance TURBELLARIA						1%	0%	0%	0%		3%		0%		1%	1%	1%
Rel. abundance PLANARIIDAE						1%	0%	0%	0%		3%		0%		1%	1%	1%
Rel. abundance EPT taxa	45%	62%	61%	59%	15%	39%	35%	9%	12%	4%	15%	27%	13%	33%	22%	20%	29%
Rel. abundance AS taxa					0%	1%	0%	0%	0%		3%		0%		1%	1%	1%
Number of total taxa	4	10	15	8	17	18	17	22	20	7	10	7	13	8	9	10	10
Standardized number of total taxa	5	12	17	9	14	12	9	11	12	8	10	8	7	9	9	10	11
Number of EPT taxa	2	5	6	3	9	9	8	12	11	2	4	4	5	4	4	4	4
Standardized number of EPT taxa	3	6	7	4	7	5	4	5	6	2	4	5	2	5	4	4	4
Number of AS taxa	0	0	0	0	1	2	2	3	1	0	1	0	2	0	1	1	1

Table 4.6 Temporal variations of the relative abundances and the number of taxa in the outlet of Lago del Starlaresc da Sgiof. ***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
Sampling times	1	2	2	1	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
Rel. abundance OLIGOCHAETA			1%	3%	3%	1%	0%	2%	10%		6%	6%		4%	4%	4%	5%
Rel. abundance HYDRACARINA			1%	1%		0%	0%	1%	2%		6%	7%	0%				
Rel. abundance COLEOPTERA	14%	2%	0%	0%	0%	0%	0%	0%	0%	1%	0%		0%	0%		1%	1%
Rel. abundance CHRYSOMELIDAE								*0%*									
Rel. abundance DYTISCIDAE	*14%*	*2%*	*0%*		*0%*	*0%*	*0%*	*0%*	*0%*	*1%*			*0%*	*0%*		*0%*	
Rel. abundance ELMIDAE														*0%*		*1%*	*1%*
Rel. abundance DIPTERA	29%	85%	91%	66%	89%	96%	85%	87%	74%	95%	69%	87%	73%	86%	83%	82%	79%
Rel. abundance ATHERICIDAE					*0%*					*25%*							
Rel. abundance CERATOPOGONIDAE		*16%*	*5%*	*10%*	*14%*	*3%*	*5%*	*14%*	*13%*	*7%*	*20%*	*15%*	*8%*	*12%*	*30%*	*33%*	*40%*
Rel. abundance CHIRONOMIDAE	*29%*	*69%*	*85%*	*56%*	*75%*	*93%*	*79%*	*71%*	*56%*	*63%*	*35%*	*59%*	*16%*	*73%*	*53%*	*47%*	*36%*
Rel. abundance LIMONIIDAE							*0%*										
Rel. abundance PSYCHIDIDAE					*0%*					*0%*							
Rel. abundance SIMULIDAE				*0%*	*0%*	*0%*	*1%*	*2%*	*4%*	*0%*	*15%*	*13%*	*49%*	*1%*		*2%*	*3%*
Rel. abundance TABANIDAE																	
Rel. abundance EPHEMEROPTERA								0%									
Rel. abundance BAETIDAE								*0%*									
Rel. abundance HETEROPTERA			1%	11%	0%	0%	0%	0%	0%	0%	0%	0%					
Rel. abundance CORIXIDAE			*0%*	*11%*	*0%*	*0%*	*0%*	*0%*	*0%*								
Rel. abundance GERRIDAE			*0%*							*0%*	*0%*	*0%*					
Rel. abundance MEGALOPTERA									0%								
Rel. abundance SIALIDAE									*0%*								
Rel. abundance ODONATA		6%	0%	13%	5%	1%	3%	2%	2%	2%	3%	0%	1%	1%	1%	2%	2%
Rel. abundance AESHNIDAE		*5%*	*0%*	*12%*	*4%*	*1%*	*3%*	*1%*	*1%*	*1%*	*2%*	*0%*	*0%*	*1%*	*1%*	*2%*	*1%*
Rel. abundance CORDULIDAE				*1%*	*1%*	*0%*	*0%*	*0%*	*0%*	*1%*							
Rel. abundance LIBELLULIDAE		*1%*									*1%*		*0%*	*0%*	*1%*	*0%*	*0%*
Rel. abundance PLECOPTERA	24%	2%	2%	5%	1%	1%	9%	8%	12%	1%	16%		26%	8%	12%	11%	13%
Rel. abundance NEMOURIDAE	*24%*	*2%*	*2%*	*5%*	*1%*	*1%*	*9%*	*8%*	*12%*	*1%*	*16%*		*26%*	*8%*	*12%*	*11%*	*13%*
Rel. abundance TRICHOPTERA	33%	5%	4%		0%	0%	1%	1%	1%				0%	1%		0%	
Rel. abundance LIMNEPHLIDAE			*0%*		*0%*	*0%*	*0%*	*0%*									
Rel. abundance PHRYGANEIDAE	*33%*	*5%*	*4%*		*0%*	*0%*	*1%*	*0%*	*0%*				*0%*				
Rel. abundance POLYCENTROPODIDAE						*0%*	*0%*	*0%*	*1%*					*0%*		*0%*	
Rel. abundance EPT taxa	57%	7%	6%	5%	2%	1%	10%	9%	13%	1%	16%		26%	9%	12%	11%	13%
Rel. abundance AS taxa								0%									
Number of total taxa	4	8	13	11	16	16	19	23	18	12	10	7	9	12	8	12	8
Standardized number of total taxa	5	8	13	12	12	6	12	13	13	13	10	7	8	11	8	12	8
Number of EPT taxa	2	3	3	1	4	6	6	8	6	1	1	0	2	2	1	2	1
Standardized number of EPT taxa	3	3	3	1	2	1	3	3	3	1	1	0	2	2	1	2	1
Number of AS taxa	0	0	0	0	0	0	0	1	0	0	0	0	0	0	0	0	0

Table 4.7 Temporal variations of the relative abundances and the number of taxa of Chironomidae in Laghetto Inferiore. ***0% indicates values between 0% and < 0.5%.***

SITE	PARAMETER	1991	2002	2003	2004	2005	2006	2007	2008	2009	2011	2012	2013	2014	2015	2016	2017	2018
OUT	Sampling times	1		3	2	3	2	2	2	2		2		2	2	2	2	2
	Individuals	24		277	204	1256	1558	2584	4661	2410		3718		2344	624	996	306	914
	Rel. abundance CHIRONOMINAE	21%		5%	0%	9%	6%	2%	1%	3%		0%		3%	2%	14%	1%	3%
	Rel. abundance Chirnonomini																	
	Rel. abundance Tanytarsini	21%		5%	0%	9%	6%	2%	1%	3%		0%		3%	2%	14%	1%	3%
	el. abundance DIAMESINAE	13%			2%		0%	1%	0%								1%	
	Rel. abundance Diamesini	13%			2%		0%	1%	0%								1%	
	Rel. abundance ORTHOCLADIINAE	67%		94%	96%	91%	90%	96%	99%	95%		100%		97%	96%	81%	88%	89%
	Rel. abundance PRODIAMESINAE																	
	Rel. abundance TANYPODINAE			0%		1%	5%	1%	0%	1%		0%		0%	1%	4%	11%	8%
	Rel. abundance Macropelopiini							0%	0%								1%	1%
	R Rel. abundance Pentaneurini			0%		1%	5%	1%	0%	1%		0%		0%	1%	4%	10%	8%
	R R Rel. abundance Procladiini																	
	Rel. abundance NOT DETERMINED			1%	1%					2%								
	Number of total taxa	8		11	10	11	25	28	19	13		18		12	11	15	20	24
	Standardized number of total taxa	8		11	10	9	26	20	11	10		14		10	11	14	20	23
LIT	Sampling times	1		3	3	3	2	2	2	2		2						
	Individuals	147		1103	945	3757		1763		1991								
	Rel. abundance CHIRONOMINAE	17%		18%	34%	36%		19%		20%		3%						
	Rel. abundance Chirnonomini			1%	1%	0%		4%		1%		1%						
	Rel. abundance Tanytarsini	17%		17%	33%	36%		15%		19%		2%						
	el. abundance DIAMESINAE	7%						0%										
	Rel. abundance Diamesini	0%						0%										
	Rel. abundance ORTHOCLADIINAE	61%		50%	28%	43%		47%		39%		86%						
	Rel. abundance PRODIAMESINAE	5%		2%	1%	1%		1%		2%		0%						
	Rel. abundance TANYPODINAE	10%		26%	36%	20%		33%		39%		10%						
	Rel. abundance Macropelopiini			2%	0%	1%		2%		5%		0%						
	R Rel. abundance Pentaneurini	10%		24%	36%	19%		31%		34%		10%						
	R R Rel. abundance Procladiini											0%						
	Rel. abundance NOT DETERMINED			4%	1%					0%								
	Number of total taxa	10		17	13	19		19		11		15						
	Standardized number of total taxa	10		16	13	13		16		9		13						

Table 4.8 Temporal variations of the relative abundances and the number of taxa of Chironomidae in Laghetto Superiore. ***0% indicates values between 0% and < 0.5%.***

SITE	PARAMETER	1991	2002	2003	2004	2005	2006	2007	2008	2009	2011	2012	2013	2014	2015	2016	2017	2018
OUT	Sampling times	1		3	2	2	2	2	2	2		2		1	2	2	2	2
	Individuals	29		415	423	1316	1482	740	2095	1401		2251		139	309	527	371	473
	Rel. abundance CHIRONOMINAE	21%		9%	6%	9%	6%	1%	1%	1%		1%			7%	8%	15%	4%
	Rel. abundance Chirnonomini											0%				0%		
	Rel. abundance Tanytarsini	21%		9%	6%	9%	6%	1%	1%	1%		1%			7%	8%	15%	4%
	el. abundance DIAMESINAE	17%			1%	0%		7%	0%	0%		0%			1%	2%	3%	0%
	Rel. abundance Diamesini	17%			1%	0%		7%	0%	0%		0%			1%	2%	3%	0%
	Rel. abundance ORTHOCLADIINAE	62%		73%	83%	90%	90%	90%	98%	96%		76%		100%	70%	46%	47%	78%
	Rel. abundance PRODIAMESINAE						0%											
	Rel. abundance TANYPODINAE			16%	5%	2%	3%	1%	1%	2%		23%			21%	44%	35%	18%
	Rel. abundance Macropelopiini					0%												
	R Rel. abundance Pentaneurini			16%	5%	1%	3%	1%	1%	2%		23%			21%	44%	35%	18%
	R R Rel. abundance Procladiini																	
	Rel. abundance NOT DETERMINED			2%	4%					1%								
	Number of total taxa	7		18	15	15	14	23	19	13		18		8	19	16	16	15
	Standardized number of total taxa	8		18	15	12	11	21	14	11		13		8	19	16	16	15
LIT	Sampling times	1		3	3	3	2	2	2	2		2						
	Individuals	487		1075	1174	5026		1689		3097		2128						
	Rel. abundance CHIRONOMINAE	3%		11%	18%	20%		14%		34%		4%						
	Rel. abundance Chirnonomini			0%	0%			0%				0%						
	Rel. abundance Tanytarsini	3%		11%	18%	20%		13%		34%		3%						
	el. abundance DIAMESINAE	13%																
	Rel. abundance Diamesini	13%																
	Rel. abundance ORTHOCLADIINAE	76%		68%	51%	61%		50%		49%		89%						
	Rel. abundance PRODIAMESINAE	3%		1%	2%	1%		1%		0%		0%						
	Rel. abundance TANYPODINAE	4%		15%	28%	19%		35%		17%		7%						
	Rel. abundance Macropelopiini			2%	2%	1%		3%		2%		1%						
	R Rel. abundance Pentaneurini	3%		13%	25%	18%		32%		15%		6%						
	R R Rel. abundance Procladiini																	
	Rel. abundance NOT DETERMINED			4%	1%					0%								
	Number of total taxa	15		17	12	15		21		13		18						

Table 4.9 Temporal variations of the relative abundances and the number of taxa of Chironomidae in Lago di Tomè. ***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
OUT	Sampling times		2	1	2	2	2	2	2		2		1	2	2	2	2
	Individuals		64	115	1035	943	1845	2956	2606		132		544	193	428	445	101
	Rel. abundance CHIRONOMINAE		16%	5%	67%	20%	45%	64%	69%		54%		93%	46%	45%	44%	34%
	Rel. abundance Chirnonomini		14%		63%	17%	42%	63%	65%		54%		93%	42%	42%	43%	31%
	Rel. abundance Tanytarsini		2%	5%	4%	3%	2%	2%	4%					4%	2%	1%	3%
	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%
	Rel. abundance PRODIAMESINAE																
	Rel. abundance TANYPODINAE		58%	18%	15%	30%	16%	7%	4%				2%	36%	40%	27%	49%
	Rel. abundance Macropelopiini																
	R Rel. abundance Pentaneurini		58%	18%	15%	30%	16%	7%	4%				2%	36%	40%	27%	49%
	R R Rel. abundance Procladiini																
	Rel. abundance NOT DETERMINED						4%		1%								
	Number of total taxa		6	8	11	13	23	18	13		13		8	11	14	13	16
	Standardized number of total taxa		6	8	10	11	18	12	9		13		7	12	14	13	16
LIT	Sampling times		2	2	2	2	2	2	2		2						
	Individuals		151	119	744		858		2009		362						
	Rel. abundance CHIRONOMINAE		25%	6%	13%		7%		21%		19%						
	Rel. abundance Chirnonomini				1%		0%		0%								
	Rel. abundance Tanytarsini		25%	6%	13%		6%		21%		19%						
	el. abundance DIAMESINAE																
	Rel. abundance Diamesini																
	Rel. abundance ORTHOCLADIINAE		18%	40%	12%		29%		27%		27%						
	Rel. abundance PRODIAMESINAE		1%		1%		1%		1%		1%						
	Rel. abundance TANYPODINAE		56%	51%	73%		60%		44%		53%						
	Rel. abundance Macropelopiini		2%	1%			0%										
	R Rel. abundance Pentaneurini		53%	50%	73%		60%		44%		53%						
	R R Rel. abundance Procladiini																
	Rel. abundance NOT DETERMINED		1%	3%			3%		7%								
	Number total taxa		11	9	11		13		12		13						
	tandardized number of total taxa		12	9	10		12		11		14						

Table 4.10 Temporal variations of the relative abundances and the number of taxa of Chironomidae in Lago del Starlaresc da Sgiof. ***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
OUT	Sampling times		2	1	2	2	2	2	2		1		1	2	2	2	2
	Individuals		625	211	1462	5641	1768	2842	1532		74		270	952	667	330	156
	Rel. abundance CHIRONOMINAE		81%	32%	58%	64%	46%	44%	60%		50%		90%	72%	62%	33%	3%
	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%
	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%
	Rel. abundance PRODIAMESINAE																
	Rel. abundance TANYPODINAE		8%	18%	5%	5%	10%	2%	3%		36%		1%	0%	1%	4%	2%
	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%
	R R Rel. abundance Procladiini		0%		0%	0%	0%		0%								
	Rel. abundance NOT DETERMINED		1%	2%			2%		1%								
	Number of total taxa		12	10	16	18	20	16	14		12		8	15	17	13	8
	Standardized number of total taxa		12	10	14	10	17	13	12		12		8	14	17	13	8
LIT	Sampling times		2	1	2	2	2	2	2		2						
	Individuals		216	148	526		1470		784		832						
	Rel. abundance CHIRONOMINAE		84%	64%	57%		60%		79%		44%						
	Rel. abundance Chirnonomini		11%	6%	2%		1%		9%		2%						
	Rel. abundance Tanytarsini		72%	57%	55%		59%		70%		42%						
	el. abundance DIAMESINAE																
	Rel. abundance Diamesini																
	Rel. abundance ORTHOCLADIINAE		7%	26%	26%		25%		9%		6%						
	Rel. abundance PRODIAMESINAE																
	Rel. abundance TANYPODINAE		10%	8%	17%		15%		9%		50%						
	Rel. abundance Macropelopiini		6%	2%	3%		3%		2%								
	R Rel. abundance Pentaneurini		2%	6%	3%		1%		1%		1%						
	R R Rel. abundance Procladiini		2%		11%		11%		6%		18%						
	Rel. abundance NOT DETERMINED			2%			0%		3%								
	Number of total taxa		9	11	14		15		12		13						
	Standardized number of total taxa		10	12	13		11		12		11						

5 POP's and metals in fish from high altitude lakes

5.1 Introduction

Persistent organic pollutants (POPs) are chemical substances that persist in the environment, bioaccumulate through the food web and can have negative effects to human health and the environment. POPs can be transported for long distances through the atmosphere from warm (low latitudes, low altitudes) to cold regions (high latitudes, high altitudes) (Wania and Mackay, 1993). Many metals are also of intermediate volatility and can be widely distributed through the atmosphere. The POPs Protocol of the CLRTAP as well as the Stockholm Convention on POPs aim at reducing and ultimately eliminating any discharges, emissions and losses of POPs into the atmosphere and the environment. The CLRTAP's POPs Protocol has been adapted in 2009 including nine new products that were not considered before. Of particular interest of this revision are the class of perfluorinated alkylated substances (PFAS particularly PFOS and PFOA) and polybrominated diphenyl ethers (PBDE). While concentrations of the less recent regulated POPs and metals have been measured sporadically in fish muscle from 2 mountain lakes in Southern Switzerland since 2000, PFAS and PBDE have never been measured.

5.2 Methods

For measuring POPs and metal concentration in fish, rainbow trouts (Oncorhynchus mykiss) and alpine chars (Salvelinus alpinus) were sampled with nets by the Office for hunting and fishing of the Canton Ticino in Laghetto Inferiore (2074 m) and in Laghetto Superiore (2128 m) by end of September 2018. Rainbow trouts are regularly stocked, but not during 2018 to guarantee that all sampled fish have lived at least one year in the lakes. Differently, alpine arctic chars are not stocked anymore. All fish were measured for length and weight. For every fish species and sampling site a homogenized samples of fish muscle was prepared. Analytical methods are described in CIPAIS (2009) for DDT, PCB, HCB, HCH, metals and in CIPAIS (2015) for PFOS and PBDE.

5.3 Results and discussion

Fish population characteristics

Fish number, average weight, length, conditioning index (C.I.), age and fat content are shown in Tab. 5.1. A C.I. above 1 stands for a good physical condition. These parameters were more variable in Laghetto Superiore compared to Laghetto Inferiore. In Laghetto Superiore a very strong correlation existed between weight, length and age (0.84-0.90) and a strong correlation between weight, lipid content and CI (0.52-0.60).

Table 5.1 Number of individuals, species, average weight, length, age and conditioning index (C.I.) of the fish sampled in Laghetto Inferiore and Superiore since 2000.

Lake	Year	Species	Number	Weight (g)	Length (cm)	C.I.	Age (months)	Fat (%)
Laghetto Inferiore	2000	*Oncorhynchus mykiss*	26	92.6	20.9	0.99	41	1.7
		Salvelinus alpinus	10	37.4	16.5	0.83	40	1.9
	2001	*Oncorhynchus mykiss*	40	52.5	17.5	0.94	36	0.9
		Salvelinus alpinus	18	50.2	18.1	0.77	41	1.1
	2002	*Oncorhynchus mykiss*	22	76.3	19.6	1.02	32	1.5
	2003	*Oncorhynchus mykiss*	17	72.4	19.2	0.99	31	1.3
	2004	*Oncorhynchus mykiss*	16	71.6	19.0	1.01	35	2.0
	2005	*Oncorhynchus mykiss*	21	87.7	20.4	1.02	39	1.2
	2007	*Oncorhynchus mykiss*	17	82.7	19.5	1.06	36	1.5
	2008	*Oncorhynchus mykiss*	17	79.6	19.6	1.01	37	1.4
	2009	*Oncorhynchus mykiss*	16	63.9	18.2	1.00	37	1.2
	2018	*Oncorhynchus mykiss*	7	68.0	17.5	1.31		0.9
		Salvelinus alpinus	21	38.3	14.5	1.02		1.8
Laghetto Superiore	2000	*Oncorhynchus mykiss*	15	103.3	21.5	1.03	40	1.8
	2001	*Oncorhynchus mykiss*	29	86.6	20.8	0.92	35	1.0
	2002	*Oncorhynchus mykiss*	19	62.2	19.2	0.85	33	0.7
	2003	*Oncorhynchus mykiss*	22	56.5	18.3	0.92	31	0.8
	2004	*Oncorhynchus mykiss*	20	60.1	18.6	0.94	34	1.1
	2005	*Oncorhynchus mykiss*	23	84.7	20.3	1.01	40	1.4
	2007	*Oncorhynchus mykiss*	11	136.2	21.8	1.22	40	2.1
	2008	*Oncorhynchus mykiss*	14	133.9	23.3	1.03	48	1.6
	2009	*Oncorhynchus mykiss*	17	106.8	21.8	1.01	41	0.8
	2010	*Oncorhynchus mykiss*	15	87.3	20.8	0.96		
	2018	*Oncorhynchus mykiss*	8	70.6	17.5	1.29		1.1
		Salvelinus alpinus	11	73.9	18.5	0.96		1.9

Concentrations of POP’s in fish muscle

Concentrations of POPs in fish muscle of rainbow trouts and arctic chars sampled in Laghetto Inferiore and Laghetto Superiore in autumn 2018 are presented in Tab. 5.2. Concentrations of POPs were significantly lower in rainbow trouts than in arctic chars, probably because they prefer to feed in the water column or at its surface, while the latter feed also on the more polluted lake bottom.

Table 5.1 Concentrations of POP's in fish muscle (µg^{-1} kg wet weight) measured in 2018

	Laghetto Inferiore		**Laghetto Superiore**	
	Oncorhynchus mykiss	*Salvelinus alpinus*	*Oncorhynchus mykiss*	*Salvelinus alpinus*
β-HCH	< 1.0	< 1.0	< 1.0	< 1.0
γ-HCH	< 1.0	< 1.0	< 1.0	< 1.0
HCB	< 1.0	< 1.0	< 1.0	< 1.0
o,p'-DDT	< 1.0	< 1.0	< 1.0	< 1.0
p,p'-DDT	< 1.0	1.8	< 1.0	3.0
o,p'-DDE	< 1.0	< 1.0	< 1.0	1.3
p,p'-DDE	2.3	26.6	2.3	31.2
o,p'-DDD	< 1.0	< 1.0	< 1.0	3.5
p,p'-DDD	< 1.0	< 1.0	< 1.0	4.7
PCB-28	< 1.0	< 1.0	< 1.0	< 1.0
PCB-52	< 1.0	< 1.0	< 1.0	< 1.0
PCB-101	< 1.0	2.9	< 1.0	4.0
PCB-138	1.0	15.5	1.5	11.6
PCB-153	1.4	18.2	2.1	12.5
PCB-180	< 1.0	16.0	1.5	8.1
PBDE-28	< 0.10	< 0.10	< 0.10	< 0.10
PBDE-47	< 0.10	0.24	< 0.10	0.48
PBDE-99	< 0.10	< 0.10	< 0.10	< 0.10
PBDE-100	< 0.10	< 0.10	< 0.10	< 0.10
PBDE-154	< 0.10	0.36	< 0.10	0.19
PBDE-153	< 0.10	< 0.10	< 0.10	< 0.10
PBDE-183	< 0.10	0.11	< 0.10	< 0.10
PBDE-209	< 0.10	< 0.10	< 0.10	< 0.10
PFPeA	< 1.50	< 1.50	< 1.50	< 1.50
PFHxA	< 0.50	< 0.50	< 0.50	< 0.50
PFHpA	< 0.50	< 0.50	< 0.50	< 0.50
PFOA	< 0.50	< 0.50	< 0.50	< 0.50
PFNA	< 0.20	< 0.20	< 0.20	< 0.20
PFDA	< 0.10	0.41	0.11	< 0.1
PFUnDA	0.17	0.73	0.25	< 0.1
PFDoDA	0.13	0.74	0.19	< 0.1
PFTrDA	0.16	2.38	0.31	0.11
PFTeDA	< 0.10	0.70	< 0.10	< 0.1
PFBS	< 1.50	< 1.50	< 1.50	< 1.50
PFHxS	< 0.20	< 0.20	< 0.20	< 0.20
PFOS	0.20	0.83	0.43	0.21

Fish sampled in Laghetto Inferiore and Laghetto Superiore at the end of 2018 were characterized by concentrations of total DDT (DDx) of 3.5 µg kg^{-1} and 2.4 µg kg^{-1}, respectively in rainbow trouts and 29.9 µg kg^{-1}and 43.9 µg kg^{-1}, respectively in arctic chars. DDT found in the fish was probably transported from a contaminated site situated along the shore of Lago Maggiore, where a factory, that produced technical DDT, discharged liquid wastes from 1948 to 1996 into the Toce River, a major inlet of Lago

Maggiore. All concentrations of DDx were below the edibility limit (4000 μg kg^{-1}) of the Swiss legislation (Ordinance on the Maximum Residue Levels for Pesticides, SR 817.022.15). The measured results are also below the environmental quality standard for biota of the Italian legislation (50 μg kg^{-1} for biota with a lipid content below 5%).
Based on the lipid content, concentrations of DDx in rainbow trouts were 389 μg kg^{-1} lipid weight (lp) in Laghetto Inferiore and 218 μg kg^{-1} lp in Laghetto Superiore and 1661 μg kg^{-1} lp and 2311 μg kg^{-1} lp, respectively in arctic chars. These concentrations are in the same range as those measured in fish muscle from other remote alpine lakes in Switzerland (130-1100* μg kg^{-1} lp; Schmid et al. 2007) and in the low altitude lakes in Southern Switzerland: 233-409** μg kg^{-1} lp in Lago di Lugano (CIPAIS, 2009) and 350-1800** μg kg^{-1} lp in Lago Maggiore (CIPAIS, 2018).

The comparison of the concentrations in rainbow trouts with former years (Fig. 5.1: 2000-2010), showed that great variations characterized concentrations of DDx, especially in Laghetto Superiore. A correlation analysis showed that in Laghetto Superiore concentrations of DDx were strongly correlated with average fish weight (0.64) and length (0.64) and moderately with the fat content (0.52) and age (0.60), suggesting that these parameters might have highly influenced the time trend. As regards Laghetto Inferiore, only the fat content correlated moderately, probably because the mean physical properties of the sampled fish varied less through the years. It can also be observed that with few exceptions DDE (p,p'-DDE) was the main cogener (on average 76% and 78% in Laghetto Inferiore and Superiore, respectively between 2000 and 2018): the relative abundances of DDD and DDT were mostly small. It is in fact known that DDT is biotransformed by the fish into DDE (Kwong et al. 2008). The same phenomena was observed for concentrations of DDx in arctic chars. DDE contributed with 90% in Laghetto Inferiore and 74% in Laghetto Superiore in autumn samples of 2018. Slightly lower were abundances of DDE in the low altitude lakes Lago di Lugano and Lago Maggiore. In Lago di Lugano the yearly average relative abundances of 4 different fish species (Alosa agone, Coregonus lavaretus, Perca fluviatilis, Rutilus rutilus) varied between 61% and 63% for DDE, 15% and 18% for DDD, 15% and 24% for DDT (CIPAIS, 2009). In Lago Maggiore the variation among the three different sampled fish species was larger and the relative importance of DDE was even lower: 44%* DDE, 42%* DDD, 15%* DDT in Alosa agone, 55%* DDE, 34%* DDD, 12%* DDT in Coregonus lavaretus and 64%* DDE, 27%* DDD, 9%* DDT in Rutilus rutilus (CIPAIS, 2018).

Total concentrations of indicator PCB (iPCB = PCB-28, PCB-52, PCB-101, PCB-138, PCB-153, PCB-181) in fish muscle samples from Laghetto Inferiore and Superiore were 3.6 μg kg^{-1} and 5.6 μg kg^{-1}, respectively in rainbow trouts and 52.6 μg kg^{-1} and 36.8 μg kg^{-1}, respectively in arctic chars. All concentrations were below the edibility limit (125 μg kg^{-1}) of the Swiss Ordinance for contaminants (SR 817.022.15).
Based on the lipid content, concentrations of iPCB in rainbow trouts were 400 μg kg^{-1} lp and 510 μg kg^{-1} lp in Laghetto Inferiore and Laghetto Superiore, respectively and 2920 μg kg^{-1} lp and 1937 μg kg^{-1} lp in arctic chars. As already observed for DDx, these concentrations are in the same range as those observed in other Swiss remote alpine lakes (176-1310* μg kg^{-1} lp; Schmid et al. 2007) and in the low altitude lakes Lago di Lugano (604-961** μg kg^{-1} lp; CIPAIS, 2009) and Lago Maggiore (370-945** μg kg^{-1} lp; CIPAIS, 2018).

Concentrations of iPCB in rainbow trouts seemed to have decreased especially in Laghetto Superiore (Fig. 5.2: 2000-2010). Compared to DDx, concentrations of the sum of iPCB were much less influenced by physical properties of the fish. Similar to observations by Schmid et al. (2007), the main cogeners were the heavier PCB-138, PCB-153 and PCB-180. The same cogener distribution was observed in arctic chars. Compared to the alpine lakes, in the lowland lakes Lago di Lugano and Lago Maggiore the relative abundance of the heavier cogener PCB-180 was in general lower and the lighter PCB-101 higher (CIPAIS, 2009; CIPAIS, 2018).

Concentrations of all measured PBDE (PBDE-28, PBDE-47, PBDE-99, PBDE-100, PBDE-154, PBDE-183, PBDE-209) were below the detection limit in rainbow trouts from Laghetto Inferiore and Laghetto Superiore. Slightly higher but still low were concentrations in arctic chars (< 1.0 µg kg^{-1}). Concentrations were comparable to those measured in other high altitude Alpine lakes (Schmid et al. 2007).

Because of their persistency and toxicity, the most worrying substances among PFAS are PFOS (perfluorooctanesulfonic acid) and PFOA (perfluorooctanoic acid) (Buck et al. 2011, Houde et al. 2011). Contrary to other POPs, PFAS are both lipo- and hydrophobe and tend to accumulate in organs as kidneys and liver. Concentrations of PFOA were always below the detection limit. Concentrations of PFOS were low (< 1.0 µg kg^{-1}). In Lago di Lugano annual mean values of 21 µg kg^{-1} and 33 µg kg^{-1} were measured in *Alosa agone* and *Perca fluviatilis*, respectively.

***refers to lake specific average concentration**
**** refers to species specific yearly average concentration**

For most POPs, concentrations in Laghetto Superiore were often higher than in Laghetto Inferiore. The phenomena may be explained by the fact that the two lakes are connected and that Laghetto Superiore is situated in the drainage basin of Laghetto Inferiore, so that part of the POPs falling over the watershed of Laghetto Inferiore is retained in the sediments of Laghetto Superiore. In addition, because of their different morphology the water column of Laghetto Superiore gets regularly completely mixed while in Laghetto Inferiore the deepest layer does not participate to the spring and fall overturn (Pradella, 2001). As a consequence, in Laghetto Inferiore POPs that reach the bottom has the tendency to remain there. Different to most POPs, concentrations of total PFAS were significantly higher in actic chars from Laghetto Inferiore, particularly as regards PFTrDA but also of PFDA, PFUnDA, PFDoDA, PFTeDA and PFOS. The reason is not clear.

Figure 5.1 Concentrations of DDx in rainbow trouts from Laghetto Inferiore and Laghetto Superiore from 2000 to 2010 and in 2018: units in µg kg-1 fish muscle (A and B) and µg kg^{-1} fat in fish muscle (C and D)

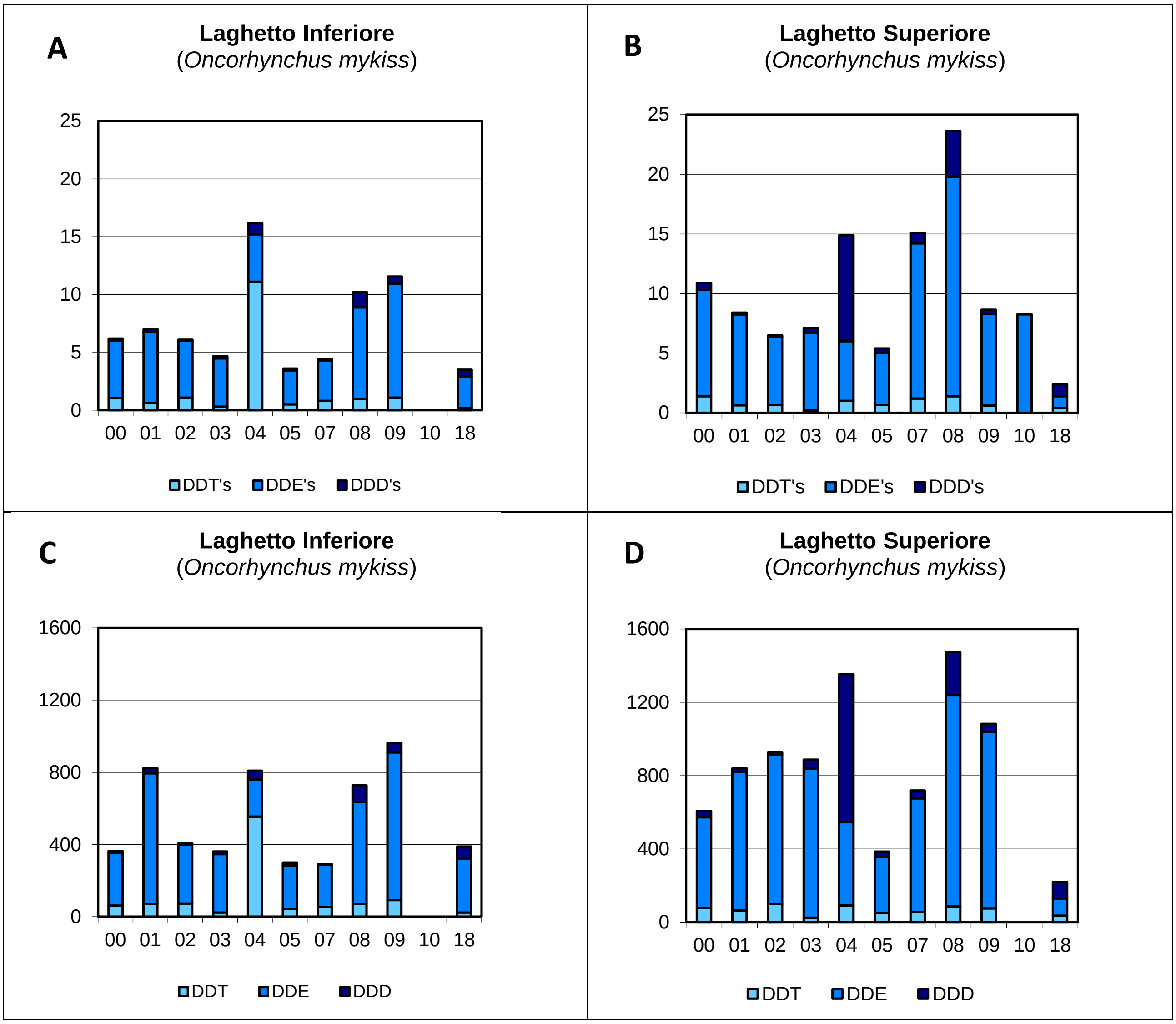
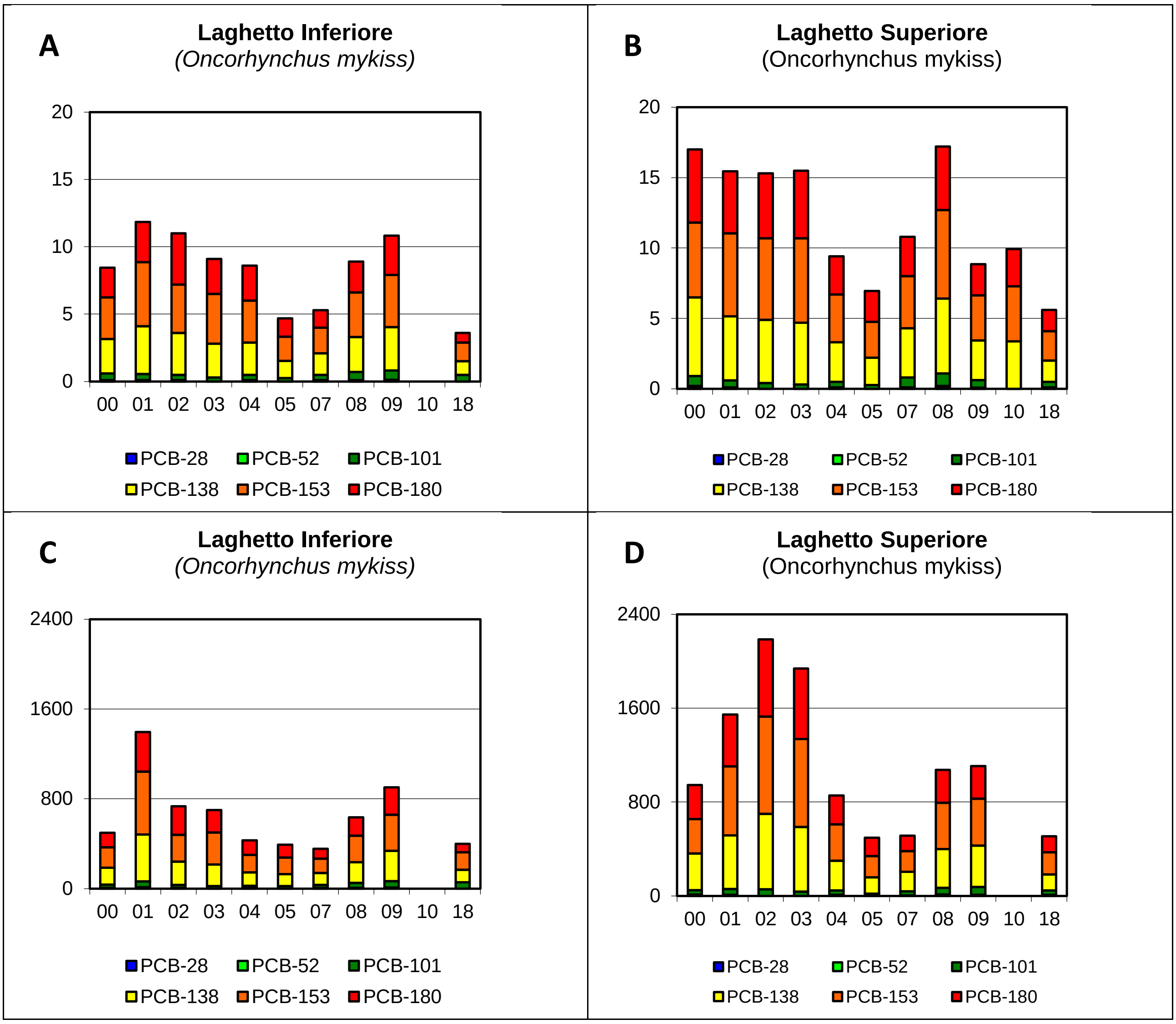


Figure 5.2 Concentrations of iPCB in rainbow trouts from Laghetto Inferiore and Laghetto Superiore from 2000 to 2010 and in 2018: units in µg kg^{-1} fish muscle (A and B) and µg kg^{-1} fat in fish muscle (C and D)



Concentrations of metals in fish muscle

An overview of the metal concentrations measured in fish muscle from Laghetto Inferiore and Superiore during 2018 is shown in Tab. 5.2. Concentrations of the most toxic metals Pb, Cd and Hg were below the Swiss edibility limits defined in the Swiss ordinance for contaminants (SR 817.022.15) (Pb: 0.3 mg kg-1, Cd: 0.05 mg kg-1, Hg: 1.0 mg kg-1). However, Hg concentrations in both fish species exceeded the environmental quality standard for biota of 0.02 mg kg-1 defined by the Directive 2013/39/UE.

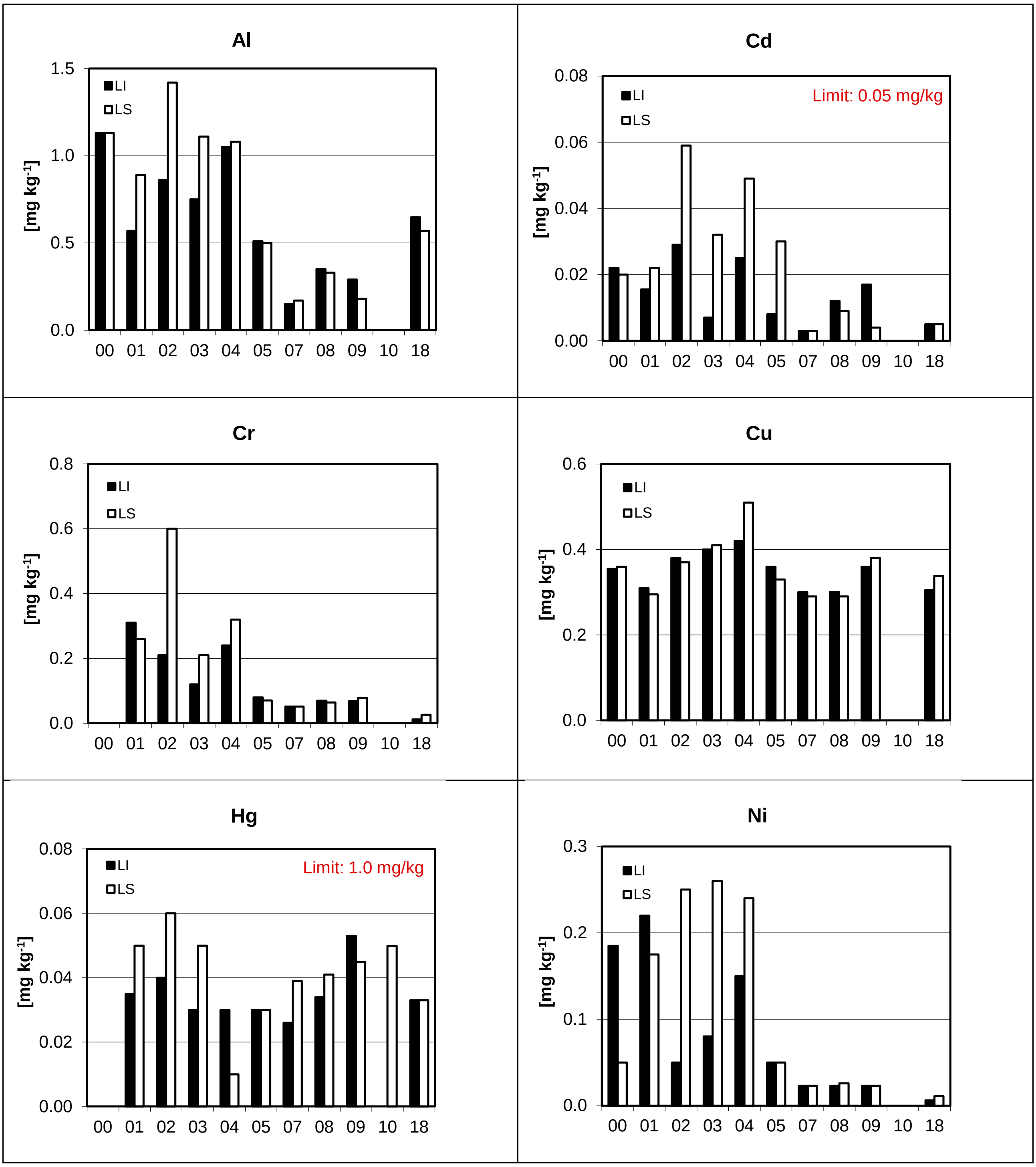
Concentrations of Hg are about a factor 2 lower compared to average concentrations in different fish species in Lago di Lugano (0.07-0.12 mg kg-1; CIPAIS, 2009) and Lago Maggiore (0.06-0.15 mg kg-1; CIPAIS, 2009).

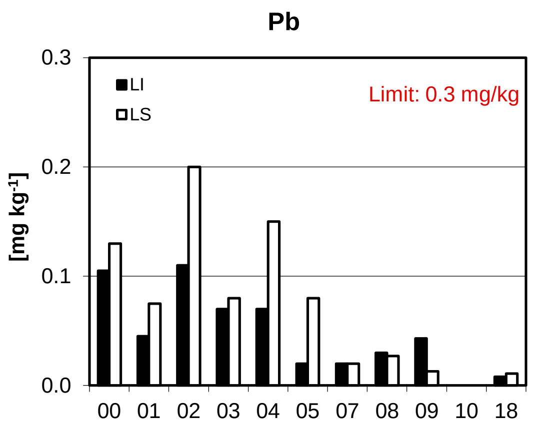
Consistently with observations from a moss monitoring in Switzerland (BAFU, 2018), concentrations of Al, Cd, Cr, Ni, Pb decreased significantly with time. The main causes for the decrease of metal concentrations were renovations of waste incineration plants (Cd), of metallurgic industries (Cd, Cr, Ni) and the introduction of unleaded fuel (Pb). Concentrations of Al are mainly of terrigenous origin, but deposition of anthropogenic sources can also occur. The main cause for the observed decrease of Al concentrations in fish muscle is probably the increase of lake pH as a consequence of chemical recovery from acidification and the subsequent decrease of Al concentrations in lake water (see paragraph 3.5.2). No significant trend was observed for Cu, Hg and Zn. The absence of a time trend for Cu has also been observed in mosses (BAFU, 2018). This result is not surprising since the use of this metal has not been a restricted.

Table 5.2 Metal concentrations in fish muscle (mg^{-1} kg wet weight) measured in 2008

	Laghetto Inferiore		**Laghetto Superiore**	
	Oncorhynchus mykiss	*Salvelinus alpinus*	*Oncorhynchus mykiss*	*Salvelinus alpinus*
Al	0.647	2.162	0.570	0.779
Cd	<0.005	0.010	<0.005	0.006
Cr	0.012	0.023	0.026	0.008
Cu	0.305	0.241	0.338	0.295
Hg	0.033	0.075	0.033	0.033
Ni	0.006	2.162	0.011	0.021
Pb	0.008	0.025	0.011	0.012
Zn	4.518	4.478	5.513	5.13

Figure 5.3 Metal concentrations in fish muscle if rainbow trouts (mg^{-1} kg wet weight) from 2000 to 2018




Pb
0.3
0.2
0.1
0.0
[mg kg-1]
■LI
□LS
Limit: 0.3 mg/kg
00
01
02
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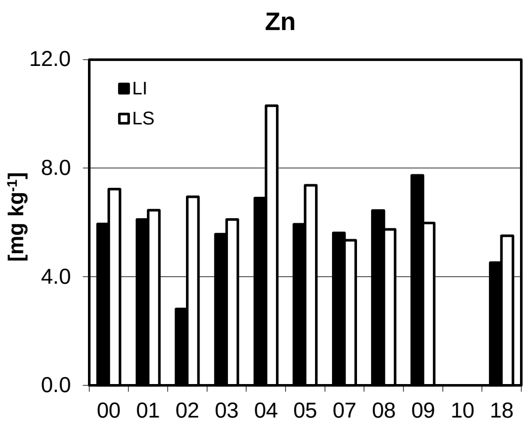
10
18


Zn
12.0
8.0
4.0
0.0
[mg kg-1]
■LI
□LS
00
01
02
03
04
05
07
08
09
10
18

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